Synthetic and structural investigations of alkali metal diamine bis(phenolate) complexes†‡§

William Clegg,[a] Matthew G. Davidson,[b] David V. Graham,[c] Gemma Griffen,[c] Matthew D. Jones,[b] Alan R. Kennedy,[c] Charles T. O'Hara,*[c] Luca Russo[a] and Calum M. Thomson[c]

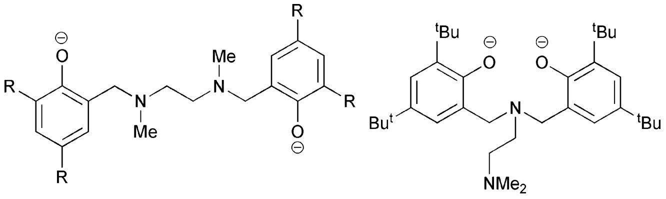
Received 26th November 2007, Accepted 2nd January 2008
First published as an Advance Article on the web 22nd January 2008
DOI: 10.1039/b718186h

Two lithium and one sodium diamine bis(phenolate) complexes have been prepared and characterised by X-ray crystallography and NMR spectroscopy. Two parent diamine bis(phenol) ligands were utilised in the study (**1**-H_2 and **2**-H_2). Dimeric (**1**-Li_2)$_2$ was prepared by treating **1**-H_2 with two molar equivalents of *n*-butyllithium in hydrocarbon solvent. It adopts a ladder-like structure in the solid state, which appears to deaggregate in C_6D_6 solution. The monomeric (hence, dinuclear) TMEDA-solvated species [**2**-Li_2·(TMEDA)] has two chemically unique Li atoms in the solid state and is prepared by reacting **2**-H_2 with two molar equivalents of *n*-butyllithium in hydrocarbon solvent, in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). Finally, the dimeric sodium-based [**2**-Na_2·(OEt_2)]$_2$ was prepared by reacting **2**-H_2 with two molar equivalents of freshly prepared *n*-butylsodium in a hydrocarbon–diethyl ether medium. The complex adopts a Na_4O_4 cuboidal structure in the solid state, which appears to remain intact in C_6D_6 solution.

Introduction

Group 1 metal phenolates are currently attracting considerable interest in several distinct fields. For instance, they can be utilised as precursors to other non-alkali metal phenolates *via* metathesis reactions,[1] as initiators in the ring opening polymerisation of cyclic esters such as ε-caprolactone and L-lactide[2–5] and for controlling network assembly in the synthesis of coordination polymers.[6] Subtle changes in ligand structure and solvent medium have highlighted interesting differences in the structural and reaction chemistry of the resultant complexes.[7–9] A subclass of the metal phenolate complexes which have come to prominence recently are the amine bis(phenolate) complexes. Of particular interest to us are ligands **1** and **2** (Fig. 1).

We have recently reported the homoleptic dimeric Mg[10] and trinuclear Ba[11] salts of **1**. By treating M(O^{i}Pr)$_4$ (where, M = Ti, Zr or Hf) with an equimolar quantity of **1** and **2**, several Group 4 heteroleptic Ti, Zr and Hf salts were prepared and characterised.[12] Mountford and Duchateau *et al.* have recently reported the structure of several Sm amine bis(phenolate) complexes.[13] Most pertinent to this particular study, Kerton *et al.* have published the structures of two dilithium diamine bis(phenolate) complexes (Fig 2).[14] The diamine bis(phenol) ligands employed in these syntheses are isomeric—the first of which is **1**-H_2, whilst the second is $Me_2NCH_2CH_2N(CH_2ArOH)_2$, **3**-$H_2$ where Ar = 3,5-C_6H_2-$^tBu_2$]. The Li complexes obtained are both dioxane adducts; however, the former, [**1**-Li_2·(dioxane)$_{1.5}$]$_2$, possesses a dimeric, tetranuclear structure whereby the dinuclear units are bridged by a molecule of dioxane. In the latter [**3**-Li_2·(dioxane)]$_\infty$, the structure adopts a polymeric arrangement in the solid state. To provide further insight into the chemistry of alkali metal bis(phenolate) complexes, we report the synthesis and characterisation of three new diamine bis(phenolate) complexes.



