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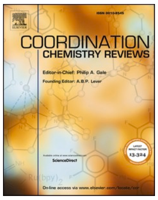

The recovery and separation of lithium by using solvent extraction methods

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ABSTRACT

Lithium, the lightest alkali metal, has been called the “new white gold” because of its limited availability and critical importance in arising applications in clean energy, like hybrid and electric vehicles. However, the rapidly growing demand for lithium, combined with its low global production rates, has led to concerns regarding the development of new technologies that require this critical mineral. For this reason, there is a need for cost-effective, energy-efficient, and environmentally friendly approaches to isolate lithium from sustainable resources like brine, ores, and seawater. In this context, solvent extraction is a promising technique for lithium recovery from these sources that has advantages over other approaches like precipitation, solid-state adsorption, and membranes. However, there are few processes in industry that use solvent extraction for lithium extraction and purification. The scarce use of this method industrially is possibly a consequence of critical knowledge gaps that need to be addressed prior to the optimization of processes with suitably high lithium selectivity and extraction efficiency. This review bridges these gaps by highlighting the coordination chemistry of lithium and discussing the requirements for developing highly selective lithium chelators for solvent extraction. Additionally, the lithium coordination properties and solvent extraction performance of macrocyclic and acyclic chelator classes, as well as ionic liquid extraction systems, used to extract lithium from artificial solutions, brines, and seawater are reviewed.

Nomenclature

List of Acronyms

AAS	atomic absorption spectroscopy
BMED	bipolar membrane electrodialysis
CN	coordination number
D2EHPA	bis(2-ethylhexyl)phosphoric acid
DFT	density functional theory
DTPA	diethylenetriamine-*N*,*N*,*N*’,*N*“,*N*”-pentaacetic acid
EDTA	ethylenediaminetetraacetic acid
EE	extraction efficiency
GFAAS	graphite furnace atomic absorption spectroscopy
HBTA	benzoyl-1,1,1-trifluoroacetone
HSAB	hard-soft acid-base
HTTA	thenoyltrifluoroacetone
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectroscopy
ILMED	ionic liquid membrane electrodialysis
Li/Al-LDHs	lithium/aluminum layered double hydroxides
LIS	lithium-ion sieves
LMO	lithium manganese oxides
LTO	lithium titanium oxides
MEHPA	(2-ethylhexyl)phosphonic acid mono-2-ethylhexyl ester
MP2	Møller–Plesset second order perturbation theory
NF	nanofiltration
SSX	synergistic solvent extraction
TALSPEAK	trivalent actinide–lanthanide separation by phosphorus reagent extraction from aqueous komplexes
TAT	Tenova Advanced Technology
TBP	tributyl phosphate
TOPO	trioctylphosphine oxide
TPPO	triphenylphosphine oxide
USGS	U.S. Geological Survey
UV/Vis	ultraviolet-visible

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1. Introduction

1.1. History and applications of lithium

The element lithium was first isolated from the mineral petalite in 1817 by Johan August Arfvedson, a student of the Swedish chemist Jöns Jakob Berzelius [1]. Its name is derived from the Greek word for stone, lithos, reflecting the source from which it was found [2,3]. Since its discovery, lithium has become an indispensable element due to its unique physical and chemical properties that render it suitable for various applications [1,2]. Recently, lithium has been referred to as the "new white gold," a moniker that signifies its particular importance and current value within the field of energy storage [4].

With the current recognition of the importance of lithium within many modern applications, it is also noteworthy that specific lithium compounds have been utilized for critical manufacturing processes since the 19th century [5]. In particular, lithium was produced in Langelsheim, Germany, after the First World War as an additive to "Bahnmetall", or bearing metal, to increase the lubricity of this material [5]. Subsequently, during World War II, lithium hydride was used for hydrogen storage applications. Currently, lithium is implemented in various industrial applications and end uses, as summarized by the U.S. Geological Survey (USGS) in 2022, as shown in Fig. 1 [6].

As depicted in Fig. 1, lithium is mainly used in the energy sector for batteries (80 %) with smaller quantities being applied in ceramics and glass (7 %), lubricating greases (4 %), continuous casting mold flux powders (2 %), air treatment (1 %), and for medical applications (1 %). In the pharmaceutical field, it is worth mentioning that lithium has been applied for over 100 years for the treatment of manic depression and has also been used as an antipsychotic drug [7–11]. The importance of lithium within new batteries has expanded significantly within the last decade. In 2010, only 23 % of lithium supplies were applied in this sector. By 2022, this number rapidly grew to 80 %. Based on forecasts, the demand for lithium will undergo significant growth in the upcoming decades due to the expansion of novel technologies, including electric and hybrid vehicles [6,12,13].

1.2. Deposits and production

Lithium is the 33rd most abundant terrestrial element. Within Earth's crust, it ranges in quantities from 20 ppm to 70 ppm [14–16]. It can be found in two primary sources: minerals, like ores and rocks, and water resources, including continental and geothermal brines and seawater [17,18]. Among these deposits, roughly 59 % of global lithium is found in continental brines, with substantially smaller quantities occurring in minerals, like pegmatites and jaderite (25 %), or in oil field brines (3 %) [5,19,20]. Although accurately determining the number of lithium reserves worldwide is challenging, the USGS releases annual estimates of the global distribution of lithium reserves and production quantities [4,6,21,22]. The recently published USGS data from the year 2022 is presented in Table 1 [6].

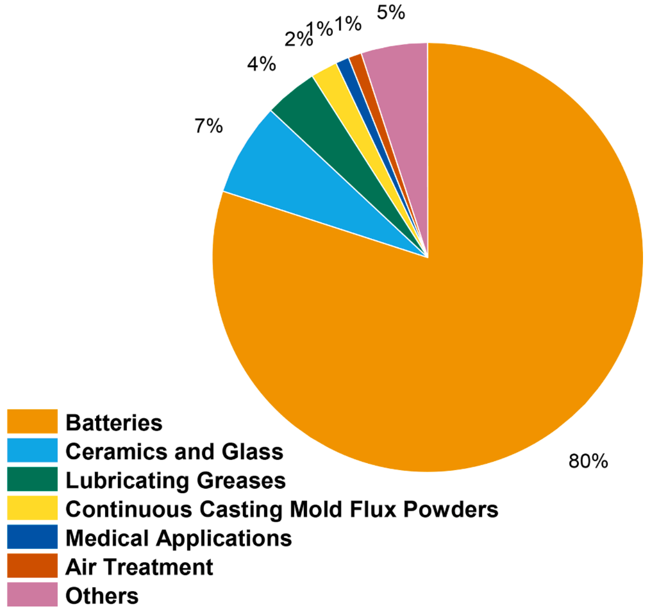


Fig. 1. Pie chart depicting major end uses and applications of lithium [6].

In analyzing Table 1, it is apparent that Australia (61,000 t), Chile (39,000 t), and China (19,000 t) are the major global suppliers of lithium with Chile (9.30 Mt), Australia (6.20 Mt), and Argentina (2.70 Mt) possessing the highest amounts of lithium in their reserves [6]. In contrast to the limited terrestrial reserves of lithium on land ($4.10\cdot 10^6$ t), the ocean is estimated to contain over 230 billion t of this critical element (Table 2) [12,22–25]. Accordingly, seawater is a lithium source that could help meet the future demands for this element. The major challenges associated with obtaining lithium from the ocean arise from its low concentration (0.1–0.2 ppm or 0.178 g/L) and the complex composition of seawater, which contains a diverse range of ions in much higher concentrations [12,24,26]. Despite these challenges, obtaining lithium from the ocean is highly desirable because of its low environmental impact and the fact that it contains enough of this element to meet the projected demands for decades to come [12].

As a reflection of the challenges associated with harvesting lithium from the ocean, Table 2 shows the most common metal ions present in seawater along with their concentrations and overall quantities [25]. Unsurprisingly, the monovalent and divalent ions sodium ($1.40\cdot 10^{16}$ t), magnesium ($1.68\cdot 10^{15}$ t), calcium ($5.34\cdot 10^{14}$ t), and potassium ($5.10\cdot 10^{14}$ t) are the most abundant elements in seawater. Their concentrations are substantially higher than those of lithium (0.178 ppm or 178 ppb), making the selective extraction of this element challenging [25]. Despite these obstacles, the Powering the Blue Economy Report from the US Department of Energy points out that the extraction of minerals from seawater can be more environmentally friendly and sustainable than terrestrial mining, even when the seawater extraction

Table 1
Estimated Data from the USGS about the Production of Lithium and Reserves Worldwide in 2022 [6].

Country	Mine Production [t]	Reserves [t]
Chile	39,000	9,300,000
Australia	61,000	6,200,000
Argentina	6,200	2,700,000
China	19,000	2,000,000
United States	–[a]	1,000,000
Zimbabwe	800	310,000
Brazil	2,200	250,000
Portugal	600	60,000
Other Countries[b]	–	3,300,000
Worldwide	**130,000**[c]	**26,000,000**

[a] Withheld to avoid disclosing company proprietary information.
[b] Other countries includes Austria, Canada, Congo (Kinshasa), Czechia, Finland, Germany, Mali, Mexico, and Serbia.
[c] Excludes U.S. production.

Table 2
The most common Metals in Seawater and on Land and their Estimated Concentrations and Total Amounts Worldwide [25].

Metal Ion	Concentration in seawater [ppm]	Total amount in seawater [t]	Total mineral reserves on land [t]
Na^+	10,800	$1.40\cdot 10^{16}$	–
Mg^{2+}	1,290	$1.68\cdot 10^{15}$	$2.20\cdot 10^{9}$
Ca^{2+}	411	$5.34\cdot 10^{14}$	–
K^+	392	$5.10\cdot 10^{14}$	$8.30\cdot 10^{9}$
Li^+	0.178	$2.31\cdot 10^{11}$	$4.10\cdot 10^{6}$

efficiency is poor [23,24,27,28]. Thus, from a cost-benefit analysis, it can be argued that obtaining lithium from the ocean can be less expensive than mining from ores and lithium-bearing minerals [19].

1.3. Demand for lithium

Worldwide lithium production has increased significantly over the last several years. In 2022, 130,000 t were produced, representing a remarkable 21 % increase from the 107,000 t produced only one year prior [6]. This trend can be attributed to the rising development and demand for lithium-ion batteries within the electric vehicle market. The surge in demand for lithium has resulted in a near-exponential increase in its price. For example, the annual price of lithium carbonate in 2010 was 5,180 U.S. dollars per ton; by 2022, this price rose to 37,000 U.S. dollars per ton – a seven-fold increase in just twelve years [29]. Moreover, the acquisition of lithium is currently limited to specific geographic sources, some of which are politically fraught and subject to geopolitical conflicts if equitable solutions for resource access are not implemented [30,31]. At the current demand rate, terrestrial lithium reserves are predicted to reach their limit by 2080 [12]. Consequently, the United States and the European Union have already added lithium to the list of critical minerals, citing its concerning rise in demand and limited domestic supply [32–34]. Novel technologies that will enable efficient strategies to isolate lithium from resources are needed to address these issues. The current technologies, however, limit the accessibility of terrestrial lithium to only a few geographic localizations, typically with brines or ores of this element, capping its current availability at 26 Mt worldwide [6].

1.4. Lithium extraction techniques

As noted above, the global lithium reserves are found in diverse types of deposits. Significant research efforts have been undertaken to isolate this element from these sources in a cost-effective and environmentally friendly manner. Lithium has been generally traded or sold as hydroxides, carbonates, chlorides, bromides, or as organic compounds like butyl lithium [5,18,19,30,35–37]. This section describes the most common strategies and techniques to isolate lithium. Because previous reviews have summarized approaches for obtaining lithium from minerals and ores from spodumene or lepidolite, this review will focus on methods for its recovery from seawater and brines [38–42].

1.4.1. Solar evaporation

Because salar brines are the most abundant terrestrial lithium source, significant efforts have been made to isolate it from these sources. Solar evaporation is the most common method for lithium recovery from salar brines, and it relies on sunlight (solar energy) to slowly evaporate these solutions, leading to highly concentrated solutions of its ionic components. In this process, brine water is pumped into shallow ponds, where evaporation is more efficient [43,44]. The evaporation rate can vary significantly, depending on the weather, region, and brine composition. Typically, sufficient brine concentration via evaporation takes at least one year. After evaporation, an excess of calcium hydroxide and calcium oxide ("lime") is added to remove residues of magnesium salts via precipitation [43]. However, this method strongly depends on the magnesium-to-lithium ratio in brine. For this reason, a pretreatment is required for brines containing higher ratios of magnesium and calcium [43,45–47]. Finally, adding sodium carbonate as soda ash will form insoluble lithium carbonate, in purities above 99 % [48]. Based on its use of large quantities of lime and soda, this method is called the "lime-soda-evaporation" process [43,46,48–50]. Although the solar radiation used to drive these brine evaporations is a clean and renewable energy source, the major disadvantage of this method is its high dependence on environmental conditions, including temperature, rainfall, humidity, and wind that make this method unpredictable and challenging, particularly in times of climate change [49,50]. Moreover, this method suffers from long processing times of up to 24 months, and the requirement for sufficient infrastructure, including spacious evaporation ponds. In addition, this process consumes large quantities of water and produces substantial amounts of waste from chemical treatments required for precipitation. These drawbacks lead to a large environmental footprint [49,51–53]. Lastly, when the composition of obtained lithium is contaminated with various salts like sodium chloride, magnesium carbonate, and magnesium hydroxide, further cost-intensive processes are required to achieve higher purity of lithium [43,51,54]. These separations, whether used in practice or under development, are discussed below.

1.4.2. Precipitation

One of the most commonly used methods to recover lithium from brines is selective precipitation. This approach is advantageous because it is operationally simple, rendering it feasible for industrial-scale production [18,19,55]. This method uses various precipitation-inducing agents. For example, aluminum salts can be added to form solid lithium aluminates from the brine [56–58]. Before precipitation processes can be performed, brine pretreatment might be required to remove competitive metal ions [55]. The major advantage of this pH–dependent precipitation process is the possibility of precipitating lithium salts from brines with high magnesium-to-lithium ratios [55,59]. Although these precipitation approaches are fairly effective at separating elementally pure lithium, magnesium salts often exhibit similar solubilities to lithium salts. The similar chemical properties and solubilities of these two ions are a consequence of their diagonal relationship in the periodic table, as well as similar ionic radii (six-coordinate ionic radius of lithium: 76 pm; six-coordinate ionic radius of magnesium: 72 pm) [2,59–63]. Therefore, brines or seawater with higher magnesium-to-lithium ratios lead to less facile separations. Consequently, higher magnesium content in brines requires lithium recovery operations that are substantially more costly [13,64]. For this reason, knowing the magnesium-to-lithium ratio is an important parameter for predicting the potential of various precipitation methods for selectively isolating this element.

Notably, the ratio of magnesium to lithium can range from less than 1 to over 7000 within different brine sources. For brines with magnesium-to-lithium ratios below six, chemical precipitation is the recommended and most efficient way to separate lithium [43,61,65–67]. Within seawater, the high amounts of other alkali and alkaline earth metals, particularly magnesium, present similar challenges [19,68]. For this reason, a successful two-step process was proposed to first precipitate calcium, magnesium, and manganese as hydroxides under basic conditions, followed by neutralization, carbonation with sodium carbonate, and evaporation of the solution to obtain lithium carbonate in purities that can exceed 99 % [68].

In addition to the concerns about magnesium, another drawback of the chemical precipitation method is that large quantities of precipitation-inducing agents are required. Furthermore, chemical precipitation leads to high amounts of byproducts in the form of sludges, and their waste disposal decreases the sustainability and cost-efficacy of these processes [69]. In most cases, lithium obtained via precipitation is not sufficiently pure for end use, and additional methods, such as solvent extraction or ion-exchange techniques, are necessary [55,70–73].

1.4.3. Chromatography

Different types of chromatography, such as gel permeation chromatography, can be used to separate alkaline earth and alkali metals from each other. These efforts date back to 1973 when the successful enrichment of lithium from calcium- and magnesium-rich solutions from the Dead Sea and concentrated brine using columns equipped with crosslinked polyacrylamide material (Bio-Gel P-2) was demonstrated [74,75]. In 1967, reversed-phase column chromatography was also used for small-scale lithium isolation by employing polytetrafluoroethylene as a stationary phase in conjunction with lithium-binding extractants in the mobile phase like tributyl phosphate (TBP) or trioctylphosphine oxide (TOPO) in dodecane. Although the experiments were performed on smaller scales, successful and quantitative separation of lithium from other alkali metals such as sodium, potassium, rubidium and cesium was reported [76]. However, no additional information about the performance of this method under realistic conditions, like in seawater or brine, and on industrial scales has been reported.

1.4.4. Ion sieves and adsorbents

Ion-exchange techniques based on ion sieves are among the most promising approaches for lithium recovery from brine or seawater [77–80]. Ion sieves can be described as adsorbents with high selectivity for specific metal ions and are derived from precursors that already contain the target metal ion [79]. The first ion sieves with high affinity and selectivity for lithium ions, called lithium-ion sieves (LIS), were reported in 1971. Since then, these materials have gained increasing attention and have arisen as the most common adsorbent materials used for lithium extraction [19,77,79,81,82]. LIS are made of a stable molecular framework with vacant positions that can be replaced by target metal ions. However, the vacant positions can only accommodate target metal ions with equal or smaller ionic radii. For this reason, only lithium ions can fit into the free spaces of LIS due to their small ionic radius compared to other metal ions. Although magnesium has a smaller four-coordinate ionic radius (57 pm) than lithium (59 pm), its incorporation into LIS is disfavored by its substantially more negative hydration energy ($\Delta_{\mathrm{hyd}}G = -1830$ kJ/mol) compared to lithium ($\Delta_{\mathrm{hyd}}G = -475$ kJ/mol) (Table 4) [62,83,84]. The replacement of protons by lithium ions in LIS is based on the LIS effect, which describes the replacement of template ions like lithium with ions of the same or smaller size, like the hydronium ion, via a redox or exchange reaction [78,79,85–87]. An ideal LIS is an inorganic material with high chemical stability and low toxicity and can be easily synthesized from commodity chemicals [78]. Furthermore, an effective LIS has high selectivity and high uptake capacities for lithium [78,79,88].

The lithium adsorption uptake capacities of several key LIS materials are summarized in Table 3. There are two major types of LIS materials, lithium manganese oxides (LMO-type) and lithium titanium oxides (LTO-type), each with different advantages and drawbacks for lithium recovery. For instance, LMOs are susceptible to dissolution effects in acidic solutions, which might lead to environmental pollution in larger industrial setups and decrease the material performance after multiple cycles of lithium recovery [78,79,89–93]. To prevent and slow this undesired dissolution, LMO was doped with various other ions like nickel, aluminum, titanium, iron, and magnesium [84,94–98]. LMO materials doped with magnesium ions showed higher resistance to dissolution than to pure LMO, even after several adsorption/desorption cycles. Furthermore, it also had higher lithium adsorption capacities of 23–25 mg/g at pH = 6.6 from salt lake brine [84]. By contrast, the LTO-type materials are more resistant to dissolution and have higher theoretical adsorption capacities, but are limited by their slower adsorption kinetics [99].

Another class of adsorbent with proven efficiency for lithium extraction are aluminum layered hydroxides [45]. In particular, lithium/aluminum layered double hydroxides (Li/Al-LDHs) show high selectivity towards lithium ions even at higher magnesium-to-lithium ratios from geothermal brine [45,101–103]. Within materials of this type gibbsite γ–Al(OH)$_3$ lithium ions are incorporated to form lithium aluminum layered double hydroxides [104]. Li/Al-LDHs can be easily synthesized at low costs. In addition, they possess faster adsorption kinetics, and the adsorbed lithium ions can be eluted by using neutral water with insignificant dissolution properties, which makes Li/Al-LDHs beneficial towards LIS [101,105,106]. However, (Li/Al-LDHs) possess lower adsorption capacities, making Li/Al-LDHs less feasible for industrial-scale production [45].

1.4.5. Membrane-based technologies

The use of nanostructured membrane technologies and nanofiltration (NF) membranes can also be applied to extract lithium from seawater and brines [107,108]. In general, membranes are known for separating contaminants like bacteria in a micrometer range. By contrast, nanostructured membranes can separate gases and ions on a nanometer scale. Further, nanostructured membrane structures are finely porous or nonporous [109]. NF is a pressure-driven membrane-based filtration process based on ultrafiltration and reverse osmosis [60,110]. The NF membranes are negatively charged, and the pore sizes in the membrane are in the nanometer-range [111,112]. For this reason, nanometer-sized pores possess a rejection range of molecules/ions comprising a cut-off molecular weight between 300 and 500 Da [108]. Due to their small pore sizes nanostructured and NF membranes are suitable for lithium separation [109]. Commercially available nanostructured and NF membranes are polymer-based materials and can be further functionalized to obtain optimal conditions for selective lithium extraction [108,113]. These membrane-based technologies are energy-efficient and have a reduced environmental impact compared to other methods. In addition, this approach can be optimized for large-scale industrial setups [60,114]. Capitalizing on these advantages, NF has received significant attention from industry [60,110].

Using membranes or nanomembranes enables the separation of monovalent ions like lithium from other multivalent ions like magnesium or uncharged small molecules based on the Donnan exclusion membrane principle. This principle describes the distribution of charged ions close to a permeable membrane [69,115–118]. Moreover, the ability to systematically modify the pore sizes and electrostatic charges of these membranes has been an effective means of developing selective lithium separations, particularly from metal ions, that would be challenging with other techniques. For instance, a recent study applied such a membrane to make the challenging separation of lithium from magnesium in salt lake brines with a high magnesium content [119–122].

Although the tunability of these membranes makes them promising for lithium recovery, when they are practically applied, they are susceptible to fouling, which decreases their performance and selectivity for lithium. These fouling effects have been a long-known limitation of membrane-based separation technology. The high susceptibility of nanoporous membranes to fouling arises from their high surface areas, which provide many regions for contaminants to deposit. These fouling agents can be a mixture of different species, including colloidal particles, salts, algae, or bacteria [119,123–125]. To address this challenge, researchers have investigated fouling-resistant membranes, which reduce the adsorption of foulants on the membrane surface by chemical or physical membrane surface engineering strategies, such as coating membranes with antibacterial layers [123,125–128]. Moreover, another way to reduce fouling in membranes can be the chemical or physical

Table 3
Different Ion Sieves Belonging to the LMO- and LTO-type and their Lithium Adsorption Capacities.

Precursor	Ion Sieve	Theoretical Adsorption Capacity	Experimental Adsorption Capacity	pH	Lithium Source	Ref.
$LiMn_2O_4$	λ-MnO_2	39.9 mg/g	1.1 mg/g	8.1	Seawater	[100]
$Li_{1.33}Mn_{1.67}O_4$	$MnO_2{\cdot}0.3H_2O$	59.5 mg/g	25 mg/g	8.1	Seawater	[100]
$Li_{1.67}Mn_{1.67}O_4$	$MnO_2{\cdot}0.5H_2O$	72.8 mg/g	37 mg/g	8.1	Seawater	[100]
Li_2TiO_3	H_2TiO_3	126 mg/g	32.6 mg/g	6.5	Salt lake brine	[99]

cleaning of membranes after each separation or the pretreatment of appropriate feed solution to remove foulants before the separation is performed [123].

Another technique that uses membranes for lithium recovery is electrodialysis. This technique relies on polymer-based ion-exchange bipolar membranes which mobilize anions and cations after applying an electric potential [129–132]. Bipolar membranes are multi-layered ion-exchange membranes, comprising a cation-selective and anion-selective membrane that are separated by a hydrophilic intermediate layer [132,133]. The membranes are made of conventional ion-exchange membranes comprising functionalized polymers, that can separate positive and negative ions from each other. However, this separation mechanism is inefficient when isolating lithium from other cations like magnesium. Innovations in this field have led to the development of ion-exchange membranes that selectively separate monovalent ions from multivalent ions [69,131,134,135]. Further innovations in this field have validated other approaches to lithium recovery, such as bipolar membrane electrodialysis (BMED) or ionic liquid membrane electrodialysis (ILMED) [69,132,134,136–138]. The BMED technology uses bipolar membranes containing a cation-selective membrane, an anion-selective membrane, and an interface between both membranes, which produces hydroxide ions and protons. For example, a BMED-based approach was recently demonstrated to separate magnesium and lithium ions from salt lake brine with a high magnesium-to-lithium ratio [139]. The ILMED is an electrodialysis-based technology that employs ionic liquid-impregnated membranes for separation. This technique has been applied for efficient separations of magnesium and lithium ions [140,141].

1.4.6. *Recycling from batteries*

Due to the rising demand for lithium in recent years, lithium recovery from batteries has become increasingly attractive [142]. However, lithium's current global recycling rate is only 1 % [5,19]. From a long-term perspective, the growing utilization of lithium-ion batteries, like those in electric vehicles, will lead to the accumulation of significant quantities of battery waste, making efforts to recycle critical elements from this waste stream appealing. The International Energy Agency forecasts that by 2040, as much as 8 million t of impractical end-of-life lithium-ion battery waste will be produced [143,144]. Thus, the recycling of end-of-life batteries can help mitigate the supply issues of critical minerals such as lithium in an environmentally friendly manner [145,146].

