

Synthetic and structural studies of mixed sodium bis(trimethylsilyl)amide-sodium halide aggregates in the presence of η^2 - N,N -, η^3 - $N,N,N/N,O,N$ - and η^4 - N,N,N,N -donor ligands

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ABSTRACT

When *n*-hexane solutions of an excess of sodium bis(trimethylsilyl)amide (NaHMDS) are combined with a cesium halide (halide = Cl, Br or I) in the presence of the tetradentate donor molecule [tris{2-(dimethylamino)ethyl}amine] (Me₆TREN), the isolation and characterization of a series of sodium amide/sodium halide mixed aggregates was forthcoming. The cesium halide was employed as it efficiently reacted with NaHMDS to produce a molecular, soluble source of the sodium halide salt (which was subsequently captured by excess of NaHMDS) via a methathetical reaction. These mixed sodium amide/sodium halide complexes are formally

sodium sodiates and are deficient in halide co-complexes with respect to the amide, and have the general formula [$\{\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-X})\}\{\text{Na}(\text{Me}_6\text{TREN})\}$] [where X = Cl (**1**), Br (**2**) or I (**3**)]. The influence of the donor ligand was studied for the NaI-NaHMDS system and when *n*-hexane solutions of this composition were treated with tridentate donors such as *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) or *N,N,N',N'*-tetramethyldiaminoether, (TMDAE), solvent-separated ion-pair co-complexes $[\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-I})]^-[\text{Na}_3(\mu\text{-HMDS})_2(\text{PMDETA})_2]^+$ (**4**) and $[\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-I})]^-[\text{Na}(\text{TMDAE})_2]^+$ (**5**) were isolated. However, on reaction with bidentate proligands such as the chiral diamine (*R,R*)-*N,N,N',N'*-tetramethylcyclohexane-1,2-diamine [(*R,R*)-TMCDA] or *N,N,N',N'*-tetramethylethylenediamine (TMEDA), neutral complexes $[\text{Na}_4(\mu\text{-HMDS})_3(\mu_4\text{-I})(\text{donor})_2]$ [donor = (*R,R*)-TMCDA, (**6**); donor = TMEDA, (**7**)] were produced. To illustrate the generality of the latter reaction with other halides, $[\text{Na}_4(\mu\text{-HMDS})_3(\mu_4\text{-Br})(\text{TMEDA})_2]$ (**8**) was also prepared by employing NaBr in the synthesis instead of NaI.

INTRODUCTION

In recent years the chemistry of alkali metal halide salts has been the subject of intense interest, both in terms of their utilization in synthesis, to gain a better understanding of their modus operandi, and their structures. For instance, in 2013 two high profile reports discussed the role of alkali metals behaving more like *p*-block than *s*-block metals in halide salts, culminating in the theoretical prediction and experimental synthesis of unexpected species such as NaCl_n and CsCl_n (where $n > 1$).¹ From a synthetic standpoint, the majority of interest has been focused on the role played by LiCl. It has been shown that the presence of this salt can play a beneficial or detrimental role in the reactivity and/or selectivity of organic transformations compared with

strictly salt-free (or assumed to be salt-free) protocols.² In this context, Knochel has comprehensively studied the favorable effect that using stoichiometric quantities of LiCl in combination with a conventional Grignard (RMgX ; R = alkyl or aryl, X = halide) or Hauser (R_2NMgX ; R = alkyl, X = halide) reagent has to produce the respective so-called *turbo*-reagents. These reagents enhance the reactivity/selectivity of a multitude of metal-halogen or metal-hydrogen exchange reactions.³ Collum has provided important structural insights into the solution state of secondary amido lithium bases in the presence of lithium halide salts illustrating the superior reactivity and stereoselectivity that the utility LiTMP (lithium 2,2,6,6-tetramethylpiperidide) exhibits in the *E*-enolization of ketones,⁴ and the catalytic activity that LiCl plays in the 1,4-nucleophilic addition of LDA (lithium diisopropylamide) to unsaturated esters⁵ and in the *ortho*-metallation of arene systems containing halogen-based directing groups.^{2b}

The reactivity of lithium amido reagents is highly dependent on their aggregation states. In this context, the solution⁶ and solid state structures⁷ of salts of sterically demanding secondary amides have been well established. For example, LDA which has been characterized as a helical polymer in the solid state^{7g} presents diverse cyclic polymorphs in arene solutions, the major species being tetrameric and trimeric but also pentamers and hexamers have been shown to exist.^{6d} LiTMP exists as a cyclic trimer and tetramer in the solid state and in hydrocarbon solution,^{7d,7j} and LiHMDS (lithium 1,1,1,3,3,3-hexamethyldisilazide) exists as an equilibrium between dimeric and tetrameric species in hydrocarbon solvents.^{6b} Although it is well known that lithium amide reagents coordinate to lithium halides, supporting solid state characterization of such aggregates is relatively scarce despite the numerous studies devoted to this chemistry over the past 40 or so years.⁸

We have recently shown that LiHMDS can efficiently trap sub-stoichiometric amounts of lithium halides to form macrocyclic LiHMDS-rich complexes $[\text{Li}_5(\mu\text{-HMDS})_5(\mu_5\text{-X})]^-[\text{Li}\{(R,R)\text{-TMCDA}\}_2]^+$ **I** [Figure 1; X = Cl and Br, (R,R)-TMCDA = (R,R)-N,N,N',N'-tetramethylcyclohexane-1,2-diamine]. These solvent-separated (*i.e.*, complexes that contains distinct anionic/cationic entities) LiHMDS/LiX aggregates have been coined as metal anionic crown complexes.^{8e} In contrast, the structural chemistry of sodium congeners of lithium anionic crowns and indeed other sodium amide-halide co-complexes appears to have been neglected. A relevant complex to this particular study is the macrocyclic hydroxyl-incorporated NaHMDS complex $[\text{Na}_4(\mu\text{-HMDS})_4(\mu_4\text{-OH})]^-[\text{Na}_2(\mu\text{-HMDS})\{(-)\text{-sparteine}\}_2]^+$ **II** (Figure 1).⁹ This complex can be considered as arising from the serendipitous trapping of an equivalent of ‘NaOH’; the OH⁻ being trapped within a tetrameric ring of $[\text{Na}(\text{HMDS})_4]$ and the Na⁺ cation coordinated by two equivalents of the chiral amine (-)-sparteine.

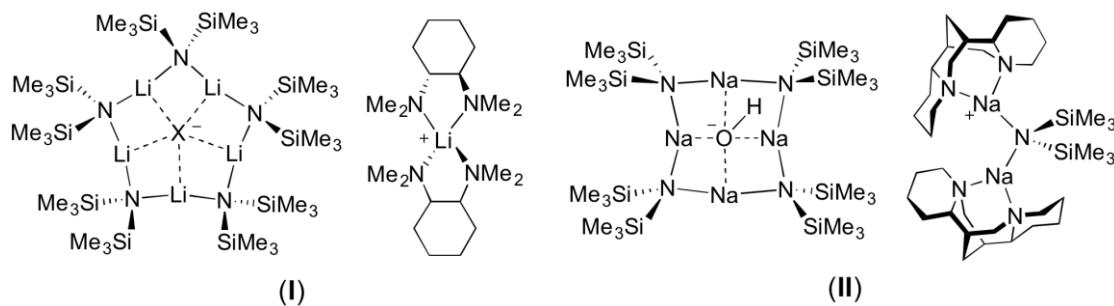


Figure 1. Structures of solvent-separated metal anionic crown complexes containing halide (**I**) and hydroxide (**II**) ions.

In this study, the structural chemistry of different aggregates of the important utility amide NaHMDS¹⁰ with several sodium halide salts in the presence of diverse Lewis donor molecules is reported. This provides further important structural insights into the way that alkali metal amide

reagents can interact with sub-stoichiometric quantities of alkali metal halide salts, a common composition encountered in certain fundamental organic transformations.^{2b,5}

RESULTS AND DISCUSSION

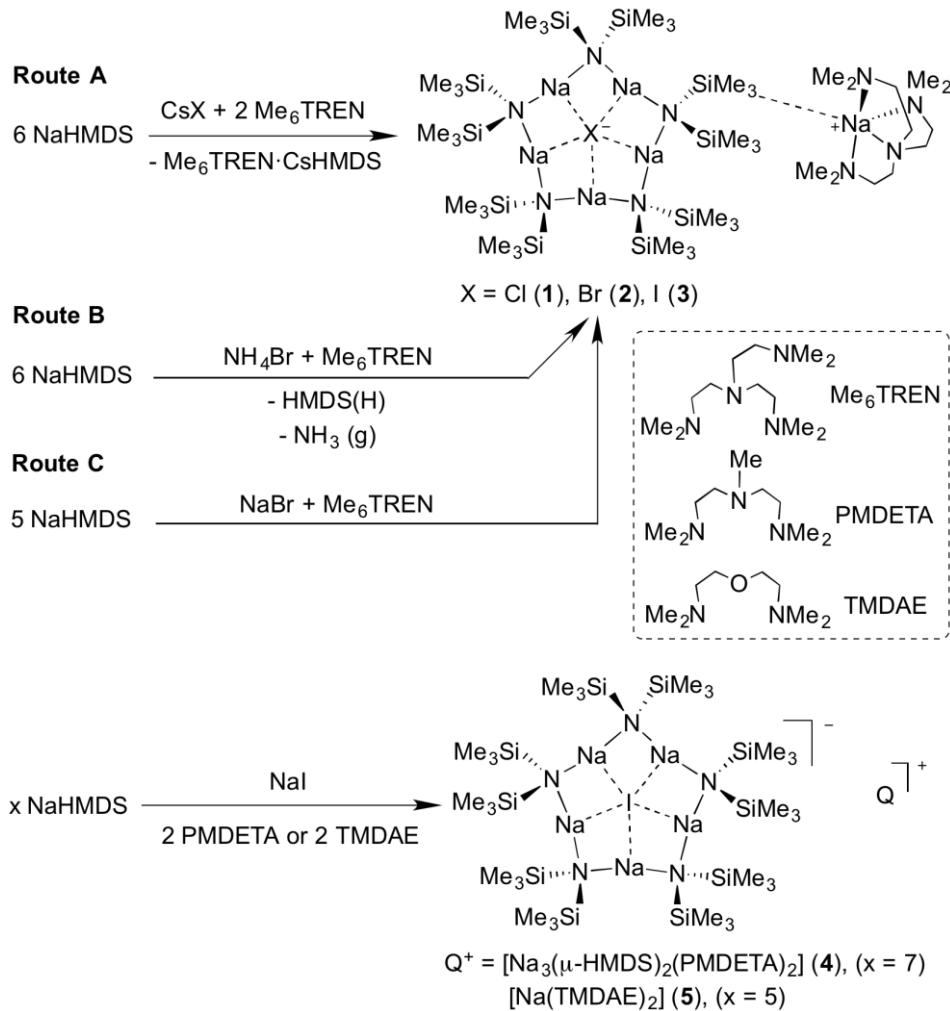
Synthesis. The main objective of this work was to accrue structural information on the halide salt capturing ability of sodium 1,1,1,3,3-hexamethyldisilazide (NaHMDS) complexes. As the primary goal was solid-state characterization, the reactions were optimized for crystallization of samples of high enough quality for X-ray crystallographic characterization. In addition, microelemental analyses in combination with NMR spectroscopy were used to determine the purity of the bulk samples and to shed light on the solution-state structures of the isolated samples.

