Exploring the solid state and solution structural chemistry of the utility amide potassium hexamethyldisilazide (KHMDS)†

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The structural chemistry of eleven donor complexes of the important Brønsted base potassium 1,1,1,3,3,3-hexamethyldisilazide (KHMDS) has been studied. Depending on the donor, each complex adopted one of five general structural motifs. Specifically, in this study the donors employed were toluene (to give polymeric 1 and dimeric 2), THF (polymeric 3), N,N,N’-tetramethylethyldiamine (TMEDA) (dimeric 4), (R,R)-N,N,N’-tetramethyl-1,2-diaminocyclohexane [(R,R)-TMCD] (dimeric 5), 12-crown-4 (dimeric 6), N,N,N,N’-tetramethyldiaminoethyl ether (TMDAE) (tetrannuclear dimeric 8 and monomeric 10), N,N,N’,N’-pentamethyldiethylenetriamine (PMDETA) (tetrannuclear dimeric 7), tris[2-dimethyl (amino)ethyl]amine (Me₂TREN) (tetrannuclear dimeric 9) and tris[2,2,6,6-tetramethylpiperidide (TMP)] (monomeric 11). The complexes were also studied in solution by 1H and 13C NMR spectroscopy as well as DOSY NMR spectroscopy.

Introduction

Alkali metal complexes of 1,1,1,3,3,3-hexamethyldisilazide (HMDS) are commonly employed reagents in synthesis due to their non-nucleophilic but Brønsted basic nature. In comparison with related alkali metal secondary amide reagents such as diisopropylamide (DA) and 2,2,6,6-tetramethylpiperidide (TMP) salts, HMDS is weakly basic due to its inherent α-silyl stabilisation. The pKₐ of LiHMDS in tetrahydrofuran (THF) solution is 24 whereas for LiDA and LiTMP are 35 and 36 respectively. Additionally, the absence of β-hydrogen atoms prevents β-hydride elimination, and their lipophilic character makes alkali metal derivatives of the HMDS group special candidates for many homogeneous reactions. Since lithium, sodium and potassium HMDS reagents are commercially available, they have become prominent transfer reagents for the synthesis of s-block metal, transition metal, lanthanide and actinide HMDS complexes via salt metathesis. In synthesis, they are used in a wide variety of chemical transformations ranging from drug synthesis to polymer production, such as in the formation of kinetic enolate anions, alkylation, arylation, isomerisation, polymerization, ring closing reactions and Wittig reactions, and also, in the deprotonative metallation of acidic C–H bonds, like cyclopentadiene, indene and fluorene. Most recently, several organic transformations have been reported which use alkali metal HMDS salt complexes in combination with a Lewis basic donor molecule to induce catalysis. In particular, KHMDs has attracted special attention due to its slightly increased Brønsted basic character when compared with its lighter lithium or sodium congeners, but also because of its relatively low toxicity and as such can be used in medical-related fields which are incompatible with conventional transition metal-catalysed approaches. In this context, the seminal work by Kobayashi has recently shown that KHMDs in combination with chiral macrocyclic crown ethers (as Lewis basic donor molecules) acts as an effective catalytic system for the carbon–carbon bond-forming reaction of alkyl-nitriles and 1,5-dicarbonyl compounds with excellent diastereo- and enantioselectivities. Wilhelm reported that KHMDs exhibits catalytic activity in the presence of THF, at temperatures as low as –78 °C, for the [2 + 2] cycloaddition of ketones with imines and aldehydes to produce biologically important β-lactam and β-lactone feedstocks. Zhang has shown that N-alkyl substituted carbamates undergo 5-exo-dig-cyclization to afford the corresponding functionalised oxazolidinone derivatives catalysed by KHMDs and 18-crown-6 in toluene solution. Panda and Carpentier have illustrated the
use of KHMDS as a pre-catalyst with a higher activity than the lithium and sodium salts for cross-dehydrocoupling of boranes and silanes, with amines for preparing aminoboranes and silazanes, respectively, with a high degree of conversion and chemoselectivity. The benefit of using potassium over lithium and sodium derivatives in synthesis could also be exemplified in the tert-butoxide congener of KHMDS (KO′Bu). For instance, Shi31 reported the use of KO′Bu in combination with the chelating Lewis base donor 1,1,1-phenanthroline as a transition metal-free catalytic system for constructing biaryl systems via radical cross-coupling between inert aromatic C–H bonds and aryl iodides or bromides. Murphy and Tuttle32 have studied in detail the mechanism of these transformations concluding that the greater basicity of KO′Bu over its sodium and lithium counterparts is a crucial factor in allowing access to these electron transfer reactions.

Since KHMDS is a widely used Brønsted base in synthesis and has recently shown excellent catalytic potential in THF or toluene solutions in the presence of Lewis basic donor molecules, it is important to understand the structural chemistry which is at play with these reagents in these solvents. The structural chemistry of LiHMDS and NaHMDS has been well studied; however, it is perhaps surprising that for the commercially available KHMDS (as toluene and THF solutions) it remains largely unexplored. To date, the solvent-free dimeric [{KHMDS}]2,33 dimeric toluene-solvated [{KHMDS}2(toluene)]34 dimeric ammonia-solvated [{KHMDS}2(NH3)]35 complexes and the monomeric species [{KHMDS}2(donor)] (donor = 1,4-dioxane16 and 18-crown-637,38) have been structurally characterized (Fig. 1a–d) alongside two examples of N-heterocyclic carbene (NHC) dimeric adducts of KHMDS, namely [{KHMDS}2(NHC)]2, where NHC are 1,3-bis-2,6-di-isopropylphenyl-imidazol-2-ylidene and 1,3-diisopropyl-3,4,5,6-tetrahydropyrimidin-2-ylidene (Fig. 1e and f).39,40 Additionally, one other related example containing a O,N-bidentate ligand derived from an ether-based backbone imidazolinium proligand [{KHMDS}2(OCH2CH2HC)NCH2CH2NiPr].2 has also been reported (Fig. 1g).41