A typical lithium-ion battery contains about 2–7 % lithium, but also cobalt (5–20 %), copper (7–25 %), aluminum (3–14 %), iron (ca. 19 %), and nickel (5–10 %) [147–150]. The low mass percentage of lithium in lithium-ion batteries has led to substantial challenges in its recovery from this waste stream, which has contributed to its poor recyclability. For example, in 2007 only 3 % of the lithium was being recovered from these battery waste sources [151]. In fact, until recently, lithium-ion battery recycling has been focused on other critical elements like cobalt [152]. The ultimate success in lithium recovery from battery waste will be dictated by the economic viability of these strategies, which in turn depends on how the market value and availability of this element change in the future [13]. A typical recycling process for lithium extraction from batteries includes identifying and quantifying the elements in the battery and then completing pretreatment steps tailored to the identified battery type. From there, common hydrometallurgical processing strategies are applied. These recycling techniques include approaches such as pyrometallurgy, mechanical treatment, and biotreatment [19,147,151,153–158].

1.4.7. *Supercritical carbon dioxide*

As an alternative to organic solvents, supercritical carbon dioxide has arisen as a promising candidate and has been used to extract lithium and other metals from many different materials, including lithium-ion batteries [159–163]. Supercritical carbon dioxide, which is obtained at pressures and temperatures that exceed the critical point of carbon dioxide, is a supercritical fluid, which has properties of both liquids and gases [164]. Supercritical carbon dioxide has a similar density and miscibility properties as many conventional solvents, and these properties have led to its investigation within extraction studies. Several key advantages of supercritical carbon dioxide arise from its low cost, non-toxicity, non-flammability, availability in pure form, its environmental friendliness, and its capacity to be used without generating significant quantities of waste [165]. Several reviews have summarized the extraction of metals, like copper and lead, via the use of chelating agents in combination with supercritical carbon dioxide [159,166]. The extraction of lithium from aqueous solutions by using this technique, however, has only begun to be investigated, but has shown significant promise [167,168]. For instance, a combination of a 14-crown-4 ether and an acidic extractant was applied in the presence of supercritical carbon dioxide to extract lithium from a solution containing a mixture of lithium, magnesium, and sodium. With these conditions, lithium extraction efficiencies of up to 30 % were obtained, but 27 % and 52 % of sodium and magnesium, respectively, were also extracted [167]. These initial studies demonstrate the potential value of using supercritical carbon dioxide for lithium extraction.

1.4.8. *Microorganisms*

Bacteria and other microorganisms have sophisticated cellular machinery regulating metal ion uptake and trafficking. These properties have been leveraged to engineer microorganisms that can extract critical minerals from their environment, presenting a novel approach for obtaining important metal ions. This strategy has been extended to the recovery of lithium, as well [169]. In particular, several gram-positive bacteria strains showed high accumulation of lithium at pH = 5.80, reaching up to 126 μmol per gram of dry-weight cells within minutes. Moreover, the immobilization of these bacteria in polyacrylamide afforded a material that could be applied for the column chromatographic separation of lithium. Lithium ions could be quantitatively desorbed from these bacteria by treating them with 1 M HCl [169]. However, no further competition experiments with other metal ions or experiments under realistic conditions, like those in brine, were reported. Following this initial study, several groups have worked on removing and recovering lithium using microorganisms [170–172]. For example, the microorganism *Rhodococcus* sp. $A5_{wh}$ sequesters 40 % of the lithium from a solution within 180 min [171].

1.5. *Scope*

As summarized above, the increasing demand for lithium has inspired the development of several different extraction technologies for both seawater and various terrestrial deposits. Among these methods, solvent extraction is probably one of the most successful techniques that have been applied to extract various metals on industrial scales, including rare earth elements [173–176]. By contrast, solvent extraction methods for large-scale lithium recovery are significantly less used. In recognition of the widespread value of the solvent extraction method for metal ion extraction and separation, significant research efforts have made this process economically and environmentally feasible for lithium. The optimization of solvent extraction relies on the development of chelating agents and extractants that possess good selectivity for lithium. Given the important role of coordination chemistry in this process, this review will focus on current and ongoing efforts towards new lithium-chelating agents that can be applied to solvent extractions. Before describing specific lithium-chelating systems, an overview of the coordination chemistry of this metal ion is presented because this information is critical to understand the rationale behind the design of new chelating agents for this metal ion.

2. Chemistry of lithium

Lithium is the lightest and least reactive metal in the alkali metal series, and therefore, possesses several unique features that have led to its importance in different applications like energy storage [2,177]. For instance, lithium, in its metallic form, is the least dense metal within the periodic table. In terms of its natural isotopic abundance, 7.5 % of it exists as ^{6}Li and 92.5 % as ^{7}Li. Like the other alkali metals, lithium attains the +1 oxidation state under ambient conditions and is present in this ionic form within natural sources like seawater, brines, and hard rock minerals [2,178]. The lithium ion is the smallest of the alkali metal ions with a four-coordinate ionic radius of 0.59 Å. The closed-shell electron configuration of lithium renders its interactions with ligand donors to be ionic in nature. As such, coordination geometries of lithium complexes are typically dictated by sterics and the small size of this ion. Most lithium complexes have coordination numbers of four and predictably attain tetrahedral geometries. With small ligands, however, higher coordination numbers of up to eight can be attained [2,179–182].

With respect to the Pearson hard-soft acid-base (HSAB) properties, the lithium(I) ion is a hard acid characterized by a relatively high charge density and low polarizability [182–184]. Consequently, lithium ions prefer hard anionic oxygen donors. In aqueous solutions, therefore, lithium tends to remain hydrated with hard water molecules rather than engaging with other ligand types, highlighting a challenge in developing chelators for this ion [182,185]. Based on these properties, most chelators and ligands that interact with lithium have alcohol, carboxylic acids, or ether functional groups with fewer examples of those with nitrogen donor atoms. In addition, lithium complexation can be achieved with other hard bases like the carboxamides of peptides, and the oxygen atoms of phosphate donors [182,186]. Lithium complexes with soft donors like sulfur, selenium, and tellurium have been reported, but are less stable under aqueous and aerobic conditions [182,187–191].

In water, lithium forms a four-coordinate aqua-complex with a tetrahedral geometry. The Li–O distance within this hydrated complex is between 1.933 and 1.948 Å [182]. In Table 4, the hydration energy of the lithium ion, compared to the other alkali metal ions, is shown. From these data, it is apparent that the lithium ion has the highest hydration energy within this series. This property makes lithium particularly challenging to extract from aqueous solutions [83,192].

A further compilation of the properties of the lithium ion in aqueous solution along with other common metal ions within seawater and brines are shown in Table 5. Although lithium is the smallest alkali metal, its hydrated cation has a radius of 382 pm, making it larger than sodium, potassium, and rubidium ions. In addition, a typical distance between lithium and the oxygen donor atom is 208 pm. As noted previously, magnesium is often the most challenging ion to separate from lithium. This challenge stems from lithium and magnesium’s similar ionic radii [193].

Table 4
Overview of Calculated and Experimental Standard State Free Energy of Hydration of Representative Alkali and Alkaline Earth Metal Ions [83].

Ion	$\Delta_{hyd}G_{calc}$ [kJ/mol]	$\Delta_{hyd}G_{ex}$ [kJ/mol]
Li^{+}	–510	–475
Na^{+}	–385	–365
K^{+}	–305	–295
Rb^{+}	–285	–275
Cs^{+}	–245	–250
Mg^{2+}	–1940	–1830
Ca^{2+}	–1515	–1505

Table 5
Overview of Relevant Metal Ions Present in Brines and Seawater and their Physical and Chemical Properties in Dependance on their Coordination Numbers (CN).

Ions	Ionic Radii/CN	Hydrated Ionic Radii at 25 °C [194]	Hydration Number (±1)[a]	M–O Distance[b] [193]
H_3O^{+}	0.10 Å [195]	2.82 Å	3 [196] 4 [193]	–
Li^{+}	0.59 Å/4 [62] 0.60 Å/4 [197] 0.76 Å/6 [62] 0.79 Å/6 [197]	3.82 Å	4 [198] 5 [199] 6 [193]	2.08 Å
Na^{+}	0.99 Å/4 [62] 1.02 Å/5 [197] 1.02 Å/6 [62] 1.07 Å/6 [197]	3.58 Å	4 [199] 5 [200] 6 [193]	2.35 Å
K^{+}	1.37 Å/4 [62] 1.38 Å/6 [62] 1.46 Å/7 [197]	3.31 Å	3 [199] 6 [201] 6–8 [193]	2.79 Å
Be^{2+}	0.27 Å/4 [62] 0.45 Å/6 [62]	4.59 Å	4 [193]	1.67 Å
Mg^{2+}	0.57 Å/4 [62] 0.72 Å/6 [62]	4.28 Å	6 [193,196]	2.09 Å
Ca^{2+}	1.00 Å/6 [62] 1.12 Å/8 [62]	4.12 Å	6 [196] 6–10 [193]	2.42 Å

[a] Estimated numbers of water molecules in the primary coordination sphere.
[b] The M–O distances are determined in aqueous solutions.

3. Solvent extraction by using chelators

3.1. Solvent extraction: general information

Liquid-liquid extraction, or solvent extraction, is a powerful approach for separating metal ions, that has been useful for various processes involving lithium. Solvent extraction employs a biphasic mixture of an organic and aqueous phase, typically containing the metal ions targeted for separation. Agitation of this mixture causes the metal ions to partition between the organic and aqueous phases with different efficacies, thereby enabling their enrichment and separation [175,176,202]. The organic phase is supplemented with lipophilic extractants that bind to metal ions with different affinities and transfer them to the organic phase, enabling their separation [175]. A schematic illustration of a typical laboratory-scale solvent extraction procedure exemplary for lithium is shown in Fig. 2 [203,204].

As shown in Fig. 2, this process ultimately leads to enrichments of the organic phase with lithium, leaving higher quantities of non-targeted metal ions in the aqueous phase. Back extraction of the organic phase, typically with acidic solutions, can transfer this ion back to water. This step is called stripping, and enables the isolation of the pure metal salt from the organic components of the extraction process [205–207].

Although most extractions use ligands or extractants within the organic phase, it is also possible to add these reagents to the aqueous phase, allowing further optimization of the separation. For example, the TALSPEAK (Trivalent Actinide–Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes) process uses a phosphorus-based extractant called D2EHPA (bis(2-ethylhexyl)phosphoric acid) in the organic phase 1,4-di-*iso*propylbenzene and the multidentate chelator diethylenetriamine-*N*,*N*,*N*’,*N*“,*N*”-pentaacetic acid (DTPA) within the aqueous lactate buffer. This process is recognized for its efficacy in separating rare earth elements from actinides, and demonstrates how modifications to the aqueous phase with appropriate chelators can be a promising strategy [174,208–212].

The success and efficacy of a solvent extraction process can be quantified by the extraction efficiency (*EE*). The *EE* is defined as the percentage of metal ions that partition into the organic phase, and it is

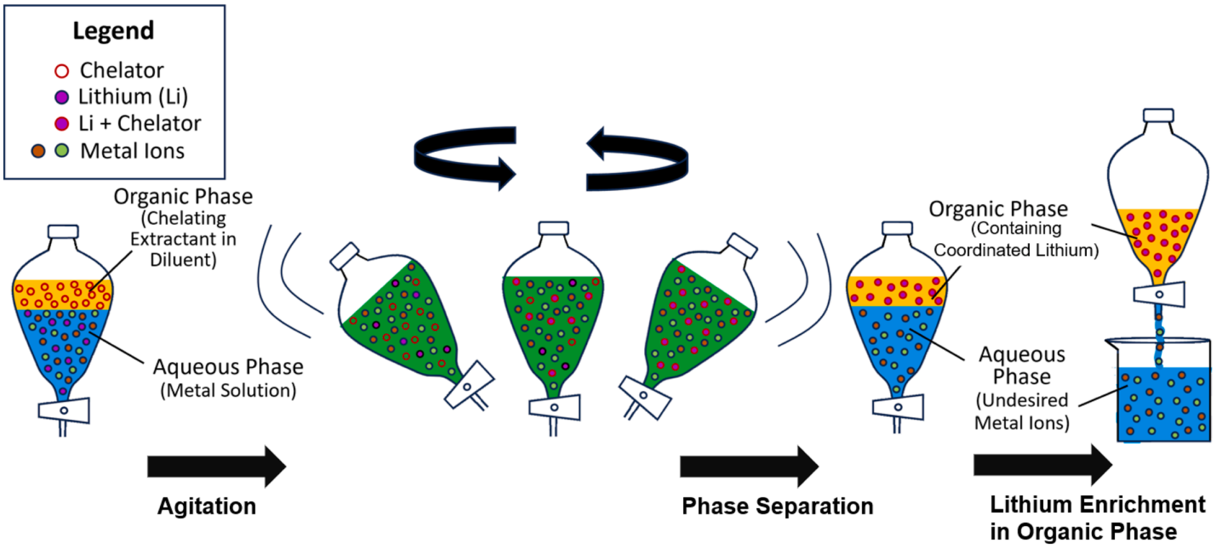


Fig. 2. Schematic illustration of a solvent extraction procedure exemplary for lithium extraction typically used in a laboratory-scale experiment. Redrawn from Ref. [204].

determined from the concentration of the metal in the aqueous phase after the extraction. The equation for calculating the *EE* is shown below, where c_0 is the initial metal concentration and c_1 is the metal concentration at equilibrium in the aqueous phase.

$$EE = \frac{c_0 - c_1}{c_0} \cdot 100\% \tag{1}$$

The amount of a given metal ion in mols within each phase can be described with the distribution coefficient D_C, which is expressed with the following equation:

$$D_C = \frac{c_0 - c_1}{c_0} \cdot \frac{V(aq)}{V(org)} \tag{2}$$

The values $V(aq)$ and $V(org)$ describe the volumes of the aqueous and organic phases, respectively. Larger D_C values signify a greater efficiency in transferring the metal ions to the organic phase.

The separation factor, $\beta_{M_1M_2}$, between two metal ions, M_1 and M_2, is another critical parameter that quantifies the efficiency of a solvent extraction process [174,175,207]. The ratio between the distribution coefficients of M_1 and M_2 determines this factor [207]. The distribution coefficient refers to the ratio of concentrations of M_1 and M_2 in the two immiscible solvents in contact with one another. It is expressed by the following equation:

$$\beta_{M_1M_2} = \frac{D_{M_1}}{D_{M_2}} \tag{3}$$

Thus, the selectivity between lithium and another metal can be described by dividing the distribution coefficients of both metals by using the following equation:

$$Selectivity = \frac{D_{C,\ Li^+}}{D_{C,\ M^+}} \tag{4}$$

Within the literature, the selectivity between two metals has been determined via different methods. For example, selectivities have been reported based on the extraction efficiencies of both metals. However, some of these efficiencies were obtained from distribution coefficients for pure metal solutions, whereas other experiments used values determined from the extraction of aqueous mixtures of metal ions. Although elemental measurement techniques, like graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), are the most common methods employed to quantify metal distributions, researchers have also used alternative techniques like NMR spectroscopy. For these reasons, the tables in this review contain information about the conditions and techniques used for the different extraction studies, and a direct comparison of values needs to take these experimental factors into consideration.

The major advantage of solvent extraction over other metal separation techniques is its high capacity and scalability which has made it the method of choice for industrial-scale operations [208,213,214]. On these large scales, the choice of solvent for the organic phase is an important consideration, given the different costs and environmental hazards associated with them. Historically, kerosene has been the most widely used solvent for the solvent extraction separation of lithium. However, the flammability and other hazards associated with kerosene have motivated researchers to explore alternative organic phases [215–219]. Thus, ionic liquids, supercritical fluids, and liquid polymers have all been investigated as safer and more sustainable alternatives [220,221].

Despite these advantages, industrial separations of lithium using this method are rare. Among the few notable examples is the solvent extraction technique from Solvay called "CYANEX® 936P," as well as the continuous process technology "LiSX™" based on pulsed columns from the company Tenova Advanced Technology (TAT) [222–225]. The technique from Solvay uses CYANEX® 936P, a proprietary organophosphorus extractant that exhibits high selectivity for lithium, to extract lithium from salar brine [224]. This extractant selectively forms a complex with lithium, enabling its extraction into the organic phase [224,225]. The LiSX™ technology from TAT uses pulsed columns, which increase the extraction efficiency compared to conventional columns [226]. As a result, the LiSX™ extraction technology offers the distinct advantages of being a multistage continuous extraction process in a single vessel that contains no internal moving parts, is fully automated, and has low maintenance and operation costs. Moreover, LiSX™ is reportedly safe and environmentally friendly [222]. In the LiSX™ process, CYANEX® 936P is used as the extractant for lithium extraction [224]. An additional solvent extraction method for lithium separation was developed by the company Adionics™ [227–229]. This method uses an organic solvent called Flionex®. Flionex contains extractants with high affinity for lithium ions, enabling high extraction efficiencies and high purity of the isolated lithium from brine. This extraction method can produce up to 250 t of lithium chloride per year [227,229,230].

Another effective solvent extraction process for lithium separation uses the organophosphorus extractant TBP, in conjunction with iron(III) chloride as a co-extraction agent. The iron(III) chloride balances the charge in the extraction process and simultaneously facilitates the formation of $LiFeCl_4$ in high chloride-containing brines. In particular, two extractant molecules of TBP and lithium form a complex, which is then be transferred into the organic phase [231–234]. These reagents can be used in different organic phases, including kerosene, Shellsol™, and ionic liquids to enrich lithium from the initial metal ion mixtures [219,221,235–241]. Although neutral organophosphorus compounds like TBP bind with high affinity and selectivity to lithium, in combination with HCl as stripping agent, they can be caustic to industrial equipment, representing a problem for large-scale applications [205,240,242]. Furthermore, at high concentrations, TBP can partition into the aqueous phase to form a third phase, leading to poor extraction efficiencies under these conditions [232,237,239,243,244]. Although these limitations are apparent, they can be potentially circumvented with several different strategies. For example, the third phase can be removed by adding different organic solvents like methyl isobutyl ketone, butyl acetate, ethyl acetate, or 2-octanol and can be used to accelerate the separation of the aqueous and organic phases [239,240,245,246]. Thus, these modifications can potentially optimize the process and make it viable for industrial applications.

A common theme within the examples above is that they all employ chelating agents to drive the metal ion selectivity to achieve separations. Thus, these chelators must be designed to have high selectivity and affinity for the metal ion of interest. Below, we summarize the ligands and chelators that have been used specifically for the solvent extraction of lithium. These compounds are classified based on their structures and types of donor atoms. The underlying coordination chemistry principles that dictate their applicability for lithium separation are also discussed. In describing the systems below, we use the term “laboratory scale” to denote solvent extractions carried out on a small scale (mL to L, or mg to g of solid) that use synthetic lithium-containing solutions. In some cases, extraction experiments were carried out using authentic samples of brine, seawater, or other industrially relevant aqueous solutions on larger scales, involving L and g of materials. We refer to these systems as being carried out under “realistic conditions,” as they match those expected to be present in the industrial setting. This terminology is used throughout the rest of this article to describe various solvent extraction ligands and approaches.

3.2. Chelator design for lithium coordination

A key requisite to developing effective solvent extraction lithium separations is a chelator with high selectivity for this ion that can partition into either phase. The design of such chelators must consider the chemical properties of lithium, such as the Pearson HSAB properties and ionic radius, which were summarized above in Section 2. An important parameter for describing the thermodynamic stability of metal complexes is the stability constant K_{ML}. The stability constant K_{ML} is a reflection of the direction and magnitude of the metal-binding reaction and is expressed with the following equation, where the concentration values represent those at equilibrium and charges of both the metal ion and ligand are omitted for clarity:

$$[M] + [L] \underset{dissociation}{\overset{complexation}{\rightleftharpoons}} [ML] \tag{5}$$

$$K_{ML} = \frac{[ML]}{[M]\cdot[L]} \tag{6}$$

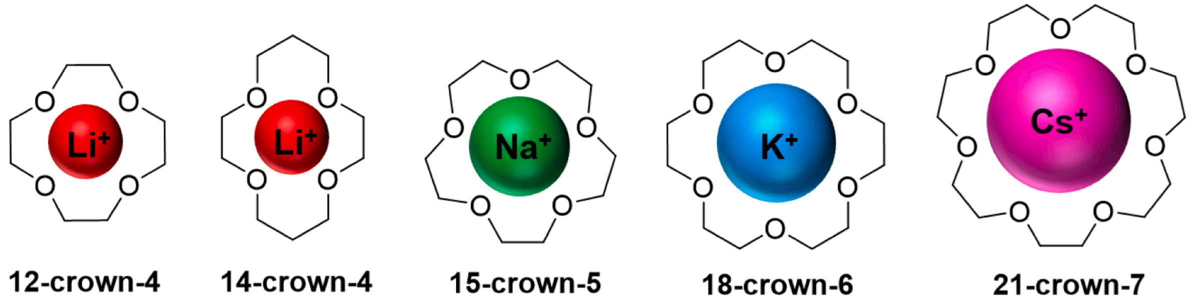
The stability constant K_{ML} describes the overall efficacy of a chelator for binding a particular metal ion [193]. Importantly, comparing stability constants for ligands and different metal ions can be used to assess selectivity, a property that is critical for applying them in chemical separations. Because stability constants can span orders of magnitude, they are more commonly expressed and compared on a logarithmic scale. For example, for lithium, the log K_{ML} values for various complexes range from 1 to 8. The magnitude of the log K_{ML} values is dictated by the factors discussed above, including ionic interactions and HSAB properties, between the metal ion and ligand donor atoms. In addition, within larger multidentate ligands the chelate and macrocyclic effects also play a critical role in the resulting complex stability. The chelate effect describes the enhancement of metal–ligand complex stability attained when using ligands with more than one donor atom compared to their monodentate analogs. The enhanced thermodynamic affinity of ethylenediamine for metal ions, compared to two monodentate methylamine ligands, is an example of the chelate effect. This effect is a consequence of enhanced entropic favorability. Similarly, the macrocyclic effect applies to cyclic chelators, comprising nine or more atoms with at least three of them being Lewis basic donor atoms. The macrocyclic effect describes the enhancement of thermodynamic stability of macrocyclic ligands to analogous acyclic and open-chain ligands [193,247–250]. In this context, chelator design for lithium extraction has focused largely on optimizing these two effects, to form stable complexes that can give rise to high extraction efficiencies. Thus, major factors like macrocycle size, topology, rigidity, and the numbers and type of donor atoms, are all important parameters to optimize for lithium chelators [251]. The following sections present an overview of chelators applied for lithium solvent extraction schemes. These ligands are classified based on their structure types (acyclic and cyclic) and their donor heteroatoms. In addition to the discussion provided below, a more concise review on lithium chelators for extraction applications was recently published, and readers are encouraged to consult this resource as well [252].

3.3. Oxygen-based chelators

Cyclic polyethers, more commonly known as crown ethers, have been thoroughly investigated for their metal-binding properties since they were first reported in 1967 by Charles J. Pedersen [253–255]. Notably, the first crown ether reported was the macrocycle dibenzo-18-crown-6 (DB18C6), which was synthesized unintentionally [253,254]. Since then, many crown ethers with different macrocycle sizes and donor atoms have been designed to optimize their complexation properties with different metal ions [254,256–258]. The significance of these crown ether ligands is reflected by the fact that Pedersen, along with Jean Marie Lehn and Donald Cram, was awarded the Nobel Prize in Chemistry in 1987 for contributions to supramolecular and host–guest chemistry [259,260].

Crown ethers are defined as cyclic oligomers of ethylene oxide $[–CH_2–CH_2O–]_n$ with $n \geq 4$. The oxygen atoms within these macrocycles act as donor atoms to Lewis acidic metal ions, mostly via conventional electrostatic and ion–dipole interactions [182,257,261,262]. An important property of simple crown ethers is that the macrocycle size can lead to selectivity for different metal ions. Scheme 1 shows the different-sized macrocyclic crown ethers, 12-crown-4, 14-crown-4, 15-crown-5, 18-crown-6, and 21-crown-7, as well as the alkali metal ions with which they form the most stable complexes. As this example highlights, modifications to the macrocycle size can significantly affect the resulting metal-binding properties and selectivities of the crown ethers [251]. The thermodynamic factors that influence the selectivity of these crown ethers is a combination of solvation, enthalpy, and entropy, as it pertains to the chelator and metal ions [263]. In general, however, crown ethers form highly stable complexes with ions that have ionic radii which are comparable to that of their cavity sizes [264,265]. Table 6, which gives the diameters of the cations and the crown ether cavity sizes determined via space-filling models, clearly shows this trend [266]. With respect to lithium, 12-crown-4 and 14-crown-4 yield the preferred macrocycle size to selectively bind this ion over the other alkali metals.

The manner by which crown ethers interact with metal ions can vary significantly depending on both the nature of the metal ion, as well as the size of the macrocycle. For example, the stoichiometric ratios of metal ion to ligand of the resulting complexes can be 1:1, 2:1, and 1:2 for



Scheme 1. A selection of the most prominent crown ethers and their preferred metal ions.

Table 6
Overview of Several Crown Ethers Including their Hole Diameter, their Preferred Metal Ions and their Ionic Diameter.

Cations	Ion Diameter [62][a]	Crown Ether	Hole Diameter of Crown Ether [266]
Li^+	1.52 Å	14-crown-4	1.20[b]–1.50 Å[c]
Na^+	2.04 Å	15-crown-5	1.70[b]–2.20 Å[c]
Ca^{2+}	2.00 Å		
K^+	2.76 Å	18-crown-6	2.60[b]–3.20 Å[c]
Ba^{2+}	2.70 Å		
NH_4^+	2.92 Å		
Rb^+	3.04 Å		
Cs^+	3.34 Å	21-crown-7	3.40[b]–4.30 Å[c]

[a] The ionic diameters were calculated based on the reported effective ionic radii for the coordination number six (excluding NH_4^+) [62].

