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Monodentate coordination of the normally chelating chiral diamine (*R,R*)-TMCDAT†

Ana I. Ojeda-Amador, Antonio J. Martínez-Martínez, Alan. R. Kennedy,
David R. Armstrong and Charles T. O'Hara*

After isolating an unusual binuclear, but monosolvated NaHMDs complex $[(R,R)\text{-TMCDAT}]\cdot(\text{NaHMDs})_2]_\infty$ which polymerises via intermolecular electrostatic $\text{Na}^+\cdots\text{Me}_{\text{HMDs}}$ interactions, further (*R,R*)-TMCDAT was added to produce the discrete binuclear amide $[(\kappa^2\text{-}(R,R)\text{-TMCDAT})\cdot(\text{NaHMDs})_2]\cdot[\kappa^1\text{-}(R,R)\text{-TMCDAT}]$, 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'*-(1*R*,2*R*)-tetramethylcyclohexane-1,2-diamine [(*R,R*)-TMCDAT] have attracted considerable attention in asymmetric synthesis in a whole host of transition metal catalysed methodologies.¹ 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.² Focusing particularly on the *C*₂-symmetric ligand (*R,R*)-TMCDAT, 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.³ In terms of its coordination chemistry, (*R,R*)-TMCDAT has worldwide interest and has been well studied. Over 50 metal complexes containing its ligated form have been reported, spanning both the s- (Li,⁴ Na,^{4e} K,^{4e} and Mg;⁵) and d-block metals (Cu,⁶ Zn,⁷ Ru,⁸ Pd,⁹ Pt¹⁰ and Hg¹¹). Within s-block chemistry and germane to this work, Strohmman has comprehensively studied (*R,R*)-TMCDAT complexes of synthetically important organolithium reagents (such as ^tBuLi,^{4a} MeLi,^{4b} ⁱPrLi,^{4b} ^sBuLi,^{4b} ⁿBuLi,^{4c} BH₃P(Ph)(Me)CH₂Li,^{4d} MeLi,^{4g} PhLi,^{4h} (allyl)Li^{4h} and (benzyl)Li⁴ⁱ derivatives). An all-encompassing feature of all known structures is that the chiral diamine ligand adopts exclusively a κ^2 -bidentate chelating mode. Due to the less flexible, fixed bite angle in (*R,R*)-TMCDAT, with respect to that of *N,N,N',N'*-tetramethylethylenediamine (TMEDA),¹² it is a stronger chelating ligand than the latter,¹³ with a recent study noting that it 'displays

no tendency to bind as a monodentate ligand.'¹⁴ This has been attributed to the κ^1 (or by implication η^1) form of (*R,R*)-TMCDAT inducing severe steric strain due to the juxtaposition of the metal-NMe₂ with the uncoordinated NMe₂ group. The structural chemistry of alkali metal amide complexes continues to be an important topic of research.¹⁵ We have recently discovered that lithium and sodium 1,1,1,3,3,3-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 $[\text{Li}\{(\text{R,R})\text{-TMCDAT}\}_2]^+[\text{Li}_5\text{HMDs}_5\text{Cl}]^-$.^{4f,16} A key starting material which remained hitherto elusive in our studies involving sodium is the (*R,R*)-TMCDAT-solvated NaHMDs complex. Crystallisation of other donor ligated [e.g., Me₆TREN¹⁷ and (–)-sparteine¹⁸] NaHMDs complexes has proven difficult, although the polymeric TMEDA $[(\mu\text{-TMEDA})\cdot(\text{NaHMDs})_2]_\infty$ ¹⁹ and *N,N,N',N'*-tetramethylpropanediamine (TMPDA) $[(\mu\text{-TMPDA})\cdot(\text{NaHMDs})_2]_\infty$ ²⁰ 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 $[(\mu\text{-TMEDA})\cdot(\text{LDA})_2]_\infty$.¹⁹

