

## RESEARCH ARTICLE

View Article Online  
View Journal

Cite this: DOI: 10.1039/d5qi01799h

## Non-aqueous separation of lithium and sodium perchlorates by selective coordination with a hexadentate semi-flexible amine ligand

Jack M. Hemingway,<sup>\*a</sup> Xiao Yang,<sup>b</sup> Paul G. Waddell,<sup>id a</sup> Joel Cornelio,<sup>b</sup> Matthew E. Lowe,<sup>a</sup> James A. Dawson,<sup>id a</sup> Peter R. Slater,<sup>id b,c</sup> Roly J. Armstrong<sup>id a</sup> and Erli Lu<sup>id \*b</sup>

Separation of lithium and sodium is a topic of substantial scientific and industrial importance. Regarding Li/Na perchlorates, which are not only environmental hazards but also useful oxidants in chemical synthesis, an efficient Li–Na perchlorate separation method has not been reported due to lack of a ligand which can selectively coordinate with one of the two. Herein, we report an efficient Li–Na perchlorate separation by using our hexadentate ligand *N,N',N''*-tris-(2-*N*-diethylaminoethyl)-1,4,7-triaza-cyclononane (DETAN), which can selectively coordinate with LiClO<sub>4</sub> at room temperature to form a monomer in excellent yield but does not coordinate with NaClO<sub>4</sub> even at elevated temperature. The structure of the monomeric complex, [LiClO<sub>4</sub>(DETAN)] (**1**), was characterised by single-crystal X-ray diffraction and NMR spectroscopy.

Received 28th August 2025,  
Accepted 22nd November 2025

DOI: 10.1039/d5qi01799h

rsc.li/frontiers-inorganic

## 1. Introduction

Lithium plays a vital role in lithium-ion batteries (LIBs),<sup>1</sup> driving exponential demand across the energy sector.<sup>2</sup> Despite the presence of Li-enriched ores such as petalite LiAl(Si<sub>2</sub>O<sub>5</sub>)<sub>2</sub>, lepidolite K(Li,Al)<sub>3</sub>(Al,Si,Rb)<sub>4</sub>O<sub>10</sub>(F,OH)<sub>2</sub> and spodumene LiAl(SiO<sub>3</sub>)<sub>2</sub>, the global Li supply largely relies on isolating Li from the sodium-rich brine,<sup>3–6</sup> which renders Li–Na separation of substantial scientific and industrial importance. However, given the close resemblance of Li<sup>+</sup> and Na<sup>+</sup> in terms of both their charge (both +1) and bonding characteristics (both form largely ionic bonds with ligand atoms, with very little covalent contribution<sup>7</sup>), their separation is challenging. So far, the reported Li–Na separation strategies include:<sup>3</sup> (i) solvent extraction; (ii) adsorption in intercalated materials; (iii) electrochemical intercalation/de-intercalation; (iv) membrane separation; (v) ligand separation; (vi) biological separation; and (vii) sedimentation separation. Among the methods, solvent extraction and ligand separation both depend on the difference of the metal cation–ligand interactions between Li<sup>+</sup> and Na<sup>+</sup>, stemming largely from the difference of the ionic radii of the

cations. Hence, designing a ligand of high selectivity between binding Li<sup>+</sup> and Na<sup>+</sup> is the key requirement for achieving an efficient Li–Na separation. Most of the current ligand systems are based on crown ethers,<sup>8</sup> while anthraquinone<sup>9</sup> and calix-[4]-arene-based<sup>10</sup> systems have been reported as well. Very recently, Nitschke, Wales and co-workers reported a proton-responsive molecular cage of the tris(2-aminoethyl)amine (TREN) and tris(formylpyridyl)benzene subcomponents, which can separate Li<sup>+</sup> from Na<sup>+</sup> in the mixture of their bis(trifluoromethanesulfonyl)imide (NTf<sub>2</sub>) salts.<sup>11</sup>

Understandably, the anion also influences the Li/Na separation by intervening with the ligand coordination to the metal cation. As such, usually a ligand system which works for one anion (such as the Li/NaNTf<sub>2</sub> in the aforementioned Nitschke/Wales system<sup>11</sup>) cannot be directly translated to another anion. In this work, we focus on the perchlorate anion (ClO<sub>4</sub><sup>−</sup>). Featuring a tetrahedral structure with distributed charge at four O atoms,<sup>12</sup> perchlorate is a potential public health concern due to its toxicity.<sup>13</sup> Also, lithium perchlorate (LiClO<sub>4</sub>) is of interest in organic synthesis (*e.g.* accelerating Diels–Alder reactions<sup>14</sup> and promoting cyanosilylation of carbonyl compounds<sup>15</sup>) and as an electrolyte component in Li-ion batteries.<sup>16</sup> In the natural environment, LiClO<sub>4</sub> usually co-exists with its heavier group-1 sister, sodium perchlorate (NaClO<sub>4</sub>), and their sensing and isolation has been of long-standing scientific interest since the early 20<sup>th</sup> century.<sup>17</sup> Yet, there is the lack of an efficient ligand that can separate LiClO<sub>4</sub> and NaClO<sub>4</sub>. In this work, we fill the knowledge gap by using a

<sup>a</sup>Chemistry-School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK. E-mail: jack.hemingway@newcastle.ac.uk<sup>b</sup>School of Chemistry, University of Birmingham, Birmingham, B15 2TT, UK. E-mail: e.lu@bham.ac.uk<sup>c</sup>The Faraday Institution, Quad One, Becquerel Avenue, Harwell campus, Didcot OX11 0RA, UK

hexadentate N-donor ligand *N,N',N''*-tris-(2-*N*-diethyl-aminoethyl)-1,4,7-triaza-cyclononane (DETAN), which was developed by us in 2021.<sup>18</sup> The DETAN ligand has exhibited versatile coordination features with group-1 alkali metal cations.<sup>19,20</sup> Herein we describe the selective binding of DETAN to LiClO<sub>4</sub> in a 1 : 1 molar mixture of Li/NaClO<sub>4</sub>, which results in the separation of the two perchlorates. The DETAN–LiClO<sub>4</sub> complex is proven to be a monomer by single-crystal X-ray diffraction (SCXRD), and its electronic structure is studied using DFT computations. The full details are elaborated on in the following sections.

