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After isolating an unusual binuclear, but monosolvated NaHMDS complex  $[(R,R)\text{-TMCDA}\cdot(\text{NaHMDS})_2]_\infty$  which polymerises via intermolecular electrostatic  $\text{Na}\cdots\text{Me}_{\text{HMDS}}$  interactions, further  $(R,R)\text{-TMCDA}$  was added to produce the discrete binuclear amide  $[(\kappa^2\text{-}(R,R)\text{-TMCDA}\cdot(\text{NaHMDS})_2\{\kappa^1\text{-}(R,R)\text{-TMCDA}\}]$ , whose salient feature is the unique monodentate coordination of one of the chiral diamine ligands.

Chiral diamine ligands, for example (–)-sparteine, its (+)-sparteine surrogate and  $N,N,N',N'$ - $(1R,2R)$ -tetramethylcyclohexane-1,2-diamine [ $(R,R)\text{-TMCDA}$ ] have attracted considerable attention in asymmetric synthesis in a whole host of transition metal catalysed methodologies.<sup>1</sup> From an s-block perspective, when paired with an organolithium reagent it can be envisaged that 'chiral carbanions' are created, which can be used in subsequent enantioselective syntheses.<sup>2</sup> Focusing particularly on the  $C_2$ -symmetric ligand  $(R,R)\text{-TMCDA}$ , it has come to prominence recently as the availability of the historically more widely utilised diamine (–)-sparteine, has been unreliable over the past few years.<sup>3</sup> In terms of its coordination chemistry,  $(R,R)\text{-TMCDA}$  has worldwide interest and has been well studied. Over 50 metal complexes containing its ligated form have been reported, spanning both the s- (Li,<sup>4</sup> Na,<sup>4e</sup> K,<sup>4e</sup> and Mg,<sup>5</sup>) and d-block metals (Cu,<sup>6</sup> Zn,<sup>7</sup> Ru,<sup>8</sup> Pd,<sup>9</sup> Pt<sup>10</sup> and Hg<sup>11</sup>). Within s-block chemistry and germane to this work, Strohmann has comprehensively studied  $(R,R)\text{-TMCDA}$  complexes of synthetically important organolithium reagents (such as <sup>1</sup>BuLi,<sup>4a</sup> MeLi,<sup>4b</sup> <sup>1</sup>PrLi,<sup>4b</sup> <sup>1</sup>BuLi,<sup>4b</sup> <sup>11</sup>BuLi,<sup>4c</sup> BH<sub>3</sub>P(Me)CH<sub>2</sub>Li,<sup>4d</sup> MeLi,<sup>4g</sup> PhLi,<sup>4h</sup> (allyl)Li<sup>4h</sup> and (benzyl)Li<sup>4i</sup> derivatives). An all-encompassing feature of all known structures is that the chiral diamine ligand adopts exclusively a  $\kappa^2$ -bidentate chelating mode. Due to the less flexible, fixed bite angle in  $(R,R)\text{-TMCDA}$ , with respect to that of  $N,N,N',N'$ -tetramethylethylenediamine (TMEDA),<sup>12</sup> it is a stronger chelating ligand than the latter,<sup>13</sup> with a recent study noting that it 'displays

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, UK. E-mail: charlie.ohara@strath.ac.uk

