Synthesis and structure of cationic guanidinate-bridged bimetallic \(\{\text{Li}_7\text{M}\}\) cubes \((\text{M} = \text{Mn, Co, Zn})\) with inverse crown counter anions†

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Received 27th May 2011, Accepted 27th July 2011
DOI: 10.1039/c1dt10999e

The reactions of the heteroleptic lithium amide \([\text{Li}_3(\mu_{-}\text{hmds})_1(\mu_4\text{-hpp})(\mu_4\text{-hmds})](1)\), where \([\text{hmds}] = \text{hexamethyldisilazide}, \text{and} [\text{ropp}] = \text{hexahydropyrimidopopyrimidide}\), with \(\text{MnCl}_2, \text{CoCl}_2\), or \(\text{ZnBr}_2\) result in the formation of the separated ion-pairs \([\text{MLi}_7(\mu_4\text{-O})(\mu_4\text{-ropp})][\text{A}^-]\), which each consist of a \({\{\text{MLi}_7}\} \text{oxo-centred cube structural motif}\) \((\text{M} = \text{Mn 2, Co 4, Zn 5})\), with each face of the cube being bridged by an \([\text{ropp}]\) ligand. In the case of \(\text{M} = \text{Mn}\) and \(\text{Co}\), the counter ion, \([\text{A}^-]\), is the pentagonal anionic inverse crown \([\{\text{Li}(\mu_{-}\text{hmds})_1,\mu_5\text{-Cl}\}^{-}\) (3), whereas the reaction with \(\text{M} = \text{Zn}\) produces the known tris-amido zincate \([\text{Zn}(_{\text{hmds}})_3]^{-}\) counter anion.

Introduction

Serendipitous assembly is a successful method for the synthesis of polymeric metal cage compounds. With this method, a proligand with molecular symmetry and structure likely to encourage cage formation is combined with a simple metal-containing precursor, such as a metal halide, in an appropriate solvent. The reaction between the various components then proceeds such that specific outcomes are not targeted. Rather, the chemical and physical conditions of the reaction result in the product self-assembling to give a stable arrangement of ligands and metal atoms. The strategy has been put to particularly effective use in the synthesis of transition metal cages, based predominantly on \(\mu_4\text{(O-donor)}\) ligands. Not only are the structures of the self-assembled compounds intrinsically interesting, the reliability and scope of the synthetic method, most notably in the case of transition metals, has allowed such cage compounds to be developed as single molecule magnets and as magnetic refrigerants.

The importance of the serendipitous assembly method for the synthesis of oxygen-bridged transition metal cages has prompted us to combine our interests in this area with our interests in the structures of alkali metal complexes of functionalized amido ligands. Here, our aim is to select \(\text{N-H}\) acidic nitrogen-containing heterocyclic ligands whose structures should encourage metal cage formation, and then to metallate these heterocycles with alkali metals. Subsequently, the alkali-metallated heterocycles can be used as ligand sources in salt metathesis reactions with transition metal halides, allowing access to nitrogen-bridged polymeric transition metal cages. In addition to the new structural chemistry of transition metal amides that could be developed, this method also potentially allows access to a range of cage compounds with magnetic properties that are influenced by \(\mu_4\text{(O-donor)}\) ligands rather than by \(\mu_4\text{(O-donor)}\) ligands.

Results and discussion

We now report the synthesis and structure of the heteroleptic trilithium complex \([\text{Li}_3(\mu_{-}\text{hmds})_1(\mu_4\text{-ropp})(\mu_4\text{-hmds})](1)\) \([\text{hmds}] = \text{hexamethyldisilazide}, \text{and} [\text{ropp}] = \text{hexahydropyrimidopopyrimidide}\), and its reaction with d-block metal(ii) halides, namely manganese(ii) chloride, cobalt(ii) chloride and zinc bromide. The reactions of \(1\) with \(\text{MnCl}_2\) or with \(\text{CoCl}_2\) result in the formation of separated ion-pairs consisting of the guanidinate-bridged, oxo-centred cationic metal cubes \([\text{MLi}_7(\mu_4\text{-O})(\mu_4\text{-ropp})][\text{A}^-]\) \((\text{M} = \text{Mn 2, M = Co 4})\), which in the case of each transition metal is accompanied by formation of the new anionic inverse crown \([\{\text{Li}(\mu_{-}\text{hmds})_1,\mu_5\text{-Cl}\}^{-}\) (3). The reaction of \(1\) with \(\text{ZnBr}_2\) produces a separated ion pair consisting of the cage complex \([\text{ZnLi}_3(\mu_{-}\text{O})(\mu_4\text{-ropp})][\text{A}^-]\) (5), which is isostructural to 2 and 4, and the known tris(amido) zincate counter anion \([\text{Zn}(_{\text{hmds}})_3]^{-}\).