In an effort to prepare the (*R,R*)-TMCDAT complex of NaHMDs, an equimolar mixture of NaHMDs and (*R,R*)-TMCDAT 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 °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*)-TMCDAT consumption). X-ray data reveal the mono- (*R,R*)-TMCDAT, binuclear $[(\text{R,R})\text{-TMCDAT}\cdot(\text{NaHMDs})_2]_\infty$ **1** (Fig. 2a). There are six crystallographically distinct but essentially chemically

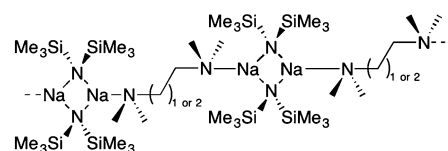
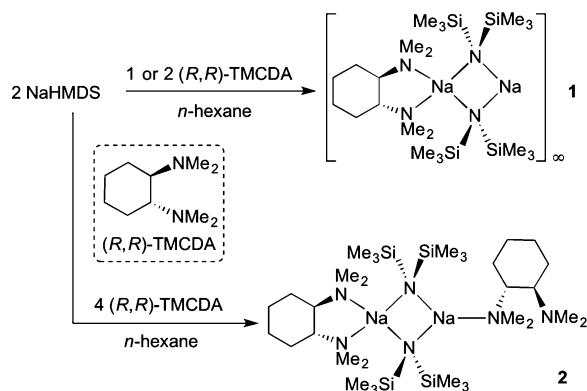


Fig. 1 Structures of previously known polymeric $[(\mu\text{-TMEDA})\cdot(\text{NaHMDs})_2]_\infty$ and $[(\mu\text{-TMPDA})\cdot(\text{NaHMDs})_2]_\infty$.

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

equivalent molecules of $\{[(R,R)\text{-TMCDAs}]_2(\text{NaHMDS})_2\}_\infty$ in the structure of **1**, thus for brevity only one is discussed here. Interestingly, the empirical formula of **1**, i.e., $[(\text{donor})\text{-}(\text{NaHMDS})_2]$ is identical to that for the aforementioned TMEDA and TMPDA derivatives; however, in keeping with previously known (R,R) -TMCDAs 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].²¹ 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) -TMCDAs 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 $\text{NaHMDS}:(R,R)\text{-TMCDAs}$ 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 $[(\text{THF})_2(\text{NaHMDS})_2]$ where one Na atom is two coordinate whilst the other binds to the ether to render it three coordinate.²² Interestingly, seven years prior to this report Dehnicke published the bis(THF) analogue $[(\text{THF})_2(\text{NaHMDS})_2]$ where both Na atoms are three coordinate.²³ 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 σ -donors would also displace the chelating (R,R) -TMCDAs ligand. Therefore to maintain synthetic simplicity, we repeated the preparation of **1** but employing an excess (two molar equivalents) of (R,R) -TMCDAs 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°C for 24 h, which were analysed by X-ray crystallography and were pleasingly found to be the target bis(solvated) derivative $\{[\kappa^2\text{-}(R,R)\text{-TMCDAs}]_2(\text{NaHMDS})_2\}[\kappa^1\text{-}(R,R)\text{-TMCDAs}]$ **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 $\text{Na}\cdots\text{C24}$ 2.976(3) Å]. However, the second sodium metal centre, Na2, is additionally coordinated to an extra molecule of (R,R) -TMCDAs, 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) -TMCDAs ligand adopts a previously unseen κ^1 -coordination mode. To change from a κ^2 - to a κ^1 -coordination mode, it appears that inversion of the N1 atom of the (R,R) -TMCDAs 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