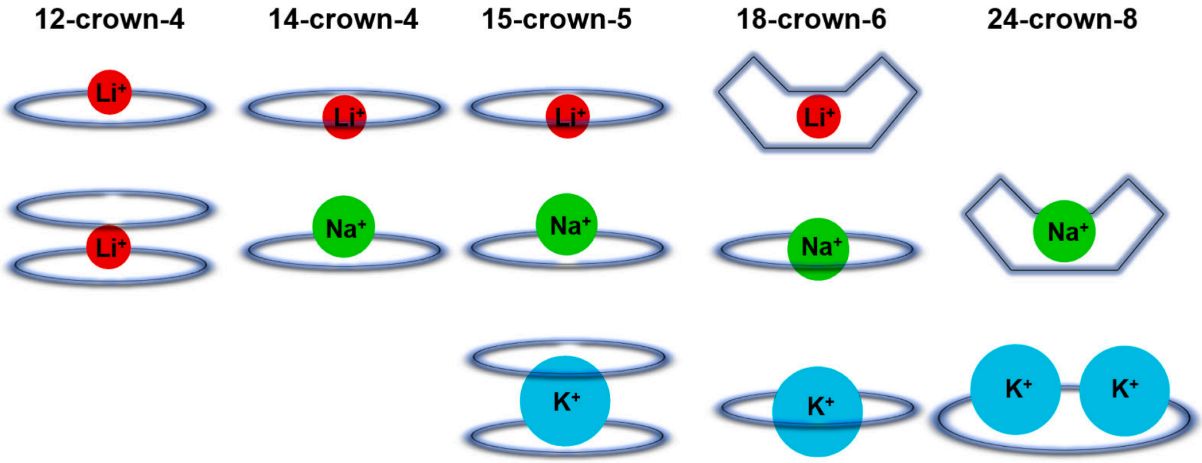
[b] Determination according to Corey-Pauling-Koltun atomic models.

[c] Determination according to Fisher-Hirschfelder-Taylor atomic models [266].

lithium, sodium, and potassium with the crown ethers shown in Scheme 2. Notably, for other crown ether and metal ion combinations even more complex stoichiometries, like 2:3, can be obtained [257]. In addition to forming complexes with different metal-to-ligand ratios, crown ethers also bind to metal ions in distinct ways, as shown in Scheme 2. For example, sodium sits on top of the 15–crown-5 ether, but is fully encapsulated by the larger 18-crown-6. The larger macrocycle 24-crown-8 is poorly matched to sodium, and therefore undergoes a significant conformational distortion in order to interact with this ion. With the larger potassium ion, different structures are formed [177,256,257,262,265,267].

Table 7 shows the stability constants of crown ethers for different alkali metal ions. These data are particularly informative with respect to understanding good choices for lithium. The smaller crown ethers like 12-crown-4 or 14-crown-4 have a higher affinity for this metal ion over the other larger alkali metal ions. This result was confirmed by Bartsch and colleagues in 1985 [275]. Furthermore, compared to 12-crown–4, 13-crown-4, and 15-crown–5 ethers 14-crown-4 shows the highest selectivity for lithium [275]. The selectivity of 14–crown–4 derivatives for lithium ions was probed by density functional theory (DFT) calculations, which suggest that this selectivity arises from the optimal geometry of 14-crown–4 for binding this ion [276–278]. Upon interacting with lithium, 14-crown-4 ethers only undergo a minimal conformational change, and the resulting Li–O interatomic distances are in the range of average Li–O interatomic distances between 2.08 and 2.28 Å [182,276,277].

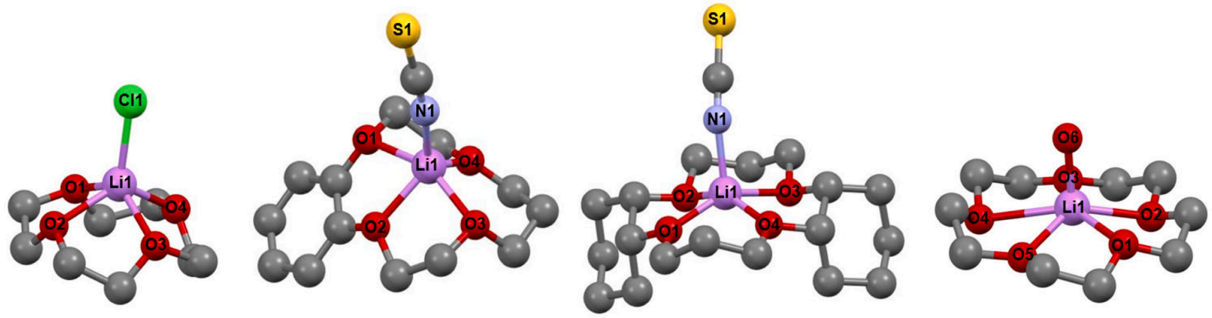
Apart from theoretical calculations, X-ray crystal structures of lithium crown ether complexes also demonstrate the suitable size-match and preference of small crown ethers like 14-crown-4 for lithium. Fig. 3 shows the crystal structures of 1:1 complexes of lithium and different crown ethers, and Li–O distances are reported in Table 8. These crystal structures show that the lithium ion attains a five-coordinate geometry, requiring the presence of an additional monodentate ligand like solvent molecules or counterions. The complexes of 12-crown-4 and 13-crown-4 ethers with lithium are five-coordinate, attaining geometries that are intermediate between square pyramidal and trigonal bipyramidal [279,280]. The Li–O interatomic distances for both crown ether complexes for 12-crown-4 and 13–crown–4 are 2.128 and 2.012–2.163 Å, respectively. These values are comparable to those found in square-pyramidal and trigonal bipyramidal complexes of lithium, where the average Li–O distances are 2.03 and 2.10 Å, respectively [182]. In contrast to the structures of the 14–crown-4 ether complexes, the 12-crown-4 and 13-crown-4 ether complexes show the lithium ion sitting above the plane of the macrocycle. This observation highlights the mismatch in size between the macrocyclic core and lithium ion within these complexes, leading to the observed convex geometry where the



Scheme 2. Oxygen-based crown ethers (labeled as blue rings) and different metal complexes with cationic metal ions like lithium (red), sodium (green) and potassium (light blue). Redrawn from Ref. [262].

Table 7
A Selection of Prominent Crown Ethers and their Stability Constants with Alkali Metal Ions.

Crown Ether	Solvent	Method/Conditions	Stability Constant log K_{ML}					Ref.
			Li^+	Na^+	K^+	Rb^+	Cs^+	
12-crown-4	MeCN	determination of stability constant in MeCN at 25 °C via titration microcalorimetry (anion: BF_4^-)	3.46					[268]
	MeOH	determination of stability constant in MeOH at 25 °C via conductometric titration (anion: Cl^-)	2.73					[269]
	d_3-MeCN	NMR, 25 °C, salt: $LiClO_4$	3.25					[270]
	MeOH	determination of stability constant in MeOH at 25 °C via calorimetric titration (anions: Cl^- for Li^+ and SCN^- for Na^+)	2.14	2.66				[271]
	MeOH	determination of stability constant in MeOH at 25 °C via potentiometric titration (anion: Cl^-)		1.70	1.74			[263]
14-crown-4	MeOH	determination of stability constant in MeOH at 25 °C via calorimetric titration (anions: Cl^- for Li^+ and SCN^- for Na^+)	2.34	1.63				[271]
15-crown-5	d_3-MeCN	NMR, 25 °C, salt: $LiClO_4$	4.73					[270]
	MeCN	determination of stability constant in MeCN at 25 °C via calorimetric titration (anion: BF_4^-)		4.91	4.33	3.98	3.11	[272]
	MeCN	determination of stability constant in MeCN at 25 °C via calorimetric titration (anion: BF_4^-)	4.44					
	$MeOH/H_2O$ 7:3	determination of stability constant in $MeOH/H_2O$ at 25 °C via conductometric titration (anion: Cl^-)	1.02	2.32	2.79	2.81	2.49	[273]
	MeOH	determination of stability constant in MeOH at 25 °C via conductometric titration (anion: Cl^-)	1.21	3.38	2.88	2.78		[273]
	MeOH	determination of stability constant in MeOH at 25 °C via calorimetric titration (anions: Cl^- for Li^+ and SCN^- for Na^+)	1.85	1.80				[271]
	MeOH	determination of stability constant in MeOH at 25 °C via potentiometric titration (anion: Cl^-)		3.24	3.43			[263]
18-crown-6	MeOH	determination of stability constant in MeOH at 25 °C via conductometric titration		4.42	>5.5	5.35	4.37	[269]
	MeCN	determination of stability constant in MeCN at 25 °C via potentiometric titration (anion: BPh_4^-)		4.71	5.72	5.24	5.07	[272]
	d_3-MeCN	NMR, 25 °C, salt: $LiClO_4$	3.07					[270]
	MeOH	determination of stability constant in MeOH at 25 °C via potentiometric titration (anion: Cl^-)		4.32	6.10	4.62		[274]
	MeOH	determination of stability constant in MeOH at 25 °C via potentiometric titration (anion: Cl^-)		4.35	6.08			[263]
21-crown-7	MeOH	determination of stability constant in MeOH at 25 °C via potentiometric titration (anion: Cl^-)			4.41	5.02		[274]
	MeOH	determination of stability constant in MeOH at 25 °C via potentiometric titration (anion: Cl^-)		2.54	4.35			[263]



[Li(12-crown-4)Cl]　[Li(13-crown-4)SCN]　[Li(14-crown-4)SCN]　[Li(15-crown-5)H_2O]$^+$

Fig. 3. Crystal structures of various lithium crown ether complexes [279,280,283,284]. The hydrogen atoms are omitted for clarity. Purple: Li, gray: C, blue: N, red: O, yellow: S, green: Cl.

Table 8
Overview of different Lithium Crown Ether Complexes and their Li–O Interatomic Distances.

	Li–O Interatomic Distances (Å)					
	Li–O (1)	Li–O (2)	Li–O (3)	Li–O (4)	Li–O (5)	Ref.
[Li(12-crown-4)Cl]	2.128	2.128	2.128	2.128	–	[279]
[Li(13-crown-4)SCN]	2.163	2.059	2.032	2.012	–	[280]
[Li(14-crown-4)SCN]	1.958	2.074	1.958	2.074	–	[283]
[Li(15-crown-5)H_2O]$^+$	2.267	2.164	2.174	2.542	2.166	[284]

lithium sits on top of the crown ether [279,280]. The smaller 12-crown-4 ethers still may have applications for binding to smaller metal ions like beryllium(II), as suggested by theoretical studies [281,282]. As the structural and binding constant data above support, the 14-crown-4 ether has a high affinity and selectivity for lithium. Thus, this macrocycle is often used as the starting point for developing new chelators for this ion.

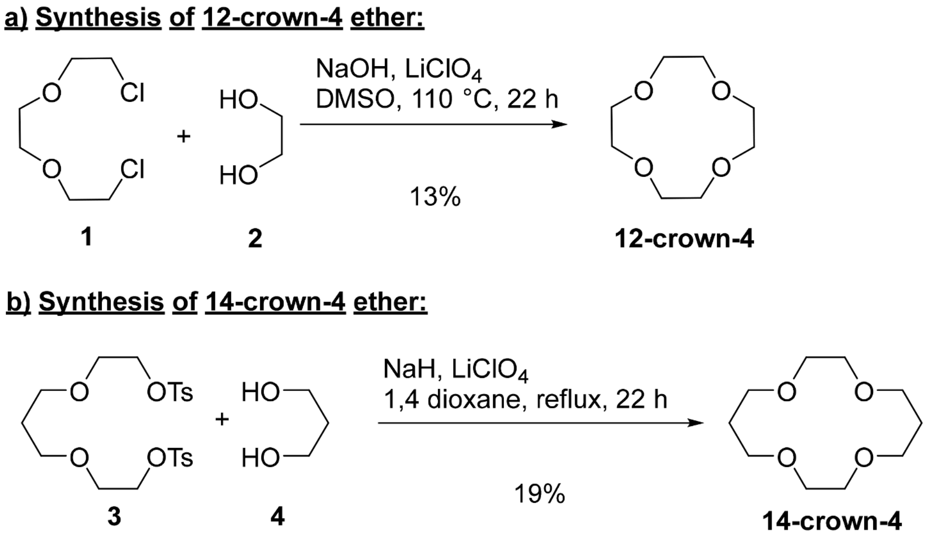
The syntheses of the unsubstituted 12-crown-4 and 14-crown-4 ethers follow the reactions shown in Scheme 3 [285–287]. These procedures use the Williamson etherification reaction, which can be employed with various leaving groups like mesylates, tosylates, chlorides, bromides, and iodides. Consistent with the known high affinity of these chelators for lithium, this ion is used as a template under high dilution conditions to facilitate their formation in good yields and minimize the generation of polymeric byproducts [258,288–290]. Even under these optimized conditions, typical yields for 12–crown–4 and 14-crown-4 ethers are low (13–19 %) [285,286]. Thus, the low yields and need for large solvent volumes to attain high dilution conditions must be considered if these ligands are to be used for industrial-scale applications.

Building upon the good lithium selectivity of 14-crown-4 ethers, various researchers have sought to further improve this ligand class for lithium chelation applications [168,251,262,271,275,291–294]. For example, the 14-crown-4 ether analogs **5**–**8** shown in Scheme 4 exhibit Li^+:Na^+ selectivities of up to 240 [275,294]. Although these compounds' Li^+:Na^+ selectivities — a critical property for successful seawater or brine extractants — were not assessed, they warrant further studies for these applications.

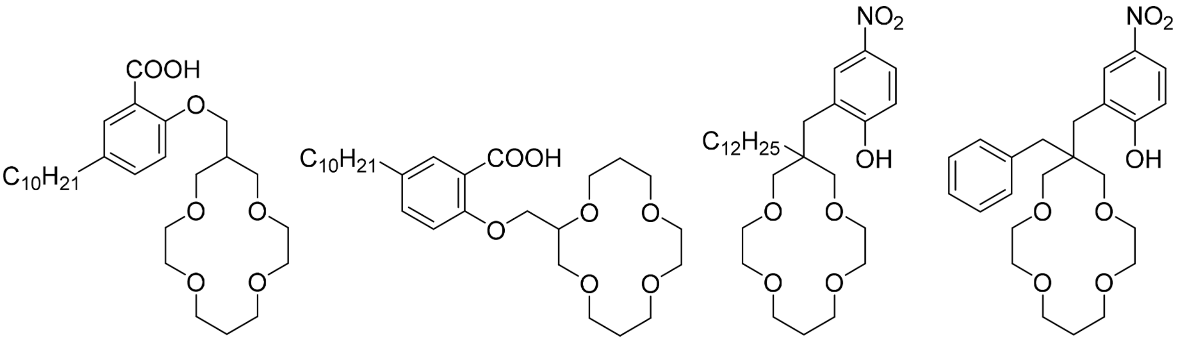
In addition to the examples shown in Scheme 4, other modifications of 12-crown-4 and 14–crown-4 ethers have been applied in order to develop new systems for lithium complexation and solvent extraction. The addition of sidearms to the crown ethers has been extensively used as a strategy to finetune their chemical properties. Moreover, the modification of these sidearms provides a means of further conjugating them to large molecules, polymers, or solid-state materials to improve their functionality. These modifications can also favorably alter their lithium ion affinity.

3.3.1. 12-Crown-4 ethers

The series of 12-crown-4 ethers bearing different R groups on the macrocycle and with the incorporation of aromatic benzene groups, shown in Scheme 5, were evaluated for their lithium ion affinity and



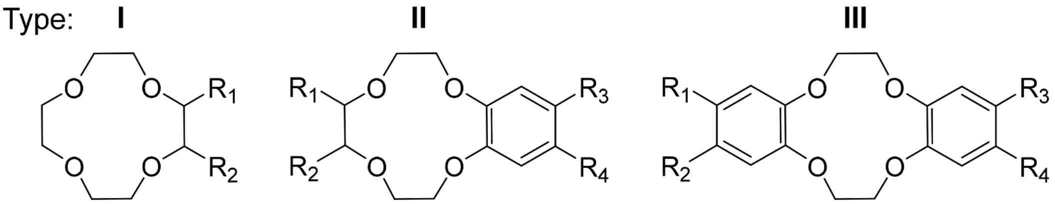
Scheme 3. a) A template-based one-pot synthesis of 12-crown-4 and b) 14-crown-4 ethers [285–287].



5 6 7 8

Li^+:Na^+ selectivity: 19[a] **20[b]** **240[b]** **200[b]**

Scheme 4. Selected 14-crown-4 ether derivatives with high selectivity for lithium ions [275,294]. [a]Value was determined in an aqueous phase with pH = 10–11 and chloroform as an organic phase. [b]Value was determined in a basic aqueous solution containing tetramethylammonium hydroxide and [tris(hydroxymethyl)methylamino]propanesulfonic acid at pH = 12, the metal chloride, and 1,2–dichloroethane as the organic phase. The experiments were performed at 25 °C.

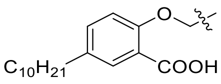
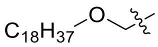
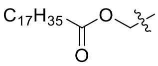
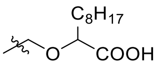


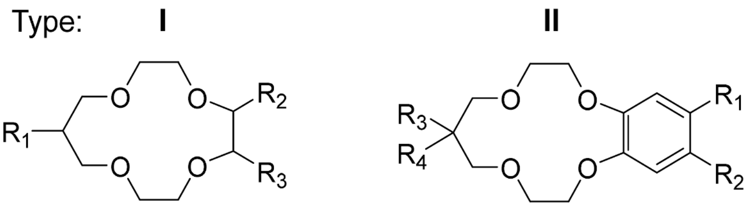
Scheme 5. Different types of 12-crown-4 ethers relevant for lithium complexation.

selectivity (Table 9).

The data within this table show that Li^+:Na^+ selectivities of the 12-crown-4 ethers derivatives containing pendent donor sidearms or alkyl chains within the positions indicated in Scheme 5 are not substantially improved compared to the parent unmodified crown ether. These results indicate that the additional pendent donor sidearm functionalization do not have a significant influence on lithium extraction performance, presumably because of the small ionic radii and low coordination numbers of these ions.

Table 9
12-crown-4 Ether Derivatives Shown in Scheme 5 and their Performance in Lithium Complexation and Separation.

Type	R_1	R_2	R_3	R_4	Solvent	Method/Conditions	log K_{ML}	Selectivity	Ref.
I **9**	H	H	–	–	MeCN	determination of Li^+-stability constant in MeCN at 25 °C via titration microcalorimetry (anion: BF_4^-)	3.46	–	[268]
I **9**	H	H	–	–	H_2O, CH_2Cl_2	solvent extraction with ligand in CH_2Cl_2 (30 mM) and aqueous metal picrates (3 mM) at 25 °C and detection via UV/Vis *EE*: Li^+: 3 % *EE*: Na^+: 14 %	–	Li^+:Na^+: 0.16	[295]
I **9**	H	H	–	–	d_3-MeCN	determination of Li^+-stability constant in d_3-MeCN at 25 °C via NMR (salt: $LiClO_4$)	3.25	–	[270]
I **10**		H	–	–	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (50 mM) and aqueous metal chloride (250 mM) at pH = 10–11 and detection via ion chromatography *EE*: Li^+: 85 %	–	Li^+:Na^+: 1.7	[275]
I **11**		H	H	–	–	ion selectivity determined by ion-selective electrodes with polyvinyl chloride matrix	–	Li^+:Na^+: low	[287]
I **12**		H	H	H	–	ion selectivity determined by ion-selective electrodes with polyvinyl chloride matrix	–	Li^+:Na^+: low	[287]
II **13**		H	H	H	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (50 mM) and aqueous metal chloride (250 mM) at pH = 10–11 and detection via ion chromatography *EE*: Li^+: 85 %	–	Li^+:Na^+: 1.8	[275]
II **14**	H	H	H	H	H_2O, CH_2Cl_2	solvent extraction with ligand in CH_2Cl_2 (30 mM) and aqueous metal picrates (3 mM) at 25 °C and detection via UV/Vis *EE*: Li^+: <1 % *EE*: Na^+: 2 %	–	Li^+:Na^+: 0.08	[295]
II **14**	H	H	H	H	H_2O, $CHCl_3$	solvent extraction with ligand in $CHCl_3$ (2.50 mM) and aqueous LiCl (2 M) at 22 °C and detection via UV/Vis *EE*: Li^+: high	–	–	[296]
III **15**	H	H	H	H	H_2O, $CHCl_3$	solvent extraction with ligand in $CHCl_3$ (2.50 mM) and aqueous LiCl (2 M) at 22 °C and detection via UV/Vis *EE*: Li^+: high	–	–	[296]



Scheme 6. Different types of 13-crown-4 ethers for lithium complexation.

3.3.2. 13-Crown-4 ethers

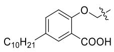
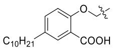
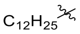
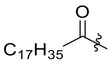
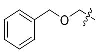
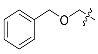
Researchers have also applied similar structural modification to the core of 13-crown-4 in an attempt to improve lithium-binding affinity and selectivity. These macrocycles are shown in Scheme 6, and Table 10 contains the relevant data regarding their performance as potential lithium extraction agents. Thus far, these 13-crown-4 ether analogs have only been evaluated for lithium-binding and extraction on a laboratory scale by using synthetic solutions containing lithium salts under basic conditions. As indicated in Table 10, however, the extraction efficiency of lithium by some of these analogs can reach values of 85 %. Despite these promising results, this class of macrocycles generally suffers from poor selectivity for lithium ions. Furthermore, the extraction experiments have used simple lithium-containing solutions instead of more complex mixtures expected to be found in lithium sources of interest, thus highlighting that additional experiments are needed to validate this promising macrocycle class.

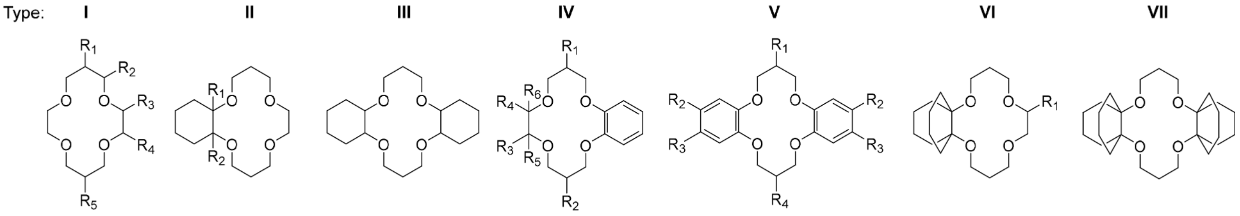
3.3.3. 14-Crown-4 ethers

Because 14-crown-4 is the most selective crown ether for lithium, this scaffold has served as the basis for many new derivatives for lithium extraction and separation purposes. In addition to the examples briefly discussed and shown in Scheme 4, Scheme 7 shows the structures of additional macrocycles of this type, and Table 11 collects relevant data and properties for them. The collected data shows that lithium extraction experiments were mainly performed on small scales by using synthetic solutions and simple laboratory equipment. Extraction experiments using realistic conditions, like seawater or brine solutions, are scarcely reported for this class of crown ethers. As expected for this crown ether type, these derivatives exhibit high Li^+:Na^+ selectivities in some cases exceeding selectivity ratios of 1000 [299]. In addition, they also show good performance for extraction of lithium (Table 11).

In analyzing the data within Table 11, it is apparent that the attachment of lipophilic side groups on 14-crown-4 ethers lead to higher

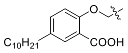
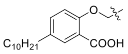
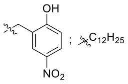
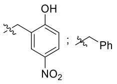
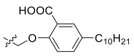
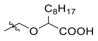
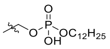
Table 10
13-crown-4 Ether Derivatives Shown in Scheme 6 and their Performance in Lithium Complexation and Separation.

Type	R_1	R_2	R_3	R_4	Solvent	Method/Conditions	Selectivity	Ref.
I 16	H	H	H	–	H_2O, CH_2Cl_2	solvent extraction with ligand in CH_2Cl_2 (30 mM) and aqueous metal picrates (3 mM) at 25 °C and detection via UV/Vis *EE*: Li^+: 1 % *EE*: Na^+: 4 %	Li^+:Na^+: 0.20	[295]
I 17	H		H	–	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (50 mM) and aqueous metal chloride (250 mM) at pH = 10–11 and detection via ion chromatography *EE*: Li^+: 85 %	Li^+:Na^+: 2.3	[275]
I 18		H	H	–	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (50 mM) and aqueous metal chloride (250 mM) at pH = 10–11 and detection via ion chromatography *EE*: Li^+: 85 %	Li^+:Na^+: 2.5	[275]
I 19		H	H	H	–	ion selectivity determined by ion-selective electrodes with polyvinyl chloride matrix	Li^+:Na^+: low	[287]
II 20	H	H	H	H	–	ion selectivity determined by ion-selective electrodes with polyvinyl chloride matrix	Li^+:Na^+: low	[287]
II 20	H	H	H	H	H_2O, $CHCl_3$	solvent extraction with ligand in $CHCl_3$ (15 mM) and LiOH (15 mM) at 25 °C and detection via AAS *EE*: Li^+: 1 %	–	[297]
II 21		H	H	H	–	ion selectivity determined by ion-selective electrodes with polyvinyl chloride matrix	Li^+:Na^+: low	[287]
II 22	H	H			$CDCl_3$	solvent extraction with ligand in $CDCl_3$ (150 μM) and aqueous metal picrates (150 mM) at 22–23 °C and detection via UV/Vis	Li^+:Na^+: 3.2	[298]



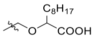
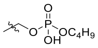
Scheme 7. Different types of 14-crown-4 ethers for lithium complexation.

Table 11
14-crown-4 Ether Derivatives Shown in Scheme 7 and their Performance in Lithium Complexation and Separation.