1 R = ^{t}Bu
2 R = Me

3

Fig. 1 Amine bis(phenolate) ligands **1**–**3**.

Results and discussion

Syntheses and solid-state structures

Complexes (**1**-Li_2)$_2$, [**2**-Li_2·(TMEDA)] and [**2**-Na_2·(OEt_2)]$_2$ were prepared using conventional deprotonation procedures (Scheme 1).

For the lithium amine bis(phenolate) complexes, a hexane–toluene solution of **1**-H_2 was treated with two molar equivalents of ^{n}BuLi. By reducing the volume *in vacuo* and cooling the mixture to −27 °C a crop of colourless, crystalline **1**-Li_2 was deposited (yield

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[a] *School of Natural Sciences (Chemistry), Newcastle University, Newcastle-upon-Tyne, UK NE1 7RU*
[b] *Department of Chemistry, University of Bath, Bath, UK BA2 7AY*
[c] *Department of Pure and Applied Chemistry, University of Strathclyde, WestCHEM, Glasgow, UK G1 1XL. E-mail: charlie.ohara@strath.ac.uk; Tel: +44 (0)141 548 2667*

† Dedicated to Professor Ken Wade—a truly inspirational inorganic chemist.

‡ CCDC reference numbers 669061–669063. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718186h

§ Electronic supplementary information (ESI) available: NMR spectra data for (**1**-Li_2)$_2$, [**2**-Li_2·(TMEDA)] and [**2**-Na_2·(OEt_2)]$_2$. See DOI: 10.1039/b718186h

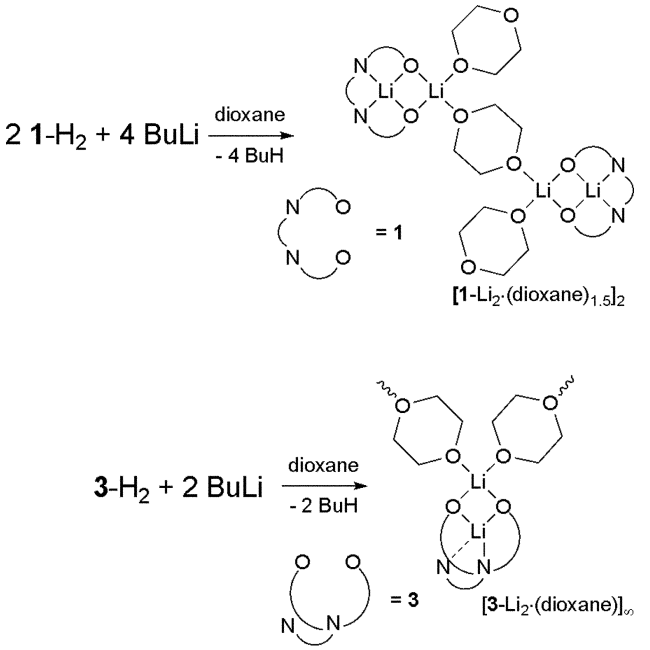
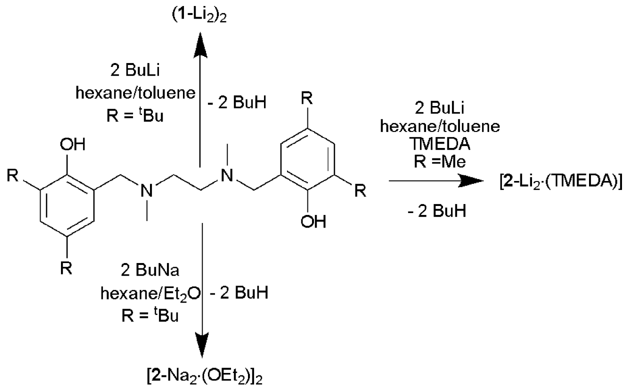