We would like to bring to our readers' awareness that this Article focuses on ligand design and aims at understanding the coordination behaviours of the DETAN ligand towards LiClO<sub>4</sub> and NaClO<sub>4</sub> in non-aqueous non-coordinative toluene solution. Water molecules, or any other coordinative solvents (such as THF), would profoundly change the coordination dynamic, hence the conclusions drawn here are not necessarily applicable in an aqueous, or coordinative solvent, environment.

## 2. Results and discussion

### 2.1 Synthesis and characterization

We initially investigated the reactions of LiClO<sub>4</sub> or NaClO<sub>4</sub> with DETAN in *d*<sub>6</sub>-benzene. The NMR-scale reaction between LiClO<sub>4</sub> and DETAN at 1 : 1 molar ratio was monitored by both <sup>1</sup>H and <sup>7</sup>Li NMR. At room temperature within approximately 2 days, the starting material LiClO<sub>4</sub> was consumed, with the con-

comitant formation of a new set of <sup>1</sup>H NMR signals corresponding to a DETAN-coordinated species, as well as a new <sup>7</sup>Li NMR signal at 0.19 ppm (see SI for the NMR spectra, Fig. S2). Scaling up the reaction in toluene at room temperature for 2 days and the following crystallisation led to the isolation of [Li(κ<sup>4</sup>-*N*-DETAN)(η<sup>1</sup>-O-ClO<sub>4</sub>)] (**1**) in 66% crystalline yield (Fig. 1a).

Single crystals of **1** suitable for SCXRD analysis were isolated from its diethyl ether solution, and its molecular structure is exhibited in Fig. 2. **1** is a monomeric LiClO<sub>4</sub> complex, joining the number of previously reported examples of such structures.<sup>21</sup> Though **1** is not the first LiClO<sub>4</sub> monomer complex, it does have a few intriguing structural features. The DETAN ligand in **1** coordinates to the Li<sup>+</sup> centre in a κ<sup>4</sup> mode, with all the three nitrogen atoms in the macrocycle and one of the three sidearms coordinated. This DETAN coordination mode is similar to our previously reported DETAN-coordinated lithium iodide [Li(κ<sup>4</sup>-*N*-DETAN)(I)].<sup>19</sup> The perchlorate anion in **1** coordinates to the Li<sup>+</sup> centre in a η<sup>1</sup> mode through one of its four oxygen atoms. The Li–O bond length is 2.063(3) Å, which is substantially shorter (by approximately 0.14 Å) than a structurally relevant monomeric LiClO<sub>4</sub> complex ligated with a tripodal tripyridyl ligand TPA, [Li(κ<sup>4</sup>-*N*-TPA)(η<sup>1</sup>-O-ClO<sub>4</sub>)], where the Li–O bond length was reported at 2.2023(3) Å.<sup>21p</sup> The short Li–O bond in **1** *cf.* that in [Li(κ<sup>4</sup>-*N*-TPA)(η<sup>1</sup>-O-ClO<sub>4</sub>)] could be a result of the weaker N → Li dative bonds in **1** (avg. 2.16 to 2.25 Å) than in the TPA complex (2.08 to 2.18 Å), which renders the Li<sup>+</sup> centre in **1** more positively charged and hence the shorter Li–O bond. The four Cl–O bonds in ClO<sub>4</sub><sup>−</sup> can be divided into two groups: (1) the Cl1–O1 bond at 1.4476(10) Å; (2) the Cl1–O2/O3/O4 bonds at 1.418–1.428 Å. The former is