Type	R_1	R_2	R_3	R_4	R_5/ R_6	Solvent	Method/Conditions	log K_{ML}	Selectivity	Ref.
I 23	H	H	H	H	H	MeOH	determination of Li^+-stability constant in MeOH at 25 °C via calorimetric titration (anions: Cl^- for Li^+ and SCN^- for Na^+)	2.34	–	[271]
I 23	H	H	H	H	H	H_2O, CH_2Cl_2	solvent extraction with ligand in CH_2Cl_2 (30 mM) and aqueous metal picrates (3 mM) at 25 °C and detection via UV/Vis *EE*: Li^+: 14 % *EE*: Na^+: 1 %	–	Li^+:Na^+: 16.3	[295]
I 24		H	H	H	H	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (50 mM) and aqueous metal chloride (250 mM) at pH = 10–11 and detection via ion chromatography *EE*: Li^+: 85 %	–	Li^+:Na^+: 19	[275]
I 25	H	H		H	H	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (50 mM) and aqueous metal chloride (250 mM) at pH = 10–11 and detection via ion chromatography *EE*: Li^+: 85 %	–	Li^+:Na^+: 20	[275]
I 26		H	H	H	H	H_2O, 1,2-dichloro-ethane	solvent extraction with ligand in 1,2-dichloroethane and aqueous metal chloride at pH = 12 and 25 °C and detection via UV/Vis	–	Li^+:Na^+: 240	[294]
I 27		H	H	H	H	H_2O, 1,2-dichloro-ethane	solvent extraction with ligand in 1,2-dichloroethane and aqueous metal chloride at pH = 12 and 25 °C and detection via UV/Vis	–	Li^+:Na^+: 200	[294]
I 28		H	H	H		H_2O, $CDCl_3$	solvent extraction with ligand in $CDCl_3$ (150 μM) and aqueous metal picrates (150 mM) at 22–23 °C and detection via UV/Vis	–	Li^+:Na^+: 41	[298]
I 29		H	H	H	H	H_2O, $CHCl_3$	solvent extraction with ligand in $CHCl_3$ and aqueous metal ions and detection via UV/Vis	–	Li^+:Na^+: 19	[300]
II 30	Ad[a]	Ad[a]	–	–	–	H_2O, CH_2Cl_2	solvent extraction with ligand in CH_2Cl_2 (700 μM) and aqueous metal picrates (100 mM) at 25 °C and detection via UV/Vis *cis* isomer: EE: Li^+: 38.9 %	–	Li^+:Na^+: 32	[301]
III 31	–	–	–	–	–	H_2O, 1-octanol	solvent extraction with ligand in 1-octanol (20 mM) and aqueous metal chloride/nitrate (400 mM) at 25 °C and stripping of extracted lithium from organic phase with H_2O and detection via ion chromatography *cis*-syn-*cis* isomer *EE*: Li^+: 21 % *cis*-anti-*cis* isomer *EE*: Li^+: 0.6 %	–	–	[302]
IV 32	H	H	H	 H	H	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (50 mM) and aqueous metal chloride (250 mM) at pH = 10–11 and detection via ion chromatography *EE*: Li^+: 85 %	–	Li^+:Na^+: 4.7	[275]
IV 33	OH	OH	Me	Me	Me Me	H_2O, CH_2Cl_2	solvent extraction with ligand in CH_2Cl_2 and aqueous LiCl (6.60 mM) at rt and detection via ICP-OES *EE*: Li^+: 4 % *EE*: Mg^{2+}: 9 %	–	–	[278]
IV 34	OH	OH	Me	Me	Me Me	H_2O, CH_2Cl_2	competitive solvent extraction with ligand in CH_2Cl_2 and aqueous LiCl (6.70 mM) and $MgCl_2$ (3.14 mM) at rt and detection via ICP-OES EE: Li^+: 4 % EE: Mg^{2+}: 9 %	–	Li^+:Na^+: low	[278]
IV 35	H	H		H	H H	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (1 mM) and aqueous MOH (10 mM) and stripping of extracted lithium from organic phase with HCl (1 M) and detection via AAS *EE*: Li^+: 40.7 %	–	Li^+:Na^+: 3.4 Li^+:K^+: 5.3	[303]

(*continued on next page*)

Table 11 (*continued*)

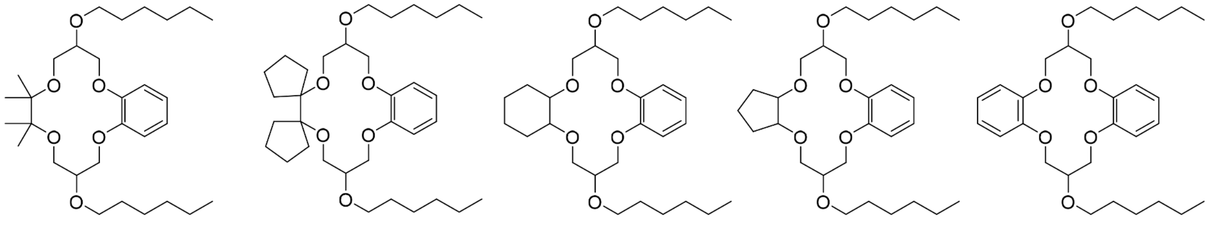
Type	R_1	R_2	R_3	R_4	R_5/ R_6	Solvent	Method/Conditions	log K_{ML}	Selectivity	Ref.
							EE: Na^+: 12.1 % *EE*: K^+: 7.7 %			
V **36**		H	H	H	–	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (50 mM) and aqueous metal chloride (250 mM) at pH = 10–11 and detection via ion chromatography *EE*: Li^+: 85 %	–	Li^+:Na^+: 0.6	[275]
V **37**	H	H	H	H	–	H_2O, CH_2Cl_2	competitive solvent extraction with ligand in CH_2Cl_2 (10 mM) and aqueous metal perchlorate (1 mM) at 27 °C and detection via ICP-MS	–	Li^+:Na^+: 125 Li^+:K^+: 312 Li^+:Cs^+: 505	[304]
V **38**		H	H	H	–	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (10 mM) and aqueous MOH (10 mM) at 25 °C and subsequent stripping of extracted lithium from organic phase with HCl (1 M) and detection via AAS *EE*: Li^+: 26.6 % *EE*: Na^+: 4.9 % *EE*: K^+: 2.9 %	–	Li^+:Na^+: 5.4 Li^+:K^+: 9.1	[305,306]
VI **39**	H	–	–	–	–	H_2O, CH_2Cl_2	solvent extraction with ligand in CH_2Cl_2 (700 μM), aqueous metal hydroxide (100 mM), and picric acid (70 μM) at 25 °C and detection via UV/Vis *EE*: Li^+: 81 % *EE*: Na^+: 5 % *EE*: K^+: 1 % *EE*: Rb^+: 1 % *EE*: Cs^+: 0 %	–	–	[307]
VI **40**	$–C_{14}H_{29}$	–	–	–	–	–	ion selectivity determined by ion-selective electrodes with polyvinyl chloride matrix	–	Li^+:Na^+: 1000	[299]
VII **41**	–	–	–	–	–	H_2O, CH_2Cl_2	solvent extraction with ligand in CH_2Cl_2 (700 μM), aqueous metal hydroxide (100 mM), and picric acid (70 μM) at 25 °C and detection via UV/Vis *EE*: Li^+: 100 % *EE*: Na^+: <20 %	–	–	[286,307]

[a] Ad: adamantyl.

extraction efficiencies as well as higher Li^+:Na^+ selectivities. The higher extraction efficiency is a consequence of enhanced lipophilicity of the resulting lithium complex that favors its partition into the organic phase. In addition, it is hypothesized that the introduction of bulky and lipophilic substituents into 14-crown-4 ethers reduces and blocks the formation of 2:1 and 3:1 complexes, which can be formed with larger metal ions. As a result, the selectivity of strongly substituted 14-crown-4 ethers are higher than unsubstituted 14-crown-4 ethers [292,301,302,304].

The most promising 14-crown-4 ethers from Table 11 for lithium extraction are the nitrophenol-functionalized crown ethers **26** and **27** (type: I), which showed Li^+:Na^+ selectivities up to 240 [294]. As an additional feature, **26** and **27** can be used as chromogenic agents to spectrophotometrically visualize the lithium complexation due to the optical properties of the nitrophenol group. It should be clarified, however, that the selectivity values were determined by performing extraction of lithium and sodium in separate solutions of the pure metal; thus, the reported selectivity values do not account for direct competition between these two ions in the same solution [294].

In addition, pendent arm functionalized 14-crown-4 ethers with ionizable groups, like alkyl phosphoric acids and others in the examples of **35** (type: IV) and **38** (type: V), have comparatively high lithium extraction efficiencies in competitive solvent extraction experiments under basic conditions that reach up to 40.7 %, leading to Li^+:Na^+ selectivities up to 5.4 [303,305,306]. The good efficacy of these phosphoric acid bearing crown ethers for lithium, may be a consequence of the optimized pK_a of this pendent group that can be easily deprotonated



42 **43** **44** **45** **46**

Scheme 8. Substituted and highly selective 14-crown-4 ethers for lithium complexation [304].

Table 12
Results of the Solvent Extraction Experiments of 14-crown-4 Ethers Shown in Scheme 8 and their Selectivity between Two Metals in Water and Dichloromethane [304].[a]

Compound	Li^+:Na^+ selectivity	Li^+:K^+ selectivity	Li^+:Cs^+ selectivity
42	2519	n.d.[b]	n.d.[b]
43	1768	n.d.[b]	n.d.[b]
44	403	827	1595
45	205	615	810
46	109	611	956

[a] The crown ethers (10 mM) were dissolved in dichloromethane and both metals were dissolved as perchlorate salts (1 mM) in water. Both phases were combined and equilibrated with agitation for 24 h at room temperature. The aqueous phases were evaluated via ICP-MS analysis.

[b] n.d.: not determined.

under the basic conditions used for solvent extraction studies and can provide an additional donor to stabilize lithium [305]. The hydrophobic decalino-functionalized 14-crown-4 ether **39** (type: VI) was analyzed in single solvent extraction experiments with various monovalent metals. In particular, the 14-crown-4 derivative **39** showed promising results with lithium extraction efficiencies up to 81 %. Moreover, the experiments revealed significantly lower extraction efficiencies for larger monovalent metal ions such as sodium, potassium, rubidium, and cesium. A related decalino–functionalized 14-crown-4 ether **40** (type: VI) was also studied for its lithium-binding properties, but not within solvent extraction experiments. An electrode functionalized with **40** was studied via electrochemistry to show a differential current response upon binding lithium versus sodium. In this investigation, Li^+:Na^+ selectivities of up to 1000 were measured, suggesting that **40** is potentially valuable for lithium solvent extraction [299].

The 14-crown-4 ether **41** (type: VII) contains two decalino units, leading to a higher lipophilicity than those of **39** and **40** [286]. For this reason, **41** was more effective than the monofunctionalized analogues **39** and **40** in laboratory-scale lithium extraction experiments, showing nearly quantitative lithium extraction efficiencies. The authors proposed that the decalin-units shield the lithium after coordination to prevent it from being complexed and solvated by water [307].

Another promising class of 14-crown-4 ethers for lithium extraction is shown in Scheme 8. First reported in 2017, these substituted 14-crown-4 ethers were synthesized in high yields by using the lithium ion as a template. These crown ethers contain different carbon ring structures within the macrocycle backbone, which act to rigidify the structure. Furthermore, they also incorporate long alkyl chains to increase their hydrophobicity and to facilitate their distribution into the organic phase [304]. The performance of these ligands was assessed on the laboratory scale via a solvent extraction experiment using dichloromethane as the organic phase. As shown in Table 12, the selectivity of these crown ethers for lithium over other metal ions like sodium are exceedingly high. For instance, 14–crown-4 ether **43** exhibits an impressive Li^+:Na^+ selectivity of 1768, and **42** shows the highest selectivity within this compound class, achieving a value of 2519. To gain an understanding of these large selectivity factors, the authors carried out DFT calculations on truncated models of these crown ethers lacking the long alkyl chains (Fig. 4). These calculations revealed that the cavity sizes of these crown ethers **42** (1.28–1.37 Å) and **43** (1.23–1.38 Å) are most compatible with that of the six-coordinate lithium ion diameter (1.36–1.52 Å), thus leading to the high observed selectivity [304,308]. Supporting this argument, the DFT calculations also show that complexes of these crown ethers with larger ions, like sodium, potassium and cesium, hold the metal above the plane of the macrocycle, showing that they are too large to be fully incorporated [304]. A potential limitation of these high-affinity chelators arises from

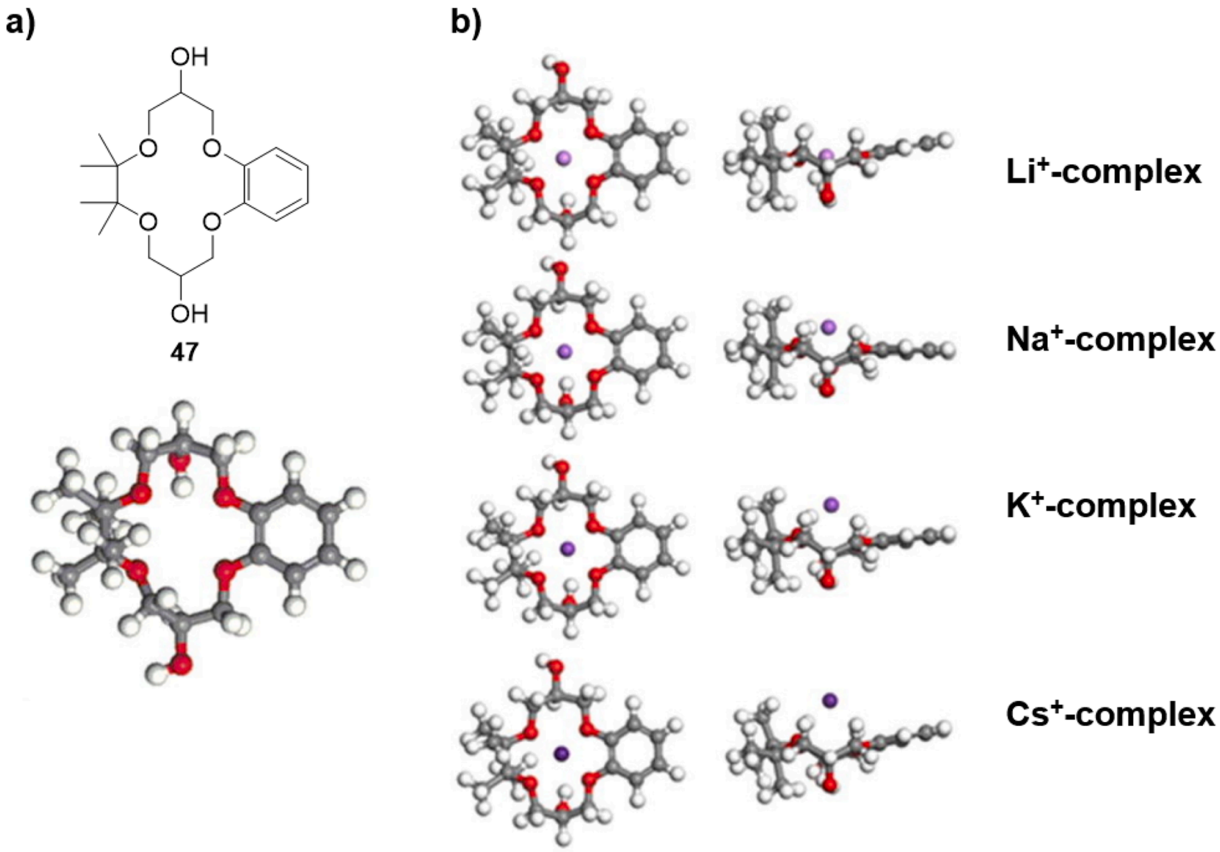


Fig. 4. a) Chemical and DFT-optimized structures of 14-crown-4 ether **47**. b) DFT-optimized structures of alkali metal complexes with crown ether **47** in a 1:1 ratio. Adapted with permission from Ref. [304]. Copyright 2017 Elsevier Inc. Purple: metal, gray: C, white: hydrogen, red: O.

the challenge in stripping lithium from their resulting complexes. However, in further studies, researchers showed that lithium can be dissociated from related 14-crown-4 ethers with dilute HCl (0.1 M). Furthermore, the recovered crown ethers could be used effectively for subsequent lithium extractions [309]. These results show the promise of this chelator class for large-scale industrial use.

3.3.4. *15-Crown-5 ethers*

The larger 15-crown-5 ethers have also been modified and studied for their use in lithium-extraction applications. In this context, it is noteworthy that several 15-crown-5 ethers have previously been applied for the isotopic separation of ^{6}Li and ^{7}Li by solvent extraction for nuclear chemistry applications [310–315]. Despite these prior applications, the cavity size of 15-crown-5 ethers (1.70–2.20 Å) is too large and generally not optimal for lithium ions, for which the six–coordinate ionic diameter is 1.36–1.52 Å [62,266,308]. DFT calculations support this conclusion, as optimized structures of the lithium complexes with 15-crown-5 ethers reveal Li–O interatomic distances of 2.10–2.38 Å that are slightly longer than preferred average Li–O interatomic distances, which range between 2.08 and 2.28 Å [182,316]. These findings were also corroborated by the experimental crystal structure of a 15-crown-5 ether lithium complex, $[Li(15C5)(H_2O)]^+$, shown in Fig. 3 [284]. In this complex, each lithium ion is bound to six donor, five oxygen atoms from the crown ether, and an oxygen from a bound water molecule. The resulting coordination geometry of the central lithium is a pentagonal pyramid. The Li–O distances found within the crystal structure are consistent with those obtained from the DFT calculations; these distances range from 2.17 to 2.54 Å and are somewhat longer than expected, reflecting the poor fit of this ion within the cavity of the macrocycle [284].

Despite the apparent poor size-match, there have been several studies that have explored the use of these chelators for lithium separation via solvent extraction [177,262]. To make these macrocycles more amenable for solvent extraction, researchers have installed hydrophobic phenyl groups on their backbones, as shown in Scheme 9. The hydrophobic groups help ensure that these chelators and their complexes partition into the organic phase effectively. This consideration is important because the unfunctionalized 15–crown-5 ether is particularly water soluble and is poor at transferring metal ions into the organic phase, a property that leads to low extraction efficiencies [296].

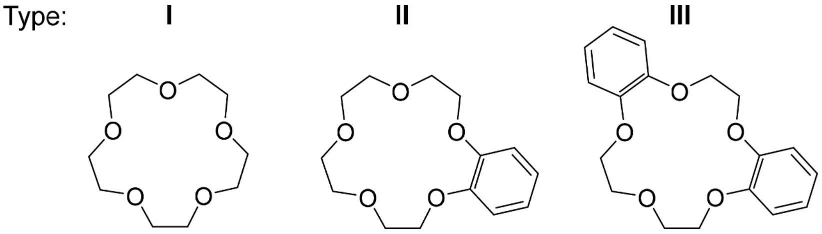
In Table 13, the stability constants and lithium extraction properties of different 15-crown-5 ethers are shown. Although there are fewer examples of these macrocycles used for this application, there are several notable studies. For instance, the benzo-15-crown-5 ether **49** was used for laboratory-scale lithium extraction from spent lithium-ion batteries [317]. Extraction efficiencies of up to 37 % via solvent extraction experiments with water (pH = 6) and dichloromethane were obtained, revealing this process to be a feasible method for isolating lithium from spent batteries [317]. Despite the disadvantages of 15-crown-5 ethers with respect to their size-mismatch and high water solubility, these macrocycles can be possibly useful for lithium extraction because of their relatively high stability constants in organic solvents. Furthermore, the water solubility of 15-crown-5 ethers can be decreased by the introduction of lipophilic groups, like alkyl chains, to facilitate the transfer into organic phase during solvent extraction. However, further investigations of this compound class are necessary to evaluate their performance for lithium solvent extraction separations.

Table 13
15-crown-5 Ether Derivatives Shown in Scheme 9 and their Performance in Lithium Complexation and Extraction.

Type	Solvent	Method/Conditions	log K_{ML}	D_C	Ref.
I **48**	MeOH/H_2O 7:3	determination of Li^+-stability constant in MeOH/H_2O at 25 °C via conductometric titration (anion: Cl^-)	1.02	–	[273]
I **48**	MeOH	determination of Li^+-stability constant in MeOH/H_2O at 25 °C via conductometric titration (anion: Cl^-)	1.21	–	[273]
I **48**	MeCN	determination of Li^+-stability constant in MeCN at 25 °C via conductometric titration (anion: ClO_4^-)	3.58	–	[318]
I **48**	MeCN	determination of Li^+-stability constant in MeCN at 25 °C via calorimetric titration (anion: BF_4^-)	4.44	–	[319]
I **48**	propylene carbonate	determination of Li^+-stability constant in propylene carbonate at 25 °C via conductometric titration (anion: ClO_4^-)	4.26	–	[320]
II **49**	H_2O, $CHCl_3$	solvent extraction with ligand in $CHCl_3$ (2.50 mM) and aqueous LiCl (2 M) at 22 °C and detection via UV/Vis	–	480	[296]
II **49**	MeOH/H_2O 7:3	determination of Li^+-stability constant in MeOH/H_2O at 25 °C via conductometric titration (anion: Cl^-)	<0.4	–	[273]
II **49**	propylene carbonate	determination of Li^+-stability constant in propylene carbonate at 25 °C via titration calorimetry (anion: ClO_4^-)	4.03	–	[321]
II **49**	acetone	determination of Li^+-stability constant in acetone with ligand and $LiClO_4$ (10 mM) at 25 °C via NMR experiment	3.22	–	[322]
II **49**	H_2O, CH_2Cl_2	competitive solvent extraction with ligand in CH_2Cl_2 (50 mM) and aqueous Li^+ and Co^{2+} (5 mM) at pH = 6 and 30 °C and detection via ICP-OES *EE*: Li^+: 37 %	–	–	[317]
III **50**	MeCN	determination of Li^+-stability constant in MeCN with ligand and $LiClO_4$ (5 mM) at 21 °C via NMR experiment	3.82	–	[323]

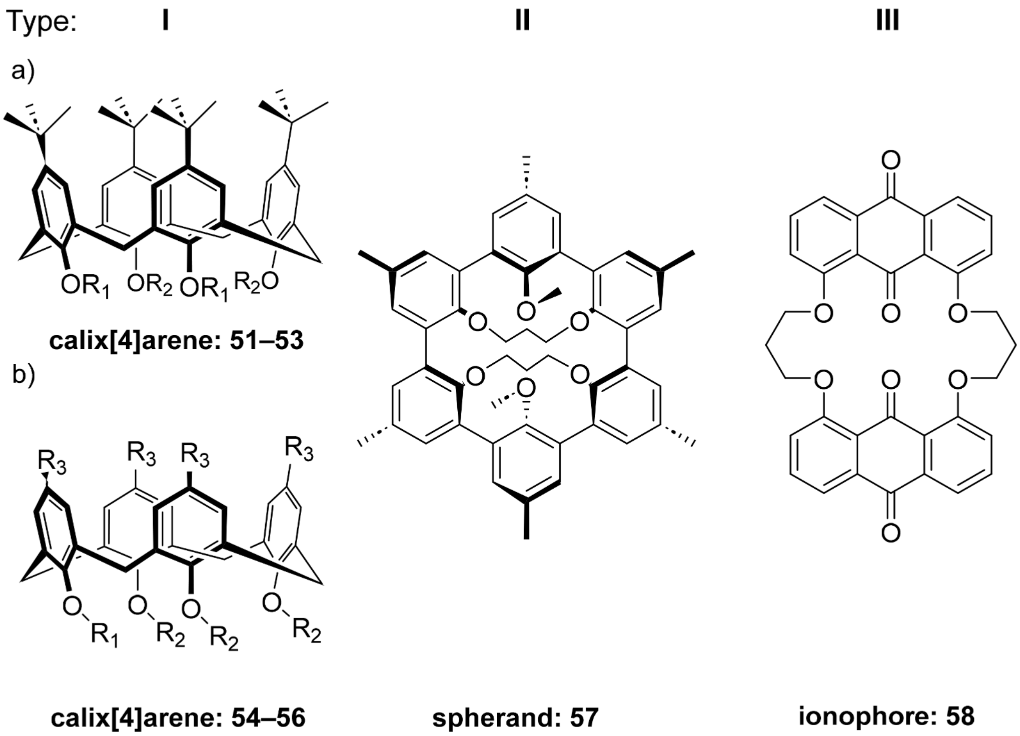
3.3.5. *Other Macrocycles*

In addition to the crown ether macrocycles, alternative macrocyclic oxygen donor ligands have been applied for lithium extraction. In



15C5: 48 **15BC5: 49** **15DBC5: 50**

Scheme 9. Different types of 15-crown-5 ethers for lithium complexation.



Scheme 10. Ionophores and other macrocyclic chelators as ligands for lithium complexation.

Scheme 10, these different types of ligands with promising properties for lithium extraction are shown, and their properties are summarized in Table 14.

The calixarenes, whose structures are displayed in Scheme 10, have shown particular promise for lithium extraction. Calixarenes are cavity-shaped cyclic oligomers of phenols [251,324]. Synthetically, these ligands are typically accessible via large-scale one-pot reactions from cheap starting materials like phenols and formaldehyde [324]. Furthermore, functionalization of the phenolate oxygens enables additional modification and tuning of their properties for different applications [251]. Calixarenes containing four phenol units, called calix[4]arenes, are the smallest of this ligand class, and have been shown to be the most effective for lithium extraction [251,325–327]. In Table 14, several derivatives of calix[4]arenes bearing different phenolate functionalization patterns, and their complexation properties are shown.