Compound \(1\) was synthesized by adding three equivalents of \([\text{Li}(_{\text{hmds}})]\) to one of \(\text{roppH}\) in toluene. A standard work-up of the reaction followed by storage of a concentrated toluene solution at \(-4^\circ\text{C}\) produced pale yellow crystals of 1 (Scheme 1). X-ray diffraction revealed that two independent molecules of 1, 1a and 1b, are found in the unit cell. The structures of 1a (Fig. 1) and 1b are essentially identical, and that of 1b is shown in Fig. S1.† The pyramidal coordination environments of Li(1/1A) in 1a consist of one \([\text{hmds}]\) nitrogen and both nitrogenos of the \([\text{ropp}]\) ligand,
the extended structure of the unsolvated cyclic trimeric rings of [Li(hmds)]$_3$–. Li(2)–N(1) distance being 1.998(8) Å, and the N(1)-Li(2)-N(1A) angle 148.9(12)°.

Table 1  Metal–ligand bond distances [Å] for 1a and for the cations 2, 4, and 5

<table>
<thead>
<tr>
<th></th>
<th>1a</th>
<th>2</th>
<th>4</th>
<th>5</th>
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<tbody>
<tr>
<td>Li/M–O</td>
<td>—</td>
<td>2.072(10)–2.192(7)</td>
<td>2.0371(14), 2.0298(15)</td>
<td>1.983(5)–2.072(7)</td>
</tr>
<tr>
<td>Li/M–N</td>
<td>—</td>
<td>1.999(8)–2.192(7)</td>
<td>1.990(3)–2.092(3)</td>
<td>1.970(7)–2.169(7)</td>
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<tr>
<td>Li–O</td>
<td>—</td>
<td>2.001(3), 2.065(3)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Li–N</td>
<td>1.959(17)–2.091(13)</td>
<td>—</td>
<td>2.054(4)–2.082(2)</td>
<td>—</td>
</tr>
</tbody>
</table>

Fig. 1 Molecular structure of 1a (upper), and the interactions between 1a and 1b (lower). Li = pink, N = blue, Si = grey.

resulting in Li(1)–N(1) and Li(1)–N(3) bond distances of 1.959(17) and 2.091(13) Å, respectively (Table 1). The bent, two-coordinate environment of Li(2) consists of two [hmds]$^-$ ligands, with the Li(2)–N(1) distance being 1.998(8) Å, and the N(1)-Li(2)-N(1A) angle 148.9(12)°. The molecular structure of 1a (and of 1b) can be regarded as being substitution of an [hmds]$^-$ ligand in the unsolvated cyclic trimeric rings of [Li(hmds)]$_3$ with an [hpp]$^-$ ligand from the guanidine-solvated dimer [Li(hpp)][hpp(H)]. In the extended structure of 1 (Fig. 1), molecules of 1a and 1b interact via CH···Li pseudo-agostic interactions involving the SiMe$_3$ substituents. This type of interaction has precedent in the structure of methyl锂itium itself and in the structures of trimethylsilyl-containing organolithiums.

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The room-temperature $^1$H NMR spectrum of 1 in benzene-$d_6$ consists of broad, overlapping resonances in the range $d(^1$H) = 1.38–3.35 ppm, and a broad singlet at 0.22 ppm (Fig. S2–S4†). Although these resonances can be assigned to the $^1$H environments of 1, it is clear that a dynamic process is occurring. A variable-temperature $^1$H NMR spectroscopic study revealed that the dynamic process can be suppressed on cooling toluene solutions to −40 °C, such that the solid-state molecular structure of 1 is observed intact. On warming to +70 °C, the resonances coalesce and sharpen, implying a dynamic equilibrium, probably involving dissociation of 1 into [Li(hpp)] and [Li(hmds)] (Scheme 1, Fig. S5†).