Fig. 2 Previously published structures of two lithium diamine bis(phenolate) complexes. For simplicity no stereochemistry is shown.[14]



Scheme 1 Preparation of $(\mathbf{1}\text{-Li}_2)_2$, $[\mathbf{2}\text{-Li}_2\cdot(\text{TMEDA})]$ and $[\mathbf{2}\text{-Na}_2\cdot(\text{OEt}_2)]$.

of first batch, 42%). A similar reaction was attempted using $\mathbf{2}\text{-H}_2$; however, no crystalline material could be isolated from solution. More success was forthcoming on introducing the coordinating diamine TMEDA to the mixture, producing colourless, crystalline $\mathbf{2}\text{-Li}_2\cdot$(TMEDA) in a yield of 48%. Akin to its Li analogue, a base-free Na complex of $\mathbf{2}\text{-H}_2$ could not be isolated—instead when a hexane/toluene solution of $\mathbf{2}\text{-H}_2$ (one molar equivalent) and ^{n}BuNa (two molar equivalents) was treated with diethyl ether, colourless $\mathbf{2}\text{-Na}_2\cdot(\text{OEt}_2)$ was formed in 34% yield.

The X-ray-determined structure of $(\mathbf{1}\text{-Li}_2)_2$ is shown in Fig. 3, and its key structural dimensions are listed in Table 1. Solvent-free $(\mathbf{1}\text{-Li}_2)_2$ is a discrete tetranuclear dimer which adopts a ladder-like conformation. The Li atoms which occupy positions in the outer rungs [Li(1) and Li(4)] are formally five-coordinate, and are coordinated by one μ_2-O, one μ_3-O, two N and one *ipso*-C from an adjacent benzene ring. Those occupying the central rungs [Li(2) and Li(3)] are three-coordinate and the attached atoms adopt a distorted trigonal pyramidal environment [*endo*-ladder angles: O(2)–Li(3)–O(4), O(3)–Li(3)–O(4), O(1)–Li(2)–O(2) and O(2)–Li(2)–O(4) are 93.5(2), 103.2(2), 104.0(2) and 93.8(2)°; *exo*-ladder angles: O(2)–Li(3)–O(3) and O(1)–Li(1)–O(4) are 158.7(3) and 156.5(3)° respectively]. The Li–O bonds range from 1.844(4) Å [for Li(3)–O(3)] to 1.978(4) Å [for Li(4)–O(4)]. As expected the