Most of the structurally known complexes contain an archetypal dinuclear (KNHMDS)2 core. This motif is also observed when ferrocene is added to KHMDS, resulting in the isolation of the unusual polymeric [{KHMDS}2(ferrocene)].∞ (Fig. 1h),42 where ferrocene π-coordinates to the potassium metal. When KHMDS is combined with alkaline earth metal amides forming mixed metallate species, it is possible to isolate inverse crown species such as hydrido-46 and oxo-variants47,48 as well as simpler binuclear heterobimetallic amide formulations49,50 also observed when the alkaline earth metal is replaced by lanthanides.51,52 As the structural chemistry of alkali metal reagents normally dictates and influences their reactivity, it was decided to isolate and characterise, (in the solid- and solution-state) a series of solvates of KHMDS containing key solubility- and reactivity-enhancing donor molecules. These molecules include toluene, THF, N,N,N′,N′-tetramethyltetrahydrophosphine oxide (TMDA), (R,R)-N,N,N′,N′-tetramethyl-1,2-diaminocyclohexane [(R,R)-TMEDA], 12-crown-4, N,N,N′,N′-tetramethylammoethyl ether (TMDAE), N,N,N′,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), tris[2-dimethyl(aminomethyl)amine (Me2TREN) and tris[2-(2-methoxyethoxy)ethyl]amine (TMEEA).

Results and discussion

Synthetic procedures

A total of eleven new solvates of KHMDS (1–11) have been prepared and structurally characterised, both in solution and in the solid state. All synthetic protocols were optimised for obtaining high-quality crystalline samples for single crystal X-ray diffraction studies.

When toluene was employed as a donor, two distinct aggregates of KHMDS were obtained depending on the reaction conditions, a polymer [{KHMDS}2(toluene)].∞ 1 and a discrete dimer [{KHMDS}2(toluene)2]. 2. The ‘toluene-deficient’ polymeric aggregate 1 was prepared by generating KHMDS in situ (via a salt metathesis reaction between equimolar quantities of LiHMDS and KO′Bu). This reaction mixture results in a pale-yellow suspension in n-hexane from which 1 was successfully crystallised by adding toluene at ambient temperature (2 : 1 mixture of n-hexane : toluene) in 38% yield (Scheme 1). However, when the reaction mixture is stored at −27 °C the 1 : 1 toluene : KHMDS dimeric solvate 2 was isolated in 46% yield. THF-solvate [{KHMDS}2(THF)].∞ 3 was obtained by adding two molar equivalents of THF to a slurry of KHMDS in n-hexane. The THF polymeric aggregate was isolated (in 34% yield) by storing the resultant solution at −27 °C (Scheme 1). To the best of our knowledge, this represents the first isolation and structural characterisation of a THF-containing derivative of KHMDS, despite this reagent-solvent combination being commonly used in synthetic chemistry. Next, two bidentate diamine donors were studied, namely TMEDA and its chiral analogue (R,R)-TMEDA. To achieve homogeneity, a single molar equivalent with respect to KHMDS was required. The corresponding dimeric complexes [{KHMDS}2(TMEDA)]. 4 and...
addition of two molar equivalents of Me₆TREN did not
−lents of Me₆TREN were required in TMDAE molecules to a suspension of KHMDS in
solutions in both cases. Complex
0.5 : 1 donor : KHMDS molar ratios, producing homogeneous
aggregates, namely \[(KHMDS)_2(PMDETA·KHMDS)_2\]
Structurally distinct (vide infra \[(KHMDS)_2(Me₆TREN·KHMDS)_2\]
amounts of KHMDS and the crown ether molecule at
(96%) from an
| 6394  
![Scheme 2](image)

**Scheme 2** Synthesis of tetranuclear \[(KHMDS)_2(PMDETA·KHMDS)_2\] 7, \[(KHMDS)_2(TMDAE·KHMDS)_2\] 8 and \[(KHMDS)_2(Me₆TREN·KHMDS)_2\] 9, and monomeric \[(KHMDS)(TMDAE)_2\] 10 and \[(KHMDS)(TMEEA)\] 11.