The ease with which 1 can be synthesized, combined with the known ability of the [hpp]$^-$ ligand to encourage cage formation, make this ligand a promising candidate for use in the synthesis of transition metal cages. To test this hypothesis, the reactions of 1 with anhydrous manganese(II) chloride, cobalt(II) chloride and zinc bromide were carried out. Addition of 1 to MnCl$_2$ produced an amber-coloured solution after stirring, and following the hot filtration of the reaction mixture and then storage of the solution, amber crystals of [MnLi$_7$]([μ$_3$-O])$_6$[Li(hpp)][Li(hmds)]$_3$ (2 toluene). [Li(hpp)][hpp(H)]. In the extended structure of 1 (Fig. 1), molecules of 1a and 1b interact via CH···Li pseudo-agostic interactions involving the SiMe$_3$ substituents.

The structures of the [MLi$_7$([μ$_3$-O])$_6$[μ$_3$'-hpp])$^+$ cations (M = Mn, Co, Zn) are essentially identical, hence only 4 will be discussed in detail. Key bond lengths for 2, 4 and 5 are shown for comparison in Table 1, and the structures of 2 and 5 are shown in Fig. S6 and S7.† The structure of 4 (Fig. 2) consists of a μ$_3$-oxo-centred {CoLi$_3$} cube, and each face of the cube is bridged by two nitrogens of an [hpp]$^-$ ligand. Four of the eight metal positions in 4 are mixed positions of cobalt and lithium, i.e. Co(1)/Li(1) and Co(2)/Li(2), both in a ratio of one quarter to three quarters. Each metal atom in 4 resides in a distorted tetrahedral environment that consists of the oxo ligand and three [hpp]$^-$ nitrogens. The mixed position Li(1)/Co(1)–O(1) bond lengths are 2.0371(14) and 2.0298(15) Å, and the Co/Li–N bond lengths are in the range 1.990(3)–2.092(3) Å (average 2.042 Å).
distances in the zinc atom in \( \text{ZnLi}_7 \). A thermal ellipsoid plot of sites of the asymmetric unit, i.e all eight metal positions of the \( \text{MnLi}_7 \) cube, with occupancies of 22, 16, 9 and 3 per cent. The manganese atom in the cation 2 is disordered over the four sites of the asymmetric unit, i.e all eight metal positions of the \( \text{MnLi}_7 \) cube, with occupancies of 22, 16, 9 and 3 per cent. The zinc atom in 5 is disordered over all eight of the metal positions in the \( \text{ZnLi}_7 \) cube, with occupancies of 31, 5, 25, 11, 14, 7, 1 and 6 per cent.

The anion 3 in \([\text{Zn(hmds)}_3]\) (Fig. 3) consists of a pentagonal arrangement of lithium cations bridged by a \( \mu_5 \)-chloro ligand, with each pair of adjacent lithiums being bridged by a \( \mu_5 \)-[hmds]\(^{3-}\) ligand. The Li(5)-Cl(1) bond coincides with a mirror plane. The range of Li–Cl distances in 3 is 2.445(4)–2.458(7) (average 2.449 Å), and the Li–N distances are in the range 2.050(5)–2.064(5) Å (average 2.058 Å). The chloride ion in 3 is co-planar with the lithium cations. The anion 3 in \([\text{Zn(hmds)}_3]\) is essentially isostructural with that in \([\text{Co(hmds)}_3]\) (Fig. S7†).

In contrast to the reactions of 1 with MnCl\(_2\) and CoCl\(_2\), the reactions of 1 with ZnBr\(_2\) produce a cation-anion pair in which the anion is the trigonal planar tris(amido) zincate \([\text{Zn(hmds)}_3]\)\(^{3-}\) (Fig. S18†), the structure of which has been reported previously by others.\(^3\) In terms of the counter anion, we attribute the different outcome in the case of \([\text{Zn(hmds)}_3]\) to the greater radius of the bromide anion, which presumably is too great to enable it to act as a template in the formation of a crown based on \([\text{Li(hmds)}_3]\) units.