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no tendency to bind as a monodentate ligand.<sup>14</sup> This has been attributed to the  $\kappa^1$  (or by implication  $\eta^1$ ) form of  $(R,R)\text{-TMCDA}$  inducing severe steric strain due to the juxtaposition of the metal-NMe<sub>2</sub> with the uncoordinated NMe<sub>2</sub> group. The structural chemistry of alkali metal amide complexes continues to be an important topic of research.<sup>15</sup> We have recently discovered that lithium and sodium 1,1,1,3,3-hexamethyldisilazide (LiHMDS and NaHMDS) can capture alkali metal halide salts in the presence of donor ligands to form ion pair metal anionic crown (MAC) complexes, for example  $[\text{Li}\{(R,R)\text{-TMCDA}\}_2]^+[\text{Li}_5\text{HMDS}_5\text{Cl}]^-$ .<sup>4f,16</sup> A key starting material which remained hitherto elusive in our studies involving sodium is the  $(R,R)\text{-TMCDA}$ -solvated NaHMDS complex. Crystallisation of other donor ligated [e.g., Me<sub>6</sub>TREN<sup>17</sup> and (–)-sparteine<sup>18</sup>] NaHMDS complexes has proven difficult, although the polymeric TMEDA  $[(\mu\text{-TMEDA})\cdot(\text{NaHMDS})_2]_\infty$ <sup>19</sup> and  $N,N,N',N'$ -tetramethylpropanediamine (TMPDA)  $[(\mu\text{-TMPDA})\cdot(\text{NaHMDS})_2]_\infty$ <sup>20</sup> complexes, which propagate via the non-chelating diamine ligand, are known (Fig. 1). These have similar structural motifs to Williard's lithium diisopropylamide (LDA) complex  $[(\mu\text{-TMEDA})\cdot(\text{LDA})_2]_\infty$ .<sup>19</sup>

In an effort to prepare the  $(R,R)\text{-TMCDA}$  complex of NaHMDS, an equimolar mixture of NaHMDS and  $(R,R)\text{-TMCDA}$  was combined in *n*-hexane medium and left to stir at ambient temperature for 1 hour (Scheme 1). The reaction mixture was then cooled to  $-33\text{ }^\circ\text{C}$  and crystals suitable for X-ray crystallographic analysis deposited after 48 hours (27% non-optimised, crystalline yield; maximum yield 50% based on  $(R,R)\text{-TMCDA}$  consumption). X-ray data reveal the mono- $(R,R)\text{-TMCDA}$ , binuclear  $[(R,R)\text{-TMCDA}\cdot(\text{NaHMDS})_2]_\infty$  **1** (Fig. 2a). There are six crystallographically distinct but essentially chemically

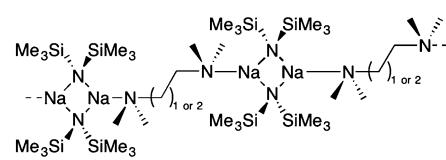
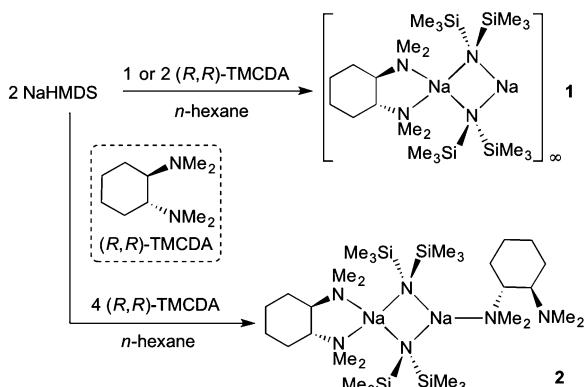


Fig. 1 Structures of previously known polymeric  $[(\mu\text{-TMEDA})\cdot(\text{NaHMDS})_2]_\infty$  and  $[(\mu\text{-TMPDA})\cdot(\text{NaHMDS})_2]_\infty$ .