As discussed earlier, depending on the crystallisation temperature, it is possible to isolate two distinct toluene solvates of KHMDS, namely polymeric \[(KHMDS)_2(toluene)_2\] 1 (Fig. 2a and b) and dimeric \[(KHMDS)_2(toluene)_2\] 2 (Fig. 2c). These crystallised in the triclinic space group \(P\overline{1}\) and in the monoclinic space group \(C2/\overline{c}\), respectively. The asymmetric unit cell of 1 is composed of a dimeric (KHMDS)₂ arrangement where one molecule of toluene is coordinated to the K metal centre in a \(\eta^6\)-manner via \(\pi\)-arene interactions \([K1···arene(centroid)] 3.045 \AA\). The structure of 1 propagates through the crystallographic a-axis via \(\pi\)-arene interactions of this toluene molecule with a second K metal centre from a neighbouring (KHMDS)₂ unit, ultimately forming a linear polymeric chain arrangement \([K2···arene(centroid)] 3.015 \AA\) (Fig. 2b). Complex 2 resembles the lattice parameters previously reported by Williard, although in this initial report the toluene solvent molecules were described as not coordinating to the K metal centres.₃₄ Here we have included our interpretation of the structural description of 2 by considering it as a four-membered \([K-N-K-N]\) cyclodimeric unit, where each K atom is solvated by a molecule of toluene in an \(\eta^6\)-manner \([K-···arene(centroid)] 2.967 \AA\). Each arene molecule binds approximately in a perpendicular array to the \(K_2N_2\) plane (87.5°) resulting in a discrete dimeric arrangement (Fig. 2c). Comparing 1 and 2, in the former the toluene molecules are disposed in a cisoid manner in the polymeric chain (Fig. 2b), whereas in 2, the toluene molecules are transoidal. This \(\eta^6\)-bonding mode of an arene to a metal is a common structural feature in heavy alkali metal organo-
metallic complexes and these K–arene(centroid) distances are similar to those found in related benzene- or toluene-solvated potassium amide complexes (range, 2.862–3.108 Å). The K,N₂ units in both the non-centrosymmetric 1 and centrosymmetric 2 resemble those of (KHMD)₃ reported by Tesh and Hanusa. Both K atoms are connected through bridging μ-HMDS ligands where the N atoms lie in approximately the same plane as the K metal centres (torsion angle K₁–N₁–K₂–N₂ of 1.5°, for 1; coplanar in 2). The inclusion of an additional molecule of toluene per potassium atom, does not have a pronounced effect on the respective K–N bond distances found in 1 and 2 [K₁–N 2.776(15) and 2.7619(15) Å and K₂–N 2.7506(15) and 2.7393(15) Å in 1; and 2.739(2) and 2.800(2) Å for 2, respectively; see Table 1]. These K–N bond distances are similar to those found for the solvent-free (KHMD)₃ [2.770(3) and 2.803(3) Å]. The distinct K–N bond lengths for K₁ and K₂ observed in 1 result in two slightly distinct N–K–N angles [N–K₁–N 94.58(4) and N–K₂–N 95.13(4)°], whilst the K–N–K
angles are identical [K1–N1–K2 85.14(4) and K1–N2–K2 85.11(4)°]. These bond angles are similar to those found in 2 [N1–K1–N1’ 94.17(7) and K1–N1–K1’, 85.83(7)°]. In addition, each K atom exhibits long K···C interactions with Me groups from the HMDS ligands in 1 and 2 [K1···C range 3.237(2)–3.2951(19) and 3.303(4)–3.402(4) Å for 1 and 2, respectively].

Complex 3 crystallises in the monoclinic space group P2₁/c. Like most known HMDS structures, 34,36,41,45,56,68,69 3 crystallises as a dimeric (HMDS)₂ unit, and it contains two molecules of THF, one coordinating to each K atom (Fig. 3a). The key features and metrics resemble those found for HMDS and for 2, two distinct K–N bond lengths [2.7442(13) and 2.8534(12) Å]. The two THF ligands are coordinated to the K atoms in a transoidal manner [K–O bond length is 2.7199 (13) Å]. Reflecting the fact that the K atoms are only partially saturated by the donor molecule in 3 (in comparison with 2), there is an intermolecular interaction with an HMDS methyl group of a neighbouring (HMDS), unit. This results in the formation of a two-dimensional layer arrangement through K···Me interactions [Fig. 3b and c, K1···C6” 3.2226(15) Å]. Each [(HMDS)],(THF)₂ unit represents a branch point towards four distinct directions in the polymeric two-dimensional sheet, two through its K atoms and two via two methyl groups from each HMDS ligand.

Fig. 3 (a) Molecular structure of [(HMDS)₂(TMEDA)], 3. Hydrogen atoms and one disordered component for the CH₂ framework in the THF ligand are omitted for simplicity. Displacement ellipsoids are displayed at 35% probability. The dashed lines illustrate K···C interactions. (b) Section of the extended framework structure showing K···C atom connectivity between K and Me and (c) the resulting two-dimensional monolayer packing. Selected bond distances (Å) and angles (°): K1–O1 2.7199(13), K1–N1 2.7442(13), K1–N1’ 2.8534(12), K1–C6” 3.2226(15), O1–K1–N1 129.65(4), O1–K1–N1’ 114.86(4), N1–K1–N1’ 96.27(3), K1–N1–K1’ 83.73(3), O1–K1–C6” 85.98(4), N1–K1–C6” 99.32(4), N1–K1–C6” 135.03(4). The symmetry operations used to generate the equivalent atoms numbered with ′ and ″ are –x + 1, –y + 2, –z and –x + 3/2, y + 1/2, –z + 1/2, respectively.