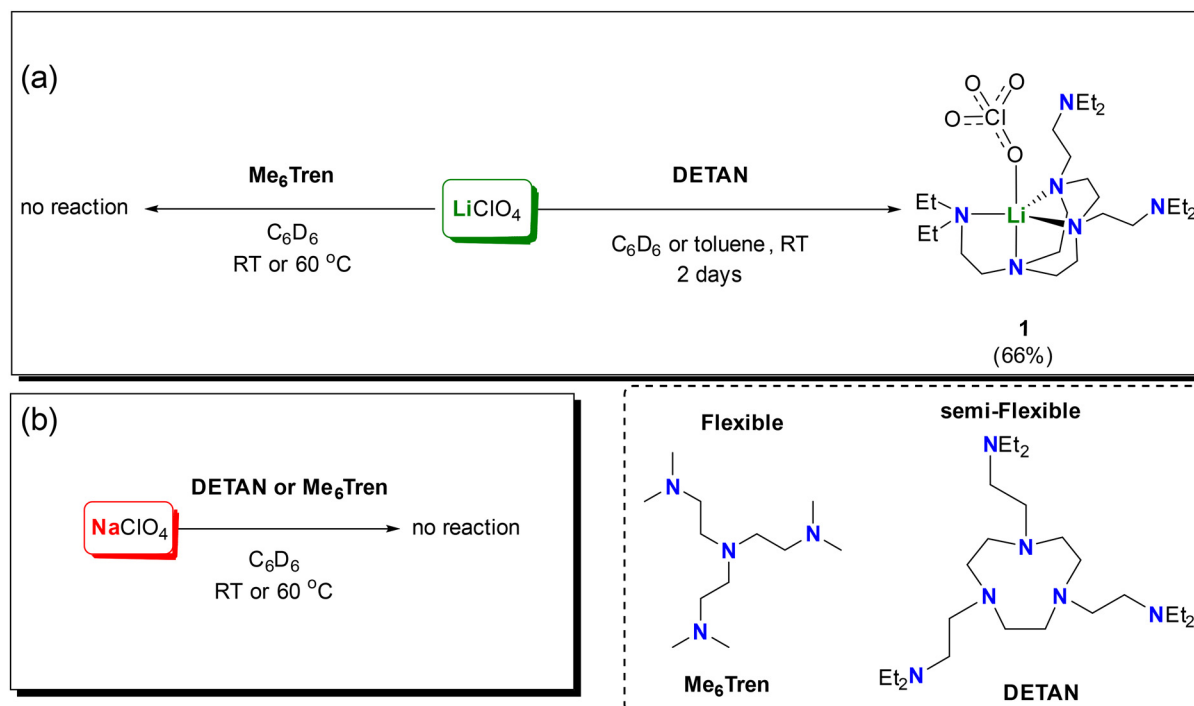
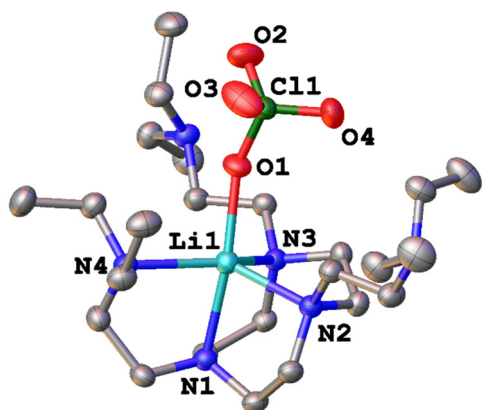


Fig. 1 Reactions between (a) LiClO<sub>4</sub> or (b) NaClO<sub>4</sub> and ligands.





**Fig. 2** Single-crystal X-ray diffraction structure of [Li(DETAN)ClO<sub>4</sub>] (**1**). Hydrogen atoms are omitted for the sake of clarity. The selected bond distances (Å) and angles (°) of **1** are Li1–O1, 2.063(3); Li1–N1, 2.183(3); Li1–N2, 2.141(3); Li1–N3, 2.164(3); Li1–N4, 2.254(2); Cl1–O1, 1.4476(10); Cl1–O2, 1.4265(12); Cl1–O3, 1.4176(12); Cl1–O4, 1.4275(11); O1–Li1–N1, 168.57(13); N1–Li1–N4, 82.35(9); N2–Li1–N1, 82.01(9); N2–Li1–N3, 86.52(9); N2–Li1–N4, 130.62(12); N3–Li1–N1, 83.00(9); N3–Li1–N4, 137.08(12); O2–Cl1–O1, 109.05(7); O2–Cl1–O4, 109.21(8); O3–Cl1–O1, 108.85(7); O3–Cl1–O2, 110.05(9); O3–Cl1–O4, 110.55(9); O4–Cl1–O1, 109.11(7); Cl1–O1–Li1, 156.05(10). The atomic colour codes in **1**: Li (cyan); C (gray); N (blue); Cl (forest green); O (red).

longer than the latter, likely due to the coordination with Li<sup>+</sup>, which withdraws the electron density. Despite the small variation, all four Cl–O bond lengths are within the normal range for a ClO<sub>4</sub><sup>−</sup> anion,<sup>21</sup> and should be treated as double bonds.

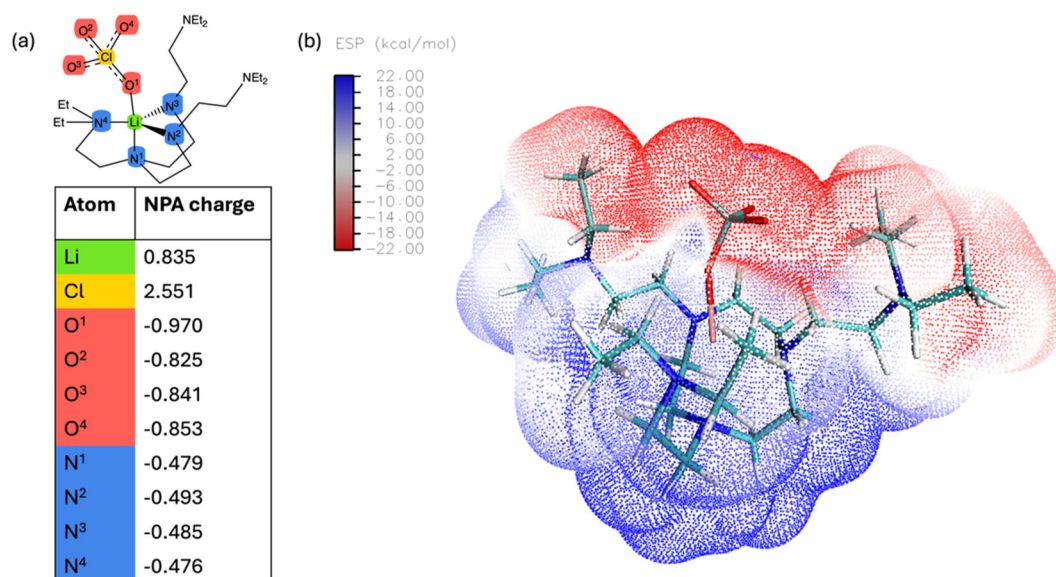
Generally speaking, all the applications and hazards of the perchlorate anion are underpinned by its unique structure of a formally high-valent chlorine centre (positively charged) and four electron-rich oxygens (negatively charged). In this regard, a similarity can be drawn between the perchlorate anion and

topical hypervalent organoiodine compounds, which are also predominantly used as oxidants.<sup>22</sup> Indeed, close examination of the inherent electronic structure of ClO<sub>4</sub><sup>−</sup> has inspired the design of an iron-catalyst system for perchlorate reduction.<sup>23,24</sup> Given this context, in an effort to explore the electronic structure of **1**, we conducted Density Functional Theory (DFT) calculations (see SI for details).