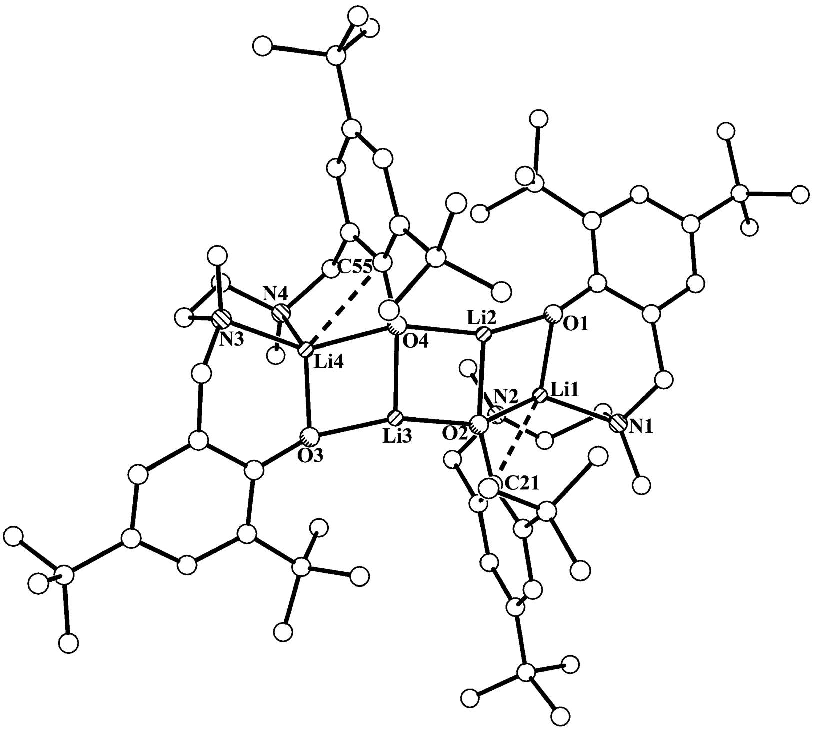


Fig. 3 Molecular structure of $(\mathbf{1}\text{-Li}_2)_2$, showing selected atom labelling with hydrogen atoms omitted for clarity. The Li···C$_{ipso}$ interactions are denoted by dashed lines.

Table 1 Bond lengths (Å) and angles (°) for $(\mathbf{1}\text{-}Li_2)_2$

Li(1)–O(1)	1.857(5)	O(1)–Li(1)–O(2)	102.5(2)
Li(1)–O(2)	1.975(5)	O(1)–Li(2)–O(2)	104.0(2)
Li(1)–N(1)	1.999(5)	O(1)–Li(2)–O(4)	156.5(3)
Li(1)–N(2)	2.054(5)	O(2)–Li(2)–O(4)	93.8(2)
Li(1)–C(21)	2.397(5)	O(2)–Li(3)–O(3)	158.7(3)
Li(2)–O(1)	1.860(5)	O(2)–Li(3)–O(4)	93.5(2)
Li(2)–O(2)	1.934(5)	O(3)–Li(3)–O(4)	103.2(2)
Li(2)–O(4)	1.931(4)	N(3)–Li(4)–N(4)	90.7(2)
Li(3)–O(2)	1.934(4)	N(3)–Li(4)–O(3)	105.4(2)
Li(3)–O(3)	1.844(4)	N(3)–Li(4)–O(4)	136.9(3)
Li(3)–O(4)	1.940(5)	N(4)–Li(4)–O(3)	124.6(2)
Li(4)–O(3)	1.852(5)	N(4)–Li(4)–O(4)	101.0(2)
Li(4)–O(4)	1.978(4)	O(3)–Li(4)–O(4)	101.5(2)
Li(4)–N(3)	2.003(5)	Li(1)–O(1)–Li(2)	77.8(2)
Li(4)–N(4)	2.046(5)	Li(1)–O(2)–Li(2)	73.3(2)
Li(4)–C(55)	2.437(5)	Li(1)–O(2)–Li(3)	150.3(2)
		Li(2)–O(2)–Li(3)	86.1(2)
N(1)–Li(1)–N(2)	90.9(2)	Li(3)–O(3)–Li(4)	79.3(2)
N(1)–Li(1)–O(1)	105.4(2)	Li(2)–O(4)–Li(3)	86.0(2)
N(1)–Li(1)–O(2)	137.4(3)	Li(2)–O(4)–Li(4)	153.1(2)
N(2)–Li(1)–O(1)	120.6(2)	Li(3)–O(4)–Li(4)	74.0(2)
N(2)–Li(1)–O(2)	101.8(2)		