Scheme 1 Syntheses of  $[(R,R)\text{-TMCDA}]\cdot(\text{NaHMDS})_2\infty$  **1** and  $[\kappa^2\text{-(}R,R\text{)-TMCDA}]\cdot(\text{NaHMDS})_2\{\kappa^1\text{-(}R,R\text{)-TMCDA}\}$  **2**.

equivalent molecules of  $[(R,R)\text{-TMCDA}]\cdot(\text{NaHMDS})_2$  in the structure of **1**, thus for brevity only one is discussed here. Interestingly, the empirical formula of **1**, *i.e.*,  $[(\text{donor})\cdot(\text{NaHMDS})_2]$  is identical to that for the aforementioned TMEDA and TMPDA derivatives; however, in keeping with previously known  $(R,R)\text{-TMCDA}$  complexes, the diamine adopts a chelating bonding mode, and with respect to the N donor atoms, renders one Na metal centre (Na1) four-coordinate in a distorted tetrahedral arrangement (bond angles range from  $68.70(9)$  to  $151.55(10)^\circ$ , see ESI† for full details). Additionally, Na1 has two long  $\text{Na}\cdots\text{Me}$  interactions with a methyl group from each HMDS ligand [ $\text{Na1}\cdots\text{C12}$  2.987(4) and  $\text{Na1}\cdots\text{C22}$  2.987(4) Å]. The second Na metal centre (Na2) remains only two-coordinate with respect to the bridging amido N atoms. To satisfy this electron deficiency, Na2

engages a solitary intermolecular  $\text{Na}\cdots\text{Me}(\text{SiMe}_2)$  [ $\text{Na2}\cdots\text{C65}$  distance, 2.818(4) Å] electrostatic interaction (Fig. 2b), which is short in comparison to known literature examples [range  $\text{Na}\cdots\text{Me}(\text{SiMe}_2)$  2.947–3.138 Å].<sup>21</sup> This sole intermolecular  $\text{Na}\cdots\text{Me}$  interaction induces propagation of binuclear units in a zigzag polymer chain. This change in the coordination chemistry of  $(R,R)\text{-TMCDA}$  in **1** with respect to the bridging TMEDA and TMPDA ligands in the aforementioned polymeric sodium amides emphasises the propensity for the chiral 1,2-diamine to remain as a chelating ligand rather than binding in a monodentate fashion. As a consequence of this coordination mismatch, significantly shorter  $\text{Na2-N}_{\text{HMDS}}$  bonds (mean distance, 2.356 Å) are observed when compared with  $\text{Na1-N}_{\text{HMDS}}$  bonds (mean distance, 2.530 Å). Despite utilising a 1:1 ratio of NaHMDS:(*R,R*)-TMCDA in this synthesis, it is clearly evident that the ultimate ratio in **1** is 2:1. When this optimised ratio is used in the synthesis, **1** was again the sole product isolated (36% crystalline yield).

Complex **1** is a rare example of a solvated sodium amide which contains an unsolvated Na site. Bochmann revealed the mono(tetrahydrofuran), mono(THF), complex  $[(\text{THF})\cdot(\text{NaHMDS})_2]$  where one Na atom is two coordinate whilst the other binds to the ether to render it three coordinate.<sup>22</sup> Interestingly, seven years prior to this report Dehnicke published the bis(THF) analogue  $[(\text{THF})_2\cdot(\text{NaHMDS})_2]$  where both Na atoms are three coordinate.<sup>23</sup> This begged the question: ‘could the coordinatively unsaturated (Lewis acidic) Na atom in **1**, act as a host for another Lewis base?’

