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

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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 $[(\mu\text{-TMPDA})\cdot(\text{NaHMDs})_2]_\infty$.

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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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Notes and references

- (a) K. Mikami and M. Yamanaka, *Chem. Rev.*, 2003, **103**, 3369; (b) R. Noyori, *Adv. Synth. Catal.*, 2003, **345**, 15; (c) V. Bette, A. Mortreux, F. Ferioli, G. Martelli, D. Savoia and J.-F. Carpentier, *Eur. J. Org. Chem.*, 2004, 3040.
- (a) D. Hoppe and T. Hense, *Angew. Chem., Int. Ed. Engl.*, 1997, 2282; (b) J. Clayden, *Organolithiums: Selectivity for Synthesis*, Pergamon, New York, 2002; (c) O. Chuzel and O. Riant, *Top. Organomet. Chem.*, 2005, **15**, 59; (d) C.-A. B. Ferber, H. B. Kagan, O. Lafon and P. Lesot, *Tetrahedron: Asymmetry*, 2008, **19**, 2666; (e) P. O'Brien, *Chem. Commun.*, 2008, 655; (f) Q. Perron, J. Praz and A. Alexakis, *Tetrahedron: Asymmetry*, 2009, **20**, 1004; (g) J. Praz, J. Graff, L. Egger, L. Guénée, S. Wagschal, E. P. Kündig and A. Alexakis, *Chem. Commun.*, 2015, **51**, 16912.
- J. D. Firth, P. O'Brien and L. Ferris, *Org. Biomol. Chem.*, 2014, **12**, 9357.
- (a) C. Strohmman and V. H. Gessner, *Angew. Chem., Int. Ed.*, 2007, **46**, 8281; (b) C. Strohmman and V. H. Gessner, *J. Am. Chem. Soc.*, 2007, **129**, 8952; (c) C. Strohmman and V. H. Gessner, *J. Am. Chem. Soc.*, 2008, **130**, 11719; (d) V. H. Gessner, S. Dilsky and C. Strohmman, *Chem. Commun.*, 2010, **46**, 4719; (e) P. García-Álvarez, A. R. Kennedy, C. T. O'Hara, K. Reilly and G. M. Robertson, *Dalton Trans.*, 2011, **40**, 5332; (f) A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, G. M. Robertson and S. D. Robertson, *Angew. Chem., Int. Ed.*, 2011, **50**, 8375; (g) K. Götz, V. H. Gessner, C. Unkelbach, M. Kaupp and C. Strohmman, *Z. Anorg. Allg. Chem.*, 2013, **639**, 2077; (h) P. K. Eckert, B. Schnura and C. Strohmman, *Chem. Commun.*, 2014, **46**, 4719; (i) S. G. Koller, U. Kroesen and C. Strohmman, *Chem. – Eur. J.*, 2015, **21**, 641.
- J. Francos, B. J. Fleming, P. García-Álvarez, A. R. Kennedy, K. Reilly, G. M. Robertson, S. D. Robertson and C. T. O'Hara, *Dalton Trans.*, 2014, **43**, 14424.
- (a) A. P. Cole, D. E. Root, P. Mukherjee, E. I. Solomon and T. D. P. Stack, *Science*, 1996, **273**, 1848; (b) E. C. Brown, J. T. York, W. E. Antholine, E. Ruiz, S. Álvarez and W. B. Tolman, *J. Am. Chem. Soc.*, 2005, **127**, 13752; (c) A. P. Cole, V. Mahadevan, L. Mirica, X. Ottenwaelder and T. D. P. Stack, *Inorg. Chem.*, 2005, **44**, 7345; (d) J. T. York, I. Bar-Nahum and W. B. Tolman, *Inorg. Chem.*, 2007, **46**, 8105; (e) J. E. Bercaw, G. S. Chen, J. A. Labinger and B.-L. Lin, *J. Am. Chem. Soc.*, 2008, **130**, 17654; (f) P. Verma, J. Weir, L. Mirica and T. D. P. Stack, *Inorg. Chem.*, 2011, **50**, 9816.
- (a) H. Y. Lee, J. U. Yoon and J. H. Jeong, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, **63**, m2471; (b) P. K. Eckert, I. d. S. Vieira, V. H. Gessner, J. Börner, C. Strohmman and S. Herres-Pawlis, *Polyhedron*, 2013, **49**, 151.
- W.-C. Cheng, W.-Y. Yu, J. Zhu, K.-K. Cheung, S.-M. Peng, C.-K. Poon and C.-M. Che, *Inorg. Chim. Acta*, 1996, **242**, 105.