Initially we tried to extend the work to heterobimetallic complexes by using a 6:1:2 stoichiometric mixture of NaHMDS, CsCl and the Lewis base Me₆TREN [where Me₆TREN is tris{2-(dimethylamino)ethyl}amine]. The cesium halide was chosen (rather than for example LiCl) as Cs is considerably larger than Na, potentially allowing us to combat the issue of mutual substitution disorder which commonly occurs when Li and Na are both present within a structure.¹¹ However, this synthetic route led to the preparation of an all sodium contacted ion pair complex [$\{\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-Cl})\}\{\text{Na}(\text{Me}_6\text{TREN})\}$] (**1**) in moderate yields (39%). Note that all yields reported in this work (*i.e.*, for the syntheses of **1-8**) are based on the consumption of alkali metal halide. Although we did not obtain the desired heterobimetallic species, this experiment showed that CsCl appears to be an ideal source of hydrocarbon-soluble molecular variant of *sodium chloride* which is formed via metathesis with NaHMDS (CsHMDS is the by-product). The NaCl appears to be trapped by the dual component NaHMDS/Me₆TREN trapping

system (Scheme 1a, route A). The by-product $[(\text{Me}_6\text{TREN})\text{Cs}(\text{HMDS})]^{12}$ is highly soluble in toluene allowing the facile isolation of crystalline **1**. Complex **1** is a rare example of a sodium sodiate.⁹

Due to the success of this reaction, we decided to explore its generality. The same synthetic methodology was applied to CsBr and again a sodium-only contacted ion pair, $[\{\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-Br})\}\{\text{Na}(\text{Me}_6\text{TREN})\}]$ (**2**) was formed in moderate yields (**2**, 39%) (Scheme 1a, route A). To assess whether it was possible to form **2** using an alternative method, ammonium halide NH₄Br and NaBr were employed as alkali metal halide sources (Scheme 1a, routes B and C, respectively). Complex **2** was indeed isolated albeit in lower yields (18 and 10%, respectively), suggesting that the salt metathesis reaction of NaHMDS with CsBr (Scheme 1a, route A) is a more convenient and efficient synthetic methodology to form **2**. NaI, generated in situ by reaction of NaHMDS with CsI, was also efficiently trapped forming a similar complex to **1** and **2** $[\{\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-I})\}\{\text{Na}(\text{Me}_6\text{TREN})\}]$ (**3**) in 35% yield.

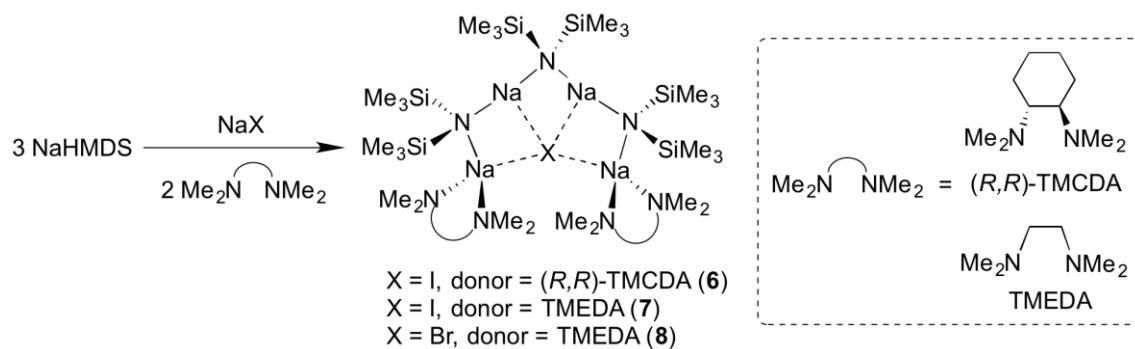
With the aim of providing additional structural insight into iodide trapped species, Me₆TREN was replaced by the tridentate amine *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA). The reaction combined NaHMDS, NaI and PMDETA initially in a 5:1:2 stoichiometric ratio to produce $[\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-I})]^-[\text{Na}_3(\mu\text{-HMDS})_2(\text{PMDETA})_2]^+$ **4**. The stoichiometry of the reaction was adjusted to 7:1:2 to produce **4** in a moderate yield of 35% (Scheme 1b). When *N,N,N',N'*-tetramethyldiaminoethylether (TMDAE) was used as the donor, $[\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-I})]^-[\text{Na}(\text{TMDAE})_2]^+$ (**5**) was isolated in a similar yield (36%) (Scheme 1b).



Scheme 1. a) Synthesis of $\left[\{\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-X})\} \{\text{Na}(\text{Me}_6\text{TREN})\}\right]$, $\text{X} = \text{Cl (1), Br (2) and I (3)}$, from cesium halide salts (Route A). Ammonium halide (Route B) and sodium halide (Route C) methodologies were used for the synthesis of **2**. b) Synthesis of $[\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-I})][\text{Na}_3(\mu\text{-HMDS})_2(\text{PMDETA})_2]$ (**4**) and $[\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-I})][\text{Na}(\text{TMDAE})_2]$ (**5**).

Following our success in the preparation of tetra- and tri-dentate donor ligand containing NaHMDS/NaI co-complexes, our work was extended to study the influence of the bidentate Lewis base donors on the formation of the complexes. The donors of choice were (*R,R*)-TMCDA [$(R,R)\text{-N,N,N',N'-tetramethylcyclohexane-1,2-diamine}$] and TMEDA (N,N,N',N' -tetramethylethylenediamine). By combining NaHMDS, NaI and the corresponding bidentate donor in a 3:1:2 stoichiometrically-precise ratio, two essentially isostructural compounds $[\text{Na}_4(\mu\text{-HMDS})_4(\mu_4\text{-I})][\text{Na}_2(\text{TMEDA})_2]$ (**6**) and $[\text{Na}_4(\mu\text{-HMDS})_4(\mu_4\text{-I})][\text{Na}(\text{TMDAE})_2]$ (**7**) were obtained.

$\text{HMDS}_3(\mu_4\text{-I})(\text{donor})_2$] [donor = (*R,R*)-TMCDA for **6** (32%) and TMEDA for **7** (44%), respectively] were formed (Scheme 2). Interestingly, by utilizing a different stoichiometric ratio of NaHMDS, NaI and donor (5:1:2) in *n*-hexane the same complexes were isolated. Therefore, it appears that an excess of NaHMDS (that was present for the syntheses of **1–5**) does not affect the preparation of **6** and **7**. To get information about the size of the halides this type of structure could accommodate, NaBr was used as the alkali metal halide reagent in the presence of the bidentate ligand TMEDA with NaHMDS introduced in the final step of the reaction. A complex having the same motif as **7** was obtained from this reaction in moderate yields (55%), namely $[\text{Na}_4(\mu\text{-HMDS})_3(\mu_4\text{-Br})(\text{TMEDA})_2]$ (**8**) (Scheme 2).



Scheme 2. Syntheses of $[\text{Na}_4(\mu\text{-HMDS})_3(\mu_4\text{-I})(\text{donor})_2]$ [donor = (*R,R*)-TMCDA (**6**) and TMEDA (**7**)] and $[\text{Na}_4(\mu\text{-HMDS})_3(\mu_4\text{-Br})(\text{TMEDA})_2]$ (**8**).

X-ray Diffraction Studies. During the course of this study, seven complexes (**1**, **2**, and **4–8**) were successfully prepared and characterized in the solid state (full details are given in Table S1 and S2). X-ray quality crystals of **1**, **2** and **4–8** were obtained from relevant NaHMDS/NaX solutions specified in experimental section. Unfortunately, several attempts to determine the solid state structure of **3** were unsuccessful. The X-ray data obtained for **3** was of poor quality, impeding any discussion of structural parameters but its chemical identity was unequivocally established as $[\{\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-I})\}\{\text{Na}(\text{Me}_6\text{TREN})\}]$ (**3**).

Our X-ray diffraction studies successfully revealed structural models for species that are potentially present in solutions containing commonly employed NaHMDS and a N-donor ligand in combination with sodium halide salts.

Complexes **1-5** all contain an anion which consists of a halide-deficient (with respect to amide) pentameric sodium amide rings [$\{\text{Na}_5\text{N}_5(\mu_5\text{-X})\}^-$, X = Cl (**1**), Br (**2**) and I (**4** and **5**)] with different-sodium based cationic counterions. Complexes **1** and **2** (Figure 2) exist as contacted ion pairs of type [$\{\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-X})\}\{\text{Na}(\text{Me}_6\text{TREN})\}$]. The cation in both complexes exhibits similar structural features and contains one sodium center tetra-coordinated to the tripodal ligand Me₆TREN giving rise to a $[\text{Na}(\text{Me}_6\text{TREN})]^+$ ion. This ion, via a Na···C long contact, is bound to the aforementioned anionic ring to generate the corresponding contacted ion pair complex. The Na···C contacts between the ions in **1** and **2** are composed of long agostic-type interactions¹³ between a Me₆TREN sequestered Na atom, and a Me group from an HMDS ligand [Na1···C16 and Na1···C13, both 2.955 Å in **1** and **2**] of the ten-atom anionic ring $[\text{Na}_5\text{N}_5(\mu_5\text{-X})]^-$. The Na···C distances in **1** and **2** are similar to those in other complexes containing Na···Me(Me₂)Si interactions [mean distance, 2.97 Å].¹⁴ Containing three donor arms emerging from a central donor, tetra-amine Me₆TREN is coordinatively flexible and has displayed all possible η^4 , η^3 , η^2 and η^1 modes to organoalkali-metal compounds.¹⁵ The donor ligand binds to the metal center in an η^4 fashion in **1** and **2**. The Na center is five-coordinate and adopts a distorted trigonal bipyramidal geometry. The metal is located in the center of the N(equatorial) plane of the Me₆TREN ligand. The Na-N(Me₆TREN) bond distances (2.44 Å, mean distance in **1** and **2**) and N-Na-N angles [mean angles, N(eq)-Na1-N(eq) 113.7 and 113.5, N(eq)-Na1-N(ax) 75.2 and 75.0, N(eq)-Na1-C16 104.9 and N(eq)-Na1-C13 106.0, N(ax)-Na1-C16 177.3 and N(ax)-Na1-C13 177.3°, in **1** and **2**, respectively] are similar to other complexes bearing a $[(\text{Me}_6\text{TREN})\text{Na}]^+$

moiety.^{15b,16} The Na atom is 0.63 Å outside of the plane formed by the equatorial N2-N3-N4 atoms (similar to the distance that the Na atom in the Me₆TREN adduct of benzylsodium protrudes from this plane, 0.74 Å)^{16c} and is projected towards a Me group of a HMDS ligand.