longest Li–O bonds are those involving the μ_3-O atoms [O(2) and O(4)], but consequently this gives rise to long (and by implication, weak) Li–O bonds to the three-coordinate Li atoms [Li(2) and Li(3)]. The mean Li–(μ_2-O) bond distance (1.853 Å) in $(\mathbf{1}\text{-}Li_2)_2$ is identical to the equivalent bond in Kerton's dioxane solvate of $(\mathbf{1}\text{-}Li_2)_2$ (1.853 Å),[14] as are the Li–N distances. As alluded to earlier, the outermost Li atoms π-bond to an adjacent benzene ring in an η^1-manner (mean distance, 2.417 Å). These bonds are in the range for those found in other related Li phenoxide systems[15–22] (2.268–2.596 Å). The ladder-like core of $(\mathbf{1}\text{-}Li_2)_2$ comprises three essentially planar Li_2O_2 rhombi [sum of endocyclic angles for Li(1)–O(1)–Li(2)–O(2), O(2)–Li(2)–O(4)–Li(3) and Li(3)–O(4)–Li(4)–O(3) rings are 357.6, 359.5 and 358.0° respectively]. Overall, the molecule adopts a convex cisoidal geometry [dihedral angles between: Li(1)–O(2)–Li(2)–O(1) and Li(2)–O(2)–Li(3)–O(3); and Li(2)–O(2)–Li(3)–O(3) and Li(3)–O(3)–Li(4)–O(4) planes are 23.7(2) and 17.7(4)° respectively] (Fig. 4). Ladder motifs akin to that in $(\mathbf{1}\text{-}Li_2)_2$ are common in lithium chemistry.[23–26]

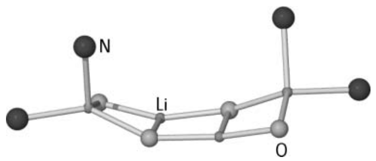


Fig. 4 The ladder-like core of $(\mathbf{1}\text{-}Li_2)_2$ showing its gentle cisoidal geometry.

Table 2 Key bond lengths (Å) and angles (°) for $[\mathbf{2}\text{-}Li_2\cdot(TMEDA)]$

Li(1)–O(3)	1.854(2)	N(11)–Li(1)–O(22)	134.80(13)
Li(1)–O(22)	1.850(2)	N(14)–Li(1)–O(3)	126.67(12)
Li(1)–N(11)	2.018(2)	N(14)–Li(1)–O(22)	102.74(10)
Li(1)–N(14)	2.056(2)	O(3)–Li(1)–O(22)	97.49(9)
Li(2)–O(3)	1.923(2)	N(29)–Li(2)–N(32)	83.4(4)
Li(2)–O(22)	1.902(2)	N(29)–Li(2)–O(3)	113.5(3)
Li(2)–N(29)	2.112(17)	N(29)–Li(2)–O(22)	123.9(3)
Li(2)–N(32)	2.245(13)	N(32)–Li(2)–O(3)	135.4(3)
		N(32)–Li(2)–O(22)	106.5(3)
N(11)–Li(1)–N(14)	88.90(9)	O(3)–Li(2)–O(22)	97.49(9)
N(11)–Li(1)–O(3)	105.52(10)		

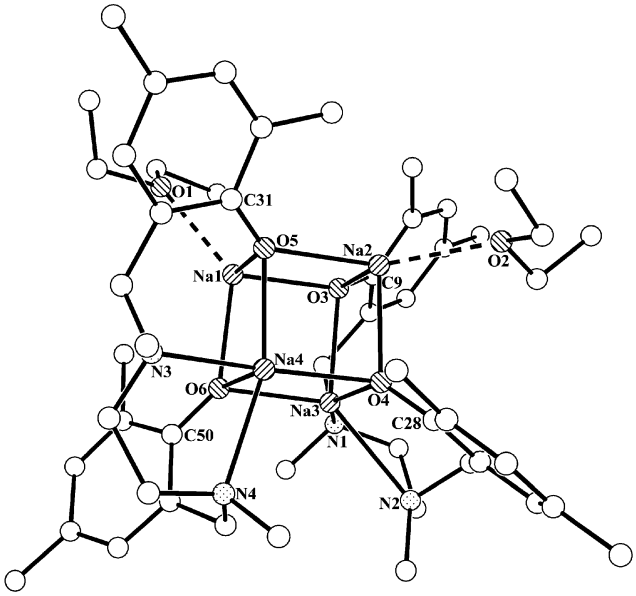


Fig. 5 The molecular structure of $[\mathbf{2}\text{-}Li_2\cdot(TMEDA)]$, showing selected atom labelling with hydrogen atoms omitted for clarity.