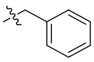
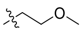
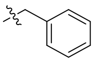
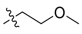
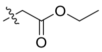
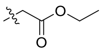
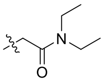
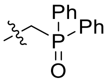
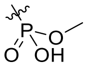
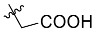
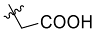
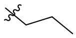
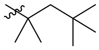
In general, most of the calix[4]arenes are not selective for lithium ions, instead exhibiting a preference for sodium ions. Consequently, in extraction experiments, sodium is more effectively extracted than lithium [251,336]. However, calix[4]arenes bearing acidic functionalities, like **55** and **56**, exhibit promising Li^+:Na^+ selectivities that may make them useful for large-scale applications. For instance, calix[4]arene **55**, which contains one carboxylic acid group, shows Li^+:Na^+ selectivities up to 57 in competitive solvent extraction studies under basic conditions (pH = 12) [332,333,336]. Like calix[4]arene **55**, calix[4]arene **56** shows promising lithium extraction properties [333]. Calix[4]arene **56** was used in a microreactor to extract lithium from seawater via solvent extraction. Specifically, lithium was extracted from untreated and natural seawater (pH = 8.21) by using calix[4]arene **56** dissolved in chloroform in a microfluidic reactor. In these extraction experiments, the ligand **56** (20 mM) was used to remove lithium quantitatively and with high selectivity, only co-extracting 3 % of the dissolved sodium ions, from seawater within seconds. Once extracted, the lithium was stripped from the organic phase with an aqueous solution of HCl (16 mM), enabling the ligand to be reused for subsequent extractions. The authors proposed that this process could be applied on a large scale, by using a series of microreactors in sequence [333].

A specific class of calixarenes are the ligands known as spherands, which exhibit enhanced preorganization and spherical structures due to crosslinks that are present between the alternating phenolate groups [334,337]. The spherand **57** shown in Scheme 10 was synthesized in seven reaction steps with an overall yield of only 1.2 %, highlighting challenges that need to be overcome for their large-scale applications [334]. This ligand forms lithium complexes that are more stable than those of sodium, and did not coordinate to the larger alkali metal ions potassium, rubidium, and cesium, or the alkaline earth metals magnesium and calcium [334]. Moreover, competition experiments showed that the lithium complex of this ligand was stable in the presence of sodium, further reflecting a high Li^+:Na^+ selectivity [334]. This class of spherands is promising for lithium extraction due to their reported high selectivity. However, further investigations of them in competitive solvent extraction studies are needed to verify their suitability for this application.

The macrocyclic ligand **58** is an ionophore with high selectivity for lithium ions [335]. In initial solvent extraction experiments, the ionophore exhibited high selectivity for this ion, as well as good extraction efficiencies that reached up to 49 % within a synthetic lithium chloride solution. Crystallographic analysis of the lithium complex of this ligand revealed a 2:1 lithium:macrocycle complex, where both lithium ions attain five-coordinate geometries, as shown in Fig. 5. The crystal structure reveals a distorted square-pyramidal geometry with Li–O ether interatomic distances between 1.990 and 2.023 Å and Li–O carbonyl interatomic distance ranges between 1.971 and 2.005 Å. The fifth coordination site of one of the two lithium ions is completed by a solvent water molecule, whereas a perchlorate counterion is bound to the second lithium ion [335]. Furthermore, the anthraquinones of this ligand confer it with rich photophysical properties that are potentially useful for quantitative analysis of lithium-ion binding. For example, the ionophore shows upon complexation with lithium perchlorate in acetonitrile a small bathochromic shift of absorption from 373 to 386 nm, whereas other metal ions such as sodium, potassium, magnesium, calcium, and strontium do not affect its UV–vis spectrum. Furthermore, lithium also quenches the fluorescence of **58** in acetonitrile at 433 nm, providing another spectrophotometric readout for binding to this ion [335].

Collectively, these prior studies on macrocyclic chelators including

Table 14
Derivatives of Ionophores and Macrocyclic Chelators Shown in Scheme 10 and their Performance in Lithium Complexation and Extraction.

Type	R_1	R_2	R_3	Solvent	Method/Conditions	log K_{ML}	Selectivity	Ref.
Ia **51**			–	MeCN	determination of Li^+-stability constant in MeCN at 25 °C via calorimetric titration (anion: ClO_4^-)	3.76	–	[328]
Ia **51**			–	H_2O, CH_2Cl_2	solvent extraction with ligand in CH_2Cl_2 (2.50 mM) and aqueous metal picrate (2.50 mM) at 20 °C and detection via UV/Vis *EE*: Li^+: 9.4 % *EE*: Na^+: 4.1 % *EE*: K^+: 2.0 % *EE*: Rb^+: 5.4 % *EE*: Cs^+: 2.5 % *EE*: Mg^{2+}: 2.5 %	–	Li^+:Na^+: moderate	[328]
Ia **52**			–	H_2O, CH_2Cl_2	solvent extraction with ligand in CH_2Cl_2 (350 μM) and aqueous metal picrate (70 mM) at 25 °C and detection via UV/Vis *EE*: Li^+: 48.9 % *EE*: Na^+: 87.7 % *EE*: K^+: 51.2 % *EE*: Rb^+: 41 % *EE*: Cs^+: 52.8 % *EE*: Ca^{2+}: 45.7 %	–	Li^+:Na^+: low	[329]
Ia **53**			–	H_2O, 1,2-dichloroethane	solvent extraction with ligand in 1,2-dichloroethane (250 μM) and aqueous metal picrate (250 μM) at 20 °C and detection via UV/Vis *EE*: Li^+: 64.5 % *EE*: Na^+: 58 % *EE*: K^+: 45 % *EE*: Rb^+: 20 % *EE*: Cs^+: 5 %	–	Li^+:Na^+: moderate	[330]
Ib **54**		Me	*tert*-butyl	H_2O, $CHCl_3$	solvent extraction with ligand in $CHCl_3$ and aqueous metal solution *EE*: Li^+: 60 % *EE*: Na^+: 57 % *EE*: K^+: 65 %	–	Li^+:Na^+: 1.05 Li^+:K^+: 0.93	[331]
Ib **55**		Me	*tert*-butyl	H_2O, $CHCl_3$	competitive solvent extraction with ligand in $CHCl_3$ (1 mM) and aqueous metal chloride/hydroxide (10 mM) at pH = 11.9 and detection via ion chromatography	–	Li^+:Na^+: 57	[332]
Ib **56**				H_2O, $CHCl_3$	solvent extraction with ligand in $CHCl_3$ (20 mM) and seawater (pH = 8.21) by using a microfluidic reactor and subsequent stripping of lithium from the organic phase with HCl (16 mM) and detection via AAS *EE*: Li^+: 100 % *EE*: Na^+: 2.56 %	–	Li^+:Na^+: high	[333]
II **57**	–	–	–	$CDCl_3$, d_6-DMSO	competitive NMR experiment of ligand in $CDCl_3$ (1.50 mM) and various metal perchlorates (40 mM) in d_6-DMSO showed Li-complexation	–	Li^+:Na^+: high	[334]
III **58**	–	–	–	H_2O, Ph-NO_2	solvent extraction with ligand in nitrobenzene (5 mM) and aqueous metal chloride/perchlorate (1 M) and subsequent stripping of lithium from organic phase with sulfuric acid (200 mM) and detection via ICP loading: 48.6 % with $LiClO_4$ and 25.6 % with LiCl	–	Li^+:Na^+: high Li^+:K^+: high Li^+:Mg^{2+}: high Li^+:Ca^{2+}: high Li^+:Sr^{2+}: high	[335]

crown ethers and other analogs, show that these entities can exhibit distinct selectivity for metal ions. The most selective crown ethers for lithium complexation typically are those of the 14-crown-4-ether family, but as the examples above show, further modification of different macrocycles can afford promising properties for these applications. Despite the proven suitability of macrocyclic crown ethers and ionophores for lithium extraction from simple laboratory separation experiments, further information about the extraction efficiency, reusability properties of crown ethers after recycling, and stabilities of lithium-selective chelators under realistic conditions, like within seawater or brine, are rarely reported. These experiments, as well as a techno-economic analysis to account for the often costly and low-yielding syntheses of these ligands, need to be carried out before they can be applied industrially.

3.3.6. *Acyclic chelators*

Although the most commonly applied oxygen-based extractants for lithium are macrocycles, a few acyclic chelators for these applications have also been reported. The relative paucity of studies on this chelator class could be a consequence of their overall lower stability due to the lack of the macrocyclic effect. Several reports within the literature on polyether diglyme ligands reveal them to possess low to moderate affinity for lithium ions, compared to their cyclic analogs [338–344]. However, the further functionalization of these ligands with ionizable carboxylic acid groups, like those shown in Scheme 11, led to improved selectivity for lithium ions over other alkali metal ions. The data for the use of these ligands in solvent extraction, as well as their selectivity for the different alkali metal ions are given in Table 15 [345].

In general, these experiments showed that these acyclic ligands possess moderate lithium extraction capabilities when the aqueous phase was at pH levels of greater than 10, even in the presence of other alkali metal ions like sodium. Among these acyclic ligands, those of the shorter polyether chains gave rise to higher Li$^+$:Na$^+$ selectivity. Hence, the acyclic chelators **59** and **61** exhibit the best performance in terms of Li$^+$:Na$^+$ selectivity of 4.9 at pH = 10–11 with a selectivity order of lithium ≫ sodium > potassium > rubidium > cesium and extraction efficiencies over 85 % [345]. Despite these promising results, there are no data reported on their selectivity between lithium and divalent metal ions, like magnesium. Furthermore, these ligands have not yet been investigated in seawater or other natural brine sources.

In a recent study, a series of lipophilic acyclic lithium ionophores containing four neutral oxygen donors like 14-crown-4 ethers were investigated for their lithium coordination and extraction properties [346]. The most promising acyclic chelators identified within this series were **64** and **65**, as shown in Scheme 11. A notable advantage of both of these ionophores, compared to more complex macrocyclic ligands, is that they can be synthesized via two steps in high yields. ^{1}H NMR spectroscopy and calorimetric titration experiments revealed this ligands to possess high affinity and good selectivity for lithium. In particular, isothermal titration calorimetry of **64** revealed a Li$^+$:Na$^+$ selectivity of 5645. As noted by the authors of this study, this selectivity is greater than 200 times that of the conventional crown ether macrocycles like dibenzo–14-crown-4 **37**. The X–ray crystal structure of **64** revealed a sterically crowded structure arising from the bulky phenyl– and cyclohexyl substituents, which presumably decrease its conformational flexibility and result in effective lithium coordination properties. A DFT-optimized structure of the lithium complex of **64** posited the presence of a four-coordinate lithium center that is well-accommodated by the small binding pocket of the ligand [346].

The related pyridine-*N*-oxide analog **65** was found to possess a Li$^+$:Na$^+$ selectivity of 1167. This chelator was studied by NMR spectroscopy within competitive solid–liquid extraction experiments with lithium chloride (0.2 %) in the presence of excess of sodium and potassium chloride [346]. These experiments revealed a high selectivity for lithium under these conditions and demonstrated the potential of this specific

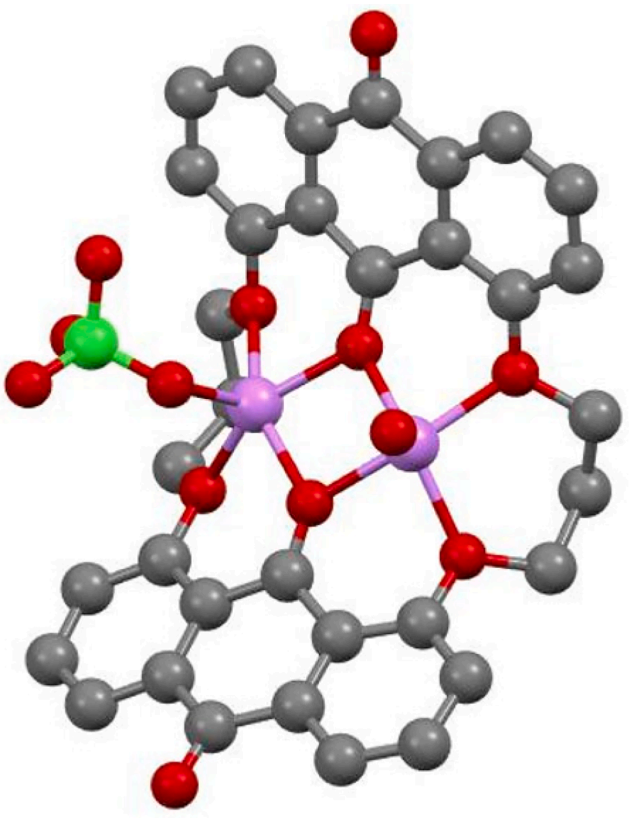
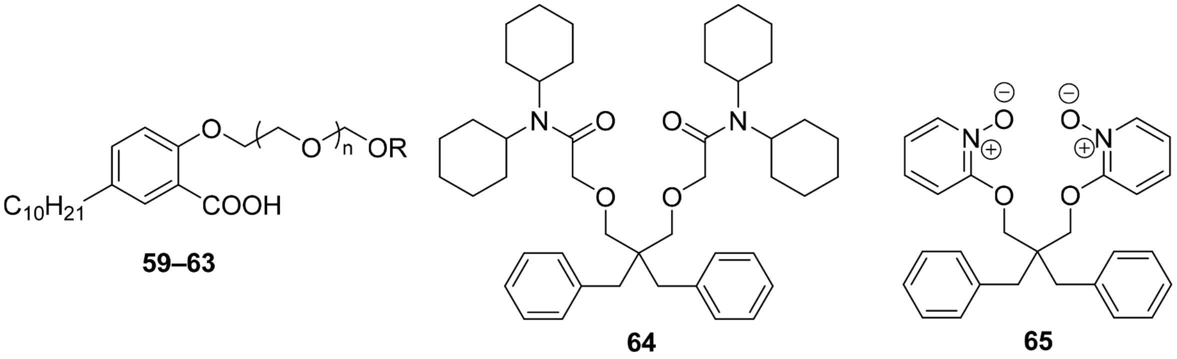


Fig. 5. X-ray crystal structure of the ionophore **58** bond to two lithium ions and as a perchlorate complex [335]. The hydrogen atoms are omitted for clarity. Purple: Li, gray: C, red: O, green: Cl.



Scheme 11. Acyclic ionizable polyethers and ionophores that have been investigated for lithium coordination and solvent extraction [345,346].

Table 15
Results of the Competitive and pH-dependent Lithium Solvent Extraction Experiments of Acyclic Polyethers Performed in Water and Chloroform [345].[a]

Compound	n	R	pH[b]	Li$^+$:Na$^+$ Selectivity[c]	Maximal Extraction Efficiency	Selectivity Order
59	0	CH$_2$Ph	10	4.9	85 %	Li$^+$≫Na$^+$>K$^+$>Rb$^+$>Cs$^+$
60	0	CH$_3$	11	2.6	90 %	Li$^+$>Na$^+$>K$^+$, Rb$^+$, Cs$^+$
61	1	CH$_2$Ph	11	3.1	90 %	Li$^+$≫Na$^+$>K$^+$>Rb$^+$>Cs$^+$
62	2	CH$_2$Ph	10	2.5	100 %	Li$^+$>Na$^+$, K$^+$>Rb$^+$, Cs$^+$
63	3	CH$_2$Ph	11	2.4	63 %	Li$^+$>Na$^+$, K$^+$>Rb$^+$, Cs$^+$

[a] The experiments were conducted at room temperature (20–23 °C) with the ligand (50 mM) dissolved in chloroform and the alkali metal chlorides dissolved (250 mM) in water, and cesium hydroxide was added for pH-control.

[b] pH at equilibrium for effective lithium uptake in organic phase in presence with other alkali metals.

[c] The selectivity of lithium ions towards other metal ions was determined by using both ion chromatography and calculating the concentrations of each metal by using UV–Vis spectroscopy [345].

binding motif for applications in lithium extraction. Like **64**, the synthesis of **65** is facile and modular, providing a launching point for a new class of lithium extracting agents.

3.3.7. *β-Diketones*

β-diketones are a common and easily tunable class of ligands that have been applied in coordination chemistry for over a century, since their initial investigation in this role by Claisen in 1889 [347]. Unsurprisingly, they have also been used for metal ion extraction and separation, although they typically require basic conditions for these purposes [348]. In Scheme 12, various *β*-diketones, including HBTA (benzoyl-1,1,1-trifluoroacetone) and HTTA (thenoyltrifluoroacetone), that have been used for lithium extraction and separation are shown [215,262,349,350].

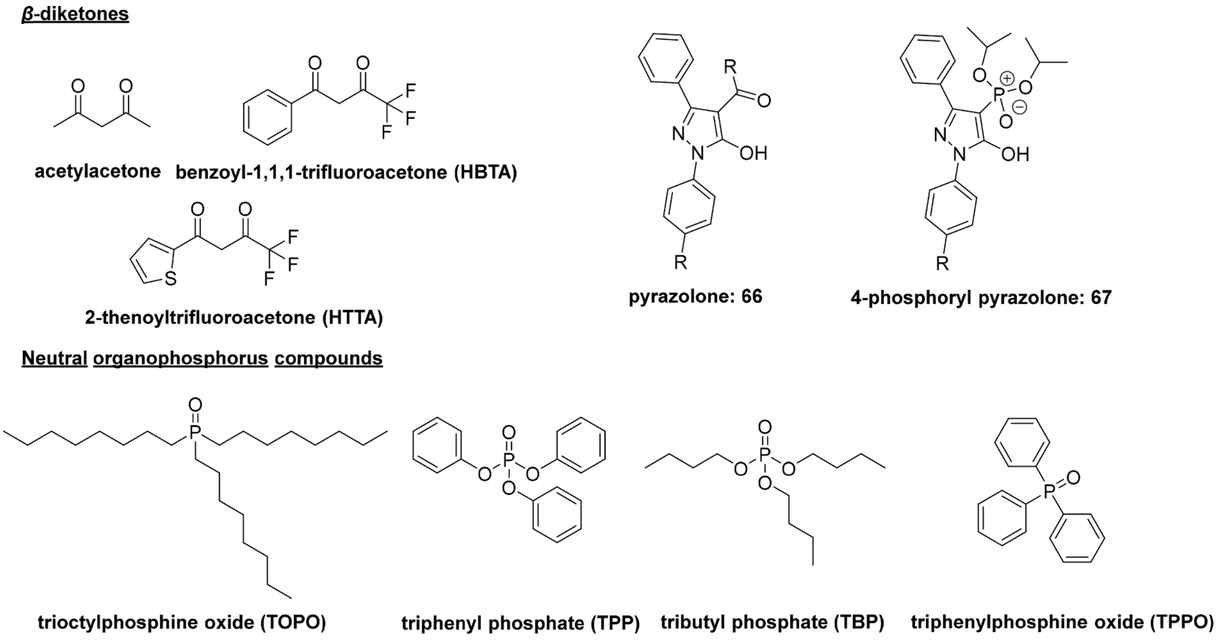
The most common means by which *β*-diketones are used for extraction is in conjunction with neutral organophosphorus extractants, like TOPO and TBP, which are dissolved in the kerosene organic phase [215,262,349,350,354–356]. In 1968, this combination was used to extract lithium from a lithium nitrate-containing aqueous carbonate solution [350]. The *β*–diketone HTTA and a series of organophosphorus donors were screened, identifying TOPO and triphenylphosphine oxide (TPPO) to be particularly promising for partitioning lithium into the benzene organic phase. This system was found to give high selectivity for lithium compared to the other alkali metal ions, but gave poorer selectivity for lithium compared to the alkaline earth metal ions [350,355,356]. In any case, this early study that combined the *β*–diketones with neutral organophosphorus reagents demonstrated a strong synergistic effect, leading to what is now known as synergistic solvent extraction (SSX). Within this method, the deprotonated anionic *β*–diketonate and the neutral organophosphorus simultaneously coordinate the metal ion of interest, leading to the observed synergistic effects that can enhance the extraction efficiency by up to 5 orders of magnitude [349,350,357]. The ideal pH-ranges required to optimize the extraction efficiency of these *β*–diketone-organophosphorus systems is dependent on several factors, including the pK_a values of the *β*–diketone ligand, which can range between p$K_a = 5$–9 [350,355,358,359]. Once extracted into the organic phase, the lithium can be stripped using aqueous HCl [241,349,355,356]. The relevant equilibrium for defining this SSX is shown as follows:

$$M^{n+} + nHA + yS \rightleftharpoons MA_nS_y + nH^+ \tag{7}$$

where M^{n+} is the metal ion, HA is the *β*-diketone, and S is the neutral organophosphorus compound. The resulting ternary complex is charge-neutralized by the *β*–diketonate and has enhanced lipophilicity from the organophosphorus reagent, factors that lead to the synergistic improvement of extraction to the organic phase [357,360].

The successful isolation of lithium from the SSX process requires the initial metal ion extraction, scrubbing of undesired metal ions, stripping of the lithium from the organic phase, and regeneration of the organic phase for subsequent extractions [215]. The extraction process, which forms the ternary complexes described above, brings metal ions into the organic phase. Although this initial step can be partially selective for lithium, it inevitably also transfers undesired metal ions, like sodium, magnesium, and calcium as well. The scrubbing step addresses this selectivity-deficiency by adjusting the pH of the solution to decrease the stability of undesired metal complex [215]. In the stripping step, the targeted metal ion is removed from the organic phase under acidic conditions. Lastly, the extractants are regenerated under basic conditions to be used in subsequent cycles [215,262].

The lithium extraction process with *β*-diketones and neutral organophosphorus compounds is often applied in laboratory scales. Hence, the performance of synergistic systems with real brine systems or seawater are required to verify the potential of this technique for industry. Reports about lithium extraction under real conditions with SSX have been reported recently. For instance, this approach was used to extract lithium ions from brine with high Na^+:Li^+ ratio (~7.5:1) by using a combination of HBTA as the *β*–diketone and TOPO as the neutral organophosphorus compound in kerosene. The brine used for these studies was obtained from preconcentrated lithium brine at a pH = 10.8, and the experiments were performed on a laboratory scale. Under these conditions, the lithium ion-extraction efficiency reached 95 %. Furthermore, a 1 M HCl solution was used in the scrubbing step to further remove sodium ions from the organic phase. This scrubbing step removed 90 % of the sodium ions, while only suffering a 10 % loss of the lithium. For stripping of the lithium, a 3 M HCl solution was needed. Lastly, the authors were able to demonstrate regeneration of the extraction solution upon basification with 2 M NaOH [215]. As this



Scheme 12. Different *β*-diketones, pyrazolones, and neutral organophosphorus compounds relevant for lithium extraction methods [349–353].

Table 16
A Selection of Different β-diketones/Neutral Organophosphorus Systems and their Efficiency in Synergistic Lithium Solvent Extraction from Different Lithium Sources.

β-diketone system	Neutral Ligand	Diluent	Lithium Source	pH	Lithium Extraction Efficiency	Separation Factor	Ref.
FDOD[a]	TOPO	kerosene (ShellSol D70)	model SWRO[c] brine	9	100 %	–	[361]
DBM[b]	TOPO	kerosene (ShellSol D70)	model SWRO[c] brine	12.2	95.4 %	–	[361]
HTTA	TOPO	kerosene	seawater	10.6	70 %	–	[362]
LIX-54	Cyanex 923	ShellSol D70	synthetic solution	11.2	97 %	$Li^+:Na^+$: 1560	[241]
HBTA	TOPO	kerosene	simulated brine	11.2	97 %	$Li^+:Na^+$: up to 2100	[356]
PHPD[d]	Cyanex 923	kerosene	synthetic solution	13.1	>97 %	$Li^+:Na^+$: up to 475	[363]
HTMPBP[e]	TOPO	benzene	synthetic solution	>10	<50 %	$Li^+:Na^+$: 1620	[364]
HTMBBP[f]	TOPO	benzene	synthetic solution	>10	<35 %	$Li^+:Na^+$: 1350	[364]

[a] FDOD: heptafluoro-dimethyloctanedione.
[b] DBM: dibenzoylmethane.
[c] SWRO: seawater reverse-osmosis.
[d] PHPD: 1-phenyl-3-heptyl-1,3-propanedione.
[e] HTMPBP: 1-tolyl-3-methyl-4-(*p*-phenylbenzoyl)-5-pyrazolone.
[f] HTMBBP: 1-tolyl-3-methyl-4-(*p*-*tert*-butyl-benzoyl)-5-pyrazolone.

example shows, the SSX system with organophosphorus and β-diketone ligands is a viable approach for the extraction and separation of lithium and shows promising results for the transfer to industrial-scale lithium production. Thus, much research has been dedicated towards improving and optimizing these ligands for this type of extraction. In Table 16, different β-diketones/neutral organophosphorus systems that have been investigated for lithium extraction are described.

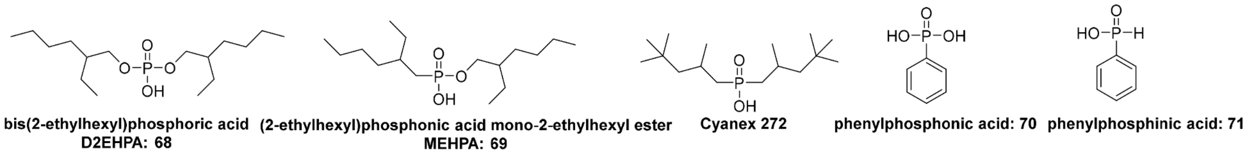
Among the novel β-diketones explored for lithium extraction are the pyrazolones **66** (Scheme 12). Pyrazolones have extensive coordination chemistry that has been studied with various d-block or f–block elements, and have been investigated for lithium extraction applications [364–366]. An early study in 1992 showed that substituted pyrazolones in solvent extraction separations using petroleum ether as the organic phase were more effective for extracting the alkaline earth elements magnesium and calcium over lithium. Therefore, the authors proposed to use the substituted pyrazolones for the separation of magnesium and calcium ions from lithium [367].