A natural population analysis was completed to probe the atomic charges in the structure of **1**, the results of which are outlined in Fig. 3(a). Additionally, the electrostatic surface potential (ESP) was calculated and is outlined.

The positive NPA charges are located on the Li and Cl and found to be +0.835*e* and +2.551*e*, respectively, whilst the negative charges are primarily located on the four O atoms, with O1 having the largest absolute charge of −0.970*e* when compared to O2, O3 and O4, which exhibit an average charge of −0.840*e*. The four nitrogen atoms that coordinate to the Li<sup>+</sup> also exhibit negative charges (average charge of −0.483*e*). The ESP diagram also highlights the negative charge build up over the perchlorate species.

Since the DETAN ligand coordinates to Li<sup>+</sup> in **1** in a κ<sup>4</sup>-N mode, and two of the three sidearms remain coordination-free, we explored the possibility of replacing the DETAN ligand with a typical κ<sup>4</sup>-N ligand, namely Me<sub>6</sub>Tren. In our previous reports, both the DETAN and the Me<sub>6</sub>Tren ligands were found to be able to coordinate to Li<sup>+</sup>, though their kinetic behaviours in solution are quite different.<sup>20</sup> Surprisingly, in this case we find that the Me<sub>6</sub>Tren does not coordinate with either LiClO<sub>4</sub> or NaClO<sub>4</sub> even at elevated temperatures (60 °C) (Fig. 1). Though the reason(s) behind this somewhat surprising finding remain unclear, we hypothesise that the substantially different kinetic features between the fully flexible Me<sub>6</sub>Tren and the semi-rigid DETAN play an important role.<sup>20</sup> This rigid nature was indeed a key part of our initial design concept of



**Fig. 3** The NPA charges of several atoms of interest in the structure of **1** (a) alongside the calculated electrostatic surface potential (b).



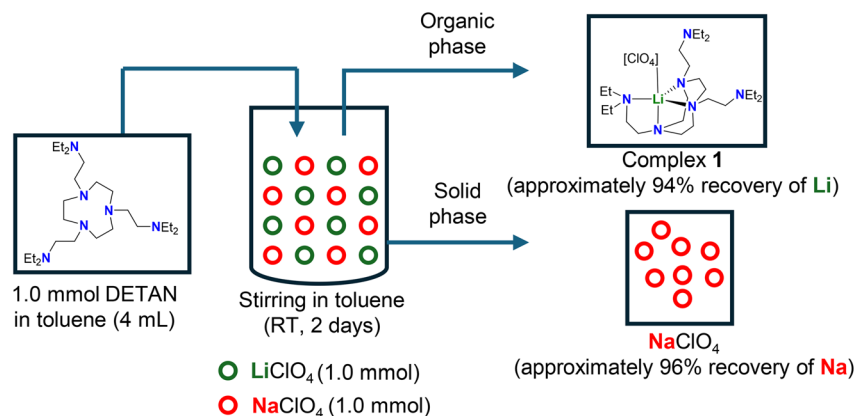


Fig. 4 Solid–liquid extraction protocol for separation of  $\text{LiClO}_4$  and  $\text{NaClO}_4$ .

the DETAN ligand.<sup>18</sup> In a very recent report, we also found that the different coordination kinetic features of  $\text{Me}_6\text{Tren}$  vs. DETAN led to a pronounced difference in their performance in a ligand-promoted alkali metal silylalkyls mediated C=O bond methylation.<sup>25</sup>

After the isolation of **1**, we tested the DETAN coordination reaction with  $\text{NaClO}_4$  also in  $d_6$ -benzene (Fig. 1b). Interestingly, there was no coordination between  $\text{NaClO}_4$  and DETAN even at 60 °C. It is obvious that the DETAN ligand exhibits highly selective coordination to  $\text{LiClO}_4$ , but not  $\text{NaClO}_4$ . This is the first ligand with such a selective coordination behaviour between Li/ $\text{NaClO}_4$ .

## 2.2 Separation experiment of Li/ $\text{NaClO}_4$

Based on the selective coordination of DETAN to  $\text{LiClO}_4$ , we designed a solid–liquid extraction protocol to isolate  $\text{LiClO}_4$  and  $\text{NaClO}_4$  from their 1:1 molar mixture. A solution of DETAN in toluene was added to a well-ground solid mixture of  $\text{LiClO}_4$  and  $\text{NaClO}_4$  and stirred at room temperature for 2 days (Fig. 4). After the reaction, the residual solid phase and the organic phase were treated *in vacuo* to remove all volatiles and subsequently analysed by  $^7\text{Li}$  and  $^{23}\text{Na}$  NMR spectroscopy. In the organic phase, a strong singlet peak corresponding to complex **1** was observed in the  $^7\text{Li}$  NMR spectroscopy, while no sodium-containing species were detected in the  $^{23}\text{Na}$  NMR. In contrast, the solid phase (dissolved in  $\text{D}_2\text{O}$ ) exhibited a strong  $^{23}\text{Na}$  NMR signal corresponding to  $\text{NaClO}_4$  and only a very weak  $^7\text{Li}$  signal, confirming a minimal  $\text{Li}^+$  retention. Only Li and Na were determined in the organic and solid phases, respectively, by inductively coupled plasma optical emission spectrometry (ICP-OES). The ICP-OES concentrations suggested that the recovery yield of Li in the organic phase was 99%, with 70% of Na recovered in the solid phase (the slightly lower yield of  $\text{NaClO}_4$  is due to the filtration, where a small amount of  $\text{NaClO}_4$  was retained on the filter paper and could not be recovered). We optimised the filtration process and the recovery of Li and Na can reach 94% and 96%, respectively (see SI for separation experiment, batch 2 and Table S1). Additionally, we can also recycle approximately 68% DETAN