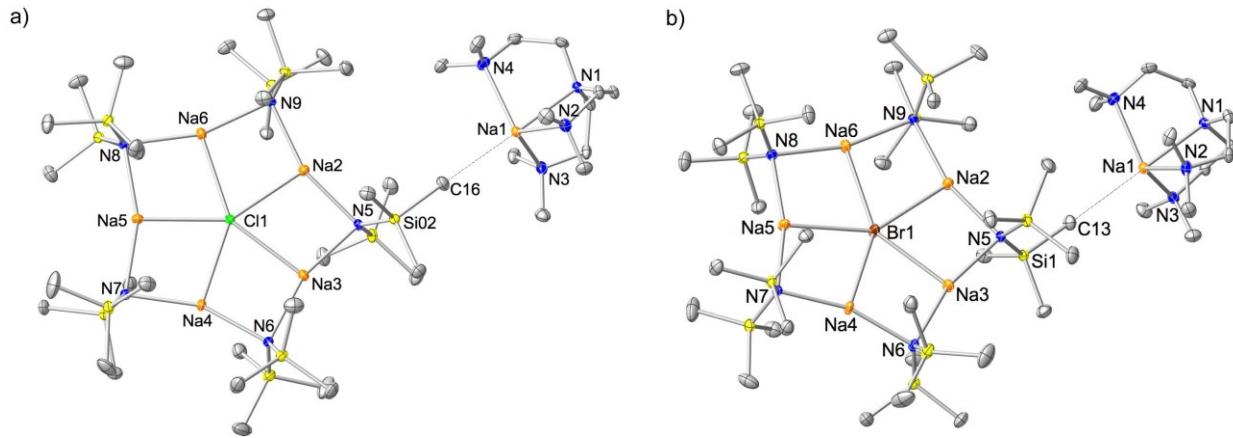


Figure 2. Molecular structure of **1** (a) and **2** (b). Hydrogen atoms are omitted for simplicity and displacement ellipsoids are displayed at 30% probability. The dashed lines illustrate Na···Me agostic interactions. Selected bond distances (Å) and angles (°) for **1**: Na3-N6 2.368(2), Na3-N5 2.380(2), Na4-N6 2.353(2), Na4-N7 2.352(2), Na5-N7 2.374(2), Na5-N8 2.387(2), Na6-N8 2.391(2), Na6-N9 2.398(2), Na2-N9 2.378(2), Na2-N5 2.384(2), Cl1-Na2 2.7988(12), Cl1-Na4 2.8112(12), Cl1-Na6 2.8302(12), Cl1-Na5 2.8366(12), Cl1-Na3 2.8452(12), N1-Na1 2.455(2), Na1-N4 2.408(2), Na1-N3 2.439(2), Na1-N2 2.443(2), Na1-C16 2.955(3); Na4-N6-Na3 87.88(8), Na4-N7-Na5 88.99(8), Na5-N8-Na6 88.65(8), Na2-N9-Na6 88.99(7), N7-Na4-N6 158.49(8), N7-Na5-N8 161.04(8), N8-Na6-N9 162.05(8), N9-Na2-N5 160.04(8), Na2-Cl1-Na6 72.99(3), Na2-Cl1-Na6 72.99(3), Na4-Cl1-Na5 71.82(3), Na6-Cl1-Na5 72.20(3), Na2-Cl1-Na3 72.16(3), Na4-Cl1-Na3 70.79(3), N4-Na1-C16 104.01(9), N3-Na1-C16 107.03(8), N2-Na1-C16 103.70(8), N1-Na1-C16 177.26(8), N2-Na1-N1 74.14(7), N3-Na1-N1 75.61(7), N4-Na1-N1 75.47(8), N3-Na1-N2 118.94(8), N4-Na1-N3 110.70(9), N4-Na1-N2 111.06(9); for **2**: Na2-N9 2.389(3), Na6-N9 2.414(3), Na6-N8 2.405(3), Na5-N8 2.405(3), Na5-N7 2.387(3), Na4-N7 2.368(3), Na4-N6 2.359(3), Na3-N6 2.380(3), Na3-N5 2.393(3), Na2-N5 2.400(3), Br1-Na2 2.8979(14), Br1-Na4 2.9144(14), Br1-Na5 2.9289(14), Br1-Na6 2.9289(15), Br1-Na3 2.9356(14), Na1-N1 2.452(3), Na1-N4 2.408(3), Na1-N3 2.442(3), Na1-N2 2.444(3), Na1-C13 2.955(4); Na2-N9-Na6 92.29(10), Na5-N8-Na6 91.66(10), Na4-N7-Na5 92.14(10), Na4-N6-Na3 91.23(11), Na3-N5-Na2 91.33(10), N8-Na6-N9 165.30(11), N7-Na5-N8 163.77(11), N6-Na4-N7 162.13(11), N6-Na3-N5 163.48(11), N9-Na2-N5 163.13(11), Na4-Br1-Na5 71.74(4), Na2-Br1-Na6 72.93(4), Na5-Br1-Na6 72.16(4), Na2-Br1-Na3 71.98(4), Na4-Br1-Na3 70.75(4), N4-Na1-C13 104.36(12), N3-Na1-C13 103.61(11), N2-Na1-C13 106.90(11), N1-Na1-C13 177.32(12), N4-Na1-N1 75.50(11), N3-Na1-N1 74.05(10), N2-Na1-N1 75.55(10), N4-Na1-N3 110.63(12), N4-Na1-N2 110.91(12), N3-Na1-N2 119.05(11).

Contrasting with **1** and **2**, co-complexes **4** and **5** have solvent-separated structures in the solid state (Figure 3). Note that **4** is the first solid-state structures of an iodide-incorporated metal anionic crown complex. The Na_5N_5 ring appears to be an adequately sized cavity to capture not only Cl and Br, as for Li_5N_5 rings,^{8e} but due to the larger perimeter of the Na_5 ring the cavity can now accommodate a larger iodide ion. The cation is rather unusual and consists of a Na atom which bridges two '(PMDETA) NaHMDS ' fragments to form $[\text{Na}_3(\mu\text{-HMDS})_2(\text{PMDETA})_2]^+$. It is trinuclear in adopting a Na-N(HMDS)-Na-N(HMDS)-Na zig-zag chain of atoms. The terminal Na atoms are η^3 -coordinated to a PMDETA ligand. This results in the terminal Na atoms adopting a distorted tetrahedral arrangement [mean angles, 116.0, 125.9 and 142.7 for N(HMDS)-Na-N(PMDETA); 73.1, 74.9 and 112.2° for N(PMDETA)-Na-N(PMDETA); mean sum of N-Na-N angles, 644.8°] while the central Na atom is two coordinated with a N(HMDS)-Na-N(HMDS) angle of 164.1° (distorted from linearity by 15.9°). A search of the Cambridge Structural Database¹⁷ appears to reveal that this is a unique example of this type of cation.

Due to the oxophilic nature of alkali metals, we decided to swap the *N,N,N*-tridentate ligand PMDETA in our reaction by the mixed donor atom *N,O,N*-tridentate ligand TMDAE (Scheme 1b). In this case the Na atom is solvated by two TMDAE molecules which fully satisfies its coordination sphere to allow formation of the solvent separated complex $[\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-I})][\text{Na}(\text{TMDAE})_2]$ (**5**). Two independent molecules constitute the asymmetric unit cell of **5**. The anionic parts resemble the same Na_5N_5 structure found in **4**. Both cationic fragments consist of a sodium atom coordinated to two TMDAE molecules in a distorted octahedral fashion, where each tridentate TMDAE ligand occupies one distorted octahedral face of the metallic center. This ligand has rarely been reported to coordinate to any alkali metal in the solid state and only two

structures have been previously reported. One of them has TMDAE ligating sodium ion in a η^2 manner in $[(\text{TMDAE})\text{Na}(\text{dpa})]_2$ (dpa is 2,2'-dipyridylamide).¹⁸ TMDAE also adopts this chelating mode towards lithium in $[\text{Li}(\mu\text{-Me}_2\text{NCH}_2\text{CH}_2\text{OCHCH}_2\text{NMe}_2)(\mu\text{-TMP})\text{Al}(\text{iBu})_2]$ where the *bis*-amide $\text{LiAl}(\text{TMP})_2\text{iBu}_2$ additionally deprotonates the Lewis base donor selectively at an α -position to the oxygen atom.¹⁹ To the best of our knowledge, **5** represents the first example of an alkali metal complex coordinating to all three heteroatoms of the TMDAE ligand in the solid state. Only one other example of TMDAE bonding in this way has been reported previously, in the copper(III) complex $[\text{CuCl}_3 \cdot \text{TMDAE}]$.²⁰ Unfortunately, due to disorder within the donor it is not meaningful to discuss its structural parameters in detail.

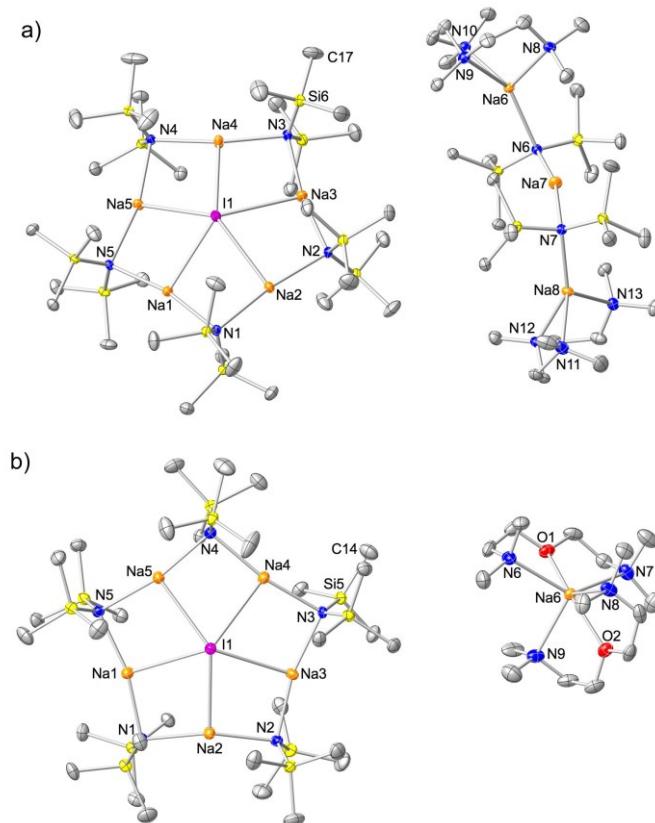


Figure 3. Molecular structure of **4** (a) and **5** (b). For both structures, hydrogen atoms have been omitted for clarity. Specifically for **4**, one disordered component of the TMDAE ligand and iodine have also been omitted. For **5** only one molecule from the asymmetric unit is shown. Displacement ellipsoids are displayed at 30% probability. Selected bond distances (\AA) and