Recent modifications of the pyrazolones **66** afforded 4–phosphoryl pyrazolones **67**, which were successfully applied for selective lithium separation from other metal ions, like cesium, potassium, sodium, and magnesium [351,352]. Notably, these 4–phosphoryl pyrazolones form multinuclear lithium complexes in the presence of co-ligands such as TBPO, TBP, and TOPO, reflecting a distinct stoichiometry compared to what is needed for generic β–diketones [351,352]. On a laboratory scale, these ligands were investigated in conjunction with TOPO for their solvent extraction capabilities. High extraction efficiencies, reaching up to 78 %, were observed for three 4–phosphoryl pyrazolones, exceeding the efficiencies obtained with pyrazolones and the common lithium extractant HBTA [351,356]. In 2023, a series of 4–phosphoryl pyrazolones for lithium extraction were reported. These 4–phosphoryl pyrazolones were used for stepwise lithium separation from solutions containing monovalent (sodium and potassium) and divalent (magnesium and calcium) metal ions by varying the pH, as described below [352]. The improved 4–phosphoryl pyrazolones, used with TOPO in *n*-octanol, reached lithium extraction efficiencies of 94 % in the presence of other metal ions, like calcium, magnesium, sodium, and potassium in pH = 6 buffer at room temperature. Under these conditions, only 3.6 % of the sodium and less than 1 % of the potassium were extracted into the organic phase, signifying the high selectivity of this system for lithium. The selectivity of this system also showed a high pH-dependency. When the buffer was equilibrated at pH = 2, this system was able to extract 64 % of the calcium and 18 % of the magnesium from a mixture of lithium, sodium, potassium, calcium, and magnesium ions. Adjusting the pH to 3 led to a 93 % extraction efficiency of magnesium from a lithium, sodium, potassium, and magnesium solution lacking calcium with negligible amounts of extracted lithium, sodium, or potassium. These experiments highlight the exquisite pH-sensitivity of this system and how this feature can be leveraged for the separation of distinct alkali and alkaline earth ions [352]. Given the promising results of the 4–phosphoryl pyrazolones, further investigation of them on the large scale and with industrially relevant solutions should be carried out.

Collectively, the results summarized above indicate the potential of the β–diketones and neutral ligand systems for efficient solvent extraction of lithium. Future work in this area should address some drawbacks to the current systems. For instance, some SSX conditions lead to a formation of a third phase that limits the extraction efficiency. Furthermore, the high costs of some of these extractants, as well as their challenging syntheses, limits their use on large industrial applications [357,368]. Developing effective recycling or regeneration strategies for these particular systems may facilitate their industrial implementation.

3.3.8. *Phosphorus-based acidic extractants*

Acidic extractants release protons at relatively low pH values which facilitate binding to metal ions in their charged anionic forms. Because the operating pH of many solvent extraction or separation procedures is low, the use of these types of reagents is valuable. In this section, several examples of these extractants as applied for lithium, specifically, are be discussed. The major classes of these ligands are shown in Scheme 13.



Scheme 13. A selection of most common acidic extractants for solvent extraction.

The acidic extractants shown in Scheme 13 are phosphorus-based. The phosphorus-based acids are reagents that have commonly been used for solvent extraction applications, including D2EHPA (**68**), MEHPA (2-ethylhexyl)phosphonic acid mono-2-ethylhexyl ester, **69**), and dialkyl phosphinic acid known as Cyanex 272. The chemical equilibrium that represents the extraction of metal ions via these reagents is shown below:

$$M^{n+}+(aq)+nHL(org)\rightleftharpoons ML_n(org)+nH^+(aq) \tag{8}$$

In this equilibrium, $M^{n+}(aq)$ is the metal cation in the aqueous phase, and HL(*org*) is the acidic extractant, which pulls the metal ion into the organic phase to form the metal complex ML_n. As depicted in this reaction, the proton of the acid is exchanged with the metal ion, a feature that has led these types of acidic extractants to be called cation exchangers [369].

Extractant **68** exists in organic non-polar solvents as a dimer (**72**), resulting in an eight-membered ring supported by strong hydrogen bonds (Scheme 14) [348,370]. The dimer **72** dissociates upon formation of metal complexes, typically exhibiting a preference for divalent cations and forming a 2:1 tetrahedral complex **73** as shown in Scheme 14a [371]. However, the binding mode of **68** and **69** to lithium is still not completely understood. A structure, in which the lithium is tetrahedrally coordinated to two oxygen donors of **68** and two water molecules has been suggested (**74**, Scheme 14b). The inner-sphere water ligands presumably increase the hydrophilicity of this complex, leading to poorer transfer of lithium into the organic phase [371].

Compound **68** has been extensively applied for metal extraction because of its high chemical stability, and low aqueous solubility, which retains it in the organic phase with good metal-binding properties [372]. **68** and **69** have been successfully used for lithium extraction and separation [373]. The lithium-extraction efficiency of **68** or **69** into kerosene from an acidic aqueous solution also containing magnesium, calcium, sodium, and potassium ions has been studied [373]. For both extractants, the following selectivity order at the optimal pH = 6 was observed: calcium > magnesium > lithium > sodium > potassium, confirming the higher affinity of these ligands for divalent metal ions [374]. Among the monovalent ions, however, lithium was most effectively extracted [373]. The same study summarizes the use of the neutral organophosphorus compounds TBP or TOPO in conjunction with **68** and **69** for lithium extraction [373]. Whereas TOPO did not show any synergistic effects in extraction experiments with **68** or **69**, experiments with TBP led to higher lithium extraction efficiencies. For instance, the extraction efficiency from a synthetic solution at pH < 5 using only **68** was 42.6 %, but when this acidic extractant was used in combination with TBP, it increased to 76.1 %. A ternary complex formation was invoked in this synergistic extraction because TBP alone was not able to partition lithium into the organic phase. Furthermore, this combination was explored to extract lithium from hot spring water in Japan. Within these solutions, lithium extraction efficiencies of up to 88 % were obtained, simultaneously with quantitative extraction of calcium and magnesium ions [373].

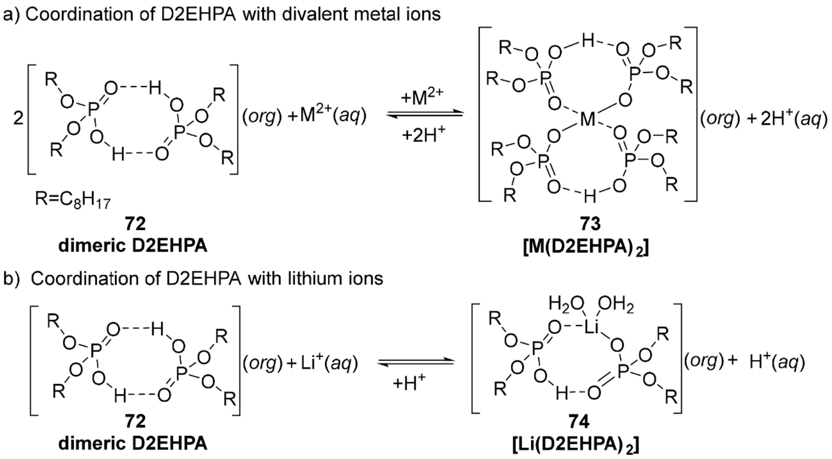
In another study, **68** was investigated in combination with crown ethers for lithium extraction to assess its synergistic effects. These experiments were performed at 25 °C with an aqueous solution of lithium hydroxide and chloroform as organic phase. The best performance was obtained with **68** in conjunction with DB14C4 in the aqueous phase. This dual-chelator system led to an extraction efficiency of 37 %, whereas an efficiency of only 15 % was obtained with the phosphoric acid analogs alone. These studies highlight the value of using two ligands for synergistic lithium extraction [297].

In related work, different phosphorus-based acids were used in conjunction with aqueous ammonia solutions to extract lithium from lithium-containing solutions [375]. The acids investigated in this work were **68**, phenylphosphonic acid (**70**), and phenylphosphinic acid (**71**) (Scheme 13). In initial laboratory-scale experiments, a biphasic mixture of pentanol, containing **68**, as representative for phosphorous-containing acidic extractant, and a 4 M aqueous ammonia solution (pH = 12.5) were used. In comparison to extractions without ammonia in the aqueous phase, the researchers found higher lithium extraction efficiencies. In particular, the extraction efficiencies increased significantly in the presence of ammonia at pH = 12.0 for **70**, **71**, and **68** from 4.0 %, 4.7 %, and 1.9 % to 43.2 %, 45.7 %, and 90.0 %, respectively. The authors hypothesized that the ammonia acts as Bronsted base, reacting with the HCl that is released upon the extractant complexation of lithium. Thus, this acid neutralization enhances the thermodynamic driving force for the extraction equilibrium, where $HOPO_3(C_8H_{17})_2$ **68** is a phosphorus-containing acidic extractant:

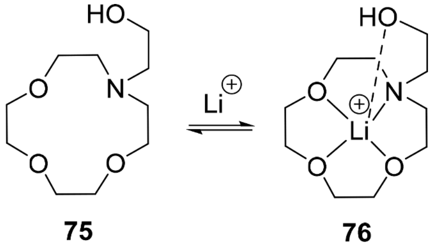
$$LiCl(aq)+\underset{68}{HOPO_3(C_8H_{17})_2}(org)\rightleftharpoons Li-OPO_3(C_8H_{17})_2(org)+HCl(aq) \tag{9}$$

$$NH_3(aq)+HCl(aq)\rightarrow NH_4Cl(aq) \tag{10}$$

In further experiments, the researchers have explored related solvent extraction experiments in the presence of 4.0 M aqueous ammonia and the acids, but using synthetic solutions containing potassium, sodium, and lithium in equal concentrations (15 mM). Compound **68** (150 mM) showed lithium extraction efficiencies of up to 81 %, indicating a high affinity for lithium ions. These conditions, however, also gave rise to sodium and potassium extraction efficiencies of 90 % and 45 %, respectively showing that this system is not selective enough for the direct use of the extracted lithium. At lower ligand concentrations (15



Scheme 14. a) The dimeric D2EHPA (**72**) in organic phase and the formation of metal complex **73** in organic phase by adding divalent metal ions. b) A proposed structure for the formation of the lithium D2EHPA complex **74** [371].



Scheme 15. An example of the interaction of a sidearm of lariat ether **75** with lithium to form **76**.

mM), however, the selectivity shifts towards lithium ions according to the selectivity order: lithium > sodium > potassium [375]. Thus, these types of extractions are particularly sensitive to the extractant concentration, and this property presents another opportunity to finetune separations via these methods. Although these initial results are promising, further studies on their selectivity for alkali compared to alkaline earth elements need to be undertaken.

Collectively, the use of acidic extractants is promising for lithium extraction. In general, such acidic extractants typically have a higher preference for divalent compared to monovalent ions. Although this property is not beneficial for the direct extraction of lithium, it can still be leveraged for useful separation approaches. A disadvantage of this method is that it requires both basic and acidic solutions for neutralization of the acidic extractant and then the resulting basic waste.

3.4. Nitrogen-based chelators

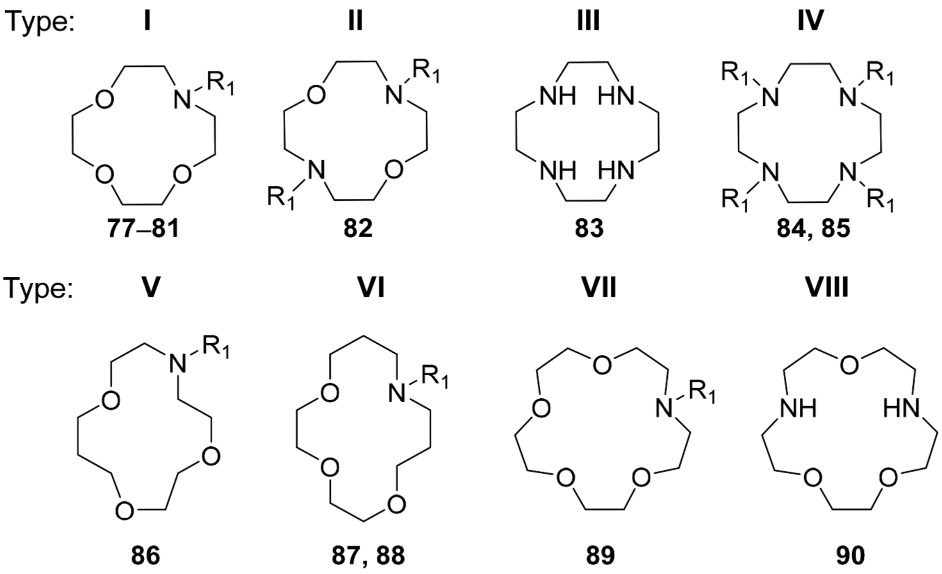
3.4.1. Macrocyclic Aza-Crown ethers

Crown ethers that contain nitrogen donor atoms incorporated into the macrocycle, also known as aza-crown ethers, are another promising class of ligands for lithium extraction. Comprehensive reviews regarding the syntheses and applications of various aza-crown ethers are reported elsewhere [376–378]. A significant benefit of aza-crown ethers is that the nitrogen can be functionalized with an additional pendent donor group that can increase complex stability and selectivity for lithium. Sidearm-functionalized crown ethers, known as lariat ethers are particularly effective. This class of macrocycles and their proposed lithium-binding mode is shown in Scheme 15 [379–381].

Aza-crown ethers typically benefit from higher thermodynamic stability compared to their oxygen analogs. The increased strength of these interactions was further verified with DFT calculations [282]. For instance, the log K_{ML} value of the lithium complex of aza-12-crown–4 is 4.24, which is greater than the value of 3.46 determined for 12–crown-4, as measured by titration microcalorimetry in acetonitrile [319]. Further theoretical studies have investigated the impact of the number of nitrogen donors within the 12-crown-4 ether macrocycle on metal ion stability. In particular, it was determined that the presence of two nitrogen donors within a macrocycle afforded the highest binding energies for lithium compared to mono-, tri- and tetraaza-12-crown–4 ethers [282].

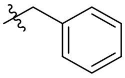
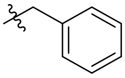
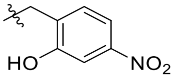
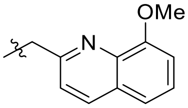
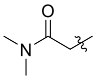
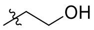
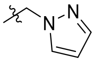
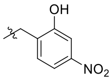
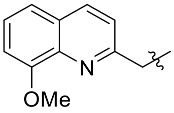
Given the potential of aza-crown ethers, these ligands have been investigated for lithium solvent extraction separations. Key examples from the literature are shown in Scheme 16, and their solvent extraction properties are collected in Table 17. As apparent from the data within Table 17, unfunctionalized aza-crown ethers without pendent donors exhibit systematically higher lithium-binding affinities, compared to those containing only oxygen donors. This enhanced stability should make aza-crown ethers more suitable for lithium extraction applications. Moreover, the monofunctionalized aza-crown ethers of type I can possess remarkably high stability constants like 4.39, signifying the beneficial effects of introducing pendent donor groups [268].

As the data collected in Table 17 show, a diverse number of these macrocycles have been investigated for laboratory-scale lithium extraction. In general, however, most of these macrocycles are not highly selective for lithium, but instead possess a high affinity for a range of different metal ions. As discussed above in Section 3.3.3, 14–crown-4 ethers show the best selectivity for lithium due to their size-match for this ion, thus making them promising reagents for extraction applications. Accordingly, nitrogen-containing aza-14-crown–4 ethers like **87** and **88** (type VI) are among the most promising candidates within this ligand class for lithium extraction, as well. For instance, the lipophilic lariat aza-14-crown-4 ether **87** (type VI) has been demonstrated in small-scale experiments to be suitable for lithium extraction, giving rise to lithium extraction efficiencies up to 32 %, while only extracting 2 % of the sodium ions [382,383]. As these particular ligands demonstrate, lipophilic groups that functionalize the macrocyclic nitrogen favor lithium complexation and the transfer to the organic phase. Although aza-14-crown-4 ethers have shown the most promising properties for this application, a chromophore-containing aza-13-crown-4 **86** (type V) exhibited an exceptional Li^{+}:Na^{+} selectivity of 525, determined within solvent extraction experiments [384]. Even though the 13–crown-4 macrocycle is not optimal for lithium-binding, the authors



Scheme 16. Different classes of aza-crown ethers for lithium complexation.

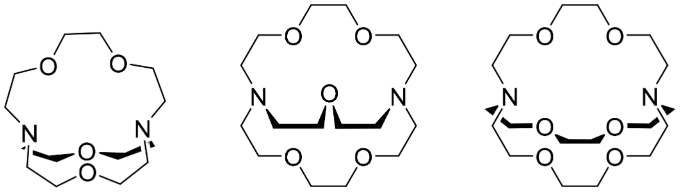
Table 17
Different Classes of Aza-Crown Ethers Shown in Scheme 16 and their Performance in Lithium Complexation and Extraction.

Type	R_1	Solvent	Method/Conditions	log K_{ML}	Selectivity	Ref.
I 77	H	MeCN	determination of Li^+-stability constant in MeCN at 25 °C via titration calorimetry (anion: BF_4^-)	4.24	–	[319]
I 77	H	propylene carbonate	determination of Li^+-stability constant in propylene carbonate at 25 °C via titration calorimetry (anion: BF_4^-)	3.69	–	[319]
I 78	CH_3	MeOH:H_2O (95:5)	determination of Li^+-stability constant in MeOH/H_2O at 25 °C via potentiometric titration (anion: Cl^-)	<2.0		[387]
I 79		MeCN	determination of Li^+-stability constant in MeCN at 25 °C via titration microcalorimetry (anion: BF_4^-)	4.30	–	[268]
I 79		propylene carbonate	determination of Li^+-stability constant in propylene carbonate at 25 °C via titration microcalorimetry (anion: BF_4^-)	4.39	–	[268]
I 80		H_2O, $CHCl_3$	solvent extraction with ligand in $CHCl_3$ (670 μM) and aqueous LiCl and NaCl at 20 °C and detection via UV/Vis	–	Li^+:Na^+: 209	[388]
I 81		H_2O, $CDCl_3$	solvent extraction with ligand in $CDCl_3$ (5 mM) and aqueous metal picrate (5 mM) and detection via UV/Vis *EE*: Li^+: 11 % *EE*: Na^+: 38 % *EE*: K^+: 41 % *EE*: Rb^+: 24 % *EE*: Cs^+: 15 %	–	–	[385]
II 82		MeOH	determination of Li^+-stability constant in MeCN at 25 °C via potentiometric titration (anion: Cl^-)	5.38	–	[389]
III 83	–	MeCN	determination of Li^+-stability constant in MeCN at 25 °C via conductometric titration (anion: ClO_4^-)	6.90	–	[390]
IV 84		MeCN	determination of Li^+-stability constant in MeCN at 25 °C via conductometric titration (anion: ClO_4^-)	8.07	–	[390]
IV 85		H_2O, CH_2Cl_2	solvent extraction with ligand (1 mM) in CH_2Cl_2 and aqueous $LiBPh_4$/$NaBPh_4$ (1 mM) *EE*: Li^+: 100 % *EE*: Na^+: 100 %	–	–	[391]
V 86		H_2O, organic phase	solvent extraction with ligand in organic phase and aqueous metal salt at 25 °C and detection via UV/Vis	–	Li^+:Na^+: 525	[384]
VI 87	$-C_2H_4OC_8H_{17}$	H_2O, CH_2Cl_2	solvent extraction with ligand (2.50 mM) in CH_2Cl_2 and aqueous MOH (50 mM), picric acid (500 μM) at 22 °C and detection via UV/Vis *EE*: Li^+: 32 % *EE*: Na^+: 1.9 % *EE*: K^+: 2.1 % *EE*: Rb^+: 2.7 % *EE*: Cs^+: 2.2 % and competitive liquid membrane transport with CH_2Cl_2 and aqueous LiCl/NaCl/KCl/Me_4NOH (100 mM), picric acid (aq, 50 μM), HCl (aq, 100 μM) at 25 °C	–	competitive passive transport: Li^+:Na^+: 24 Li^+:K^+: 97	[383]
VI 88	$-C_3H_6OC_8H_{17}$	H_2O, CH_2Cl_2	competitive liquid membrane transport with CH_2Cl_2 and aqueous LiCl/NaCl/KCl/Me_4NOH (100 mM), picric acid (aq, 50 μM), HCl (aq, 100 μM) at 25 °C	.-	Li^+:Na^+: 20 Li^+:K^+: 136	[383]
VII 89		H_2O, $CDCl_3$	solvent extraction with ligand in $CDCl_3$ (5 mM) of aqueous metal picrate (5 mM) and detection via UV/Vis *EE*: Li^+: 8.9 % *EE*: Na^+: 46 % *EE*: K^+: 46 % *EE*: Rb^+: 21 % *EE*: Cs^+: 10 %	–	–	[385]
VIII 90	–	–	determination of relative binding selectivity of metal complexes by ESI-MS	–	Na^+>Li^+>K^+	[386]

propose that the pendent phenolic oxygen donor enhances the stability for lithium, in part due to the formation of a six–membered chelate ring [384]. Larger macrocycles bearing pendent donor arms, like **89** or **90** (type VII/VIII), have not demonstrated success for lithium extraction, yet. The larger macrocycle sizes most likely disfavor lithium-binding, leading to ligands that are more useful for extracting larger ions like sodium or potassium ions [385,386].

3.4.2. *Cryptands*

Cryptands, another class of promising ligands for lithium, are cage-like macrobicyclic ligands that possess three-dimensional cavities for the encapsulation of metal ions or small molecules. The cryptands possess at least two substituted atoms, like nitrogen, carbon, or phosphorus, which link the macrocyclic units that give rise to the bridges within these structures. The cavity sizes of the cryptands can be systematically modified by altering the length of the bridging atoms and optimized for binding to metal ions of different ionic radii [392].



cryptand 2.1.1: 91 cryptand 2.2.1: 92 cryptand 2.2.2: 93

Scheme 17. Several cryptands as potential ligands for lithium complexation.

Complexes of macrobicycles exclude solvent molecules from coordinating to the metal ion, thereby leading to higher stability compared to their crown ether analogs. This effect is known as the cryptate effect [251]. Furthermore, the high preorganization of the cryptands enhances the stability of their complexes, compared to normal macrocycles, and modification of the types of donor atoms and rigidity of these systems can be used to fine tune their ion-binding properties [392–395]. The influence of the cryptand can have a remarkable effect on complex properties. For example, several cryptands called "fast proton sponges," are even more basic than hydroxide ions in organic solution, a noteworthy property in the context of the normally lower basicity of tertiary amines compared to hydroxide anions [251,395,396]. Examples of relevant cryptands that have been studied for lithium solvent extraction separations are shown in Scheme 17.

Analogous to how the metal ion preference of crown ethers is dictated by their respective sizes, the cavity sizes of different cryptands also lead to distinct metal ion preferences. In Table 18 the stability constants of the alkali metal ion complexes of different cryptands are shown as a representative example of this phenomenon. Cavity sizes of the cryptands, determined by using the Corey-Pauling-Koltun atomic models and X-ray crystallography, are also collected within this table [397]. The smallest cryptand 2.1.1 (**91**) has a cavity size of 1.50–1.68 Å that is well-matched to the ionic diameter of the lithium ion, resulting in the very large stability constants for this metal in aqueous and methanolic solutions [251,390,393,397–402]. The cryptate effect is particularly apparent for the lithium complex of **91**; its lithium log K_{ML} value in methanol is 8.04, 200,000-fold greater than that of 12-crown-4 ether (log $K_{ML} = 2.73$) [269,400]. The appropriate size-match of **91** also confers it with a high Li^+:Na^+ selectivity and poor binding affinity towards alkaline earth ions like magnesium [401].

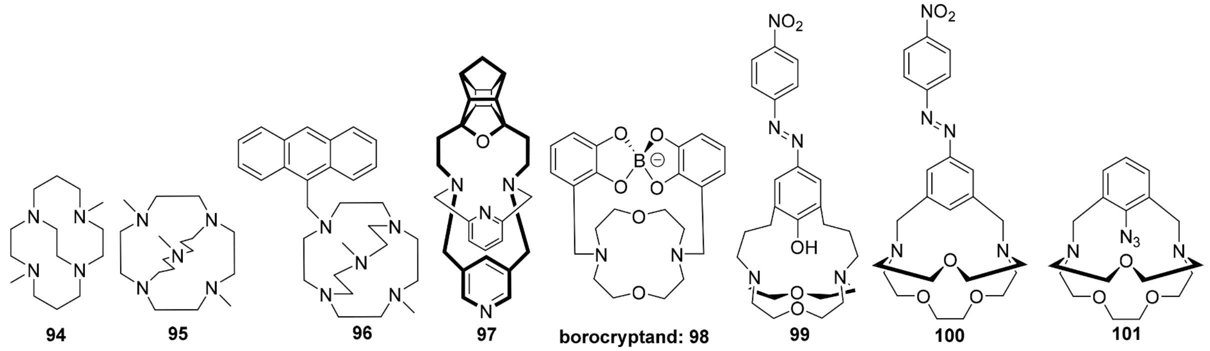
Accordingly, cryptands 2.2.1 (**92**, cavity size: 2.00–2.50 Å) and 2.2.2 (**93**, cavity size: 2.70–2.80 Å) with larger cavity sizes are poorly compatible with the small lithium ion, and thus have a thermodynamic preference for larger metal ions like sodium or potassium [397,401]. Although **91** is ideal for lithium, its poor lipophilicity limits its direct use in solvent extraction because it cannot effectively transfer this ion to the organic phase [401,403]. Thus, the functionalization of this ligand with more hydrophobic groups could improve its use for lithium solvent extraction.