Analytically pure samples of \([\text{Zn(hmds)}_3]\), \([\text{Co(hmds)}_3]\) and \([\text{Mn(hmds)}_3]\) were obtained by placing the crystalline materials under vacuum. In the case of \([\text{Zn(hmds)}_3]\) and \([\text{Co(hmds)}_3]\) the lattice toluene was evaporated. The Q-band EPR spectrum of \([\text{Zn(hmds)}_3]\) at 5 K features a broad resonance centred on 11963 G (\(g = 2.001\)). The resonance is a six-line multiplet with a separation of 80 G between the components of the multiplet. The EPR spectrum is consistent with high-spin manganese(II). The X- and Q-band EPR spectra of \([\text{Co(hmds)}_3]\) at 5 K show resonances at 1062 G (full width at half-maximum = 89 ± 1.5 G) and 3650 G (full width at half-maximum = 228 ± 4 G), respectively, consistent with \(g = 6.518 ± 0.058\), and there is an inflection in the X-band spectrum at 12040 G (\(g = 0.588\)) (Figs. S15 and S16). These \(g\)-values fall within a typical range for low-symmetry Co(II) coordination environments.\(^9\)

The paramagnetism of \([\text{Co(hmds)}_3]\) resulted in the \(^1\)H NMR spectrum of this compound consisting of a series of broad, overlapping resonances approximately in the region \(\delta(\text{H}) = 0.9–3.6\) ppm (Fig. S8†). These resonances are likely due to be due to the \([\text{hpp}]\)-protons, and the two sharp singlets at \(\delta(\text{H}) = 0.29\) and 0.10 ppm can be assigned to the SiMe\(_3\) substituents (Fig. S9†). The \(^7\)Li NMR spectrum of \([\text{Zn(hmds)}_3]\) consists of three sharp resonances at \(\delta(\text{Li}) = 1.52, 1.92\) and 2.39 ppm, and a broad resonance approximately in the range \(\delta(\text{Li}) = -0.5–3.5\) ppm, centred on 1.71 ppm (Fig. S9†). Structural assignments based on the paramagnetic NMR spectra of \([\text{Zn(hmds)}_3]\) cannot be completely free from ambiguity, however the \(^7\)Li NMR spectrum may indicate that the compound exists as two components in benzene: one type that contains manganese(II) and one that does not, although there is no evidence to suggest that the solid-state structure of \([\text{Zn(hmds)}_3]\) is preserved in solution. Similarly, the paramagnetism of \([\text{Co(hmds)}_3]\) resulted in the \(^1\)H NMR spectrum of this compound consisting of a series of broad, low-intensity resonances in the region \(\delta(\text{H}) = 0.79–4.45\) ppm assignable to the hpp protons, two sharp singlets at \(\delta(\text{H}) = 0.62\) and 0.01 ppm assignable to the SiMe\(_3\) substituents, and seven resonances at lower field with \(\delta(\text{H}) = 15.14–44.72\) ppm (Fig. S13†). The \(^{25}\)M NMR spectrum of \([\text{Co(hmds)}_3]\) consists of four sharp resonances in the region \(\delta(\text{Li}) = 2.33–2.86\) ppm, and six broad, overlapping resonances in the region \(\delta(\text{Li}) = -0.06–2.17\) ppm (Fig. S14†). As with \([\text{Zn(hmds)}_3]\), the NMR spectroscopic data may again indicate that \([\text{Co(hmds)}_3]\) exists as a cobalt(II)-containing component and a lithium-only component.