angles ($^{\circ}$) for **4**: Na1-N5 2.424(2), Na5-N5 2.362(2), Na1-N1 2.371(2), Na2-N1 2.397(2), Na2-N2 2.387(2), Na3-N2 2.417(2), Na3-N3 2.428(2), Na4-N3 2.402(2), Na4-N4 2.404(2), Na5-N4 2.408(2), mean Na-I 3.076, Na6-N8 2.533(2), Na6-N9 2.498(2), Na6-N10 2.515(2), Na6-N8 2.533(2), Na6-N6 2.461(2), Na7-N6 2.360(2), Na7-N7 2.406(2), Na8-N7 2.403(2), Na8-N11 2.466(2), Na8-N12 2.518(2), Na8-N13 2.594(2); Na5-N5-Na1 92.89(7), Na1-N1-Na2 97.85(8), Na2-N2-Na3 97.19(8), Na4-N3-Na3 96.54(8), Na4-N4-Na5 95.72(8), N1-Na1-N5 166.98(8), N2-Na2-N1 171.03(8), N2-Na3-N3 169.67(8), N3-Na4-N4 166.71(8), N5-Na5-N4 164.00(8), mean Na-I-Na 70.883, Na7-N6-Na6 108.31(8), Na8-N7-Na7 107.94(8), N6-Na7-N7 164.05(8), N6-Na6-N9 142.53(8), N6-Na6-N10 125.58(7), N9-Na6-N10 74.95(7), N6-Na6-N8 116.00(8), N9-Na6-N8 73.19(7), N10-Na6-N8 112.10(8), N7-Na8-N11 117.31(8), N7-Na8-N12 146.67(8), N11-Na8-N12 75.40(8), N7-Na8-N13 122.01(8), N11-Na8-N13 112.32(8), N12-Na8-N13 72.89(7); for **5**: Na1-N1 2.388(4), Na1-N5 2.377(4), Na2-N1 2.382(4), Na2-N2 2.379(4), Na3-N2 2.406(4), Na3-N3 2.414(4), Na4-N3 2.399(4), Na4-N4 2.435(4), Na5-N4 2.401(4), Na5-N5 2.438(4), I1-Na2 3.105(2), I1-Na4 3.117(2), I1-Na1 3.118(2), I1-Na5 3.123(2), I1-Na3 3.1383(19); Na2-N1-Na196.00(15), Na2-N2-Na3 95.54(15), Na4-N3-Na3 94.95(14), Na5-N4-Na4 98.47(16), N5-Na1-N1 162.79(17), N2-Na2-N1 164.18(17), N2-Na3-N3 166.98(16), N3-Na4-N4 168.38(16), N4-Na5-N5 167.94(16).

The structure of the ten-atom Na_5N_5 ring can be compared with the structural chemistry of salt-free NaHMDS aggregates²¹ (e.g. donor-free NaHMDS exists as a zig-zag polymeric chain of alternating N and Na atoms²² and as a near-planar cyclo-trimer²³ in the solid state). Complexes **1**-**5** expand the reported lithium amide anionic crowns to sodium, and can be considered to resemble inverse crown polymetallic complexes. An inverse crown ether complex (**IV**, Figure 4) is a macrocyclic compound which exhibits an inverse topological relationship to conventional crown ethers (**III**).²⁴ It is also possible to encapsulate non-oxygen containing species (such as aryl dianions) within the polymetallic ring and these are classed as inverse crowns. The main differences between these types of complexes are alkali metal anionic crowns (**VI**) are generally solvent-separated or are contact ion-pairs which have weak agostic-type interactions holding the ions together whereas inverse crown ethers/inverse crowns (**IV** and **V**) contain an alkali metal and a divalent metal within a neutral molecule.

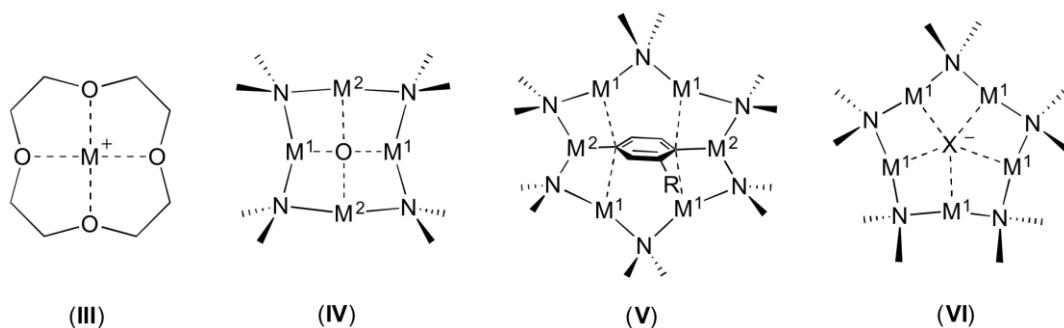


Figure 4. Structures of 12-crown-4 ether (**III**), inverse crown ether (**IV**), inverse crown (**V**) and metal anionic crown (**VI**) complexes.

The Na_5N_5 anionic cavity in **1**, **2**, **4** and **5** can be described as a ten pointed star of alternating Na and N atoms which act as a homometallic host-guest type complex accommodating a chloride (**1**) bromide (**2**) or iodide (**4** and **5**) ions. Only one other anion fragment akin to that in **1** appears to have been crystallographically characterized, namely the ytterbium amido sodiate complex, $[(\text{Na}_5(\mu\text{-HMDS})_5(\mu_5\text{-Cl}))][\text{L}_2\text{Yb}]^+$.²⁵ It can be envisaged that the ‘star’ is constructed of two interpenetrating essentially regular pentagons – one small pentagon composed of five Na atoms, the other a larger pentagon composed of five N atoms. Assuming the pentagons are concentric, they are disposed at angles of approximately 36° with respect to each other in all the cases (**1**, **2**, **4** and **5**, Figure 5a). In order to compare the homometallic sodium amide anionic cavities found for **1–5**, structural parameters for the chloride (**1**), bromide (**2**) and iodide (**4** and **5**) derivatives are shown in Table 1, including dimensions related to the aforementioned pentagon cavities.

Table 1. Selected bond parameters and angles for co-complexes **1**, **2**, **4–7**.

	1 (Cl)	2 (Br)	4 (I)	5 (I)	6 (I)	7 (I)
Na-X ^a	2.82	2.92	3.11	3.10	3.13	3.12
Na-N(HMDS) ^a	2.38	2.39	2.40	2.39	2.39	2.38
Na-X-Na ^b	72.0	71.9	70.3	69.9	67.8	67.3
N(HMDS)-Na-N(HMDS) ^b	160.5	163.6	167.8	166.5	160.3	159.9
Na-N(HMDS)-Na ^b	88.6	91.7	96.1	96.1	93.8	92.6
N ₅ -pentagon angles ^c	539.3	539.4	538.7	539.4	-	-
Na ₅ -pentagon angles ^c	539.6	536.7	539.6	539.5	-	-

^a Mean distance (Å). ^b Mean angles (°). ^c Sum of internal angles (540° for a regular pentagon).

As expected, the mean Na- μ_5 -halogen distance increases in the series Cl < Br < I. The ten-atom Na₅N₅ ring is planar for chloride and bromide, slightly puckered for iodide (mean Na-N-Na-N torsion angles, 170.7, 169.6 and 156.0° in **1**, **2** and **5**, respectively), but of similar perimeter for **1-5** as judged by comparing the Na-N bond distances (mean Na-N, 2.38-2.40 Å, in **1-5**, Table 1). This provides an adequately sized cavity to satisfactorily accommodate chloride, bromide or iodide ions. Figure 5 shows the different positions that the halide occupies in the planar Na₅N₅ cavity. The halide atoms are geometrically positioned in the center of both concentric pentagons: the chloride ion is approximately co-planar with the ten-atom Na₅N₅ ring (0.09 Å above) in **1**, the bromide is 0.15 Å out of the Na₅N₅ plane in **2**. Chloride and bromide have been previously trapped within a Li₅N₅ ring, but the cavity of Na₅N₅ seems to be of an appropriate size to also accommodate the larger iodide atom in **4** and **5** (Figure 5). The anionic moiety is structurally identical for **4** and **5**, a ten-atom Na₅N₅ ring hosting an iodide ion which is situated farther from the Na₅N₅ plane (0.67 Å above the plane, Figure 5b) when compared with chloride (**1**) and bromide (**2**), suggesting that the Na₅N₅ ring is too small to accommodate the anion in the same plane.

Based on the calculated areas, the N₅ pentagon is approximately double the size of the Na₅ pentagon (calculated areas for the Na₅/N₅ pentagons, 19.0/37.8, 20.3/38.5, 21.9/39.1, 21.8/39.1, Å², for **1**, **2**, **4** and **5**, respectively). The N₅ cores of the complexes are similar in size (mean N···N separation, 4.68, 4.73, 4.77 and 4.77 Å for **1**, **2**, **4** and **5**, respectively) whilst the Na₅ cores modestly increase in size with respect to the size of the captured halide, Cl < Br < I (mean Na···Na separations, 3.32, 3.43, 3.57 and 3.55 Å, for **1**, **2**, **4** and **5**, respectively). As expected, the Li₅ cavities of the previously reported complexes, of the form [Li₅(μ -HMDS)₅(μ_5 -X)]⁻[Li{(*R,R*)-TMCDA}₂]⁺ (X = Cl, Br), have shorter Li···Li separations and therefore smaller areas

for the Li₅-pentagons [mean Li···Li separation (Å)/area (Å²): 2.86/14.1 (Cl), 2.97/15.2 (Br)].^{8e} In keeping with the results for **1**, **2**, **4** and **5**, the area of the N₅ pentagon is still approximately twice as large as the Li₅ pentagon, due to the inherent shortening of the N···N separations. It can be postulated that due to the relatively small area generated by the Li atoms in the Li₅ cavities, it is not possible to accommodate iodide as a substitute for the bromide ion in the latter complex as it is already 0.4 Å out of the plane.