ligand and recover 78% of Li through a following liquid–liquid back extraction using deionised water (see SI for back-extraction experiment, batch 5 and Table S2). The following test for the solubility of perchlorates ( $\text{LiClO}_4$  and  $\text{NaClO}_4$ ) showed that the perchlorates were not dissolved in both toluene and benzene (see SI for solubility test, batches 3 to 4 and Table S1).

In order to explore the influence of the anionic component on the coordination of DETAN to the Li/Na salts, we selected an additional salt (tetrafluoroborate,  $\text{BF}_4^-$ ) on the basis of its similar tetrahedral geometry and charge distribution. Once again, the DETAN ligand preferentially bound to the Li salt ( $\text{LiBF}_4$ ) over the Na salt, mirroring the selectivity in the case of the perchlorate anion (see SI for details regarding selectivity and solubility experiments, batches 6–8 and Table S3). This is particularly interesting as previous work focusing on iodide ( $\text{I}^-$ ) and tetraphenylborate ( $\text{BPh}_4^-$ ) anions has shown that coordination utilising DETAN is achievable for both Li/Na salts, unlike  $\text{ClO}_4^-$  and  $\text{BF}_4^-$ .<sup>19</sup>

## 3. Conclusion and outlook

In this work, we describe the first example of a ligand (DETAN) that is able to efficiently separate  $\text{LiClO}_4$  and  $\text{NaClO}_4$  through selective complexation of the Li containing species. The semi-flexible framework of DETAN may potentially influence the cation recognition, as the more flexible  $\text{Me}_6\text{Tren}$  ligand fails to react with  $\text{LiClO}_4$ . A separation experiment at 1.0 mmol scale was conducted to demonstrate the feasibility of the isolation. With the concept demonstrated, further work is underway in three directions: (i) to explore the influence of the anionic component, such as halides and pseudo-halides; (ii) to modify the DETAN ligand with a variety of alkyl and aryl substituents and examine their separation performance; (iii) to expand the scope to the aqueous environment, which is closer to the potential application scenario.

## Author contributions

X. Y., M. E. L., J. C. and P. R. S.: syntheses and experimental characterisations. J. M. H. and J. A. D.: design and conduct the





computational studies. P. G. W.: collect and refine the single-crystal X-ray diffraction data. R. J. A., J. A. D. and E. L.: secure and manage the resources used in this work; direct the project. E. L., J. M. H. and X. Y.: write the manuscript with input from all authors.

## Conflicts of interest

The authors declare no competing financial interest.

## Data availability

Supplementary information (SI): additional experimental details, materials, and methods. See DOI: <https://doi.org/10.1039/d5qi01799h>.

CCDC 2481385 (1) contains the supplementary crystallographic data for this paper.<sup>26</sup>

## Acknowledgements

The authors gratefully acknowledge the Rocket HPC based at Newcastle University for high performance computing services. The authors thank the Leverhulme Trust for their generous financial support *via* two Research Grant projects RPG-2023-159 (R. J. A., E. L. and M. E. L.) and RPG-2022-231 (J. M. H., J. A. D. and E. L.). X. Y. thanks Newcastle University, University of Birmingham and the EPSRC for a PhD studentship *via* the Doctoral Training Partnerships (DTP). P. R. S. thanks the Faraday Institution for funding (ReLiB project FIRG085).

