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


After isolating an unusual binuclear, but monosolvated NaHMDS complex [(R,R)-TMCDAD]2 NaHMDS], which polymerises via intermolecular electrostatic Na·MeHMDS interactions, further (R,R)-TMCDAD was added to produce the discrete binuclear amide [k2-(R,R)-TMCDAD].(NaHMDS)2{κ3-(R,R)-TMCDAD}], 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′′-tetramethylethylene-1,2-diamine ([R,R]-TMCDAD) have attracted considerable attention in asymmetric synthesis in a whole host of transition metal catalysed methodologies. 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. Focusing particularly on the C2-symmetric ligand (R,R)-TMCDAD, it has come to prominence recently as the availability of the historically more widely used diamine (−)-sparteine, has been unreliable over the past few years. In terms of its coordination chemistry, (R,R)-TMCDAD has worldwide interest and has been well studied. Over 50 metal complexes containing its monodentate coordination of the normally chelating chiral diamine (−)-sparteine, are known (Fig. 1). These have similar structural motifs to Williard’s lithium diisopropylamide (LDA) complex [μ-TMEDA]2{LDA}2.10

In an effort to prepare the (R,R)-TMCDAD complex of NaHMDS, an equimolar mixture of NaHMDS and (R,R)-TMCDAD 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)-TMCDAD consumption). X-ray data reveal the mono-(R,R)-TMCDAD, binuclear [(R,R)-TMCDAD](NaHMDS)2.11 (Fig. 2a). There are six crystallographically distinct but essentially chemically

 nak3bidentate chelating mode. Due to the less flexible, fixed bite angle in (R,R)-TMCDAD, with respect to that of N,N′N,N′-tetramethylethylenediamine (TMEDA), it is a stronger chelating ligand than the latter, with a recent study noting that it ‘displays no tendency to bind as a monodentate ligand.’ This has been attributed to the κ3′ or by implication κ1′ form of (R,R)-TMCDAD 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. 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 [Li[(R,R)-TMCDAD],][LiHMDS2Cl]−.4,16 A key starting material which remained hitherto elusive in our studies involving sodium is the (R,R)-TMCDAD–solvated NaHMDS complex. Crystallisation of other donor ligated [e.g., Me3TREN]7 and (−)-sparteine18] NaHMDS complexes has proven difficult, although the polymeric TMEDA [μ-TMEDA](NaHMDS)2.19 and N,N,N′,N′-tetramethylenediamine (TMEDA) [μ-TMPDA](NaHMDS)2.20 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 [μ-TMEDA](LDA)2.10

Fig. 1 Structures of previously known polymeric [μ-TMEDA](NaHMDS)2.19 and [μ-TMPDA](NaHMDS)2.20.
The empirical formula of the atoms labelled with $\text{Na}$, $\text{Me}$, and $\text{SiMe}_2$ interactions. The symmetry operation used to generate $\text{Na}$ and $\text{Me}$ interactions with a methyl group from each HMDS engagement with a solitary intermolecular Na$\cdot$Me$\cdot\text{SiMe}_2$ [Na2$\cdot$C65 distance, 2.818(4) Å] electrostatic interaction (Fig. 2b), which is short in comparison to known literature examples [range Na$\cdot$Me$\cdot\text{SiMe}_2$ 2.947–3.138 Å]. This sole intermolecular Na$\cdot$Me interaction induces propagation of binuclear units in a zigzag polymer chain. This change in the coordination chemistry of (R,R)-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 Na2–N$_{\text{HMDS}}$ bonds (mean distance, 2.356 Å) are observed when compared with 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 [(THF)$\cdot$(NaHMDS)$_2$] where one Na atom is two coordinate whilst the other binds to the ether to render it three coordinate. Interestingly, seven years prior to this report Dehnicke published the bis(THF) analogue [(THF)$_2$:(NaHMDS)$_2$] where both Na atoms are three coordinate. 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)-TMCDA ligand. Therefore to maintain synthetic simplicity, we repeated the preparation of 1 but employing an excess (two molar equivalents) of (R,R)-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 °C for 24 h, which were analysed by X-ray crystallography and were pleasingly found to be the target bis(solvated) derivative [(k$^2$-(R,R)-TMCDA)-(NaHMDS)$_2$](k$^1$-(R,R)-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 [Na1$\cdot$C27 2.968(3) and Na1$\cdot$C24 2.976(3) Å]. However, the second sodium metal centre, Na2, is additionally coordinated to an extra molecule of (R,R)-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)-TMCDA ligand adopts a previously unseen $k^1$-coodination mode. To change from a $k^2$- to a $k^1$-coodination mode, it appears that inversion of the N1 atom of the (R,R)-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
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). The $\kappa^1$-coordinated (RR)-TMCD is disordered over two domains, but its atomic connectivity and geometry are unequivocal. The $\kappa^2$- and the hitherto unseen $\kappa^3$-coordination mode (RR)-TMCD observed in 2 can be compared with DFT calculations (at the B3P86/6-311+G* level) performed for its dihedral relative (-)-sparteine (Fig. 4).

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 $\kappa^3$-coordinated (RR)-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 (RR)-TMCD and have shown that there is negligible difference (less than 1 kcal mol$^{-1}$) 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 $^1$H NMR spectroscopy, it was evident that the expected 1:2 and 2:2 (RR)-TMCDA:HMDS ratios were observed respectively. For 1, a single amido resonance (at $\delta$ 0.25) was observed and the (RR)-TMCDA resonances (at $\delta$ 2.01, 1.90, 1.47 and 0.74) in CD$_2$Cl$_2$ 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 (RR)-TMCDA resonances would be expected. In reality a single set of resonances (at $\delta$ 2.06, 1.99, 1.51 and 0.80 in CD$_2$Cl$_2$ solution) is observed. This indicates that a single (RR)-TMCDA environment exists at 300 K in arene solution, indeed, a variable temperature NMR spectroscopic study of 2 in [D$_8$]toluene solution unveiled that this situation was maintained even at low temperature (down to 206 K, see ESI†). In addition, $^1$H and $^{13}$C NMR spectra obtained in non-polar [D$_8$]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 (RR)-TMCDA ligands], it is likely that the spectra show a time-averaged situation between dynamic $\kappa^1$- and $\kappa^2$-coordinated (RR)-TMCDA ligands.

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

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Notes and references