Fig. 4 (a) Molecular structure of [(HMDS), (TMEDA)], 4, showing one of the three crystallographically independent molecules within the asymmetric unit. (b) Molecular structure of [(HMDS), (R,R)-TMCDA)], 5. (c) Molecular structure of the centrosymmetric [(HMDS),[12-crown-4)], 6. Hydrogen atoms, one disordered component of one SiMe₃ group of 4 and one disordered molecule of toluene of crystallisation of 6 are omitted for simplicity. Displacement ellipsoids are displayed at 35% probability. The dashed lines illustrate K···C and K···O long interactions. Selected bond distances (Å) and angles (°): for 4, K5–N13 2.8365(16), K5–N14 2.7942(17), K5–N15 2.8762(17), K6–N13 2.7876(17), K6–N14 2.8765(17), K6–N15 2.9489(19), K6–N16 2.8529(19), K5···C71 3.373(3), K5···C59 3.397(3), K6···C66 3.313(2), N13–K5–N14 98.99(5), N13–K5–N17 135.20(5), N13–K5–N18 120.17(5), N14–K5–N17 115.45(5), N14–K5–N18 136.69(5), N17–K5–N18 63.27(5), N13–K6–N16 133.38(5), N13–K6–N14 98.19(5), N16–K6–N14 117.74(5), N13–K6–N15 118.70(5), N15–K6–N16 62.86(5), N14–K6–N15 133.61(5), N15–K6–N14 69.09(4), K5–N13–K6 91.81(4); for 5, K1–O2 2.844(2), K1–N1 2.808(2), K1–N5 2.959(2), K1–N6 3.035(2), K2–N1 2.785(2), K2–N3 2.878(2), K2–N4 2.764(2), K2–N5 2.878(2), K1–C11 3.369(3), K1–C12 3.185(3), K2–C4 3.223(3), K2–C9 3.180(3), K2–C14 3.347(3), K2–C15 3.299(3), N1–K1–N2 92.04(5), N2–K2–N1 128.17(7), N1–K1–N5 125.61(7), N2–K1–N6 130.71(7), N1–K1–N6 125.71(7), N5–K1–N6 57.22(6), K1–N1–K2 84.78(6), N1–K2–N2 97.37(7), N2–K2–N3 138.81(7), N1–K2–N3 115.27(6), N2–K2–N4 106.44(7), N1–K2–N4 144.64(7), N3–K2–N4 60.14(6), K1–N2–K2 85.62(6); for 6, K1–O1 2.9124(19), K1–O2 2.773(2), K1–O3 2.8024(18), K1–O4 3.121(2), K1–N1 3.073(2), K1–N1’ 2.913(2), K1–N1’’ 2.913(2), K1–C6” 3.313(3), O2–K1–O3 61.01(6), O2–K1–O1 59.05(6), O3–K1–O1 84.81(5), O2–K1–N1 91.72(6), O3–K1–N1 79.98(6), O1–K1–N1’ 150.78(6), O2–K1–N1 138.32(6), O3–K1–N1 160.67(6), O1–K1–N1 105.29(6), O1–K1–N1’ 138.08(5), N1–K1–N1 96.52(5), O2–K1–O4 88.27(6), O3–K1–O4 55.82(5), O1–K1–O4 56.26(6), N1–K1–O4 128.82(6), N1–K1–O4 116.04(5). The symmetry operation used to generate the equivalent atoms numbered with ′ and ″ is x′, y′, z′.
Derivatives 4–6 crystallised as discrete dimers (Fig. 4a–c). Whilst 4 and 6 are both in the monoclinic space group P2₁/c, 5 is in the orthorhombic Sophncke space group P2₁₂₁. TMEDA and its chiral analogue (R,R)-TMCDCA are widely utilised bidentate Lewis donor ligands in the chemistry of alkali metals, thus surprisingly, 4 and 5 represent the first structural examples of a KHMDMS species solvated by these important diamine ligands. The asymmetric unit of 4 contains three distinct molecules of [(KHMDMS)₂(TMEDA)]ₙ; two of them present some degree of disorder, which hampers their structural discussion. The third is discussed below. Complexes 4–6 resemble the archetypical planar four-membered K₂N₂ metalla-cyclo-dimer [sum of endocyclic angles, 359° for 4 and 357° for 5] previously seen in 1–3 and in the solvent-free [(KHMDMS)]ₙₜₗ. In 4 and 5, each K atom is coordinated to two bridging μ-HMDS amido groups and to the chelating TMEDA and (R,R)-TMCDCA ligands, respectively, resulting in the metals being four coordinate in a distorted tetrahedral geometry [N–K–N range 63.27(5)–135.20(5) and 62.86(5)–133.38(5)° for K5 and K6 in 4, and 55.22(6)–130.71(7) and 60.14(6)–138.81(7)° for K1 and K2 in 5; Fig. 4a and b, respectively]. However, each K in the centrosymmetric 6 binds a tetradentate 12-crown-4 ligand resulting in six-coordinated metal centres. In 4, the K–NHMDMS bond distances are identical [2.7942(17) and 2.7876(17) Å], whilst for 5 there is a short and long set of K–NHMDMS bonds [short K2–N1 and K2–N2 lengths of 2.785(2) and 2.764(2) Å, and long K1–N1 and K1–N1 lengths of 2.908(2) K1–N2 2.884(2) Å, respectively]. As expected, these are shorter than the K–NTMDA lone-pair dative interactions with either TMEDA or (R,R)-TMCDCA ligands in 4 and 5, respectively [K–N–TMDA range 2.8529(19)–2.9489(19) Å in 4 and K–N–(R,R)–TMCDCA range 2.878(2)–3.035(2) Å in 5]. The coordination modes of the K atoms in 4 and 5 closely resemble those found in related dimeric [{(KDA)₂(TMEDA)]₇ and [{KTMP]₂(TMEDA)]₇. Turning to 6 (Fig. 4c), the K–NHMDMS bond distances are noticeably longer [2.913(2) and 3.073(2) Å] than those for 4 and 5, and as expected longer than that in the donor-free reagent [mean 2.787 Å]. This is presumably the result of the different nature and higher denticity of the 12-crown-4 ligand resulting in six coordinate K atoms. The 12-crown-4 ligand coordinates the K metal centres being slightly distorted, thus resulting in four distinct K–O bond lengths. Three of them are in the range 2.773(2)–2.912(2) Å; however, the fourth K–O distance (K1–O4) is considerably longer at 3.121(2) Å. The K atoms are located approximately 2.1 Å above the mean plane of O atoms within the 12-crown-4 molecules. The internal angles at the K atoms in the centrosymmetric K₂N₂ ring are approximately 14° wider than the angles at the N atoms [N–K–N 96.92(5), K–N–K 83.08 (5)°], where the latter present an intermediate value between those found in 4 and 5. The mean K–N bond distance of the central (KHMDMS)₂ ring of 6 is 2.99 Å. In keeping with the other complexes discussed herein, the coordination spheres of both K atoms in 4–6 are completed by a series of long intramolecular K–C_HMDMS interactions [range 3.313(3)–3.397(2) and 3.180(3)–3.369(3) Å in 4 and 5, respectively] while a single K–C_HMDMS interaction can be found in 6 for each potassium atom [3.313(3) Å]. Complex 6 is a rare example of a potassium amide 12-crown-4 dimer, only two other examples have been reported with different amides, (2-phenylamido)pyridine and (trimethylsilylamido)pyridine.