## References

- 1 R. Zhao, Z. Ying, H. Sun, Q. Wei and X. Ren, Extracting Li<sup>+</sup> from high Na/Li solution and comparing the affinity of nonylphenol oxygen anion to Na<sup>+</sup> and Li<sup>+</sup>, *Sep. Purif. Technol.*, 2023, **320**, 124189, DOI: [10.1016/j.seppur.2023.124189](https://doi.org/10.1016/j.seppur.2023.124189).
- 2 C. B. Tabelin, J. Dallas, S. Casanova, T. Pelech, G. Bournival, S. Saydam and I. Canbulat, Towards a low-carbon society: A review of lithium resource availability, challenges and innovations in mining, extraction and recycling, and future perspectives, *Miner. Eng.*, 2021, **163**, 106743, DOI: [10.1016/j.mineng.2020.106743](https://doi.org/10.1016/j.mineng.2020.106743).
- 3 C. Zhang, N. He, X. Meng and H. Zhao, Advances in lithium and sodium separation techniques for brine lithium extraction processes, *J. Environ. Chem. Eng.*, 2025, **13**, 116471, DOI: [10.1016/j.jece.2025.116471](https://doi.org/10.1016/j.jece.2025.116471).
- 4 F. Fan, Y. Ren, S. Zhang, Z. Tang, J. Wang, X. Han, Y. Yang, G. Lu, Y. Zhang, L. Chen, Z. Wang, K. Zhang, J. Gao, J. Zhao, G. Cui and B. Tang, A Bioinspired Membrane with Ultrahigh Li<sup>+</sup>/Na<sup>+</sup> and Li<sup>+</sup>/K<sup>+</sup> Separations Enables Direct Lithium Extraction from Brine, *Adv. Sci.*, 2024, **11**, 2402898, DOI: [10.1002/advs.202402898](https://doi.org/10.1002/advs.202402898).
- 5 S. Sun, Y. Deng, J. Chen, D. Zou, Y. Han and M. Liu, Recovery of lithium from the desorption solutions of salt lakes using  $\beta$ -diketone synergistic extraction system, *Sep. Purif. Technol.*, 2025, **354**, 128748, DOI: [10.1016/j.seppur.2024.128748](https://doi.org/10.1016/j.seppur.2024.128748).
- 6 A. Razmjou, M. Asadnia, E. Hosseini, A. H. Korayem and V. Chen, Design principles of ion selective nanostructured membranes for the extraction of lithium ions, *Nat. Commun.*, 2019, **10**, 5973, DOI: [10.1038/s41467-019-13648-7](https://doi.org/10.1038/s41467-019-13648-7).
- 7 The subtle differences in the covalence of metal–ligand bond underpins lanthanide–actinide separation. For representative recent examples, see: (a) Y. Q. Wan, H. X. Hao, Y. Y. Zhang, Y. X. Guo, Z. J. Ma, Z. P. Wang, J. Li and P. Mocilac, Efficient Trivalent Actinide–Lanthanide Separations Using Hydrophilic CHON-Compliant Phenanthroline-Dicarboxamide Ligands, *Ind. Eng. Chem. Res.*, 2025, **64**, 12185–12199, DOI: [10.1021/acs.iecr.5c00795](https://doi.org/10.1021/acs.iecr.5c00795); (b) X. Yang, D. Fang, L. Chen, Y. Liu, S. Wang, L. Xu, A. Zhang, J. Su, C. Xu and C. Xiao, Computation-Aided Development of Next-Generation Extractants for Trivalent Actinide and Lanthanide Separation, *JACS Au*, 2024, **4**, 4744–4756, DOI: [10.1021/jacsau.4c00684](https://doi.org/10.1021/jacsau.4c00684); (c) H. Zhang, A. Li, K. Li, Z. Wang, X. Xu, Y. Wang, M. V. Sheridan, H.-S. Hu, C. Xu, E. V. Alekseev, Z. Zhang, P. Yan, K. Cao, Z. Chai, T. E. Albrecht-Schonzart and S. Wang, Ultrafiltration separation of Am(VI)-polyoxometalate from lanthanides, *Nature*, 2023, **616**, 482–487, DOI: [10.1038/s41586-023-05840-z](https://doi.org/10.1038/s41586-023-05840-z); (d) J. A. Bogart, B. E. Cole, M. A. Boreen, C. A. Lippincott, B. C. Manor, P. J. Carroll and E. J. Schelter, Accomplishing simple, solubility-based separations of rare earth elements with complexes bearing size-sensitive molecular apertures, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 14887–14892, DOI: [10.1073/pnas.1612628113](https://doi.org/10.1073/pnas.1612628113).
- 8 For a few recent representative examples, see: (a) Y. Luo, N. Marets and T. Kato, Selective lithium ion recognition in self-assembled columnar liquid crystals based on a lithium receptor, *Chem. Sci.*, 2018, **9**, 608–616, DOI: [10.1039/c7sc03652c](https://doi.org/10.1039/c7sc03652c); (b) S. J. Warnock, R. Sujanani, E. S. Zofchak, S. Zhao, T. J. Dilenschneider, K. G. Hanson, S. Mukherjee, V. Ganesan, B. D. Freeman, M. M. Abu-Omar and C. M. Bates, Engineering Li/Na selectivity in 12-Crown-4-functionalized polymer membranes, *Proc. Natl. Acad. Sci. U. S. A.*, 2021, **118**, e2022197118, DOI: [10.1073/pnas.2022197118](https://doi.org/10.1073/pnas.2022197118); (c) A. A. Bezdomnikov, V. E. Sharov, L. I. Demina, M. I. Skrebtsov, A. B. Ilyukhin and A. Y. Tsivadze, Specific features of lithium solvent extraction from perchlorate media with benzo-15-crown-5, *Polyhedron*, 2023, **244**, 116612, DOI: [10.1016/j.poly.2023.116612](https://doi.org/10.1016/j.poly.2023.116612); (d) Y. Deng, Y. Sun, B. Wang, Y. Lin, G. Chai and Y. Zhang, A crown-like ether for lithium extraction from brine, *Sep. Purif. Technol.*, 2025, **364**, 132591, DOI: [10.1016/j.seppur.2025.132591](https://doi.org/10.1016/j.seppur.2025.132591); (e) J. M. Mahoney, A. M. Beatty and B. D. Smith, Selective Solid-Liquid extraction of lithium halide salts using a ditopic macrobicyclic