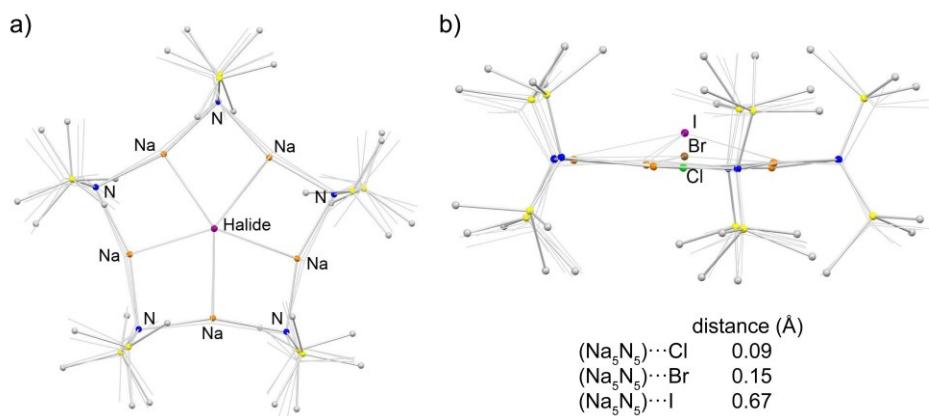


Figure 5. Ball and stick superimposed top (a) and side view (b) for the anionic [Na₅(μ -HMDS)₅(μ ₅-halide)]⁻ fragments containing chloride (**1**), bromide (**2**) and iodide (**5**). N and Na atoms from **1** have been chosen as a reference to overlay **2** and **5**.

We also studied the influence of the denticity of the Lewis base donor of choice on the formation of these halogen-deficient sodium anionic ring complexes by replacing the tetradeятate Me₆TREN and tridentate PMDETA and TMDAE donors with the bidentate (*R,R*)-TMCDA and TMEDA ligands. Co-complexes **6–8** crystallized in the monoclinic crystal system, and they are found to have similar structures consisting of a Na₄N₃ chain, with the two terminal metal centers each being coordinated to a bidentate ligand (*R,R*)-TMCDA (**6**) or TMEDA (**7** and **8**) (Figures 6 and 7). The employment of these donors produced three essentially isostructural complexes, structures which contained a novel neutral "open ring" motif, with general formula [Na₄(μ -

$\text{HMDS}_3(\mu_4\text{-X})(\text{donor})_2$] [donor = (*R,R*)-TMCDA, X = I for **6**; donor = TMEDA, X = I for **7**; donor = TMEDA, X = Br for **8**]. It can be envisaged that a tetranuclear sodium amide chain acts as a host towards iodide (**6** and **7**) or bromide (**8**) ions.

The Na_4N_3 chain is essentially planar and the iodide ion occupies a position 0.26 Å out of the plane containing the Na-Na-N-Na-Na chain in **6** whilst it is almost co-planar in **7** (0.07 Å above). This is perhaps due to the more constrained and less flexible nature of (*R,R*)-TMCDA forcing the halide further away from the Na_4N_3 plane. In both cases the corresponding bidentate ligands are η^2 coordinate to the two terminal sodium atoms, rendering them four-coordinate. The separation between the terminal sodium atoms ($\text{Na}_4 \cdots \text{Na}_1$ and $\text{Na}_4 \cdots \text{Na}_3$, 6.10 and 6.14 Å in **6** and **7**, respectively, Figure 6), are longer than the analogous Na···Na separations in **4** and **5** (mean Na···Na separation, 5.77 Å, Figure 3). The open ring, more flexible nature of **6** and **7** means that the Na_4 cavity can accommodate an iodide ion more easily and thus it protrudes less from the metal plane. The Na-I bond distances are similar in **6** and **7** (mean Na-I distance, 3.13 and 3.11 Å, respectively; Table 1) and to those found in the solvent-separated complexes **4** and **5** (3.11 and 3.10 Å, respectively), being shorter than the shortest Na-I distances in NaI salt itself (3.231 Å), albeit that the Na and I coordination numbers in **4** and **5** are lower than those encountered in NaI.²⁶ The diglyme and 18-crown-6 adducts of sodium iodide [$\text{NaI}(\text{L})$, L = $(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{O}$ or 18-crown-6] present similar Na-I bond lengths to those in complexes **4-7** (3.164 and 3.138 Å, respectively).²⁷ The Na-N(HMDS) and Na-N(donor) dimensions are similar to those in **6** and **7** [mean Na-N(HMDS)/Na-N(donor) distance, 2.39/2.50 and 2.38/2.49 Å, respectively] and as expected, in both compounds, the Na-N(amine) bonds are longer than Na-N(amide) bonds.²⁸ The two terminal Na atoms in **6** and **7** have distorted tetrahedral coordination spheres [range of angles, 70.10(2)-135.90(2)° for Na1 and 70.90(2)-133.9(3)° for Na4 in **6**;

75.99(11)-136.32(12) $^{\circ}$ for Na3 and 75.78(11)-138.38(12) $^{\circ}$ for Na4 in **7**] primarily due to the acute bite angle of the bidentate ligand when coordinating to the sodium atom. In an attempt to extend the scope of the reaction employed in the preparation of **7**, NaBr was utilized instead of NaI. This produced $[\text{Na}_4(\mu\text{-HMDS})_3(\mu_4\text{-Br})(\text{TMEDA})_2]$ **8**, but due to disorder the structural parameters cannot be discussed in detail (Figure 7).

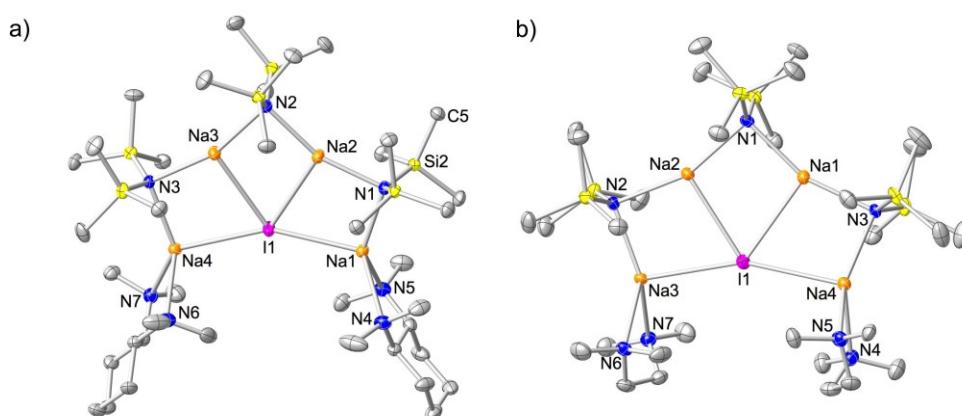


Figure 6. Molecular structure of **6** (a) and **7** (b). Hydrogen atoms, and one disordered component of one TMEDA ligand has been omitted for clarity. Displacement ellipsoids are displayed at 30% probability. Selected bond distances (\AA) and angles ($^{\circ}$) for **6**: Na1-N1 2.425(5), Na2-N2 2.369(5), Na2-N1 2.377(5), Na3-N3 2.378(5), Na3-N2 2.382(5), Na4-N3 2.417(5), Na1-N4 2.479(7), Na1-N5 2.528(7), Na4-N7 2.496(6), Na4-N6 2.498(7), Na1-I1 3.128(2), Na2-I1 3.127(2), Na3-I1 3.139(2), Na4-I1 3.123(2); Na2-N1-Na1 94.75(19), Na2-N2-Na3 91.29(17), Na3-N3-Na4 95.29(16), N2-Na2-N1 159.5(2), N3-Na3-N2 160.96(18), Na2-I1-Na1 68.78(6), Na4-I1-Na3 68.94(5), Na2-I1-Na3 65.66(6), N1-Na1-N4 127.1(2), N1-Na1-N5 135.9(2), N4-Na1-N5 70.1(2), N1-Na1-I1 97.65(13), N4-Na1-I1 119.47(18), N5-Na1-I1 106.90(17), N3-Na4-N7 128.4(2), N3-Na4-N6 133.9(3), N7-Na4-N6 70.9(2), N3-Na4-I1 97.56(12), N7-Na4-I1 120.18(16), N6-Na4-I1 105.83(19); for **7**: Na3-N2 2.392(3), Na2-N1 2.383(3), Na2-N2 2.394(3), Na1-N3 2.369(3), Na1-N1 2.384(3), Na4-N3 2.374(3), Na3-N7 2.475(3), Na3-N6 2.491(3), Na4-N4 2.454(4), Na4-N5 2.518(3), Na1-I1 3.1049(15), Na2-I1 3.0964(14), Na3-I1 3.1184(15), Na4-I1 3.1297(14); Na3-N2-Na2 91.45(11), Na2-N1-Na1 93.64(11), Na1-N3-Na4 92.75(12), N1-Na2-N2 159.41(12), N3-Na1-N1 160.47(12), Na2-I1-Na1 68.17(4), Na2-I1-Na3 66.92(4), Na1-I1-Na4 66.82(4), N2-Na3-N7 136.32(12), N2-Na3-N6 135.12(12), N7-Na3-N6 75.99(11), N2-Na3-I1 100.53(8), N7-Na3-I1 96.01(9), N6-Na3-I1 106.09(9), N3-Na4-N4 138.38(12), N3-Na4-N5 133.18(12), N4-Na4-N5 75.78(11), N3-Na4-I1 99.61(9), N4-Na4-I1 101.20(9), N5-Na4-I1 102.59(9).

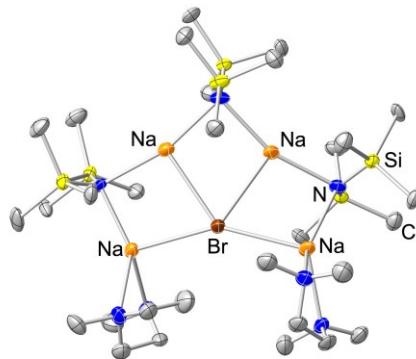


Figure 7. Molecular structure of **8** displaying its atom connectivity. Hydrogen atoms, and disordered components of TMEDA and HMDS ligands have been omitted for clarity. Displacement ellipsoids are displayed at 30% probability.

Some Li containing structures which are related to **6-8** have been reported. During investigations into enolization and addition reactions, Williard isolated a tetralithium mixed amido/enolate/bromide complex $[(\text{LiBr})(\text{TMEDA}_2(\text{LiOR})_2\text{LiHMDS})]$ (where OR is $\text{OC}=\text{CH}_2'\text{Bu}$) (Figure 8, **VII**),²⁹ which closely resembles the metal-anion framework of **6-8**. Also related to this work are the trilithium amide/chloride structures $[(\text{LiCl})(\text{donor}\cdot\text{LiNR}_2)_2]$ [$\text{NR}_2 = \text{HMDS}$, DA; donor = TMEDA, DMAE [2-(*N,N*-dimethylamino)ethyl methyl ether], which formally contain one unit less of MNR_2 to complete the structure (Figure 8, **VIII-X**).^{8b,8c}

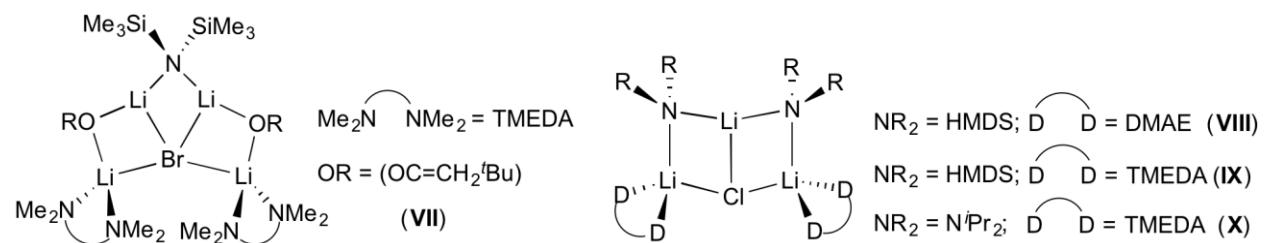


Figure 8. Structural representation of $[(\text{LiBr})(\text{TMEDA}_2(\text{LiOR})_2\text{LiHMDS})]$ (**VII**) and $[(\text{LiCl})(\text{donor}\cdot\text{LiNR}_2)_2]$ (**VIII-X**) reagents.