Complexes 7 and 8 both crystallised in the monoclinic system space group P2₁/c, whilst 9 crystallised in the triclinic system P1. Complexes 7–9 (Fig. 5a–c) are essentially isostructural and can be considered as being composed of two [(donor)K–N–K–N] chains which are linked together though two K–NHMDMS bonds forming a 1 : 2 donor : KHMDMS tetranuclear discrete arrangement with a central cyclo-dimer (KHMDMS)₂ unit. The central K₂N₂ ring is planar in 7–9 (sum of endocyclic angles, 360° for 7–9). Two distinct types of K atoms are found in 7–9 occupying ‘internal’ and ‘external’ positions. Tridentate PMDETA and TMDAE, and the tetradentate Me₆TREN ligand respectively coordinate the external K atoms in an anti-disposition. The terminal metals are in a distorted tetrahedral environment in 7 and distorted square planar environment in 8. In 9, the tetradentate amine Me₆TREN coordinates the external K centres in a η⁴-manner, rendering these metals five-coordinated [N–K–N range 62.42(7)–165.97(6)°]. The three N-donor arms emerging from the central N donor in the tripodal Me₆TREN ligand are disposed in a plane in which the K atoms occupy a position approximately 1.41 Å above it. The internal K atoms bind to two bridging NHMDMS atoms forming the cyclic (KHMDMS)₂ motif (mean K–NHMDMS 2.83, 2.85 and 2.88 Å for 7, 8 and 9, respectively) and additionally to a bridging NHMDMS atom from a [(KHMDMS)(donor)] unit [K1–N2 2.8808(11) Å for 7, K2–N3 2.9254(11) Å for 8 and K2–N5 2.906(2) Å for 9]. The K atoms in the central cyclo-dimer present a distorted trigonal planar geometry in the three examples [range N–K–N 95.93(3)–141.54(4) for 7, N₄–K2–N3 95.65(3)–140.39(3)° for 8 and 95.58(6)–132.40(6)° for 9]. The K–NHMDMS bond distances are similar in 7–9 and as alluded to previously it is they are shorter than the corresponding K–N_donor bond length [mean K–N_PMDETA distance 2.90 Å for 7, mean K–N_TMDEA and K–O_TMDEA distances 2.98 and 2.7362(10), respectively, for 8, and mean K–N_Me6TREN distance 3.00 Å for 9]. Additionally, the K atoms in 7, 8 and 9 show stabilizing long K–C contacts with methyl groups from the HMDS and donor ligands [K–C range 3.3233(17)–3.3663(3) Å for 7, 3.3147(14)–3.3353(15) Å for 8, 3.239(4)–3.4023(3) Å for 9]. A search of the Cambridge Crystallographic Database reveals only four solid state structures with Me₆TREN coordinating to a K metal centre, including benzyl potassium complexes [PhCH₂K(Me₆TREN)] and 3,5-dimethylbenzyl potassium [3,5-Me₂C₆H₃CH₂K].

In an effort to prepare and characterise the solid state structures of monomeric KHMDMS species we used TMDEA and the heptadentate TMEEA donor molecules in 2:1 and 1:1 donor : HMDS molar ratios yielding 10 and 11, respectively. X-ray crystallographic analysis reveals that 10 crystallises in the monoclinic space group P2₁/a whilst 11 crystallises in the triclinic space group P1. The structures of 10 and 11 (Fig. 6a and b, respectively) consist of discrete solvated monomeric species of KHMDMS containing two molecules of TMDEA and one molecule of the multidentate TMEEA molecule coordinating the K...
metal centres, respectively. Two chemically identical but crystallographically distinct molecules of 10 are observed within its asymmetric cell; however, for simplicity and due to disorder in one of the molecules, the structural parameters of only one molecule will be discussed. The K metal centre is seven-coordinated in one of the molecules, the structural parameters of only one its asymmetric cell; however, for simplicity and due to disorder.

NMR spectroscopic studies
Crystalline compounds 1–11 were studied by $^1$H, $^{13}$C and DOSY NMR spectroscopies in CD$_2$Cl$_2$ solution. The $^1$H and $^{13}$C NMR spectra of 1–11 showed two distinct set of signals corresponding to the Lewis base donor of choice and the HMDS group. In general, the Lewis donor ligand : HMDS ratio found in the $^1$H NMR spectra is in agreement with the proportions found in the crystalline structures of complexes. However, the observed toluene:HMDS ratios in the $^1$H NMR spectra of 1 and 2 were slightly smaller than expected (1:2 and 1:1, respectively) presumably due to the partial removal of the labile arene ligand during their isolation. The $^1$H NMR chemical shifts for the HMDS ligand in the toluene-containing compounds 1 and 2, and in the PMDETA-solvate 7 are practically identical (0.13 ppm for 1 and 2, and 0.14 ppm for 7), whilst it is marginally shifted downfield for the THF-solvate 3 (0.16 ppm). For the dimeric complexes containing the bidentate N-donor ligands TMEDA and (R,R)-TMCDCA, 4 and 5, the HMDS singlet appears only slightly shifted downfield (0.23 ppm in both) with respect to 1–3, and is similar to that found for the TMEDA species 4 (0.24 ppm). However, the $^1$H NMR resonance for the HMDS ligand for the 12-crown-4,
Me₆TREN and TMDA derivatives 6, 9 and 10 appears markedly further downfield (0.35, 0.30 and 0.37 ppm, respectively), being even farther shifted for the monomeric TMEEA species 11 (0.49 ppm). The HMDMS resonance in the ¹³C NMR spectra for the complexes 1–11 appears in the range 7.2–7.5 ppm.