- receptor, *Inorg. Chem.*, 2004, **43**, 7617–7621, DOI: [10.1021/ic049066b](#); (f) C. Xu, Q. Tran, L. Wojtas and W. Liu, Harnessing ion–dipole interactions: A simple and effective approach to high-performance lithium receptors, *J. Mater. Chem. A*, 2023, **11**(23), 12214–12222, DOI: [10.1039/D3TA01831H](#).
- 9 N. Choudhary, D. Rajpurohit, D. Rajpurohit, A. Saha, S. Yadav, S. Tothadi, B. Ganguly and A. R. Paital, Lithium sequestration from dilute solutions and sea bittern inspired by the self-assembled complexation, *Chem. Eng. J.*, 2023, **470**, 144408, DOI: [10.1016/j.cej.2023.144408](#).
- 10 (a) Y. S. Kurniawan, R. R. Sathuluri, K. Ohto, W. Iwasaki, H. Kawakita, S. Morisada and M. Miyazaki, A rapid and efficient lithium-ion recovery from seawater with tripropyl-monoacetic acid calix[4]arene derivative employing droplet-based microreactor system, *Sep. Purif. Technol.*, 2019, **211**, 925–934, DOI: [10.1016/j.seppur.2018.10.049](#); (b) H. Wang, L. O. Jones, I. Hwang, M. J. Allen, D. Tao, V. M. Lynch, B. D. Freeman, N. M. Khashab, G. C. Schatz, Z. A. Page and J. L. Sessler, Selective separation of lithium chloride by organogels containing strapped calix [4] pyrroles, *J. Am. Chem. Soc.*, 2021, **143**, 20403–20410, DOI: [10.1021/jacs.1c10255](#).
- 11 X. Sun, K. Wu, P. C. Teeuwen, P. Pracht, D. J. Wales and J. R. Nitschke, Proton-driven lithium separation using alkali-templated coordination cages, *Chem*, 2025, **11**, 102556, DOI: [10.1016/j.chempr.2025.102556](#).
- 12 C. J. Koester, H. R. Beller and R. U. Halden, Analysis of perchlorate in groundwater by electrospray ionization mass spectrometry/mass spectrometry, *Environ. Sci. Technol.*, 2000, **34**, 1862–1864, DOI: [10.1021/es991209j](#).
- 13 Q. Fang and B. Chen, Adsorption of perchlorate onto raw and oxidized carbon nanotubes in aqueous solution, *Carbon*, 2012, **50**, 2209–2219, DOI: [10.1016/j.carbon.2012.01.036](#).
- 14 A. Heydari, Organic synthesis in an unconventional solvent, 5.0 M lithium perchlorate/diethyl ether, *Tetrahedron*, 2002, **58**, 6777–6793, DOI: [10.1016/S0040-4020\(02\)00745-7](#).
- 15 N. Azizi and M. R. Saidi, An improved synthesis of cyanohydrins in the presence of solid LiClO<sub>4</sub> under solvent-free conditions, *J. Organomet. Chem.*, 2003, **688**, 283–285, DOI: [10.1016/j.jorganchem.2003.09.014](#).
- 16 G. Zubi, R. Dufo-López, M. Carvalho and G. Pasaoglu, The lithium-ion battery: State of the art and future perspectives, *Renewable Sustainable Energy Rev.*, 2018, **89**, 292–308, DOI: [10.1016/j.rser.2018.03.002](#).
- 17 (a) H. H. Willard and G. F. Smith, The Separation and Determination of Sodium and Lithium by Precipitation from Alcoholic Perchlorate Solution, *J. Am. Chem. Soc.*, 1922, **44**, 2816–2824, DOI: [10.1021/ja01433a015](#); (b) R. Khurana, F. Alami, C. A. Nijhuis, E. Keinan, J. Huskens and O. Reany, Selective Perchlorate Sensing Using Electrochemical Impedance Spectroscopy with Self-Assembled Monolayers of semiaza-Bambusurils, *Chem.* – *Eur. J.*, 2024, **30**, e202302967, DOI: [10.1002/chem.202302968](#).
- 18 N. Davison, E. Falbo, P. G. Waddell, T. J. Penfold and E. Lu, A monomeric methyllithium complex: synthesis and structure, *Chem. Commun.*, 2021, **57**, 6205–6208, DOI: [10.1039/D1CC01420J](#).
- 19 N. Davison, K. Zhou, P. G. Waddell, C. Wills, C. Dixon, S. X. Hu and E. Lu, Versatile Coordination Modes of Multidentate Neutral Amine Ligands with Group 1 Metal Cations, *Inorg. Chem.*, 2022, **61**, 3674–3682, DOI: [10.1021/acs.inorgchem.1c03786](#).
- 20 N. Davison, J. A. Quirk, C. Wills, C. Dixon, P. G. Waddell, J. A. Dawson and E. Lu, Elucidating Solution-State Coordination Modes of Multidentate Neutral Amine Ligands with Group-1 Metal Cations: Variable-Temperature NMR Studies, *Inorg. Chem.*, 2022, **61**, 15204–15212, DOI: [10.1021/acs.inorgchem.2c02457](#).
- 21 (a) W. A. Henderson, N. R. Brooks, W. W. Brennessel and V. G. Young Jr., Triglyme-Li<sup>+</sup> Cation Solvate Structures: Models for Amorphous Concentrated Liquid and Polymer Electrolytes (I), *Chem. Mater.*, 2003, **15**, 4679–4684, DOI: [10.1021/cm034351z](#); (b) I. S. Ivanova, A. B. Ilyukhin, G. S. Tsebrikova, I. N. Polyakova, E. N. Pyatova, V. P. Solov'ev, V. E. Baulin and A. Y. Tsivadze, 2,4,6-Tris[2-(diphenylphosphoryl)-4-ethylphenoxy]-1,3,5-triazine: A new ligand for lithium binding, *Inorg. Chim. Acta*, 2019, **497**, 119095, DOI: [10.1016/j.ica.2019.119095](#); (c) J. H. Buttery, Effendy, G. A. Koutsantonis, S. Mutfon, N. C. Plackett, B. W. Skelton, C. R. Whitaker and A. H. White, Complexes of Group 1 Salts with N,N'-Aromatic Bidentate Ligands, of Mononuclear ('Molecular') 1 : 2 Salt : Base Ratio, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1829–1838, DOI: [10.1002/zaac.200600080](#); (d) A. A. Bezdomnikov, V. E. Sharov, L. I. Demina, M. I. Skrebtsov, A. B. Ilyukhin and A. Y. Tsivadze, Specific features of lithium solvent extraction from perchlorate media with benzo-15-crown-5, *Polyhedron*, 2023, **244**, 116612, DOI: [10.1016/j.poly.2023.116612](#); (e) R. R. Burnette and I. A. Guzei, CCDC 761188: Experimental Crystal Structure Determination. *CSD Communication*, 2016, DOI: [10.5517/ccdc.csd.ctk2gw](#); (f) H. Gohil, S. Chatterjee, S. Yadav, E. Suresh and A. R. Paital, An Ionophore for High Lithium Loading and Selective Capture from Brine, *Inorg. Chem.*, 2019, **58**, 7209–7219, DOI: [10.1021/acs.inorgchem.9b00135](#); (g) J. Dale, J. Eggstad, S. B. Fredriksen and P. Groth, 1,5,9-Trioxacyclododecane and 3,3,7,7,11,11-hexamethyl-1,5,9-trioxacyclododecane: novel lithium cation complexing agents, *J. Chem. Soc., Chem. Commun.*, 1987, 1391–1393, DOI: [10.1039/C39870001391](#); (h) K. Ueno, K. Hiratani, K. Taguchi, T. Okada and H. Sugihara, Crystal Structure of a 1 : 1 Complex of 1,3-Bis(8-quinolyloxy)propane and Lithium Perchlorate, *Chem. Lett.*, 1987, **16**, 949–952, DOI: [10.1246/cl.1987.949](#); (i) B. S. Bouley, F. Tang, D. Y. Bae and L. M. Mirica, C–H bond activation via concerted metalation–deprotonation at a palladium(III) center, *Chem. Sci.*, 2023, **14**, 3800–3808, DOI: [10.1039/D3SC00034F](#);