NMR Spectroscopic studies. Compounds **1-8** were characterized by ¹H and ¹³C NMR spectroscopy. All the reactions where cesium halides were used as reactants, led to the formation of CsHMDS/MX (where M = Na or Cs) co-complexes as by-products via partial salt metathesis. This was confirmed by ¹³³Cs NMR spectroscopic studies of the corresponding reaction mixtures.³⁰ The NMR spectroscopic data for a genuine sample of [(Me₆-TREN)CsHMDS] were significantly different from that of the by-products above, likely indicating the incorporation of metal halide salts. Full details can be found in the Supporting Information (Figures S22-26).

Co-complexes **1-5** are poorly soluble in C₆D₆ and *d*₈-toluene solvents at ambient temperature whilst co-complexes **6-8** display good solubility in C₆D₆ at ambient temperature. Therefore, ¹H and ¹³C NMR spectroscopic experiments utilizing more polar *d*₈-THF solutions were undertaken for **1-5**, presumably at the cost of altering the aggregation state found in the respective solid state structures and resulting in the preclusion of dynamic equilibrium. In an effort to study the solution state of **5** in a less polar and less coordinating *d*₈-toluene solvent, ¹H and ¹³C NMR spectroscopic studies of **5** were additionally studied at 363 K, the temperature at which a homogeneous solution was observed. The ¹H and ¹³C NMR spectra obtained of **1-8** in their respective solvents, were relatively simple, and the resonances were limited to two distinct regions corresponding to the Lewis base donor of choice and the HMDS ligand present in the corresponding complex.

¹H NMR spectra obtained for *d*₈-THF solutions of **1-3** are coincident and show resonances for uncoordinated Me₆TREN ligand. Altering the sodium halide (Cl, Br and I) salts has little effect on the ¹H and ¹³C chemical shifts of both Me₆TREN and HMDS ligands in **1-3**. Moreover, the observed chemical shifts for Me₆TREN and HMDS ligands in **1-3** in *d*₈-THF are similar to those found for a salt-free sample of Me₆TREN·NaHMDS³¹ in the same solvent for which a total

dissociation of Me₆TREN from the metal amide complex is also observed,³² presumably due to the high coordinating ability of the vast excess of *d*₈-THF, breaking the structure found in the solid state. The Me₆TREN/HMDS ratio found was approximately 1:5 as expected from the solid state structure of **1-3**.

Looking at the solvent-separated complexes **4** and **5**, ¹H and ¹³C NMR spectra in *d*₈-THF show the corresponding resonances for HMDS and Lewis base (PMDETA and TMDAE, respectively) ligands at the same chemical shifts as for "(*d*₈-THF)·NaHMDS" and non-coordinated PMDETA or TMDAE ligands for **4** and **5**, respectively (Table S3 and S4, Supporting Information). In addition, PMDETA/HMDS and TMDAE/HMDS ratios of approx. 1:3.5 and 1:2.5 are found for **4** and **5**, respectively, being in agreement with the proportions found in the solid state structures. In an attempt to study the unaltered structure for **5** in solution, ¹H and ¹³C NMR spectroscopic studies of **5** in *d*₈-toluene at 363 K were carried out as **5** is soluble in *d*₈-toluene at this temperature. Under these conditions, the chemical shifts for TMDAE and HMDS groups are coincident to those of an *in situ* prepared sample of TMDAE·NaHMDS in *d*₈-toluene at the same temperature (Table S4, Supporting Information), suggesting that the sodium halide present in the structure of **5**, which is silent by NMR spectroscopy, has a marginal effect on the chemical shifts of both NaHMDS and free TMDEA ligand when comparing with those of TMDAE·NaHMDS.

¹H and ¹³C NMR spectroscopic studies of **6-8** in C₆D₆ solutions reveal that the resonances for the bidentate Lewis base [*i.e.*, (*R,R*)-TMCDA and TMEDA] have been shifted upfield with respect to the free donor due to coordination to the electropositive sodium metal (Tables S5 and S8, Supporting Information). In contrast, a downfield shift in ¹H signals is observed for the HMDS groups in **6-8** (0.41, 0.36 and 0.35 ppm for **6**, **7** and **8**, respectively) when compared with C₆D₆ solutions of (*R,R*)-TMCDA·NaHMDS, [(TMEDA)(NaHMDS)₂]_∞³³ and NaHMDS (0.35, 0.19,

and -0.19 ppm, respectively). If the solution state chemistry for **6-8** mirrors that of the solid state, then two different resonances for the HMDS ligand should exist due to the different chemical environments present. Looking specifically at **7**, at 300 K for a d_8 -toluene solution of the complex, this is not the case – only one resonance at 0.28 ppm is observed. However, on cooling the solution significant resonance broadening is observed and the resonance drifts downfield (at 253 K, 0.37 ppm). At 233 K a shoulder (0.25 ppm) appears on the main resonance (0.44 ppm). At 223 K, two distinct resonances are observed (at 0.47 ppm and 0.27 ppm) in a $2:1$ integral ratio, which is consistent with the solid state structure of **7**. It was also noted that the solubility of **7** decreased markedly in d_8 -toluene at lower temperatures.

Previously, it was noted that **7** could be prepared and crystallized from a solution containing an excess of NaHMDS. It was decided to probe the solution structure (hence stability) of **7** in the presence of an excess of NaHMDS. One, two and three equivalents of NaHMDS were added to one equivalent of **7** in a C_6D_6 solution (Figure S18). On adding one equivalent of NaHMDS only one HMDS resonance was observed (0.29 ppm). This signal could not be attributed to free NaHMDS (or indeed a TMEDA solvate of NaHMDS – the previously reported diamine solvate (TMEDA)NaHMDS has a HMDS chemical shift of 0.19 ppm).³³ Instead one HMDS resonance which gradually drifted upfield from 0.36 ppm (when no additional NaHMDS is added) to 0.21 (when three additional equivalents of NaHMDS are added). Interestingly, the two resonances for TMEDA [at 2.01 (CH_3) and 1.81 (CH_2) ppm] remain consistent throughout the series of experiments and differ significantly from those in (TMEDA)NaHMDS [1.99 (CH_2) and 1.97 (CH_3) ppm]. These data therefore suggest that the additional NaHMDS is in fast dynamic exchange with the NaHMDS units within the open ring framework of **7**. This suggests that **7** does not incorporate further NaHMDS units to generate a metal anionic crown motif akin to **3-5**.

If this were to occur, it is likely that the TMEDA environment in such a species would differ significantly from that found in **7**. These data help to explain why **7** can be crystallized from a solution containing an excess of NaHMDS [*i.e.*, **7** is less soluble in arene solution than (TMEDA)NaHMDS].

Providing further evidence for these conclusions, one, two and three equivalents of TMEDA were added to one equivalent of **7** in a C₆D₆ solution (Figure S19). Here the HMDS resonance remains essentially constant throughout (0.37-0.39 ppm); however, the TMEDA resonances alter significantly ranging from 2.01 (CH₃) and 1.81 (CH₂) ppm for **7** to 2.08 (CH₃) and 2.14 (CH₂) for **7** with three additional equivalents of TMEDA. It can be envisaged that adding a large excess of TMEDA could deaggregate **7** as there are two formally unsolvated Na ions present. However, as the HMDS signal remains constant, it seems that the open ring framework is staying intact. The TMEDA ligands initially attached to the Na atoms in **7** appear to be in dynamic equilibrium with the excess TMEDA.

CONCLUSIONS

In summary, we report the synthesis of a family of chloro (**1**), bromo (**2**) and iodo (**3**) deficient sodium bis(trimethylsilyl)amide complexes by salt metathesis of an excess of NaHMDS with the corresponding halide Cs halide salt in the presence of the tetradentate Me₆TREN ligand. The halide is trapped within a pentameric cavity of NaHMDS whilst Me₆TREN formally η^4 -coordinates to the Na⁺ counterion enabling the formation of the corresponding contacted ion pair complexes with long agostic-type Na \cdots Me(HMDS) interactions. When a tridentate Lewis base is used, the solvent separated co-complexes **4** and **5** are obtained in which an iodide ion is trapped by formal ionization of NaI with NaHMDS in the presence of PMDETA and TMDAE,

respectively. On switching to bidentate ligands [(*R,R*)-TMCDA and TMEDA], novel open ring co-complexes **6-8** were obtained instead of Na₅N₅ closed ring species. In short, our X-ray diffraction studies provide useful structural insights into the aggregation state of NaHMDS with NaCl, NaBr and NaI in the presence of Lewis donor ligands of different nature and denticity.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under a protective dry argon atmosphere using standard Schlenk techniques. *n*-Hexane and toluene were distilled under reflux within a nitrogen atmosphere in the presence of sodium metal and benzophenone. In addition, toluene was stored under argon over activated molecular sieves (4 Å) prior to use. C₆D₆ and *d*₈-toluene were degassed and stored under argon over activated molecular sieves (4 Å) prior to use. *d*₈-THF was degassed, dry and stored under argon over a potassium mirror prior to use. *n*-BuNa was prepared according to literature methods and stored in a glove box.³⁴ 1,1,1,3,3,3-Hexamethyldisilazane [HMDS(H)], *N,N,N',N'*-tetramethylethylenediamine (TMEDA), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) and *N,N,N',N'*-tetramethyldiaminoethylether (TMDAE) were purchased from Aldrich, distilled under nitrogen atmosphere in the presence of CaH₂ and stored under argon over activated molecular sieves (4 Å). Tris{2-(dimethylamino)ethyl}amine] (Me₆TREN) and *N,N,N',N'*-(*R,R*)-tetramethylcyclohexane-1,2-diamine [(*R,R*)-TMCDA] were prepared according to literature methods,³⁵ and stored under argon over activated molecular sieves (4 Å). CsCl, CsBr and CsI were purchased from Aldrich and dried under vacuum at 150 °C for five days and stored in a glove box. NH₄Br, NaBr and NaI were purchased form Aldrich, dried under vacuum at 150 °C for two days and stored in a glove box. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.1, 100.6, and 52.5 for ¹H, ¹³C and ¹³³Cs NMR, respectively. ¹H

and $^{13}\text{C}\{\text{H}\}$ NMR chemical shifts are expressed in parts per million (ppm) and referenced to residual solvent peaks. ^{133}Cs NMR spectra were referenced against an external standard solution of CsF (1M in D₂O, δ = 0 ppm). Microanalysis was obtained for all compounds using a Perkin Elmer 2400 elemental analyzer; however, for **2-4** variable values were obtained due to the high reactivity of the sodium sodiate species.