**Solution studies by DOSY NMR spectroscopy.** In an effort to gain more information regarding the solution state structures of the different solvates of KHMDMS isolated, 1, 3, 4, 6 and 9–11 were fully studied by DOSY NMR spectroscopy in arenė [C₆D₆ and D₈-toluene] and D₈-THF solutions (see the ESI† for full details). The NMR spectroscopic data in arenė solution show a similar trend for all the complexes, consisting of partial dissociation of the corresponding Lewis basic donor molecule present in the crystalline structures and replacement by arenė molecules. Additionally, this process is accompanied by monomeration of KHMDMS to form [KHMDMS[[deutero-arene]₂] as a major species in arenė solutions of 1, 3, 4 and 9–11 [range of MW(DOSY, C₆D₆) for 1, 3 and 4 and 9–11, 314–373 g mol⁻¹, MW(calc.) for [KHMDMS(C₆D₆)]₂] is 368 g mol⁻¹, 12% error; MW(DOSY, D₈-toluene) for 6, 361 g mol⁻¹, [KHMDMS(D₈-toluene)]₂] is 400 g mol⁻¹, 9% error]. This effect is more prominent when more polar D₈-THF is used. The DOSY NMR data for 3, 4, 6, 9, 10 and 11 in D₈-THF solutions reveal full dissociation of the corresponding Lewis basic donor ligand and replacement by molecules of D₈-THF producing the monomeric [KHMDMS(D₈-THF)]₂ as major species in solution [MW(DOSY, D₈-THF) range for 3, 4, 6, 9, 10 and 11, 317–375 g mol⁻¹, MW(calc.) for [KHMDMS(D₈-THF)]₂] is 360, 4–12% error.

**Conclusions**

The solid and solution structural chemistry of KHMDMS has been developed by exploring its coordination with a series of Lewis donor molecules. In the solid state, four different aggregation forms of KHMDMS have been found, namely, a linear polymeric chain array (in the presence of tolène), two-dimensional polymeric layer arrangement (with THF), dimeric arrangements (with tolène, TMEDA, R,R-TMCD and 12-crown-4), tetranuclear aggregates (with PMDETA, TMDA, Me₆TREN), and discrete monomeric species (with TMDA and TMEEA). Solution studies by DOSY NMR spectroscopy in D₈-THF and arenė (C₆D₆ and D₈-toluene) reveal that monomerisation of KHMDMS and displacement of the Lewis donor by these solvents occur in all the examples studied at ambient temperature.

**Experimental**

**General procedures**

All manipulation and reactions were performed under an atmosphere of dry pure argon gas using standard high vacuum Schlenk and glove box techniques. n-Hexane, tolène and tetrhydrofuran (THF) were distilled under reflux with sodium metal and benzophenone under a nitrogen atmosphere. Tolène was additionally stored over activated 4 Å molecular sieves. C₆D₆, [D₈]tolène and [D₁₂]cyclohexane were degassed and dried over activated 4 Å molecular sieves. [D₈]THF was stored over a potassium metal mirror. KHMDMS was purchased from Aldrich and used as received. N,N,N′,N″-Tetramethylethylendiamine (TMEDA), N,N,N′,N″,N‴-penta-methyldiethylenetriamine (PMDETA) and N,N,N′,N″,N‴-tetramethyldiaminoethylether (TMDA) were purchased from Aldrich, distilled with CaH₂ under a nitrogen atmosphere and stored under vacuum atmosphere. Solutions of KHMDMS and its derivatives with THF and arenė were stored over activated 4 Å molecular sieves. Tris[2-{2-methoxyethoxy}ethyl]amine (TMEEA) and 12-crown-4 were purchased from Aldrich and stored under vacuum atmosphere. Tris[2-dimethyl (amino)ethyl]amine was prepared by a previously reported method⁸⁷ and stored over activated 4 Å molecular sieves. NMR spectra were collected on a Bruker AV400 MHz spectrometer operating at 400.1 and 100.6 MHz for ¹H and ¹³C, respectively. ¹H and ¹³C(¹H) NMR chemical shifts are expressed in parts per million (δ, ppm) and referenced to residual solvent peaks. Microanalyses were obtained using a PerkinElmer 2400 elemental analyser.

Fig. 6 (a) Molecular structure of [KHMDMS(TMDA)]₁ showing one of the two crystallographically independent molecules within the asymmetric unit. (b) Molecular structure of [KHMDMS(TMEEA)]₁. Hydrogen atoms are omitted for simplicity. Displacement ellipsoids are displayed at 35% probability. The TMDA and TMEEA ligands are pictured in 10 and 11 as capped sticks with translucent space-filling van der Waals surfaces for a probe of 1.5 Å radius. Selected bond distances (Å) and angles (°): for 10, K₂–N₁ 2.794(3), K₂–O₁ 2.814(2), K₂–O₄ 2.824(2), K₂–N₉ 2.960(3), K₂–N₁₀ 3.559(3), K₂–N₈ 2.975(3), Kₐ–N₇ 3.337(4), N₆–K₂–O₁ 111.44(8), N₆–K₂–O₄ 106.42(9), O₃–K₂–O₄ 141.91(8), N₆–K₂–N₉ 132.63(8), O₃–K₂–N₉ 95.50(9), O₄–K₂–N₉ 60.13(9), N₆–K₂–N₈ 134.58(9), O₃–K₂–N₈ 59.22(8), O₄–K₂–N₈ 90.93(9), N₉–K₂–N₈ 92.54(9), N₆–K₂–N₇ 83.46(9), O₃–K₂–N₇ 55.33(8), O₄–K₂–N₇ 135.52(8), N₉–K₂–N₇ 81.01(9), N₈–K₂–N₇ 113.00(9), N₆–K₂–N₁₀ 83.97(8), N₁₀–K₂–N₁₀ 166.99(8); for 11, K₁–O₁ 2.7613(8), K₁–N₂ 2.7889(9), K₁–O₆ 2.831(8), K₁–O₄ 2.8736(8), K₁–O₅ 2.9078(8), K₁–O₃ 2.9652(8), K₁–N₁ 3.1364(9), K₁–O₂ 3.3145(10), O₁–K₁–N₂ 80.00(5), O₁–K₁–O₆ 150.12(8), N₂–K₁–O₆ 83.93(3), O₁–K₁–O₄ 137.21(8), N₂–K₁–O₄ 121.03(3), O₆–K₁–O₄ 72.63(2), O₁–K₁–O₅ 111.53(2), N₂–K₁–O₅ 122.61(2), O₆–K₁–O₅ 57.96(2), O₄–K₁–O₅ 88.90(2), O₁–K₁–O₃ 90.45(2), N₂–K₁–O₃ 161.50(2), O₆–K₁–O₃ 111.12(2), O₄–K₁–O₃ 57.56(2), O₅–K₁–O₃ 75.61(2), O₁–K₁–N₁ 57.01(2), N₂–K₁–N₁ 126.60(2), O₆–K₁–N₁ 117.35(2), O₄–K₁–N₁ 112.19(2), O₅–K₁–N₁ 59.71(2), O₃–K₁–N₁ 72.78(2), O₁–K₁–O₂ 56.12(2), N₂–K₁–O₂ 85.08(3), O₆–K₁–O₂ 147.03(2), O₁–K₁–O₂ 86.86(2), O₅–K₁–O₂ 149.24(2), O₃–K₁–O₂ 76.45(2), N₁–K₁–O₂ 94.02(2).
X-ray crystallography