- (j) G. W. Buchanan, R. A. Kirby and J. P. Charland, An example of conformational disorder in solids: X-ray crystallographic and  $^{13}\text{C}$  CPMAS NMR studies of dibenzo and dicyclohexano-13-crown-4 ethers and some lithium complexes, *Can. J. Chem.*, 1990, **68**, 49, DOI: [10.1139/v90-011](#);
- (k) D. M. Seo, T. Afroz, J. L. Allen, P. D. Boyle, P. C. Trulove, H. C. De Long and W. A. Henderson, Structural Interactions within Lithium Salt Solvates: Cyclic Carbonates and Esters, *J. Phys. Chem. C*, 2014, **118**, 25884–25889, DOI: [10.1021/jp5079168](#);
- (l) T. N. Y. Hoang, M. Humbert-Droz, T. Dutronc, L. Guénée, C. Besnard and C. Piguet, A Polyaromatic Terdentate Binding Unit with Fused 5,6-Membered Chelates for Complexing s-, p-, d-, and f-Block Cations, *Inorg. Chem.*, 2013, **52**, 5570–5580, DOI: [10.1021/ic400526j](#);
- (m) J. J. Vittal, X. Wang and J. D. Ranford, Influence of the  $\text{Li}^+$  on the Structure of the  $[\text{Cu}_3(\text{phis})_3]^{3+}$  Cation, *Inorg. Chem.*, 2003, **42**, 3390–3392, DOI: [10.1021/ic026311n](#);
- (n) A. Merz, T. Futterer, J. Lex and H. Inerpicwicz, Alkali Metal Complexes of o, o'-(Tetraethyleneglycoldiyl)-(Z)-stilbene: One Common Ligand Conformation for Li, Na, K, and Rb Ions, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 278–280, DOI: [10.1002/anie.199702781](#);
- (o) K. Ziach and J. Jurczak, Mirror symmetry breaking upon spontaneous crystallization from a dynamic combinatorial library of macrocyclic imines, *Chem. Commun.*, 2015, **51**, 4306–4039, DOI: [10.1039/C4CC10083B](#);
- (p) N. G. Spiropoulos, E. A. Standley, I. R. Shaw, B. L. Ingalls, B. Diebels, S. V. Krawczyk, B. F. Gherman, A. M. Arif and E. C. Brown, Synthesis of zinc and cadmium O-alkyl thiocarbonate and dithiocarbonate complexes and a cationic zinc hydrosulfide complex, *Inorg. Chim. Acta*, 2012, **386**, 83–92, DOI: [10.1016/j.ica.2012.01.040](#).
- 22 A. Yoshimura and V. V. Zhdankin, Recent Progress in Synthetic Applications of Hypervalent Iodine(III) Reagents, *Chem. Rev.*, 2024, **124**, 11108–11186, DOI: [10.1021/acs.chemrev.4c00303](#).
- 23 C. L. Ford, Y. J. Park, E. M. Matson, Z. Gordon and A. R. Fout, A bioinspired iron catalyst for nitrate and perchlorate reduction, *Science*, 2016, **354**, 741–743, DOI: [10.1126/science.aah6886](#).
- 24 M. J. Drummond, T. J. Miller, C. L. Ford and A. R. Fout, Catalytic Perchlorate Reduction Using Iron: Mechanistic Insights and Improved Catalyst Turnover, *ACS Catal.*, 2020, **10**, 3175–3152, DOI: [10.1021/acscatal.9b05029](#).
- 25 X. Yang, N. Davison, M. E. Lowe, P. G. Waddell, R. J. Armstrong, C. L. McMullin, M. N. Hopkinson and E. Lu, C=O methylenation mediated by organo-alkali metal reagents: metal identity and ligand effects, *Chem. Sci.*, 2025, **16**, 11151–11160, DOI: [10.1039/D5SC02313K](#).
- 26 CCDC 2481385: Experimental Crystal Structure Determination, 2025, DOI: [10.5517/ccdc.csd.cc2p92ps](#).