Synthesis of $[\{\text{Na}(\mu\text{-HMDS})_5(\mu\text{s-Cl})\}\{\text{Na}(\text{Me}_6\text{TREN})\}]$ (1). *n*-Butylsodium (480 mg, 6 mmol) was suspended in *n*-hexane (20 mL) and 1,1,1,3,3-hexamethyldisilazane (1.26 mL, 6 mmol) was added via syringe to give a white suspension which was stirred for 3 h. CsCl (168 mg, 1 mmol) was added using a solid addition tube to give a light brown suspension which was stirred for 24 h. Me₆TREN (0.53 mL, 2 mmol) was then added via syringe and the reaction mixture was stirred for 24 h. Toluene (10 mL) was then added, the reaction mixture was heated with a heat-gun and the hot reaction mixture was then filtered to give an orange solution. The solvent was partially removed under vacuum (4 mL) and **1** was crystallized as colorless crystals suitable for an X-ray diffraction study allowing to cold down the hot solution in a Dewar containing hot water for 24 h. **1** was filtered, washed with *n*-hexane (10 mL) and dried under vacuum for 30 min. Yield: 470 mg, 0.39 mmol, 39%. ^1H NMR (400.1 MHz, *d*₈-THF, 300 K): δ –0.20 (br s, 90 H, Me₃Si), 2.16 (br s, 18 H, Me₆TREN), 2.31 (t, 6 H, $^3\text{J}_{\text{HH}} = 6.8$ Hz, CH₂, Me₆TREN), 2.55 (t, 6 H, $^3\text{J}_{\text{HH}} = 6.8$ Hz, CH₂, Me₆TREN). $^{13}\text{C}\{\text{H}\}$ NMR (100.6 MHz, *d*₈-THF, 300 K): δ 6.6 (Me₃Si), 46.0 (Me₆TREN), 53.9 (α -CH₂, Me₆TREN), 58.8 (β -CH₂, Me₆TREN). Anal. Calcd (Found) for C₄₂H₁₁₉ClN₉Na₆Si₁₀: C, 41.84 (42.40); H, 10.03 (10.23); N, 10.46% (10.87%).

Synthesis of $[\{\text{Na}(\mu\text{-HMDS})_5(\mu\text{s-Br})\}\{\text{Na}(\text{Me}_6\text{TREN})\}]$ (2). **Method A.** *n*-Butylsodium (480 mg, 6 mmol) was suspended in *n*-hexane (20 mL) and bis(trimethylsilyl)amine (1.26 mL, 6

mmol) was added via syringe to give a white suspension which was stirred for 3 h. CsBr (213 mg, 1 mmol) was added using a solid addition tube to give a pale orange suspension which was stirred for 24 h. Me₆TREN (0.53 mL, 2 mmol) was then added via syringe and the reaction mixture was stirred for 24 h. The solvent was removed under vacuum until dryness to give a light brown residue from which **2** was extracted with hot toluene (10 mL) to give a light yellow solution. The solvent was removed under vacuum until dryness and **2** was crystallized as colorless block crystals suitable for an X-ray diffraction study from a 1:1.6 mixture of toluene:*n*-hexane (6.5 mL) at -25 °C for 24 h. **2** was filtered, washed with *n*-hexane (10 mL) and dried under vacuum for 30 min. Yield: 490 mg, 0.39 mmol, 39%. **Method B.** *n*-Butyl sodium (480 mg, 6 mmol) was suspended in *n*-hexane (20 mL) and bis(trimethylsilyl)amine (1.05 mL, 5 mmol) was added via syringe to give a white suspension which was stirred for 3 h. NH₄Br (98 mg, 1 mmol) was then added using a solid addition tube to give a light orange suspension which was stirred for 24 h. Me₆TREN (0.53 mL, 2 mmol) was then added via syringe and the reaction mixture was stirred for 24 h. Then, toluene (10 mL) was added, heated with a heat-gun and the hot reaction mixture was filtered to give an orange solution. The solvent was removed under vacuum until dryness and **2** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 2:1 mixture of *n*-hexane:toluene (6 mL) at -25 °C for 24 h. **2** was filtered, washed with *n*-hexane (5 mL) and dried under vacuum for 30 min. **2** was filtered, washed with *n*-hexane (2 mL) and dried under vacuum for 30 min. Yield: 230 mg, 0.18 mmol, 18%. **Method C.** *n*-Butyl sodium (401 mg, 5 mmol) was suspended in *n*-hexane (20 mL) and bis(trimethylsilyl)amine (1.05 mL, 5 mmol) was added via syringe to give a white suspension which was stirred for 3 h. NaBr (103 mg, 1 mmol) was then added using a solid addition tube and the reaction mixture was stirred for 24 h. Me₆TREN (0.54 mL, 2 mmol) was then added to

give a light brown suspension which was stirred for 24 h. The solvent was removed under vacuum until dryness to give a pale brown residue from which **2** was extracted in hot toluene (10 mL) to give a pale yellow solution. The solvent was removed under vacuum until dryness and **2** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 1:1 mixture of *n*-hexane:toluene (4 mL) at -25 °C for 24 h. **2** was filtered, washed with *n*-hexane (2 mL) and dried under vacuum for 30 min. Yield: 130 mg, 0.10 mmol, 10%. NMR spectroscopy and X-ray diffraction studies of the crystalline sample isolated in methods A, B and C proved the compound to be **2**. ¹H NMR (400.1 MHz, *d*₈-THF, 300 K): δ -0.19 (br s, 90 H, Me₃Si), 2.18 (br s, 18 H, Me₆TREN), 2.32 (t, 6 H, ³J_{HH} = 6.6 Hz, CH₂, Me₆TREN), 2.55 (t, 6 H, ³J_{HH} = 6.8 Hz, CH₂, Me₆TREN). ¹³C{¹H} NMR (100.6 MHz, *d*₈-THF, 300 K): δ 6.6 (Me₃Si), 46.0 (Me₆TREN), 53.5 (α -CH₂, Me₆TREN), 58.6 (β -CH₂, Me₆TREN). Anal. Calcd (Found) for C₄₂H₁₁₉BrN₉Na₆Si₁₀: C, 40.35 (41.27); H, 9.67 (9.81); N, 10.08% (10.21%).

Synthesis of [{Na₅(μ -HMDS)₅(μ ₅-I)}{Na(Me₆TREN)}] (3). n-Butylsodium (480 mg, 6 mmol) was suspended in *n*-hexane (20 mL) and bis(trimethylsilyl)amine (1.26 mL, 6 mmol) was added via syringe to give a white suspension which was stirred for 3 h. CsI (260 mg, 1 mmol) was then added using a solid addition tube and the reaction mixture was stirred for 24 h. Me₆TREN (0.52 mL, 2 mmol) was then added via syringe to give a light brown suspension which was stirred for 60 h. The solvent was removed under vacuum to give a light brown residue from which **3** was extracted in hot toluene (10 mL) to give a light yellow solution. The solvent was removed under vacuum until dryness and **3** was crystallized as a colorless crystals suitable for an X-ray diffraction study from a 1:1.25 mixture of *n*-hexane:toluene (4.5 mL) at -25 °C for 24 h. Yield: 460 mg, 0.35 mmol, 35%. ¹H NMR (400.1 MHz, *d*₈-THF, 300 K): δ -0.19 (br s, 90 H, Me₃Si), 2.23 (br s, 18 H, Me₆TREN), 2.36 (br t, 6 H, ³J_{HH} = 6.0 Hz, CH₂, Me₆TREN), 2.52 (br t, 6 H,

$^3J_{HH} = 6.0$ Hz, CH₂, Me₆TREN). ¹³C{¹H} NMR (100.6 MHz, *d*₈-THF, 300 K): δ 6.6 (Me₃Si), 45.7 (Me₆TREN), 52.5 (α -CH₂, Me₆TREN), 58.0 (β -CH₂, Me₆TREN). Anal. Calcd (Found) for C₄₂H₁₁₉IN₉Na₆Si₁₀: C, 38.89 (39.47); H, 9.32 (9.57); N, 9.72% (9.95%).

Note that the NMR spectroscopic data for **1-3** are identical.

Synthesis of [Na₅(μ -HMDS)₅(μ ₅-I)][Na₃(μ -HMDS)₂(PMDETA)₂] (4). *n*-Butylsodium (560 mg, 7 mmol) suspended in *n*-hexane (20 mL) and bis(trimethylsilyl)amine (1.47 mL, 7 mmol) was added via syringe to give a white suspension which was stirred for 2 h. NaI (150 mg, 1 mmol) was then added using a solid addition tube and the reaction mixture was stirred for 24 h. PMDETA (0.42 mL, 2 mmol) was added via syringe and the resulting brown suspension was stirred for 15 h. The solvent was removed under vacuum until dryness to give a pale brown residue from which **4** was extracted in hot toluene (20 mL) to give a pale yellow solution. The solvent was removed under vacuum until dryness and **4** was crystallized as colorless crystals suitable for an X-ray diffraction study from *n*-hexane (2 mL) at -25 °C for 24 h. Yield: 630 mg, 0.35 mmol, 35%. ¹H NMR (400.1 MHz, *d*₈-THF, 300 K): δ -0.19 (s, 63 H, Me₃Si), 2.18 (s, 12 H, Me₂N, PMDETA), 2.22 (s, 3 H, MeN, PMDETA), 2.33 (t, 4 H, $^3J_{HH} = 6.4$ Hz, CH₂, PMDETA), 2.42 (t, 4 H, $^3J_{HH} = 6.4$ Hz, CH₂, PMDETA). ¹³C{¹H} NMR (100.6 MHz, *d*₈-THF, 300 K): δ 6.8 (Me₃Si), 43.5 (MeN, PMDETA), 46.2 (Me₂N, PMDETA), 57.0 (CH₂, PMDETA), 58.6 (CH₂, PMDETA). Anal. Calcd (Found) for C₆₀H₁₇₂IN₁₃Na₈Si₁₄: C, 40.48 (41.04); H, 9.74 (9.67); N, 10.23% (11.01%).