Crystallographic data were collected at 123(2) K on Oxford Diffraction Xcalibur (Mo-Kα radiation, λ = 0.71073 Å, for 3, 4, 6, and 11) and Gemini (Mo-Kα radiation, λ = 0.71073 Å, for 9; Cu-Kα radiation, λ = 1.5418 Å, for 1, 2, 5, 7, 8 and 10) diffractometers. The structures were solved and refined to convergence on F² and against all independent reflections by full-matrix least-squares using SHELXL and SHELXS programs, respectively. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed and allowed to ride on their parent atoms. The THF ligand in 3, SiMe₃ groups and a TMEDA ligand in 4, the chelate group of 10, and toluene molecules of crystallisation in 6 and 9 were modelled as disordered over two sites with the geometry and displacement parameters of these groups restrained to approximate typical values. Selected crystallographic and refinement details are provided in Tables S1 and S2.†

Synthesis of [(KHMDS)₂(toluene)]∞ (1). KO'Bu (0.56 g, 5 mmol) was reacted with LiHMDS (0.84 g, 5 mmol) in n-hexane (20 mL) for 5 days. After this time, the solvent was removed under vacuum and the product was extracted in hot toluene (30 mL). Suitable crystals of 1 for an X-ray diffraction study were grown by cooling down a hot solution of 1 in a 2:1 mixture of n-hexane/toluene (9 mL) in a hot water bath (24 h). The crystalline material was filtered, washed with cold n-hexane (5 mL) and dried under vacuum for 10 min. Yield: 0.44 g, 0.94 mmol, 38%. In agreement with ¹H NMR and microelemental analyses toluene is partially removed (approximately 45%) during isolation of 1. ¹H NMR (400.1 MHz, C₆D₆, 298 K): δ 0.13 (s, 36 H, toluene), 7.12 (d, 2 H, 3H-JHH = 8.0 Hz, toluene), 137.9 (C13'H) NMR (100.6 MHz, C₆D₆, 300 K): δ 7.0 (Me₂Si), 25.7 (β-CH₂-THF), 67.8 (α-CH₂-THF). Anal. calc. (found) for C₁₂H₁₅K₂N₆Si₄: C, 51.97 (52.01); H, 10.90 (10.74); N, 11.36% (11.34%).

Synthesis of [(KHMDS)₂(TMEDA)]²⁻ (2). KHMS (1.00 g, 5 mmol) was taken up in hot toluene (10 mL) and then filtered to give a colourless solution. This solution was then cooled down to room temperature. The reaction mixture was then heated and filtered to give a colourless solution which was concentrated under vacuum (10 mL). Crystals of 4 suitable for an X-ray diffraction study were grown by cooling down the resulting solution at −27 °C (12 h). The crystalline material was filtered, washed with cold n-hexane (5 mL) and dried under vacuum for 10 min. Yield: 0.58 g, 0.92 mmol, 46%. ¹H NMR (400.1 MHz, C₆D₆, 300 K): δ 0.13, 7.0 (Me₂Si), 21.4 (β-TMCDA), 40.4 (para-CH, TMCDA). Anal. calc. (found) for C₂₃H₄₈K₂N₆Si₄: C, 45.66 (45.45); H, 9.04 (9.25); N, 5.98% (5.69%).

Synthesis of [(KHMDS)₂(12-crown-4)]²⁻ (3). (R,R)-TMCDA (0.68 mL, 2 mmol) was added via a syringe to a stirred solution of KHMS (0.40 g, 2 mmol) in n-hexane (20 mL) producing a slightly cloudy reaction mixture after 20 min at room temperature. The reaction mixture was then filtered to give a colourless solution which was concentrated under vacuum (5 mL). Crystals of 5 suitable for an X-ray diffraction study were obtained by cooling down the resulting solution at −27 °C (12 h). The crystalline material was filtered, washed with cold n-hexane (5 mL) and dried under vacuum for 10 min. Yield: 0.34 g, 0.68 mmol, 34%. In agreement with ¹H NMR and microelemental analyses THF is partially removed (approximately 20%) from 3 during isolation. ¹H NMR (400.1 MHz, C₆D₆, 300 K): δ 0.16 [s, 18 H, Me₂Si], 1.40 [m, 4 H, β-CH₂-THF], 3.52 (m, 4 H, α-CH₂-THF). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 300 K): δ 14.3 (Me₂Si), 57.6 (CH₂-THF). Anal. calc. (found) for C₁₂H₁₅K₂N₆Si₄: C, 42.97 (43.86); H, 9.56 (9.94); N, 5.45% (5.41%).