A logical route to address this question would be to utilise monodentate donors such as THF and diethylether, in an attempt to saturate the deficient metal centre; but, it is highly likely that these strong  $\sigma$ -donors would also displace the chelating  $(R,R)\text{-TMCDA}$  ligand. Therefore to maintain synthetic simplicity, we repeated the preparation of **1** but employing an excess (two molar equivalents) of  $(R,R)\text{-TMCDA}$  with respect to NaHMDS in an attempt to coordinate a second molecule of the Lewis base ligand to the donor-free metal centre. High quality crystals (39% crystalline yield) were obtained by storing the resultant solution at  $-33^\circ\text{C}$  for 24 h, which were analysed by X-ray crystallography and were pleasingly found to be the target bis(solvated) derivative  $[\kappa^2\text{-(}R,R\text{)-TMCDA}]\cdot(\text{NaHMDS})_2\{\kappa^1\text{-(}R,R\text{)-TMCDA}\}$  **2** (Fig. 3). The distorted tetrahedral coordination sphere of Na1 in **2** (bond angles around Na1 range from  $66.90(6)$  to  $151.05(8)$ , see ESI†) is essentially identical to that found in **1**, exhibiting additional long contacts with a methyl group from each HMDS amido ligand [ $\text{Na1}\cdots\text{C27}$  2.968(3) and  $\text{Na1}\cdots\text{C24}$  2.976(3) Å]. However, the second sodium metal centre, Na2, is additionally coordinated to an extra molecule of  $(R,R)\text{-TMCDA}$ , giving rise to a distorted trigonal planar geometry. As such there are two distinct coordinated diamine ligands within the structure of **2**. Undoubtedly, the most eye-catching feature is that one  $(R,R)\text{-TMCDA}$  ligand adopts a previously unseen  $\kappa^1$ -coordination mode. To change from a  $\kappa^2$ - to a  $\kappa^1$ -coordination mode, it appears that inversion of the N1 atom of the  $(R,R)\text{-TMCDA}$  has occurred, no longer allowing the ligand to chelate to Na2 (Fig. 3).

Complex **2** is a discrete dimeric entity, despite the potential availability for N2 to coordinate further. In theory, this could be

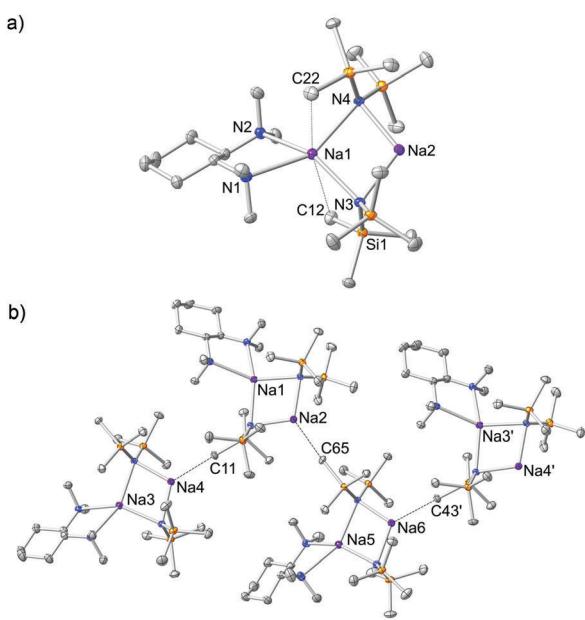


Fig. 2 (a) Molecular structure of  $[(R,R)\text{-TMCDA}]\cdot(\text{NaHMDS})_2\infty$  **1** showing one molecule from the asymmetric unit. Hydrogen atoms omitted for simplicity and thermal ellipsoids are displayed at 35% probability. (b) Section of the zigzag polymeric chain of **1**. The dashed lines illustrate  $\text{Na}\cdots\text{Me}(\text{SiMe}_2)$  interactions. The symmetry operation used to generate the atoms labelled with ' is  $-x + 1, y + 1/2, -z + 1$ .

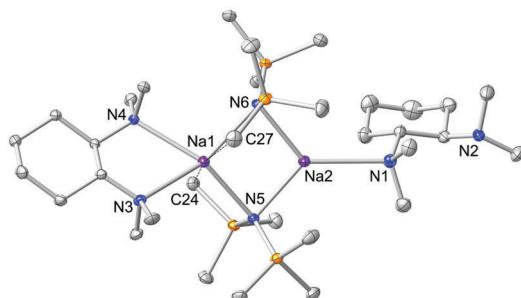


Fig. 3 Molecular structure of  $[\kappa^2\text{-(}R,R\text{)-TMCDA}\cdot(\text{NaHMDS})_2\cdot\kappa^1\text{-(}R,R\text{)-TMCDA}]$  **2**. Hydrogen atoms and one disordered component of the mono-dentate  $(R,R)$ -TMCDA ligand are omitted for simplicity. Thermal ellipsoids are displayed at 35% probability.