- 9 (a) S. V. Pavlova, Y.-S. Wen and S. I. Chan, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2003, **59**, m792; (b) G. Lu and H. C. Malinakova, *J. Org. Chem.*, 2004, **69**, 4701; (c) N. Miklasova, E. Fischer-Fodor, R. Miklas, L. Kuckova, J. Kozisek, T. Liptaj, O. Soritau, J. Valentova and F. Devinsky, *Inorg. Chem. Commun.*, 2014, **46**, 229.
- 10 M. Benedetti, G. Tamasi, R. Cini and G. Natile, *Chem. – Eur. J.*, 2003, **9**, 6122.
- 11 P. K. Eckert, V. H. Gessner, M. Knorr and C. Strohmman, *Inorg. Chem.*, 2012, **51**, 8516.
- 12 (a) D. Barr, W. Clegg, R. E. Mulvey, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1987, 716; (b) M. Westerhausen, M. Wieneke, W. Ponikwar, H. Nöth and W. Schwarz, *Organometallics*, 1998, **17**, 1438; (c) M. A. Beswick, C. N. Hamer, P. R. Raithby, A. Steiner, M. Tombil and D. S. Wright, *J. Organomet. Chem.*, 1999, **573**, 267; (d) E. Hevia, D. J. Gallagher, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara and C. Talmard, *Chem. Commun.*, 2004, 2422; (e) M. M. Meinholz and D. Stalke, *Eur. J. Inorg. Chem.*, 2011, 4578.
- 13 (a) B. L. Lucht, M. P. Bernstein, J. F. Remenar and D. B. Collum, *J. Am. Chem. Soc.*, 1996, 10707; (b) J. F. Remenar, B. L. Lucht and D. B. Collum, *J. Am. Chem. Soc.*, 1997, **119**, 5567; (c) D. Hoffmann and D. B. Collum, *J. Am. Chem. Soc.*, 1998, **120**, 5810; (d) J. L. Rutherford, D. Hoffmann and D. B. Collum, *J. Am. Chem. Soc.*, 2002, **124**, 264.
- 14 T. S. De Vries, A. M. Bruneau, L. R. Liou, H. Subramanian and D. B. Collum, *J. Am. Chem. Soc.*, 2013, **135**, 4103.
- 15 (a) R. Michel, T. Nack, R. Neufeld, J. M. Dieterich, R. A. Mata and D. Stalke, *Angew. Chem., Int. Ed.*, 2013, **52**, 734; (b) R. E. Mulvey and S. D. Robertson, *Angew. Chem., Int. Ed.*, 2013, **52**, 11470–11487; (c) R. Neufeld, R. Michel, R. Herbst-Irmer, R. Schöne and D. Stalke, *Chem. – Eur. J.*, 2016, **22**, 12340–12346.
- 16 A. I. Ojeda-Amador, A. J. Martínez-Martínez, A. R. Kennedy and C. T. O'Hara, *Inorg. Chem.*, 2015, **54**, 9833.
- 17 D. M. Cousins, M. G. Davidson, C. J. Frankis, D. García-Vivo and M. F. Mahon, *Dalton Trans.*, 2010, **39**, 8278.
- 18 N. M. Clark, P. García-Álvarez, A. R. Kennedy, C. T. O'Hara and G. M. Robertson, *Chem. Commun.*, 2009, 5835.
- 19 M. P. Bernstein, F. E. Romesberg, D. J. Fuller, A. T. Harrison, D. B. Collum, Q. Y. Liu and P. G. Williard, *J. Am. Chem. Soc.*, 1992, **114**, 5100.
- 20 K. W. Henderson, A. E. Dorigo, Q. Y. Liu and P. G. Williard, *J. Am. Chem. Soc.*, 1997, **119**, 11855.
- 21 A recent CCDC search (C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2016, **72**, 171) reveals a selection of examples comprising Na⁺⋯Me(Si) interactions, for example see: F. Antolini, P. B. Hitchcock, M. F. Lappert and P. Merle, *Chem. Commun.*, 2000, 1301; O. Bénaud, J.-C. Berthet, P. Thuéry and M. Ephritikhine, *Inorg. Chem.*, 2010, **49**, 8117.
- 22 Y. Sarazin, S. J. Coles, D. L. Hughes, M. B. Hursthouse and M. Bochmann, *Eur. J. Inorg. Chem.*, 2006, 3211.
- 23 M. Karl, G. Seybert, W. Massa, K. Harms, S. Agarwal, R. Maleika, W. Stelter, A. Greiner, W. Heitz, B. Neümmüller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1301.
- 24 K. B. Wiberg and W. F. Bailey, *J. Mol. Struct.*, 2000, **556**, 239.