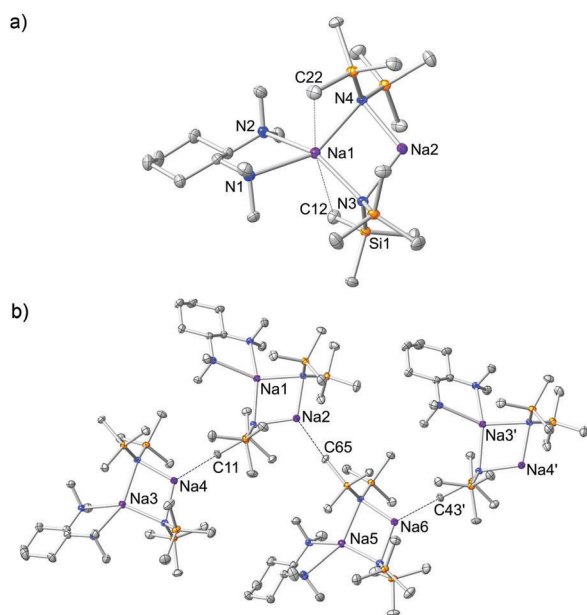


Fig. 2 (a) Molecular structure of $\{[(R,R)\text{-TMCDAs}]_2(\text{NaHMDS})_2\}_\infty$ **1** showing one molecule from the asymmetric unit. Hydrogen atoms omitted for simplicity and thermal ellipsoids are displayed at 35% probability. (b) Section of the zigzag polymeric chain of **1**. The dashed lines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



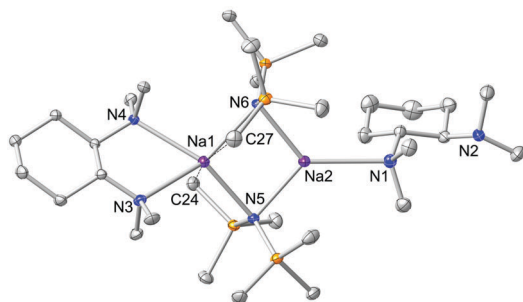


Fig. 3 Molecular structure of $[(\kappa^2-(R,R)\text{-TMCD})\cdot(\text{NaHMDs})_2(\kappa^1-(R,R)\text{-TMCD})]$ **2**. Hydrogen atoms and one disordered component of the mono-dentate (R,R) -TMCD ligand are omitted for simplicity. Thermal ellipsoids are displayed at 35% probability.

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 (butterflying).¹⁴ The κ^1 -coordinated (R,R) -TMCD is disordered over two domains, but its atomic connectivity and geometry are unequivocal. The κ^2 - and the hitherto unseen κ^1 -coordination mode (R,R) -TMCD observed in **2** can be compared with DFT calculations (at the B3P86/6-311+G* level) performed for its diamine relative (–)-sparteine (Fig. 4).²⁴ 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^{–1}) in a ring-flipped ‘*trans*’ configuration [akin to our κ^1 -coordinated (R,R) -TMCD] 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) -TMCD and have shown that there is negligible difference (less than 1 kcal mol^{–1}) between the potentially κ^1 - and κ^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 ¹H NMR spectroscopy, it was evident that the expected 1:2 and 2:2 (R,R) -TMCD:HMDs ratios were observed respectively. For **1**, a single amido resonance (at δ 0.25) was observed and the (R,R) -TMCD resonances (at δ 2.01, 1.90, 1.47 and 0.74) in C₆D₆ solution appeared to correspond to a metal-coordinated ligand (see ESI† for full details). For **2**, the amido resonance appears at δ 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) -TMCD resonances would be expected. In reality a single set of resonances (at δ 2.06, 1.99, 1.51 and 0.80 in C₆D₆ solution) is observed. This indicates that a single (R,R) -TMCD environment exists at 300 K in arene solution, indeed, a variable temperature

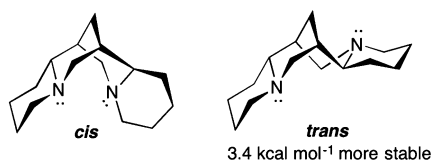


Fig. 4 Relative stabilities of *cis* and *trans* isomers of uncoordinated (–)-sparteine.²⁴

NMR spectroscopic study of **2** in [D₈]-toluene solution unveiled that this situation was maintained even at low temperature (down to 206 K, see ESI†). In addition, ¹H and ¹³C NMR spectra obtained in non-polar [D₁₂]-cyclohexane also reveal this situation (see ESI†). Therefore due to the steric bulk of the HMDs ligands within the molecule [thus precluding a dual κ^2 -situation for the (R,R) -TMCD ligands], it is likely that the spectra show a time-averaged situation between dynamic κ^1 - and κ^2 -coordinated (R,R) -TMCD ligands.

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

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