A selection of other cryptands with relevance for lithium extractions are shown in Scheme 18, and their lithium complexation and extraction properties are shown in Table 19. The cyclam-derived cryptand **94** exhibited high Li^+:Na^+ selectivities, reaching up to 200. This selectivity pattern was determined with NMR spectroscopy, but solvent extraction or separation studies have not yet been carried out [405]. Likewise, the cross-bridged aza-12-crown–4 ether ligands **95** and **96** have a strong binding affinity for lithium with selectivity over sodium [406,407]. The high selectivity of both cryptands is a consequence of their smaller and more rigid metal-binding cavities that cannot effectively accommodate sodium ions, compared to the conventional, more flexible tetraaza non-cross-bridged macrocycles [392]. The cryptand **97**, which incorporates a pyridine-bridge, was applied in single metal solvent extraction studies in which the alkali metals were studied separately. It was found that **97** transferred 82 % of the lithium from the aqueous into the organic phase. In separate experiments in the absence of lithium, extraction efficiencies of 71 % for sodium, 40 % for potassium, 46 % for rubidium, and 41 % for cesium were obtained, indicating poor selectivity of this ligand for lithium [408].

Table 18
Alkali Metal Ions and Cryptands and their Performance in Complexation and Extraction.

Cations	Ion Diameter[a]	Cryptand	Cavity Diameter of Cryptand[b] [397]	log K_{ML}	Selectivity
Li^+	1.36 Å [308] 1.52 Å [62]	**91**	1.50–1.68 Å	Li^+: 5.50[c] [401] Li^+: 8.04[d] [400] Li^+: 11.80[e] [404] Na^+: 3.20[c] [401] Na^+: 6.10[d] [401] K^+: <2.00[c] [401] K^+: 2.30[d] [401] Mg^{2+}: <2.0[c] [401]	Li^+:Na^+: 200
Na^+	1.94 Å [308] 2.04 Å [62]	**92**	2.00–2.50 Å	Li^+: 2.50[c] [401] Li^+: 5.38[d] [400] Na^+: 5.40[c] [401] Na^+: 9.65[d] [400] K^+: 3.95[c] [401] K^+: 8.54[d] [400]	Li^+:Na^+: ~0.001
K^+	2.66 Å [308] 2.76 Å [62]	**93**	2.70–2.80 Å	Li^+: <2.0[c] [401] Li^+: 2.60[d] [401] Na^+: 3.90[c] [401] Na^+: 7.98[d] [400] K^+: 5.40[c] [401] K^+: 10.41[d] [400]	–

[a] The ionic diameters were calculated based on reported ionic radii of metal ions for the coordination number six [62,308].
[b] From X-ray crystallographic data and Corey-Pauling-Koltun atomic models [378,397].
[c] Stability constant in water via pH titration, 25 °C, anion: Cl^-, supporting electrolyte: $N(CH_3)_4Br$ (50 mM).
[d] Stability constant in methanol, 25 °C.
[e] Stability constant in acetone via calorimetric titration, 25 °C.



Scheme 18. Different cryptands investigated for lithium binding with potential applications in solvent extraction separations.

Table 19
Cryptands Shown in Scheme 18 and their Performance in Lithium Complexation and Extraction.

Compound	Solvent	Method/Conditions	Selectivity	Ref.
94	CD_3CN	competitive NMR experiment of ligand, $LiClO_4$ and $NaBPh_4$ (1:1:1) in CD_3CN	Li^+:Na^+: 200	[405]
95	$CDCl_3$	competitive NMR experiment of ligand and various metal ions (Li^+, Na^+, K^+) showed only Li–complexation	Li^+:Na^+: high	[406]
96	MeOH	synthesis of lithium complex was performed in the presence of an excess of sodium perchlorate	Li^+:Na^+: high	[407]
97	H_2O, $CHCl_3$	solvent extraction with ligand (5 mM) in $CHCl_3$ and aqueous metal picrates (5 mM) at 25 °C and detection via UV/Vis *EE*: Li^+: 81.9 % *EE*: Na^+: 70.7 % *EE*: K^+: 40.3 % *EE*: Rb^+: 46.0 % *EE*: Cs^+: 40.9 %	Li^+:Na^+: moderate	[408]
98	DMSO	competitive NMR experiment of ligand in DMSO with Li^+ and Na^+	Li^+:Na^+: high	[411]
99	H_2O/ DEGMEE[a] (9:1)	competitive selectivity experiment with ligand (50 μM) and LiCl, NaCl and KCl at pH = 12 at 25 °C and detection via UV/Vis	Li^+:Na^+: high Li^+:K^+: high	[412]
100	H_2O, $CHCl_3$	solvent extraction with ligand in $CHCl_3$ and aqueous LiCl, NaCl and KCl at pH = 7–9 and detection via UV/Vis	Li^+:Na^+: 10^4 Li^+:K^+: high	[413]
101	H_2O, CH_2Cl_2	solvent extraction with ligand (5 mM) in $CHCl_3$ and metal picrates (aq, 5 mM) at 25 °C and detection via UV/Vis *EE*: Li^+: 81 % *EE*: Na^+: 14 % *EE*: K^+: 12 % *EE*: Rb^+: 13 % *EE*: Cs^+: 14 %	–	[414]

[a] DEGMEE: diethylene glycol monoethyl ether.

Another subgroup of cryptands are borocryptands with the general structure of **98** (Scheme 18) [409–411]. The borocryptands contain a diaza-12-crown-4 center which is linked to two anionic catechol units coordinated to a boron. This bridge is formed by the condensation of two pendent catechol groups with boronic acid. The resulting borocryptand forms stable six-coordinate complexes with lithium. In competition experiments, borocryptand **98** binds lithium more strongly than sodium [410,411]. Despite their interesting anionic structures and promising lithium selectivity, further experiments to evaluate the performance of borocryptands for lithium extraction applications have not yet been performed.

The cryptands **99** and **100** contain *p*-nitrophenylazo-chromophores and therefore possess rich photophysical properties [412,413]. In addition to being more selective under neutral to basic pH (pH = 7–12) for lithium over sodium, they also undergo a significant change in their absorption spectra upon lithium complexation including a bathochromic shift that can potentially be used for quantitative lithium sensing. The azide-bearing cryptand **101** shows selective and highly efficient lithium extraction properties in initial small-scale solvent extraction experiments. In particular, **101** showed lithium extraction efficiencies up to 81 %. For larger alkali metal ions, the extraction efficiency was less than 14 % [414]. However, its extraction properties with alkaline earth metal ions like magnesium or calcium ions has not yet been studied.

3.4.3. *Calix[4]pyrroles*

Calix[4]pyrroles are a class of ligands that contain four pyrroles linked in a cyclic structure that are analogs to calix[4]arenes discussed above [415–417]. A key difference between these ligands, however, are the pK_a values of the cyclic monomeric units. The phenol protons of calix[4]arenes can be deprotonated under basic conditions, allowing them to directly coordinate to metal ions [332]. Calix[4]pyrroles, by contrast, typically remain protonated, even under highly basic conditions. This property is advantageous because the N–H groups can hydrogen bond with anions, leading to systems that can extract ion pairs [416,418–420]. Fig. 6, for example, shows a crystal structure of the calix

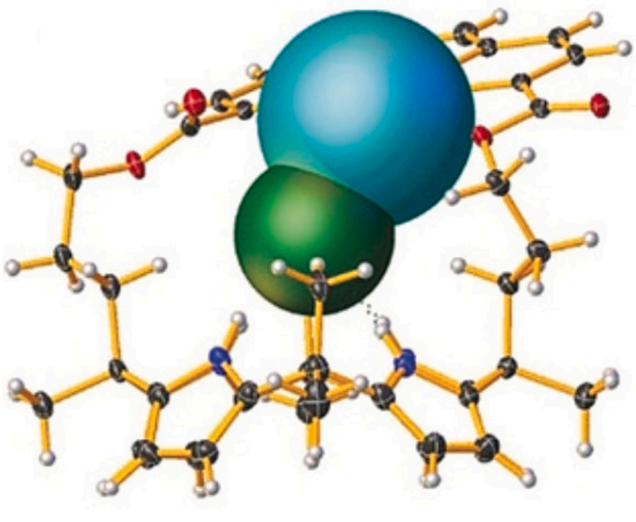
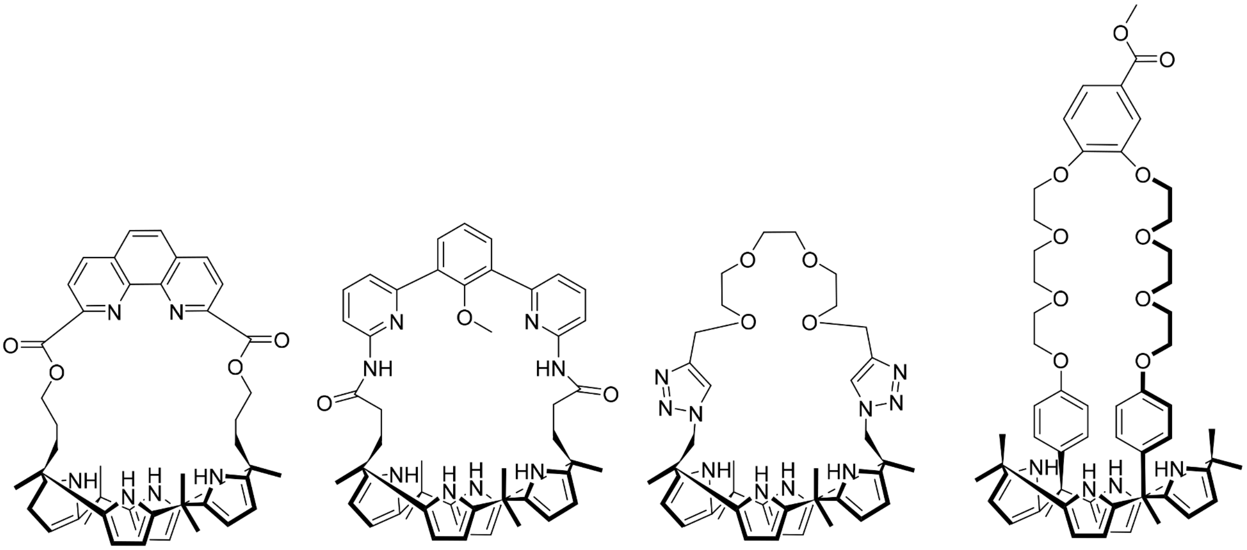


Fig. 6. X-ray crystal structure of calix[4]pyrrole **102** complexing the lithium (teal) chloride (green) ion pair. Reproduced with permission from Ref. [421]. Copyright 2018 John Wiley and Sons Inc.



calix[4]pyrrole: 102 calix[4]pyrrole: 103 calix[4]pyrrole: 104 calix[4]pyrrole: 105

Scheme 19. Calix[4]pyrroles as chelators for selective lithium salt extraction.

[4]pyrrole **102,** which is binding to the lithium chloride ion pair via pyrrole hydrogen bonding with the chloride, and metal ion coordination via the phenanthroline group to the lithium [421].

Ditopic receptors that can bind ion pairs are typically more effective in extracting them to the organic phase, because their charge remains neutralized throughout the process [420,422]. Furthermore, calix[4]pyrroles have been designed to exhibit cooperative binding with ion pairs. For these compounds, hydrogen bonding of the pyrroles can trigger a conformational change that enhances the cation-π interactions with metal ions [418–420,423].

Like calix[4]arenes, the syntheses of calix[4]pyrroles can be accomplished in very few steps, following a procedure that requires the coupling of pyrrole-containing units and a metal-recognizing counterpart via condensation. Recently, several calix[4]pyrroles have been designed to bind and extract lithium salt ion pairs. These examples are shown in Scheme 19 and their extraction properties are given in Table 20.

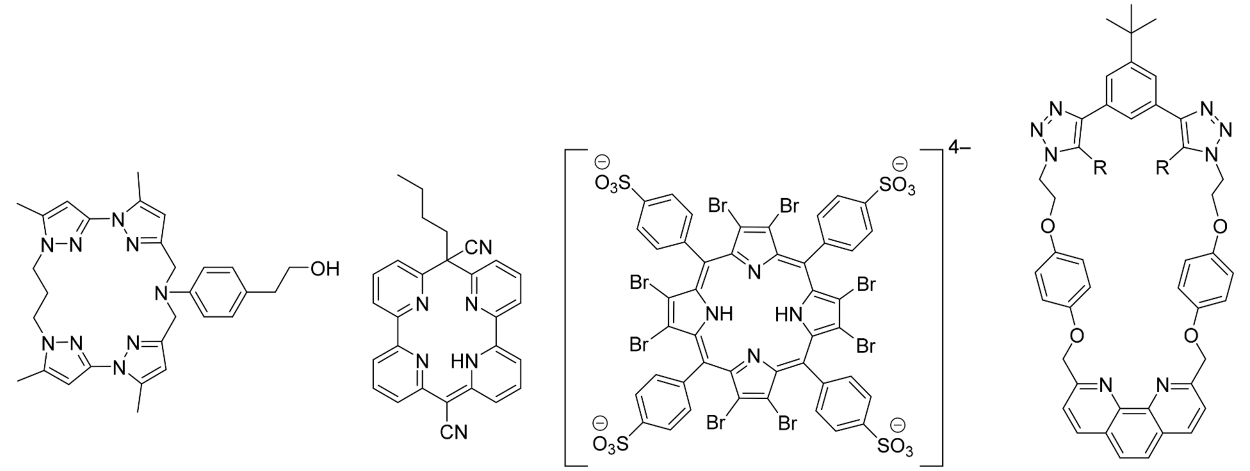
Although simple calix[4]pyrroles can be synthesized in few steps, more complex structures within this ligand class require more sophisticated multi-step syntheses and are obtained in lower yields [421,424–426]. These synthetic efforts, however, are often worthwhile, as the complex calix[4]pyrroles, like those shown in Scheme 19, can exhibit impressive affinity and selectivity for lithium salt ion pairs even in the presence of other alkaline earth and alkali metals. For example, calix[4]pyrroles **102** and **103** were studied by NMR spectroscopy, showing that they were able to selectively extract the ion pair lithium salts lithium chloride and lithium nitrite from an aqueous phase containing sodium and potassium salts into the organic phase [421,424]. In addition, calix[4]pyrrole **105** was demonstrated to have impressive selectivity for solid lithium chloride over other alkali and alkaline earth metal salts, such as magnesium and calcium chloride [426]. These NMR experiments provide qualitative demonstration of metal ion selectivity of these receptors. Further quantitative binding studies in the form of titrations or solvent extractions would be valuable to more precisely characterize their metal ion preferences. X-ray crystal structures of calix[4]pyrroles **102**, **103**, and **105** revealed a 1:1 complex of ligand and various lithium salts like lithium chloride, lithium nitrite, and lithium nitrate, whereas the triazole-functionalized calix[4]pyrrole **104** formed a 2:2 complex with lithium chloride [425]. These structures clearly highlight how the donor atoms like nitrogen and π-interactions of the aromatic groups bind effectively to lithium, while the pyrrole NH groups form effective hydrogen bonds with the anions. Moreover, DFT calculations on the ion pair-binding properties of these calix[4]pyrroles explained the lithium ion pair selectivity of these ligands based on their higher binding energies for lithium salts [424].

Table 20
Calix[4]pyrroles shown in Scheme 19 and their Performance in Lithium Complexation and Extraction.

Compound	Solvent	Method/Conditions	Selectivity	Ref.
102	D_2O, $CDCl_3$	competitive solvent extraction experiment with ligand (3 mM) in $CDCl_3$ and saturated aqueous metal chloride in D_2O and detection via NMR *EE*: LiCl: high *EE*: NaCl: low *EE*: KCl: low	LiCl:NaCl: high LiCl:KCl: high	[421]
103	D_2O, $CDCl_3$	solvent extraction experiment with ligand (10 mM) in $CDCl_3$ and saturated aqueous metal nitrite in D_2O and detection via NMR *EE*: $LiNO_2$: high *EE*: $NaNO_2$: low *EE*: KNO_2: low	$LiNO_2$: $NaNO_2$: high $LiNO_2$: KNO_2: high	[424]
104	D_2O, CD_2Cl_2	competitive solvent extraction experiment with ligand (5 mM) in CD_2Cl_2 and saturated aqueous metal chloride in D_2O and detection via NMR *EE*: LiCl: high *EE*: NaCl: low *EE*: KCl: low	LiCl:NaCl: high LiCl:KCl: high	[425]
105	CD_3CN	competitive NMR experiment of ligand in CD_3CN (5 mM) and an excess of solid metal chloride at 25 °C showed selective Li–complexation	LiCl:NaCl: high LiCl:KCl: high LiCl:$MgCl_2$: high LiCl:$CaCl_2$: high	[426]

In addition to their value for solvent extraction, these ligands have also been shown to be effective for solid–liquid extraction, a process where metal salts in their solid-state can be extracted via transfer into the liquid phase [421,424,425].

The calix[4]pyrrole extractants show high selectivity for lithium



tetrapyrazolic macrocycle: 106 **107** **porphyrin: 108** **109**

Scheme 20. Different classes of nitrogen-containing macrocycles and ionophores for lithium complexation.

Table 21
Different Aromatic Nitrogen Donor Classes Shown in Scheme 20 and their Performance in Lithium Complexation and Extraction.

Compound	Solvent	Method/Conditions	Selectivity	Ref.
106	H_2O, CH_2Cl_2	competitive solvent extraction experiment with ligand in CH_2Cl_2 (70 μM) and various metal nitrates (aq, 17.5 μM; pH = 7) at 25 °C and detection via AAS *EE*: Li^+: 42 % *EE*: Na^+: 10 % *EE*: K^+: 2 % *EE*: Cs^+: 0 % extracted lithium complex shows desorption from organic phase by using pure water of up to 50 %	Li^+:Na^+: 4.2	[427]
107	H_2O, CH_2Cl_2	LiCl was enriched from 0.005 % to 80 % in two steps by using the ligand with membrane support	Li^+:Na^+: high	[428]
108	H_2O/ seawater, $CHCl_3$	solvent extraction experiment with ligand and tetrabutylammonium chloride (600 μM) in $CHCl_3$ and aqueous lithium (10 μM) at pH = 12.7 and detection via UV/Vis/AAS *EE*: Li^+: 100 % seawater extraction: pretreatment to remove Mg^{2+}/Ca^{2+} was occurred before extraction was performed and detection via flame photometry or UV/Vis	Li^+:Na^+: 10^4	[432]
109	$CDCl_3$/CD_3CN (1:1)	ligand (1 eq.) in $CDCl_3$ and $LiClO_4$ (1 eq.) in CD_3CN were combined to form the lithium complex followed by the addition of tetrabutylammonium salts at 25 °C to determine anion association, detection and analysis via NMR and binding software Bindfit: anion association constant: tetrabutylammonium chloride: $K_a = 1147\ M^{-1}$ anion association constant: tetrabutylammonium bromide: $K_a = 1214\ M^{-1}$ anion association constant: tetrabutylammonium iodide: $K_a = 1236\ M^{-1}$	–	[437]

salts and are able to remove both the lithium cation and their anion simultaneously. The advantage of extracting ion pairs provides a strong impetus for exploring these systems in complex media like seawater and brine.

3.4.4. Other aromatic nitrogen-containing macrocycles

The use of several other classes of aromatic nitrogen-based macrocycles, distinct from those described in the sections above, for lithium extraction have been reported. These structures are shown in Scheme 20, and their relevant properties are summarized in Table 21.

The tetrapyrazolic macrocycle **106** was evaluated for lithium extraction applications [427]. In laboratory-scale solvent extraction experiments with various alkali metal ions, this ligand showed high lithium extraction efficiencies of up to 42 % with a Li^+:Na^+ selectivity of 4.2. Upon extraction of lithium into the organic phase, the authors demonstrated that they could use deionized water to strip 50 % of this ion within two hours [427].

The tetrapyridyl macrocycle **107** was also found to be useful for lithium extraction and separation [428]. The cavity size of this macrocycle is optimal for lithium, leading to a preference for this ion compared to other alkali and alkaline earth metal ions [428–430]. As a result, the ligand is able to enrich lithium chloride from 0.005 % to 80 % from seawater after two separation steps by using a liquid membrane system designed by the authors of this study. Additionally, the ligand exhibits significant changes in its optical absorbance spectra upon binding to lithium. The free ligand absorbs light in the visible region, characterized by absorption bands at 281, 359, and 378 nm [431]. However, upon lithium binding the resulting complex becomes colorless [429,431]. This color change provides a valuable means of monitoring lithium extraction by this ligand [428]. These properties make this ligand interesting for further investigations for lithium solvent extraction.

The porphyrin **108** has also been used for lithium extraction and as an optical sensor for this ion [432]. The rigid and preorganized structure of porphyrins often confers them high selectivity for metal ions with well-matched ionic radii [433,434]. Although the crystal structure of the lithium complex with porphyrin **108** was not reported, related lithium porphyrin complexes show that the metal ion is incorporated into the cavity of the porphyrin and is coordinated to the four pyrroles [435]. Furthermore, the rich optical properties of porphyrin **108** give rise to diagnostic spectral changes upon metal binding. In particular, upon lithium complexation there was a hypsochromic shift in the absorption spectrum with an absorption maximum at 491 nm observed [433]. For these reasons, the use of porphyrins for metal ion extraction is interesting. The porphyrin **108**, which contains eight electron-withdrawing bromine atoms and four water-solubilizing sulfonate groups, was investigated for lithium extraction. The bromine substituents act to decrease the basicity of the pyrrole, enabling metal-binding extraction studies to take place at relatively low pH values. Moreover, **108** showed high affinity for lithium, achieving Li^+:Na^+ selectivity ratios on the order of 10^4 in biphasic aqueous solution at $pH = 12.7$ containing tetrabutylammonium chloride and chloroform mixture [432,436]. The high selectivity of porphyrin **108** prompted further studies on its use to extract lithium from seawater [432,433]. Prior to solvent extraction with this ligand, the seawater was pretreated with ethylenediaminetetraacetic acid (EDTA) to remove the alkaline earth ions magnesium and calcium [432]. Under these conditions, the porphyrin **108** was able to spectrophotometrically quantify the concentration of lithium in seawater. Because the primary effort of this study was to detect lithium, the researchers did not report approaches to decomplex the lithium so that it could be recovered. A major disadvantage in the use of porphyrins for this application is the need for highly basic conditions ($pH > 10$) within the extraction step.

Recently, the heteroditopic macrocyclic chelator **109** and other derivatives were analyzed for lithium ion-pair recognition (Scheme 20) [437]. NMR titration experiments, which involved treating **109** with lithium perchlorate in deuterated acetonitrile, revealed a strong interaction between these species. Notably, the subsequent addition of tetrabutylammonium salts of different anions to this lithium complex revealed substantial changes in the NMR spectrum, indicating that the macrocycle has captured discrete lithium ion pairs of different anions. Through these titration experiments, the authors determined association constants for the ion pairs, showing the lithium complex has higher preference for iodide ($K_a = 1236\ M^{-1}$) compared to bromide ($K_a = 1214\ M^{-1}$) and chloride ($K_a = 1147\ M^{-1}$). Demonstrating selectivity for lithium ion pairs, attempts to titrate sodium and potassium perchlorate complexes of this ligand with the different halides led to precipitation of alkali metal halide salts. Building upon these properties, **109** was able to dissolve lithium salts in organic solvents in solid–liquid extraction experiments [437]. Thus, **109** has potential applications for the direct extraction of lithium salts from solid materials and minerals.

3.5. Phosphorus- and sulfur-based chelators

Heavier heteroatoms, like sulfur and phosphorus, undergo less orbital hybridization than their 2p counterparts. Accordingly, their introduction as donor atoms within crown ethers leads to significant structural distortions due to their more acute bond angles, generally making them less suitable for this application [293]. Furthermore, both sulfur and phosphorus are soft Lewis bases, a property that is not favorable when interacting with hard acids like lithium. Thus, crown ethers containing these heavier heteroatoms have not been substantially explored for this application.

Computational studies, however, have investigated the effect of adding these heteroatoms on lithium ion binding affinity and selectivity [438]. The theoretically calculated heteroatom-to-lithium (Li–X) interatomic distances within complexes of various heteroatom substituted 12-crown-4 ethers were determined with Møller–Plesset second order perturbation theory (MP2) (Table 22). These calculations show that the Li–O and Li–N distances, 1.869 and 1.991 Å respectively, in the substituted 12–crown-4 complexes are substantially shorter than the corresponding Li–P and Li–S distances, 2.385 and 2.487 Å respectively. The longer distances in the phosphorus- and sulfur-substituted macrocycles are expected based on the larger atomic radii of these 3p elements, but also highlight a significant deviation from average Li–O atom distances of 2.08–2.28 Å [182]. Building upon these initial theoretical structural studies, metal-binding affinities of these macrocycles were calculated at the same level of theory [438]. As shown in Table 22, the lithium-binding affinities follows the sequence aza–12–crown–4 ~ oxa–12–crown–4 > thia-12-crown–4 > phospha-12-crown-4. These results indicate that the sulfur and phosphorus-containing cyclic crown ethers are poorer ligands for lithium, as expected from HSAB theory.