The X-ray-determined structure of $[\mathbf{2}\text{-}Li_2\cdot(TMEDA)]$ is shown in Fig. 5, and its key structural dimensions are listed in Table 2. As for $(\mathbf{1}\text{-}Li_2)_2$, there are two chemically distinct Li atoms within the dinuclear, monomeric structure of $[\mathbf{2}\text{-}Li_2\cdot(TMEDA)]$; however, their overall chemical environments are more similar. Both Li(1) and Li(2) are in a distorted tetrahedral arrangement (mean angle: 110.1 and 110.0° respectively) and are bound to two μ_2-O and two N atoms, where the N atoms belong to internal **2** for Li(1) and external TMEDA for Li(2). The central four-membered Li_2O_2 ring is almost planar (sum of endocyclic angles: 358.6°). There appears to be no appreciable Li–C π-bonding in $[\mathbf{2}\text{-}Li_2\cdot(TMEDA)]$ [shortest Li···C_{aryl} distance: 2.596(2) Å for Li(1)···C(4)], although the aryl rings tend to tilt considerably more toward Li(1) than Li(2) {*c.f.* Li(1)–O(3)–C(4) [108.52(9)°] with Li(2)–O(3)–C(4) [162.30(10)°]; and Li(1)–O(22)–C(21) [109.51(9)°] with Li(2)–O(22)–C(21) [168.51(10)°]}. The shortest Li–O and Li–N distances in $[\mathbf{2}\text{-}Li_2\cdot(TMEDA)]$ are those involving Li(1)—highlighting the excellent metal-binding properties of the N_2O_2 chelating ligand. For instance, the Li(2)–N_{TMEDA} bonds (mean distance: 2.179 Å) are significantly longer than the Li(1)–N bonds associated with the amine bis(phenolate) ligand (mean distance: 2.037 Å). An identical scenario is found for the Li–O bonds: mean Li–O bond distance is 1.852 and 1.913 Å for Li(1) and Li(2) respectively. The TMEDA bite angle [83.4(4)°] is 5.5° more acute than the corresponding angle attributed to the amine bis(phenolate) ligand. To the best of our knowledge, three other TMEDA solvates of lithium phenolates have been crystallographically characterised: a hexanuclear adduct of dilithiated 2-*tert*-butyl-5-methylphenol, lithiated TMEDA and TMEDA (in a ratio of 2 : 2 : 2);[15] a dodecanuclear adduct of trilithiated 2,5-dimethylphenol and TMEDA (in a 4 : 4 ratio);[16] and octanuclear $[(salen)Li_2]_3\cdot Li_2O\cdot(TMEDA)_2\cdot H_2O]$ where salen-H_2 = *N*,*N*′-ethylenebis(salicylideneimine).[27] Additionally, the crystal structure of a TMEDA-solvated mixed lithium–magnesium phenolate has also been published.[28]