Synthesis of [(KHMDS)₂(TMEDA)₂]²⁻ (4). TMEDA (0.6 mL, 4 mmol) was added via a syringe to a stirred solution of KHMS (0.80 g, 4 mmol) in n-hexane (20 mL) producing a slightly cloudy reaction mixture after 20 min at room temperature. The reaction mixture was then heated and filtered to give a colourless solution which was concentrated under vacuum (10 mL). Crystals of 6 suitable for an X-ray diffraction study were grown by cooling down the resulting solution at −27 °C (12 h). The crystalline material was filtered, washed with cold n-hexane (5 mL) and dried under vacuum for 10 min. Yield: 0.35 g, 0.68 mmol, 34%. In agreement with ¹H NMR and microelemental analyses THF is partially removed (approximately 20%) from 3 during isolation. ¹H NMR (400.1 MHz, C₆D₆, 300 K): δ 0.16 [s, 18 H, Me₂Si], 1.40 [m, 4 H, β-CH₂-THF], 3.52 (m, 4 H, α-CH₂-THF). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 300 K): δ 14.3 (Me₂Si), 57.6 (CH₂-THF). Anal. calc. (found) for C₁₂H₁₅K₂N₆Si₄: C, 42.97 (43.86); H, 9.56 (9.94); N, 5.45% (5.41%).
study were obtained at −27 °C (3 days). In agreement with $^1$H NMR and microelemental analyses the toluene solvent molecule of crystallisation present in the crystal lattice of 6 is removed upon isolation. Yield: 0.36 g, 0.48 mmol, 96%. $^1$H NMR (400.1 MHz, C$_6$D$_{12}$, 300 K): δ 0.43 (s, 18 H, Me$_3$Si), 3.06 (s, 16 H, CH$_2$). $^{13}$C($^1$H) NMR (100.6 MHz, C$_6$D$_{12}$, 300 K): δ 7.4 (Me$_3$Si), 67.1 (CH$_2$). Anal. calcd (found) for C$_{23}$H$_{46}$K$_4$N$_8$O$_2$Si$_8$: C, 44.76 (44.51); H, 9.12 (9.12); N, 7.33% (7.43%).

**Synthesis of [(KHMDS)$_2$[(PMDETA-KHMDS)$_2$]](7).** PMDETA (0.21 mL, 1 mmol) was added via a syringe to a stirred gently heated suspension of KHMDS (0.40 mg, 2 mmol) in hexane (20 mL) to give a slightly cloudy reaction mixture. The reaction was filtered to yield a colourless solution. The solution was concentrated (4 mL) and placed inside a hot water bath (24 h) to give crystals of 7 suitable for an X-ray diffraction study. The crystalline material was filtered, washed with cold n-hexane (5 mL) and dried under vacuum for 15 min. Yield: 0.30 g, 0.26 mmol, 52%. $^1$H NMR (400.1 MHz, C$_6$D$_{12}$, 300 K): δ 0.22 (s, 36 H, Me$_3$Si), 2.00 (s, 12 H, Me$_2$N-PMDETA), 2.01 (s, 3 H, MeN-PMDETA), 2.06 (br t, 4 H, $^3$J$_{HH}$ = 6 Hz, CH$_2$-PMDETA), 2.15 (br t, 4 H, $^3$J$_{HH}$ = 6 Hz, CH$_2$-PMDETA). $^1$H NMR (400.1 MHz, [D$_3$]toluene, 300 K): δ 0.14 (s, 36 H, Me$_3$Si), 2.02 (s, 12 H, Me$_2$N-PMDETA), 2.04 (s, 3 H, MeN-PMDETA), 2.08 (br t, 4 H, $^3$J$_{HH}$ = 6 Hz, CH$_2$-PMDETA), 2.17 (br t, 4 H, $^3$J$_{HH}$ = 6 Hz, CH$_2$-PMDETA). $^{13}$C($^1$H) NMR (100.6 MHz, [D$_3$]toluene, 300 K): δ 7.3 (Me$_3$Si), 42.7 (Me$_2$N-PMDETA), 45.7 (Me$_2$N-PMDETA), 55.9 (CH$_2$-PMDETA), 57.6 (CH$_2$-PMDETA). Anal. calcd (found) for C$_{44}$H$_{110}$K$_4$N$_{10}$Si$_8$: C, 44.08 (44.15); H, 10.39 (11.40); N, 12.24% (12.36%).

**Synthesis of [(KHMDS)$_3$[(TMDAE-KHMDS)$_2$]] (8).** TMDAE (0.19 mL, 1 mmol) was added via a syringe to a stirred gently heated suspension of KHMDS (0.40 g, 2 mmol) in n-hexane (20 mL) yielding a pale-yellow solution. The solution was concentrated to (5 mL) and suitable crystals of 8 for an X-ray diffraction study were obtained by cooling down the solution at −27 °C (24 h). The crystalline material was filtered, washed with cold n-hexane (5 mL) and dried under vacuum for 10 min. Yield: 0.37 g, 0.33 mmol, 66%. $^1$H NMR (400.1 MHz, C$_6$D$_{12}$, 300 K): δ 0.24 (s, 36 H, Me$_3$Si), 1.99 (s, 12 H, MeO-TMDAE), 2.13 (t, 4 H, $^3$J$_{HH}$ = 5.6 Hz, CH$_2$N-TMDAE), 3.13 (t, 4 H, $^3$J$_{HH}$ = 5.6 Hz, CH$_2$O-TMDAE). $^{13}$C($^1$H) NMR (100.6 MHz, C$_6$D$_{12}$, 300 K): δ 7.4 (Me$_3$Si), 45.4 (MeO-TMDAE), 59.1 (CH$_2$N-TMDAE), 68.4 (CH$_2$O-TMDAE). Anal. calcd (found) for C$_{46}$H$_{64}$K$_4$N$_{12}$O$_2$Si$_8$: C, 42.96 (41.99); H, 10.09 (9.82); N, 7.02% (7.04%). 

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