Synthesis of [Na₅(μ -HMDS)₅(μ ₅-I)][Na(TMDAE)₂] (5). *n*-Butylsodium (401 mg, 5 mmol) was suspended in *n*-hexane (20 mL) and bis(trimethylsilyl)amine (1.05 mL, 5 mmol) was added via syringe to give a white suspension which was stirred for 2 h. NaI (150 mg, 1 mmol) was then

added using a solid addition tube and the reaction mixture was stirred for 24 h. TMDAE (0.38 mL, 2 mmol) was then added via syringe and the reaction mixture was stirred for 15 h. The solvent removed under vacuum until dryness and the white residue from which **5** was extracted with hot toluene (30 mL) to give a pale yellow solution. The solvent was removed under vacuum until dryness and **5** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 2:1 mixture of *n*-hexane:toluene (3 mL) at -25 °C for 24 h. Yield: 480 mg, 0.36 mmol, 36%. ¹H NMR (400.1 MHz, *d*₈-THF, 300 K): δ -0.19 (br s, 45 H, Me₃Si), 2.20 (s, 12 H, Me TMDAE), 2.42 (t, 4 H, ³J_{HH} = 6.0 Hz, NCH₂, TMDAE), 3.49 (t, 4 H, ³J_{HH} = 6.0 Hz, OCH₂, TMDAE). ¹H NMR (400.1 MHz, *d*₈-toluene, 363 K): δ 0.16 (s, 45 H, Me₃Si), 1.99 (s, 12 H, Me-TMDAE), 2.01 (t, 4 H, ³J_{HH} = 5.2 Hz, NCH₂, TMDAE), 2.92 (t, 4 H, ³J_{HH} = 5.2 Hz, OCH₂, TMDAE). ¹³C{¹H} NMR (100.6 MHz, *d*₈-THF, 300 K): δ 6.7 (Me₃Si), 46.1 (Me TMDAE), 59.8 (NCH₂, TMDAE), 68.8 (OCH₂, TMDAE). ¹³C{¹H} NMR (100.6 MHz, *d*₈-toluene, 363 K): δ 7.0 (Me₃Si), 45.0 (Me, TMDAE), 58.8 (NCH₂), 67.0 (OCH₂). Anal. Calcd (Found) for C₄₆H₁₃₀IN₉Na₆O₂Si₁₀: C, 39.83 (40.27); H, 9.45 (9.45); N, 9.02% (9.37%).

Synthesis of [Na₄(μ-HMDS)₃(μ₄-I){(R,R)-TMCDA})₂] (6). *n*-Butyllsodium (240 mg, 3 mmol) was suspended in *n*-hexane (20 mL) and bis(trimethylsilyl)amine (0.63 mL, 3 mmol) was added via syringe to give a white suspension which was stirred for 2 h. NaI (150, 1 mmol) was added through via addition tube and the reaction mixture was stirred for 24 h. (R,R)-TMCDA (0.39 mL, 2 mmol) was then added via syringe and the reaction mixture was stirred for 15 h to give a yellow suspension. The solvent was removed under vacuum until dryness to give a yellow residue from which **6** was extracted in hot toluene (30 mL) to give a yellow solution. The solvent was removed under vacuum and **6** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 3:5 mixture of *n*-hexane:toluene (8 mL) at -25 °C for 24 h. Colorless

crystals grew after 24 hours. **6** was filtered, washed with *n*-hexane (5 mL) and dried under vacuum for 30 min Yield: 330 mg, 0.32 mmol, 32%). ^1H NMR (400.1 MHz, C_6D_6 , 300 K): δ 0.41 (s, 27 H, Me_3Si), 0.69 [br s, 4 H, CH_2 , (*R,R*)-TMCDA], 1.42 [br s, 4 H, CH_2 , (*R,R*)-TMCDA], 2.00 [br s, 2 H, CH , (*R,R*)-TMCDA], 2.12 [br s, 12 H, Me, (*R,R*)-TMCDA]. $^{13}\text{C}\{\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 300 K): δ 7.5 (Me_3Si), 21.5 [CH_2 , (*R,R*)-TMCDA], 25.3 [CH_2 , (*R,R*)-TMCDA], 41.0 [v br s, CH , (*R,R*)-TMCDA], 63.7 [Me, (*R,R*)-TMCDA]. Anal. Calcd (Found) for $\text{C}_{38}\text{H}_{98}\text{IN}_7\text{Na}_4\text{Si}_6$: C, 43.86 (43.45); H, 9.49 (9.03); N, 9.42% (9.31%).

Synthesis of $[\text{Na}_4(\mu\text{-HMDS})_3(\mu\text{-I})(\text{TMEDA})_2]$ (7). *n*-Butylsodium (240 mg, 3 mmol) was suspended in *n*-hexane (20 mL) and bis(trimethylsilyl)amine (0.63 mL, 3 mmol) was added via syringe to give a white suspension which was stirred for 2 h. NaI (150 mg, 1 mmol) was added via addition tube and the reaction mixture was stirred for 24 h. TMEDA (0.3 mL, 2 mmol) was added via syringe to give a dark yellow suspension which was stirred for 15 h. The solvent was partially removed under vacuum (15 mL) and toluene (30 mL) was added. The reaction was heated with a heat-gun and the hot reaction mixture was filtered to give a yellow solution. The solvent was removed under vacuum until dryness and **7** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 3:5 mixture of *n*-hexane:toluene (8 mL) at -25°C for 24 h. **7** was filtered, washed with *n*-hexane (5 mL) and dried under vacuum for 30 min. Yield: 410 mg, 0.44 mmol, 44%. ^1H NMR (400.1 MHz, C_6D_6 , 300 K): δ 0.36 (s, 27 H, Me_3Si), 1.81 (s, 4 H, CH_2 , TMEDA), 2.01 (s, 12 H, Me, TMEDA). ^1H NMR (400.1 MHz, d_8 -toluene, 300 K): δ 0.28 (s, 27 H, Me_3Si), 1.85 (s, 4 H, CH_2 , TMEDA), 2.03 (s, 12 H, Me, TMEDA). ^1H NMR (400.1 MHz, d_8 -toluene, 253 K): δ 0.37 (s, 27 H, Me_3Si), 1.73 (s, 4 H, CH_2 , TMEDA), 1.98 (s, 12 H, Me, TMEDA). ^1H NMR (400.1 MHz, d_8 -toluene, 233 K): δ 0.25 (bs, 9 H, Me_3Si), 0.44 (bs, 18 H, Me_3Si), 1.68 (s, 4 H, CH_2 , TMEDA), 1.96 (s, 12 H, Me, TMEDA). ^1H NMR

(400.1 MHz, d_8 -toluene, 223 K): δ 0.27 (bs, 9 H, Me₃Si), 0.47 (bs, 18 H, Me₃Si), 1.63 (s, 4 H, CH₂, TMEDA), 1.96 (s, 12 H, Me, TMEDA). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 300 K): δ 7.2 (Me₃Si), 46.4 (Me, TMEDA), 57.2 (CH₂, TMEDA). Anal. Calcd (Found) for C₃₀H₈₆IN₇Na₄Si₆: C, 38.64 (38.71); H, 9.30 (9.04); N, 10.52 % (11.23 %).

Synthesis of [Na₄(μ -HMDS)₃(μ ₄-Br)(TMEDA)₂] (8). TMEDA (0.30 mL, 2 mmol) was added via a syringe to a suspension of NaBr (150 mg, 1 mmol) in *n*-hexane (10 mL) and the reaction mixture was stirred for 24 h. NaHMDS prepared *in situ* [*n*-butylsodium (240 mg, 3 mmol) in *n*-hexane (10 mL) and bis(trimethylsilyl)amine (0.63 mL, 3 mmol)] was added via cannula to the NaBr/TMEDA reaction mixture to give a white suspension which was stirred for 5 days. The solvent was removed under vacuum until dryness and toluene (30 mL) was added. The reaction was heated with a heat-gun and the hot reaction mixture was filtered to give a yellow solution. The solvent was partially removed under vacuum (4 mL) and the solution was placed at -33 °C (24 h) to yield **8** as colorless crystals suitable for an X-ray diffraction study. **8** was filtered, washed with cool *n*-hexane (10 mL) and dried under vacuum for 30 min. Yield: 470 mg, 0.55 mmol, 55%. ¹H NMR (400.1 MHz, C₆D₆, 300 K): δ 0.35 (s, 27 H, Me₃Si), 1.84 (s, 4 H, CH₂, TMEDA), 2.00 (s, 12 H, Me, TMEDA). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 300 K): δ 7.2 (Me₃Si), 46.2 (Me, TMEDA), 57.2 (CH₂, TMEDA). Anal. Calcd (Found) for C₃₀H₈₆BrN₇Na₄Si₆: C, 40.70 (40.71); H, 9.79 (9.65); N, 11.07% (10.99 %).

Crystallographic Analysis. Crystallographic data were recorded at 123(2) K on Oxford Diffraction Xcalibur and Gemini Diffractometers with Mo-K α (λ = 0.71073 Å, for **1-5**) and Cu-K α (λ = 1.5418 Å, for **6-8**) radiation, respectively. Structures were refined to convergence on F² and against all independent reflections by full-matrix least-squares using SHELXL-2013

programs.³⁶ The iodine atom in **4**, two TMEDAE ligands in **5**, one TMEDA ligand in **7** were modeled as disordered over two sites. The geometries of the disordered groups were restrained to approximate typical values. SQUEEZE routine of PLATON³⁷ was used in the structure of **5** to remove the effects of disordered solvent molecules. Approximately the equivalent of 272 and electrons were removed from approx. 2210 Å³ of "void" cell space. This approximated to five to six molecules of *n*-hexane per unit cell. Selected crystallographic parameters are given in Tables S1 and S2 and full details are given in the deposited cif files (CCDC 1411192-1411198 for **1**, **2** and **4-8** respectively). These data in cif format can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

Supporting Information. Crystallographic data for complexes **1**, **2**, and **4-8**, in cif format, and copy of ¹H, ¹³C NMR and spectra for complexes **1-8**, ¹³³Cs NMR spectroscopic data for [(Me₆TREN)Cs(HMDS)]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes. The authors declare no competing financial interest.

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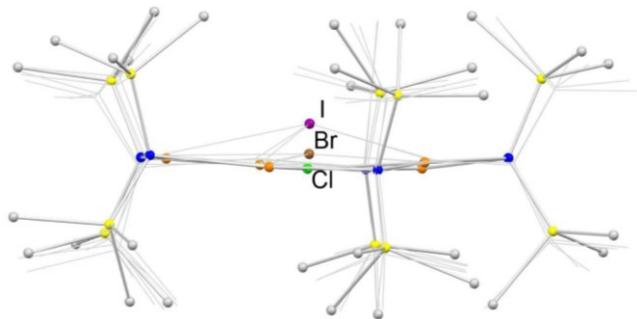
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Synopsis

When the important utility amide sodium bis(trimethylsilyl)amide (NaHMDS) is combined with hydrocarbon-soluble molecular forms of sodium halide salts a complex structural chemistry is observed. By utilizing several different multidentate donor molecules, it is possible to isolate a series of compounds which have structural motifs previously not observed in sodium chemistry.