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

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

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

Chiral diamine ligands, for example \((-\text{sparteine})\), its \((+)-\text{sparteine}\) surrogate and \(N,N',N''\text{-}(1R,2R)\text{-tetr methylcyclohexane-1,2-diamine}\) \([\{(R,R)\text{-TMCDA}\}]\) 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 carbamions’ are created, which can be used in subsequent enantioselective syntheses. Focusing particularly on the \(C_2\text{-symmetric ligand } (R,R)\text{-TMCDA}\), it has come to prominence recently as the availability of the historically more widely utilised diamine \((-\text{sparteine})\), has been unreliable over the past few years. 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 \(s\)-\((\text{Li}, \text{Na}, \text{K}, \text{Mg})\) and \(d\)-block metals (\(\text{Cu}, \text{Zn}, \text{Ru}, \text{Pd}, \text{Pt}\) and \(\text{Hg}\)). 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 \(\text{BuLi}, \text{MeLi}, \text{PrLi}\), \(\text{BuLi}, \text{BuLi}, \text{BH}_3\text{P(Ph)Me}_2\text{Li}, \text{MeLi}, \text{PhLi}\) and (allyl)Li\(^+\) and (benzyl)Li\(^+\) 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 \(N,N',N''\text{-tetramethylhexamethylene}diamine\) (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 \(\kappa^1\) form of \((R,R)\text{-TMCDA}\) inducing severe steric strain due to the juxtaposition of the metal–NMe\(_2\) with the uncoordinated NMe\(_2\) 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 \(1,1,1,3,3,3\text{-hexamethyldisilazide} (\text{LiHMDS} \text{and NaHMDS})\) can capture alkali metal halide salts in the presence of donor ligands to form ion pair metal anionic crown (MAC) complexes, for example \([\text{Li}\{\{(R,R)\text{-TMCDA}\}\}^+\{\text{LiHMDS}_2\text{Cl}\}]^-\). 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 [\(e.g., \text{Me}_3\text{TREN}\) and \((-\text{sparteine})\)] NaHMDS complexes has proven difficult, although the polymeric TMEDA \([\{\mu\text{-TMEDA}\} (\text{NaHMDS})_2]\) and \(NN'NN''\text{-tetr am ethyl propanediamine} (\text{TMPDA}) [\{\mu\text{-TMPDA}\} (\text{NaHMDS})_2]\) 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 \([\{\mu\text{-TMEDA}\} (\text{LDA})_2]\).

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 \(-33^\circ\text{C}\) 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 \([\{\{(R,R)\text{-TMCDA}\}\} (\text{NaHMDS})_2]\) (Fig. 2a). There are six crystallographically distinct but essentially chemically

![Fig. 1 Structures of previously known polymeric \([\mu\text{-TMEDA}\] (NaHMDS)\)](c6cc07190b)
expected molecules of \([[(R,R)\text{-TMCDA}](\text{NaHMDS})_2]\) in the structure of 1, thus for brevity only one is discussed here. Interestingly, the empirical formula of 1, i.e., \([\text{donor}](\text{NaHMDS})_2\) 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), see ESI† for full details). Additionally, Na1 has two long Na···Me interactions with a methyl group from each HMDS ligand \([\text{Na}1\cdots\text{C12} 2.987(4) \text{ Å} \text{and Na}1\cdots\text{C22} 2.987(4) \text{ Å}]\). 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 Na····Me(SiMe₃) \([\text{Na}2\cdots\text{C65} \text{ distance, } 2.818(4) \text{ Å}]\) electrostatic interaction (Fig. 2b), which is short in comparison to known literature examples [range Na····Me(SiMe₃) 2.947–3.138 Å]. This sole intermolecular Na····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 Na2–N;HMDS bonds (mean distance, 2.356 Å) are observed when compared with Na1–N;HMDS bonds (mean distance, 2.530 Å). Despite utilising a 1:1 ratio of NaHMDS: \((R,R)\text{-TMCDA}\) 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 \([(\text{THF})(\text{NaHMDS})_2]\) 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 coordinately 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 \((R,R)\text{-TMCDA}\) 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 °C for 24 h, which were analysed by X-ray crystallography and were pleasingly found to be the target bis(solvated) derivative \([(\text{Na}1\cdots\text{Na}2\text{-}k^1\text{-}(R,R)\text{-TMCDA})]_2(\text{NaHMDS})_2(\text{Na}1\cdots\text{Na}2\text{-}k^1\text{-}(R,R)\text{-TMCDA})]\) (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 \([\text{Na}1\cdots\text{C27} 2.968(3) \text{ Å and Na}1\cdots\text{C24} 2.976(3) \text{ Å}]\). 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 k¹-coordination mode. To change from a k²- to a k¹-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
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 κ²-coordinated (R,R)-TMCDA is disordered over two domains, but its atomic connectivity and geometry are unequivocal. The κ²- and the hitherto unseen κ¹-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). 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 κ¹-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⁻¹) between the potentially κ¹- and κ²-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)-TMCDA:HMDS ratios were observed respectively. For 1, a single amido resonance (at δ 0.25) was observed and the (R,R)-TMCDAs resonances (at δ 2.01, 1.90, 1.47 and 0.74) in CD₆ solution corresponded to a metallo-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 sets of (R,R)-TMCDAs resonances would be expected. In reality a single set of resonances (at δ 2.06, 1.99, 1.51 and 0.80 in CD₆ solution) is observed. This indicates that a single (R,R)-TMCDA environment exists at 300 K in arene solution, indeed, a variable temperature NMR spectroscopic study of 2 in [D₆]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 [D₆]cyclohexane also reveal this situation (see ESI†). Therefore due to the steric bulk of the HMDS ligands within the molecule [thus precluding a dual κ²-situation for the (R,R)-TMCDA ligands], it is likely that the spectra show a time-averaged situation between dynamic κ¹- and κ²-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 κ¹-manner.

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Notes and references