Table 22
Møller–Plesset (MP) Perturbation Calculations Based Interatomic Distances Li–X and Binding Energies of Heteroatom Substituted 12-crown-4 Ethers with Lithium [438].

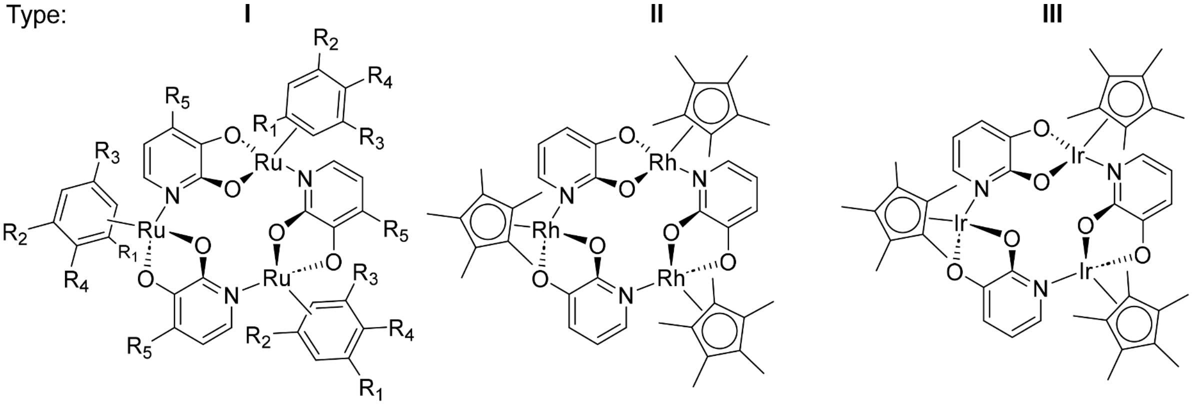
Crown Ether	Li–X (X = O, N, S, P) Distance	Calculated Binding Energy
oxa-12-crown-4	1.869 Å	–381.83 kJ/mol
aza-12-crown-4	1.991 Å	–382.17 kJ/mol
thia-12-crown-4	2.385 Å	–377.90 kJ/mol
phospha-12-crown-4	2.487 Å	–361.92 kJ/mol

Experimentally, the metal-binding and selectivity properties of the sulfur-containing thia-14-crown-4 ethers were investigated by using ion-selective electrodes equipped with the chelator in a polymer matrix in selectivity experiments [439]. As expected, these sulfur-containing crown ethers possess low affinity for lithium, but strongly bind soft metals like silver(I) and mercury(II) [439]. Similarly, sulfur-containing cryptands were also found to be poor lithium ligands and did not show any promise for use as extractants of this ion [414]. Collectively, these experimental and computational studies suggest that the incorporation of sulfur and phosphorus donor atoms is not beneficial for the design of effective lithium extractants.

3.6. Metallacrowns

Metallacrowns are analogs of crown ethers that provide multiple oxygen donor atoms within a macrocyclic core. In metallacrowns, however, the oxygen atoms are typically provided by bridging oxygen donors between metal centers, which comprise the remainder of the macrocycle [440,441]. In particular, trinuclear complexes of the general formula $[M(arene/Cp)(pyO_2)_3]$ like those shown in Scheme 21, where M is a transition metal, arene is a neutral η^6 ligand, Cp is an anionic cyclopentadienyl ligand, and pyO_2 is the bridging ligand, afford a metallacrown with similar topology as the 12-crown-3 ether with promising lithium- and sodium-binding properties. Following the initial discovery of this ligand class in 1989, several metallacrowns with high affinity for lithium and sodium ions have been characterized [442–445]. These metallacrowns can be easily synthesized via self-assembly and were obtained in quantitative yields [440,446–452]. The metallacrowns **110** and **111** bind sodium chloride and lithium chloride in the solid-state and in polar protic organic solvents. The cations of these ion pairs interact with the three bridging oxygen donors, and the chloride anions remain bound to the alkali metal [446,451]. Their high stability is afforded by the rigidity of the metallacrown and the size-match of the cavity to the alkali metal ions. These properties are advantageous over conventional organic crown ethers and cryptands [440]. For these reasons, 12-metallacrown-3 complexes have been investigated for the solvent extraction of lithium. Scheme 21 and Table 23 collect structures of metallacrowns and their lithium coordination and extraction properties.

Table 23 shows that in laboratory-scale experiments, the trinuclear ruthenium and rhodium metallacrown complexes **110–115** exhibit high Li^+:Na^+ selectivity that reaches 10,000, with even greater selectivity over larger monovalent and divalent metal ions [446,451–453]. The ruthenium 12–metallacrown–3 complex **113** was used to extract lithium from seawater [448]. Excellent extraction efficiencies and good selectivity for lithium, even in the presence of other metal ions like sodium and magnesium were achieved. After the initial extraction, the sodium ions can be easily and selectively removed from the organic phase by washing with deionized water. This washing step leads to a high enrichment of lithium ions in the organic phase including high selectivity between lithium and other competitive metals like sodium and



12-metallacrown-3: 110–114 **12-metallacrown-3: 115** **12-metallacrown-3: 116**

Scheme 21. Trinuclear 12-metallacrown-3 ether complexes as ligands for lithium complexation.

magnesium with Li^+:Na^+ and Li^+:Mg^+ ratios of 5.6 and 250, respectively [448]. However, no further experiments to strip the lithium ions from the organic phase have been reported.

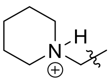
The iridium 12-metallacrown-3 complex **116**, a structural analog of the rhodium metallacrown **115**, was shown to bind lithium salts like lithium chloride and lithium fluoride as ionic pairs [447]. Interestingly, it was found in ^{1}H NMR experiments that the rhodium 12-metallacrown-3 complex **115** incorporated lithium chloride within eight min, whereas the iridium 12-metallacrown-3 complex **116** took more than one h to bind lithium chloride [447]. In addition, the iridium complex **116** showed higher affinity for lithium fluoride over lithium chloride. Given the high affinity for lithium fluoride, this metallacrown **116** was used for fluoride detection and sensing [447]. Despite the promising lithium affinity of **116**, no further studies involving its use for solvent extraction separations of this ion were reported.

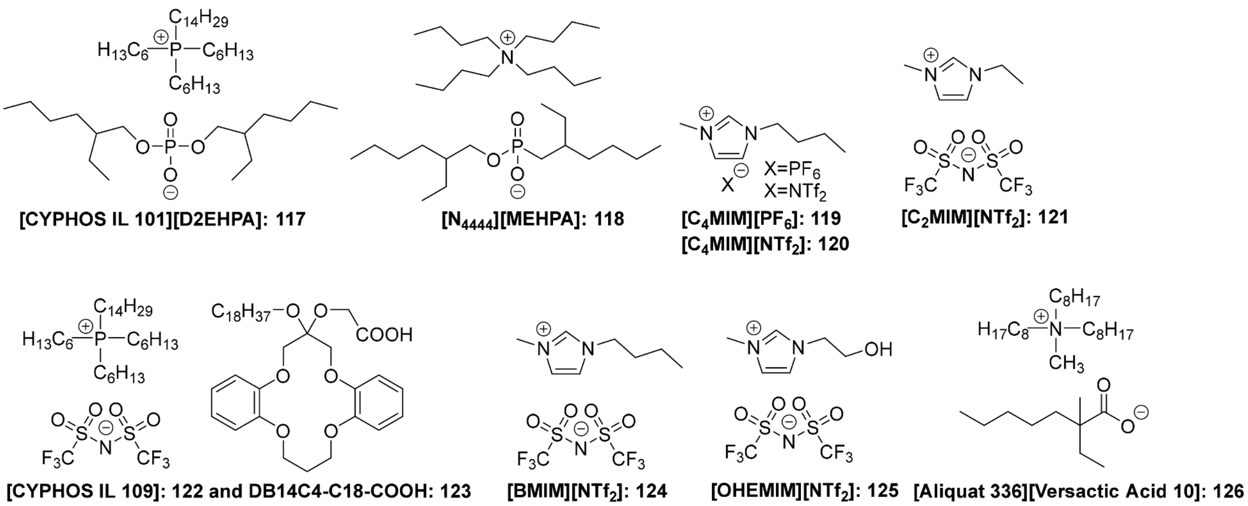
As these data indicate, the trinuclear 12–metallacrown–3 complexes are promising agents for lithium extraction. Further studies need to verify that the extracted lithium could be stripped and isolated from the organic phase. In addition, large-scale applications will most likely be limited by the cost of the precious metal metallacrown complexes. The development of metallacrowns with similar extraction capabilities using more cost-affordable base metals would help address this limitation.

4. Ionic liquids

The use of ionic liquids for green solvent extraction was first proposed and investigated in 1998 [454]. Since then, ionic liquids have received increasing attention for this application over the last few decades. Compared to conventional organic solvents, like benzene, acetonitrile, and toluene, ionic liquids have a negligible vapor pressure over a wide range temperatures, making them non-flammable and non-combustible [455–458]. Ionic liquids are typically composed of bulky and asymmetric organic cations and an inorganic or organic anion, and are characterized by their low melting points, which are commonly below room temperature. Their unusual ionic nature confers them with high thermal and radiation stability, low aqueous solubility, good ionic conductivity, and low volatility, making them well suited for the extraction of metals from aqueous phases [309,455,459–465]. Another advantage of ionic liquids is that their physicochemical properties can be finetuned via structural modifications to the cations and anions, allowing them to be optimized for their desired applications [456]. In the context of metal ion extraction, the ionic liquid themselves can be altered to serve both as extractant and as the organic phase [462]. In this case, the cationic metal ion from the aqueous phase exchanges with the cation of the ionic liquid, resulting in transfer of the metal ion to the ionic liquid by maintaining charge neutrality [459].

Table 23
Trinuclear 12-metallacrown-3 Ether Derivatives Shown in Scheme 21 and their Performance in Lithium Complexation and Extraction.

Compound	R_1	R_2	R_3	R_4	R_5	Solvent	Method/Conditions	Selectivity	Ref.
I **110**	Me	H	H	*i*Pr	H	H_2O, $CDCl_3$	competitive solvent extraction experiment with ligand in $CDCl_3$ (10 mM) and LiCl and NaCl (aq, 2 M) and detection via NMR	Li^+>Na^+	[451]
I **111**	COOEt	H	H	H	H	H_2O, $CDCl_3$	competitive solvent extraction experiment with ligand in $CDCl_3$ (10 mM), LiCl (aq, 50 mM) and various metal chlorides (aq, 1 mM) and detection via NMR/ICP	Li^+:Na^+: 1000	[446]
I **112**	OMe	H	H	H	H	H_2O, CH_2Cl_2	competitive solvent extraction experiment with ligand in CH_2Cl_2, Li/Na-picrate (aq) at 25 °C and detection via AAS	$\beta_{Li:Na}$: 4,390	[448]
I **113**	OMe	CH_3	CH_3	H	H	H_2O, CH_2Cl_2	competitive solvent extraction experiment with ligand in CH_2Cl_2, Li/Na-picrate (aq)/natural seawater at 25 °C and detection via AAS	$\beta_{Li:Na}$: 71,430 seawater: Li^+:Na^+: 5.6 Li^+:K^+: 10 Li^+:Mg^{2+}: 250 Li^+:Ca^{2+}: 9.1	[448]
I **114**	H	Me	H	*i*Pr		D_2O	NMR experiment of ligand in D_2O (5 mM) and different concentrations of $LiOAc/Na_2HPO_4$ in neutral aqueous buffer	Li^+:Na^+: 10,000	[452]
II **115**	–	–	–	–	–	H_2O, CH_2Cl_2	solvent extraction experiment with ligand in CH_2Cl_2, Li/Na/K-picrate (aq) at 25 °C and detection via AAS	Li^+:Na^+: 27 Li^+>Na^+>K^+	[453]
III **116**	–	–	–	–	–	C_6H_6, MeOH	metallacrown•LiCl was converted to metallacrown•LiF with KF in C_6H_6 and MeOH and detection via NMR	–	[447]



Scheme 22. Different ionic liquids and the crown ether DB14C4-C18-COOH **123** relevant for the solvent extraction separation of lithium.

The successful application of ionic liquids for metal extraction has been demonstrated for a range of different metal ions, including transition metals, precious metals, heavy main group metals, lanthanides, and actinides [465–473]. In this section, several promising ionic liquid-based extraction systems used for lithium will be discussed. In Scheme 22, various examples of ionic liquids used for lithium extraction and their chemical structures are shown, and Table 24 collects the relevant extraction parameters of these systems.

The ionic liquid and extractant combination of CYPHOS IL 101 and D2EHPA (**117**) dissolved in the diluent kerosene as organic phase was used for a laboratory-scale lithium extraction [474]. This combination led to lithium extraction efficiencies of up to 53 % at pH = 6 from an aqueous lithium nitrate solution. Moreover, under the same conditions, the extractant D2EHPA (**68**) alone was only able to extract less than 20

Table 24
Overview of Different Ionic Liquids Shown in Scheme 22 and their Extraction Systems for Lithium Solvent Extraction.

Ionic Liquid	Liquids	Method/Conditions	Selectivity	Ref.
117	H_2O, [CYPHOS IL 101][D2EHPA] in kerosene	solvent extraction with [CYPHOS IL 101][D2EHPA] (100 mM) in kerosene and aqueous $LiNO_3$ (3 mM) at pH = 6 at 30 °C and detection via AAS and photometer *EE*: Li^+: 53 %	–	[474]
118	H_2O, $[N_{4444}]$[MEHPA] in dichloroethane	solvent extraction with $[N_{4444}]$[MEHPA] in dichloroethane and aqueous LiCl (12 mM) at 20 °C and detection via ICP-OES *EE*: Li^+: 94.6 %	–	[464]
118	H_2O, $[N_{4444}]$[MEHPA] in dichloroethane	competitive solvent extraction with $[N_{4444}]$[MEHPA] in dichloroethane and aqueous LiCl, NaCl, KCl, RbCl, CsCl at 20 °C and detection via ICP-OES	Li^+:Na^+: high Li^+:K^+: high Li^+:Rb^+: high Li^+:Cs^+: high	[464]
119	salt lake brine, $[C_4MIM][PF_6]$ in TBP	competitive solvent extraction with $[C_4MIM][PF_6]$ (10 % v/v) in TBP and aqueous lithium from salt lake brine at pH = 5.58 at 20 °C and detection via AAS *EE*: Li^+: >90 %	Li^+:Mg^{2+}: high	[475]
119	salt lake brine, $[C_4MIM][PF_6]$ in TBP	competitive solvent extraction with $[C_4MIM][PF_6]$ (20 % v/v) in TBP and aqueous lithium from salt lake brine with $NaClO_4$ as co-extraction reagent at pH = 5.58 at 20 °C and detection via AAS *EE*: Li^+: >87 %	Li^+:Mg^{2+}: high	[476]
120	salt lake brine, $[C_4MIM][NTf_2]$ in TBP	competitive solvent extraction with $[C_4MIM][NTf_2]$ (10 % v/v) in TBP and aqueous lithium from salt lake brine with at pH = 5.58 at 30 °C and detection via AAS *EE*: Li^+: >90 %	Li^+:Mg^{2+}: high	[221]
121	salt lake brine, $[C_2MIM][NTf_2]$ in TBP	competitive solvent extraction with $[C_4MIM][NTf_2]$ (10 % v/v) in TBP and aqueous lithium from salt lake brine at 30 °C and detection via AAS *EE*: Li^+: >80 %	Li^+:Mg^{2+}: high	[477]
122	H_2O, [CYPHOSIL IL 109]	competitive solvent extraction with DB14C4-C18-COOH **123** in CYPHOSIL IL 109 (55 mM) and aqueous LiCl, NaCl, and KCl at pH = 12 at 25 °C and detection via ICP-MS *EE*: Li^+: 72.8 % *EE*: Na^+: <0.1 % *EE*: K^+: 0.5 %	Li^+:Na^+: 1954 Li^+:K^+: 138	[309]
124	H_2O, $[BMIM][NTf_2]$ in CH_2Cl_2	solvent extraction with crown ether (200 mM) and $[BMIM][NTf_2]$ (500 mM) and aqueous $LiNTf_2$ (1 M) at 20 °C and detection via ICP-OES *EE*: Li^+: 26.4 %	–	[478]
125	H_2O, $[OHEMIM][NTf_2]$ in Cyanex923	competitive solvent extraction with $[OHEMIM][NTf_2]$ (15 % v/v) in Cyanex923 and aqueous LiCl and NaCl at initial pH = 10.68 and 25 °C and detection via ICP-OES *EE*: Li^+: >80 % *EE*: Na^+: <20 %	Li^+:Na^+: high	[459]
126	H_2O, [Aliquat 336][Versatic Acid 10] in *p*-cymene	competitive solvent extraction with [Aliquat 336][Versatic Acid 10] (1.0 M) in *p*-cymene and aqueous LiCl (4.72 mM), NaCl (137 mM), and $MgCl_2$ (158 mM) and detection via ICP-OES *EE*: Li^+: ca. 15 % *EE*: Na^+: <5% *EE*: Mg^{2+}: ca. 90 %	Mg^{2+}:Li^+: high	[479]

% of the lithium. These experiments illustrate that the ionic liquid **117** provides synergistic advantages with respect to the extraction of lithium from aqueous solutions [474].

The lithium extraction efficiency was studied in a laboratory-scale experiment from an aqueous solution of lithium chloride by using the ionic liquid tetrabutylammonium 2-ethylhexyl hydrogen-2-ethylhexylphosphonate ($[N_{4444}]$[MEHPA], **118**) dissolved in dichloroethane as organic phase [464]. Under these conditions, lithium extraction efficiencies from an aqueous solution containing lithium of up to 94 % were achieved. By contrast, the acidic extractant MEHPA **69** alone showed an extraction efficiency of only 5 %, providing further validation on the synergistic functionality of the ionic liquid. Moreover, competitive solvent extraction experiments in the presence of other alkali metal ions like potassium, sodium, rubidium, and cesium revealed the high selectivity of **118** for lithium ions. In further experiments, the authors used a 500 mM HCl solution to quantitatively strip the lithium from the ionic liquid-containing organic dichloroethane phase [464].

Imidazolium-based ionic liquids have also been investigated for lithium extraction [221,475–477]. For instance, the imidazolium-based ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$, **119**) dissolved in TBP at 10 % v/v was able to extract lithium efficiently from salt lake brine [475]. In particular, the authors reported that lithium extraction efficiencies of greater than 90 % in the presence of other competing metal ions present in the brine can be achieved. By contrast, the extraction efficiency of magnesium, one of the most highly abundant metal ions within brine, was less than 7 %, reflecting the high selectivity of this system for lithium. The mechanism of the extraction was postulated to be via a cationic extractant complex “$[Li(TBP)_2]^+$” that is transferred into the organic phase. This process can be described according to the following equation:

$$Li^+(aq) + [C_4mim][PF_6](org) + 2TBP(org) \rightarrow Li(TBP)_2[PF_6](org) + [C_4mim]^+(aq) \tag{11}$$

In additional experiments, the authors also showed that the lithium ions could be quantitatively stripped from the organic phase by using 0.1 M HCl at 20 °C [475]. Subsequent studies on the use of imidazolinium-based ionic liquids **120** and **121** for extracting and obtaining lithium from salt lake brines have further validated this approach [221,476,477].

The imidazolium-based ionic liquid **120** was used in combination with the ligand dibenzo–14-crown-4 **37** for lithium isotope separation, but the efficacy of this system for extraction of lithium from complex mixtures like brine or seawater has not yet been studied [403]. Other researchers, however, have explored the use of chelators in combination with ionic liquids for these applications [309,478,480]. For instance, the phosphonium-based ionic liquid CYPHOSIL IL 109 (**122**) was explored in conjunction with lipophilic and lithium-selective ligands like DB14C4-C18-COOH (**123**, Scheme 22). These studies showed that successful extraction of lithium with greater than 70 % efficiency in the presence of sodium and potassium required the organic ligand, as the ionic liquid itself was insufficient for this purpose. The experiments used basic conditions (pH = 12) to deprotonate the sidearm carboxylic acid group on the DB14C4-C18-COOH **123** ligand to increase its lithium ion affinity via formation of a five-coordinate 1:1 ligand to metal complex. Dilute HCl (0.1 M) could be used to strip the extracted lithium from the ionic liquid organic phase, and the ionic liquid-crown ether combination could be used through at least five subsequent extraction cycles [309]. The reusability of this system as well as its stability to the acidic conditions required for lithium stripping reflects its promise for large-scale industrial applications.

The use of a 15–crown-5 crown ether in combination with 16 different ionic liquids for lithium extraction has also been studied [478]. The most effective crown ether-ionic liquid combination identified from these investigations employed the 15-crown-5 ether dissolved in the imidazolium-based ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ($[BMIM][NTf_2]$, **124**) and dichloromethane as the organic phase. This biphasic extraction system transfers lithium from a synthetic solution containing 1 M aqueous lithium bis(trifluoromethanesulfonyl)imide ($LiNTf_2$) with an extraction efficiency of 26 %. These studies generally identified imidazolinium-based ionic liquids to be the most effective. The anions of the imidazolium-based ionic liquid investigated (NTf_2^-, PF_6^-, CF_3COO^-, BF_4^-, Cl^-) also impacted the lithium extraction efficiency; anions with greater water solubility were less effective. Consequently, the bulky, non-coordinating NTf_2^- anion was found to be the most effective for lithium extraction applications [478].

The ionic liquid 1–hydroxyethyl-3-methyl imidazolium bis(trifluoromethane)sulfonimide ($[OHEMIM][NTf_2]$, **125**) was dissolved in the neutral phosphine oxide-containing extractant Cyanex923 forming the organic phase [459]. The pH of the aqueous phase was adjusted to an initial pH of 10.7 by using an aqueous solution of lithium carbonate and sodium hydroxide. The aqueous to organic phase ratio was kept at 1:1. These conditions gave rise to lithium extraction efficiencies exceeding 80 % from synthetic solutions of lithium and sodium. Under analogous conditions, additional experiments showed that the ionic liquid or the neutral extractant Cyanex923 alone were not effective for lithium extraction, indicating that their combination is critical. Upon optimization for the Cyanex923 concentration, the sodium extraction efficiency could be minimized (<20 %) to afford highly pure solutions of lithium. Mechanistically, it was proposed that two Cyanex923 molecules are required to transfer lithium to the organic phase, as shown below:

$$Li^+(aq) + [OHEMIM][NTf_2] + 2Cyanex923(org) \rightarrow \left[Li(Cyanex923)_2\right][NTf_2](org) + [OHEMIM]^+(aq) \tag{12}$$

Finally, the authors of this study demonstrated that the lithium could be quantitatively stripped from the organic phase with 1 M HCl [459].

The ionic liquid [Aliquat 336][Versatic Acid] (**126**) was investigated for the separation of magnesium from lithium in a synthetic solution containing lithium, sodium, and magnesium via solvent extraction. This ionic liquid comprises both the ammonium-based extractant [Aliquat 336] and the acidic extractant [Versatic Acid 10] [479]. This system was used to selectively separate magnesium from lithium within the brine solution. This enrichment of lithium in the brine could prove valuable for facilitating the isolation of this ion.

Collectively, the studies described above indicate that the use of ionic liquids in combination with extractants leads to synergistic effects and shows promise for lithium extraction and separation. In addition, the high stability of ionic liquids provides relatively facile means of using dilute HCl to remove lithium from the organic phase. The recyclability of these ionic liquid systems is important when considering the environmental impact of these processes, especially on large industrial-scales.

5. Conclusion and outlook

The rising demand for lithium worldwide requires more efficient and environmentally friendly approaches to extract and separate this metal from different sources. In this review, we discussed strategies that have been investigated with a key focus on solvent extraction. Although there are many factors that can be modified and optimized for a given solvent extraction process, the use and choice of chelator is critically important. The different efficacies of the extractions described in this article were a consequence of the different chelators applied. Collectively, these studies highlight the importance of inorganic and coordination chemistry for the isolation of lithium. Among the chelators surveyed, the most widely used and promising ones are those based on the 14-crown-4 ether, whose size is optimally matched to the ionic radii of lithium. In addition, the examples discussed in this article show that these macrocycles can be systematically modified to further alter and optimize their lithium-binding properties and ability to partition into the organic phase. Lastly, most of these macrocycles could easily be recycled by stripping the lithium with dilute aqueous HCl. A major limitation of these ligands, however, is their challenging syntheses and consequently high costs, factors that are important for large-scale applications.

Accordingly, most of the new ligands applied for lithium solvent extraction are studied with laboratory-scale experiments, using synthetic solutions of metal ions. To further develop these separation processes using novel chelators, they need to be tested on larger scales using industrially relevant solutions like brine and seawater. Lastly, many studies do not report on the efficacy of the lithium stripping step and the potential recyclability of the chelators for subsequent extractions. Given the high cost and synthetic challenges associated with making novel chelators, the ability to reuse them for multiple extraction cycles will be critical for their industrial success.

All in one, we think that after careful optimization, solvent extraction methods in support with chelators can be a major way to extract lithium from lithium-containing resources. In addition, disadvantages of solvent extraction methods can be compensated by using newly reported dual technologies in which two or more extraction techniques will be combined to achieve maximum efficiency. For instance, ion sieves or polymer-based membranes functionalized with chelators can be an another powerful tool for effective lithium recovery, due to potential synergistic effects [481].

CRediT authorship contribution statement

Thines Kanagasundaram: Conceptualization, Writing, Investigation, Formal analysis. **Olivia Murphy:** Writing. **Maha N. Haji:** Writing, Review and Editing, Supervision. **Justin J. Wilson:** Writing, Conceptualization, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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