achieved if this N atom could also invert thus allowing an additional *exo*-coordination site; however, it is unlikely that this would occur due to high steric strain (buttressing).<sup>14</sup> The  $\kappa^1$ -coordinated  $(R,R)$ -TMCDA is disordered over two domains, but its atomic connectivity and geometry are unequivocal. The  $\kappa^2$ - and the hitherto unseen  $\kappa^1$ -coordination mode  $(R,R)$ -TMCDA observed in **2** can be compared with DFT calculations (at the B3P86/6-311+G\* level) performed for its diamine relative  $(-)$ -sparteine (Fig. 4).<sup>24</sup> It has been shown that when  $(-)$ -sparteine binds to a metal complex, it always adopts a chelating '*cis*' configuration. However, in the absence of a metal complex, it is actually slightly more stable (by 3.4 kcal mol<sup>-1</sup>) in a ring-flipped '*trans*' configuration [akin to our  $\kappa^1$ -coordinated  $(R,R)$ -TMCDA] where the lone pairs of electron present on the N atoms are not adjacent to each other. We have performed similar DFT studies (ESI†) on  $(R,R)$ -TMCDA and have shown that there is negligible difference (less than 1 kcal mol<sup>-1</sup>) between the potentially  $\kappa^1$ - and  $\kappa^2$ -coordination modes.

As **1** and **2** are both highly soluble in non-polar hydrocarbon and arene solutions, solutions of these compounds were studied by NMR spectroscopy. Using <sup>1</sup>H NMR spectroscopy, it was evident that the expected 1:2 and 2:2  $(R,R)$ -TMCDA:HMDS ratios were observed respectively. For **1**, a single amido resonance (at  $\delta$  0.25) was observed and the  $(R,R)$ -TMCDA resonances (at  $\delta$  2.01, 1.90, 1.47 and 0.74) in C<sub>6</sub>D<sub>6</sub> solution appeared to correspond to a metallo-coordinated ligand (see ESI† for full details). For **2**, the amido resonance appears at  $\delta$  0.31 in the same solvent. If the solid state structure of **2** was to be retained in solution, two unique sets of  $(R,R)$ -TMCDA resonances would be expected. In reality a single set of resonances (at  $\delta$  2.06, 1.99, 1.51 and 0.80 in C<sub>6</sub>D<sub>6</sub> solution) is observed. This indicates that a single  $(R,R)$ -TMCDA environment exists at 300 K in arene solution, indeed, a variable temperature

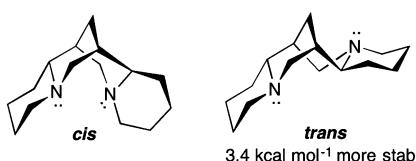


Fig. 4 Relative stabilities of *cis* and *trans* isomers of uncoordinated  $(-)$ -sparteine.<sup>24</sup>

NMR spectroscopic study of **2** in [D<sub>8</sub>]-toluene solution unveiled that this situation was maintained even at low temperature (down to 206 K, see ESI†). In addition, <sup>1</sup>H and <sup>13</sup>C NMR spectra obtained in non-polar [D<sub>12</sub>]-cyclohexane also reveal this situation (see ESI†). Therefore due to the steric bulk of the HMDS ligands within the molecule [thus precluding a dual  $\kappa^2$ -situation for the  $(R,R)$ -TMCDA ligands], it is likely that the spectra show a time-averaged situation between dynamic  $\kappa^1$ - and  $\kappa^2$ -coordinated  $(R,R)$ -TMCDA ligands.

In closing, we have shown that counter to previous studies,  $(R,R)$ -TMCDA can indeed bind to an alkali metal in a non-chelating  $\kappa^1$ -manner.

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