The \(^1\)H and \(^{13}\)C NMR spectra of \([\text{Zn(hmds)}_3]\) in benzene show environments characteristic of the \([\text{hpp}]\)- and \([\text{hmds}]^{-}\) ligands (Fig. S19 and S20†). Thus the \(^1\)H NMR spectrum consists of group of mutually coupled resonances in the region \(\delta(\text{H}) = 3.43–1.54\) ppm corresponding to the \([\text{hpp}]^{-}\) environments and sharp singlets at 0.81 and 0.10 ppm corresponding to the SiMe\(_3\) substituents. The \(^{13}\)C NMR spectrum has the \([\text{hpp}]^{-}\) environments at \(\delta(\text{C}) = 25.42,
The structures of the cationic cubes 2, 4 and 5 are similar to that of \( \mu_2\)-hydride-containing cation \([\text{Li}_n(\mu_2-H)(\text{hphp})_n]^+\), which has been reported with several different counter anions, including \([\text{Zn Bu}_3]^-\). The observation of \( \mu_2\)-oxo ligands in molecular compounds is rare. A search of the Cambridge Structural Database reveals that the few previously reported \( \mu_2\)-oxo compounds are based entirely on alkali metals,\(^{11}\) meaning that the cations 2, 4 and 5 are the first d-block metal complexes of \( \mu_2\)-oxo ligands. The oxygen-scavenging ability of alkali metal organometallics is well known.\(^{11}\) Indeed, several examples of oxo-containing lithium organozincates are known in which \( \mu_2\)-oxo ligands \((n = 3-6)\) derive either from molecular oxygen or from adventitious water from the reaction solvent.\(^{16}\) A lithium-manganese(II) amido inverse crown ether has also been shown to be able to accommodate a \( \mu_2\)-oxo ligand.\(^{17}\) The oxygen scavenging ability of bimetallic alkali metal organometallics is seen consistently with the synthesis of \([\text{Zn(hmds)}]_2\), \([\text{Mn(hmds)}]_2\) and \([\text{Zn(hmds)}]_5\). Molecular oxygen is unlikely to be the source of the oxo ligands in the three \([\text{MLi}_2]_5\) cubes because performing the syntheses using rigorous anaerobic conditions either with a Schlenk line or in an efficient glove box (dioxygen levels less than 0.5 ppm) does not affect the outcome. The \( \mu_2\)-oxo ligand in the structure of the cation 2 therefore most likely derives from the presence of adventitious water in the toluene solvent. To test this hypothesis, a small amount of degassed water was added to rigorously dried toluene (approximately 50 \( \mu\)L in 15 mL) and stirred vigorously for 30 min, and the mixture then subsequently added to \( \text{MX}_2\). A dry toluene solution of 1 was then added to the suspension of \( \text{MX}_2\), and following the same reaction time and workup conditions as in the case of the serendipitous formation of the oxo-centred cubes, formation of crystalline \([\text{Zn(hmds)}]_5\) was again observed, but in slightly higher yields.

The structural chemistry of lithium amido zirconates\(^{18,19,20,21}\) and, to a lesser extent, lithium amido manganates\(^{18,19,20,21}\) has been investigated in some detail. In recent years, interest in both types of amido metallate has increased substantially owing to their organic heterocycles.\(^{9,17,20,21}\) The cation 4 in \([\text{Zn(hmds)}]_5\) provides the first crystallographically characterized example of a lithium amido cobaltate.

Lithium amide/halide co-complexes are widely used to enhance the efficiency of key organic syntheses, such as the aldol reaction,\(^{22}\) however crystallographically characterized examples such as 3 are rare. The anion 3 is also a new member of the s-block metal inverse crown family, a term describing complexes consisting of a macrocyclic arrangement of metal amide units that host an anionic guest within the crown.\(^{24}\) The majority of inverse crowns are heterobimetallic combinations of an alkali metal with a less polar divalent metal, so it is notable that the inverse crown in 3 is a cyclic pentamer of \([\text{Li(hmds)}]_5\).\(^{25}\) The solid-state structure of lithium hexamethyldisilazide is the cyclic trimer \([\text{Li(hmds)}]_3\), however in hydrocarbon solution a tetrammer-dimer equilibrium has been observed.\(^{26}\) To account for the formation of 3, an aggregation process involving \([\text{Li(hmds)}]_n\) units with \( n = 1, 2, 3 \) or 4 templating around the nascent chloride ion can be envisaged, although proof for this cannot be obtained by NMR spectroscopy owing to the paramagnetism of \([\text{Zn(hmds)}]_2\) and \([\text{Mn(hmds)}]_2\). A mechanism qualitatively similar to that which we propose for 3 is thought to account for the formation of the anionic phospha(V)zane cyclic pentamer \([\{\mu-N-Bu_3, \mu-NH\}_3(HCl)\] in which the chloride ion templates the formation of the macrocycle via a series of hydrogen bonds.\(^{27}\) A pentameric structural motif related to 3 was also observed in the mercury-based inverse crown \([\{\text{F}_2\text{C}, \text{CH}_2\}_2(\mu_2-\text{Cl})_5\], although in this instance the macrocycle was pre-synthesized and the chloride guest added subsequently.\(^{28}\)

**Conclusions**

In summary, the heteroleptic lithium amide 1 has been used as a precursor for the synthesis of the ion-separated compounds \([\text{Zn(hmds)}]_2\), \([\text{Mn(hmds)}]_2\) and \([\text{Zn(hmds)}]_5\). The heterobimetallic cations 2, 4 and 5 contain \( \mu_2\)-oxo-centred \([\text{MLi}_2]_5\) cubes (M = Mn, Co, Zn), with each face of the cube capped by a \( \mu_2\)-oxo ligand. An additional serendipitous outcome was the formation of the anionic inverse crown 3. The apparent ability of d-block metals to replace lithium in a structural type more commonly found in s-block chemistry may enable more extensive investigations of the less common coordination environment for the transition metals, such as tetrahedral cobalt(II), which would add to the considerable current interest in cage compounds of octahedral cobalt(II).\(^{29}\) Our ongoing research in this area will also extend the synthetic described for \([\text{Zn(hmds)}]_5\), to other N–H acidic organic heterocycles.

**Experimental**

**Synthesis of 1**

A solution of Li(N(SiMe_3)_2 (0.50 g, 3.0 mmol) in toluene (15 mL) was added to hphpH (0.14 g, 1.0 mmol) at \(-78^\circ\) C and stirred for 30 min. The reaction was warmed to room temperature and stirred for 1 h, producing a colourless precipitate. Gentle heating of the reaction mixture produced a pale yellow solution, which was filtered and stored overnight at \(-4^\circ\) C, resulting in the formation of 1 as pale yellow crystals (0.32 g, 66%). Elemental analysis calculated for C_{12}H_{20}NLi: C 47.56, H 10.08, N 14.60; found: C 47.42, H 9.93, N 14.51. Crystal data for 1: C_{12}H_{20}NLi, M = 479.80, tetragonal, \( P_{4}bc\), \( a = 16.4053(3), c = 21.4837(10) \) \( \AA\), \( V = 5781.99(31) \) \( \AA^3\), \( T = 100(2) \) \( K\), \( Z = 8\), 12200 reflections collected, 4177 independent reflections (\( R_{int} = 0.0397\)), 89.6% completeness to \( \theta = 28.66^\circ\) (\( \lambda = 0.71073 \) \( \AA\)), final \( R \) indices \( |I| > 2\sigma(I)\) \( R_I = 0.0393\) and \( wR_I = 0.0989\), \( R \) indices (all data) \( R_I = 0.0551\), \( wR_I = 0.1060\).

**Synthesis of [2][3]**

A solution of LiN(SiMe_3)_2 (0.48 g, 1.0 mmol) in toluene (10 mL) was added to a stirred suspension of MnCl_2 (0.06 g, 0.5 mmol) in toluene (15 mL) at room temperature. The pale pink reaction mixture was stirred overnight, resulting in a pale amber solution and a precipitate. Filtration of the hot reaction mixture (Celite, porosity 3) produced an amber solution, which was reduced in volume to approximately 5 mL and stored at \(-4^\circ\) C. After two days, amber crystals of \([\text{Zn(hmds)}]_5\) formed. For spectroscopic and analytical studies, the nascent solvent was removed by syringe and the crystalline material then washed with hexane (2 x 5 mL), before being dried in vacuo, which resulted in evaporation of the lattice toluene to give \([\text{Zn(hmds)}]_5\) (0.05 g, 30% isolated yield). An alternative synthesis of \([\text{Zn(hmds)}]_5\), using the same amounts of each reagent but with the suspension of MnCl_2 in toluene containing 50 \( \mu\)L of...
degassed water, was also accomplished (0.06 g, 36% isolated yield). Elemental analysis for C$_{2}$H$_{12}$N$_{2}$O$_{5}$Cl$_{3}$Mn: calculated C 48.42; H 18.04; found C 48.11, H 8.99, N 17.51. Crystal data for I: C$_{2}$H$_{13}$N$_{3}$O$_{5}$Cl$_{2}$LiCl: M = 1988.96, monoclinic, C2/c, a = 20.1096(12), b = 24.4769(15), c = 24.9736(17) Å, β = 105.769(6)°, V = 11829.9(13) Å$^3$, T = 100(1) K, Z = 4, 21119 reflections collected, 7584 independent reflections ($R_{int}$ = 0.0906), 99.7% completeness to $θ = 21.00$° ($λ = 0.71073$ Å), final R indices ($I > 2σ(I)$) $R_I$ = 0.0857 and $wR_I$ = 0.1799, R indices (all data) $R_I$ = 0.1783, $wR_I$ = 0.2215.

**Synthesis of [4][3]**

This compound was synthesized in an identical manner to [2][3] using a suspension of anhydrous CoCl$_{2}$ (0.11 g, 0.5 mmol) in toluene (10 mL) and a solution of I (0.24 g, 0.5 mmol) in toluene (10 mL). The resulting blue solution was stored overnight at room-temperature to result in blue crystals of [4][3](2-toluene). Drying the crystals in vacuo resulted in evaporation of the lattice toluene to give [2][3] (0.42 g, 24% isolated yield; with water 0.49 g, 28%). Elemental analysis calculated for C$_{2}$H$_{12}$N$_{2}$O$_{5}$Cl$_{2}$Co: C 48.31; H 9.12, N 18.00; found C 47.82, H 8.98, N 17.51. Crystal data for I: the SQUEEZE function of PLATON was applied to two independent toluene molecules, which could not be refined owing to severe disorder at special positions.$^{86}$ C$_{2}$H$_{13}$N$_{3}$O$_{5}$Cl$_{3}$Li-Co: M = 2009.07, monoclinic, C2/c, a = 20.1096(4), b = 24.5598(4), c = 24.9957(5) Å, β = 105.786(2)°, V = 11874.2(4) Å$^3$, T = 100(1) K, Z = 4, 43649 reflections collected, 12325 independent reflections ($R_{int}$ = 0.0275), 98.8% completeness to $θ = 76.56$° ($λ = 1.54178$ Å), final R indices ($I > 2σ(I)$) $R_I$ = 0.0629 and $wR_I$ = 0.1746, R indices (all data) $R_I$ = 0.0653, $wR_I$ = 0.1763.

**Synthesis of [5][3]**

This compound was synthesized in an identical manner to [2][3] using anhydrous ZnBr$_{2}$ (0.11 g, 0.5 mmol) and I (0.24 g, 0.5 mmol). The resulting yellow solution stored overnight at room-temperature to result in yellow crystals of [5][3] (0.04 g, 32% isolated yield; with water 0.06 g, 48%). Elemental analysis calculated for C$_{2}$H$_{12}$N$_{2}$O$_{5}$Li$_{2}$Zn$_{2}$: C 47.93; H 8.31, N 19.56; found C 47.78, H 8.19, N 19.59. Crystal data for [5][3]: C$_{2}$H$_{13}$N$_{3}$O$_{5}$Li$_{2}$Zn$_{2}$: M = 1505.70, orthorhombic, Pha$_{2}$a, a = 27.7860(13), b = 24.4421(10), c = 12.1310(7) Å, $V = 8232.3(7)$ Å$^3$, $T = 100(2)$ K, Z = 4, 33772 reflections collected, 10107 independent reflections ($R_{int}$ = 0.1008), 94.5% completeness to $θ = 23.25$° ($λ = 0.71073$ Å), final R indices ($I > 2σ(I)$) $R_I$ = 0.0481 and $wR_I$ = 0.1150, R indices (all data) $R_I$ = 0.1317, $wR_I$ = 0.1268.

**Acknowledgements**

The authors acknowledge the EPSRC, The EPSRC UK National Electron Paramagnetic Resonance Facility at The University of Manchester, the Alexander von Humboldt Foundation (Fellowship for Experienced Researchers awarded to RAL) and the Royal Society (Wolfson Merit Award to REPW). We thank Prof. D. Collison (Manchester) for helpful discussions.

**References**