The X-ray-determined structure of [**2**-Na_2·(OEt_2)]$_2$ is shown in Fig. 6 and and its key structural dimensions are listed in Table 3. Table 4 collects together the crystal and structure refinement data for (**1**-Li_2)$_2$, [**2**-Li_2·(TMEDA)] and [**2**-Na_2·(OEt_2)]$_2$. [**2**-Na_2·(OEt_2)]$_2$ exhibits a tetranuclear distorted cubane structure. Each corner-positioned Na atom is coordinated by three μ_3-O atoms. Na(1) and Na(2) are further stabilised by the coordination of a molecule of diethyl ether, whilst Na(3) and Na(4) are further stabilised by internal chelation by two N atoms [N(1) and N(2), and N(3) and N(4) respectively for Na(3) and Na(4)]. Due to the presence of disorder in the diethyl ether molecules the pseudo-tetrahedral geometry around Na(1) and Na(2) can not be discussed in detail. Interestingly, the geometries around the five-coordinate Na(3) and Na(4) atoms are significantly different in the solid state. Firstly, the Na(3) atom appears to adopt a distorted trigonal bipyramidal arrangement where N(1) and O(4) adopt the axial positions [N(1)–Na(3)–O(4) angle: 152.65(17)°]. Secondly, the Na(4) atom appears to adopt a distorted square pyramidal arrangement. Unlike the Na(3) case, there are two angles which are tending towards 180°—O(4)–Na(4)–N(3) and O(5)–Na(4)–N(4) are 163.47(15)° and 162.46(15)° respectively—hence O(6) adopts the axial coordination site. The Na–(μ^3-O) bond distances range from 2.259(4) to 2.389(3) Å, the shortest and longest are attributed to Na(3)–O(4) and Na(3)–O(3) respectively. Turning to the Na–N bonds in [**2**-Na_2·(OEt_2)]$_2$, the Na(3)–N(1) [2.349(4) Å] and Na(3)–N(2) [2.522(4) Å] distances differ signifcantly. On the other hand the Na(4)–N bonds are more uniform [Na(4)–N(3) and Na(4)–N(3) distances: 2.427(4) and 2.435(4) Å]; however, the mean Na(3)–N (2.436 Å) and Na(4)–N (2.431 Å) distances are almost identical. From a search of the Cambridge Structural Database,[29]

Table 3 Key bond lengths (Å) and angles (°) for [**2**-Na_2·(OEt_2)]$_2$

Na(1)–O(3)	2.263(4)	O(3)–Na(2)–O(5)	92.50(13)
Na(1)–O(5)	2.285(4)	O(4)–Na(2)–O(5)	93.49(12)
Na(1)–O(6)	2.307(3)	O(3)–Na(3)–O(4)	91.48(12)
Na(2)–O(3)	2.350(4)	O(3)–Na(3)–O(6)	91.51(12)
Na(2)–O(4)	2.268(3)	O(3)–Na(3)–N(1)	86.44(13)
Na(2)–O(5)	2.311(3)	O(3)–Na(3)–N(2)	132.63(14)
Na(3)–O(3)	2.389(3)	O(4)–Na(3)–O(6)	96.36(13)
Na(3)–O(4)	2.259(4)	O(4)–Na(3)–N(1)	152.65(17)
Na(3)–O(6)	2.275(4)	O(4)–Na(3)–N(2)	86.55(14)
Na(4)–O(4)	2.309(4)	O(6)–Na(3)–N(1)	110.94(16)
Na(4)–O(5)	2.304(4)	O(6)–Na(3)–N(2)	135.77(14)
Na(4)–O(6)	2.332(4)	N(1)–Na(3)–N(2)	75.16(15)
Na(3)–N(1)	2.349(4)	O(4)–Na(4)–O(5)	92.59(12)
Na(3)–N(2)	2.522(4)	O(4)–Na(4)–O(6)	93.44(13)
Na(4)–N(3)	2.427(4)	O(4)–Na(4)–N(3)	163.47(15)
Na(4)–N(4)	2.435(4)	O(4)–Na(4)–N(4)	104.78(14)
		O(5)–Na(4)–O(6)	89.61(12)
		O(5)–Na(4)–N(3)	88.83(12)
O(3)–Na(1)–O(5)	95.52(13)	O(5)–Na(4)–N(4)	162.46(15)
O(3)–Na(1)–O(6)	94.03(12)	O(6)–Na(4)–N(3)	103.05(14)
O(5)–Na(1)–O(6)	90.73(12)	O(6)–Na(4)–N(4)	86.99(14)
O(3)–Na(2)–O(4)	92.28(13)	N(3)–Na(4)–N(4)	75.23(14)

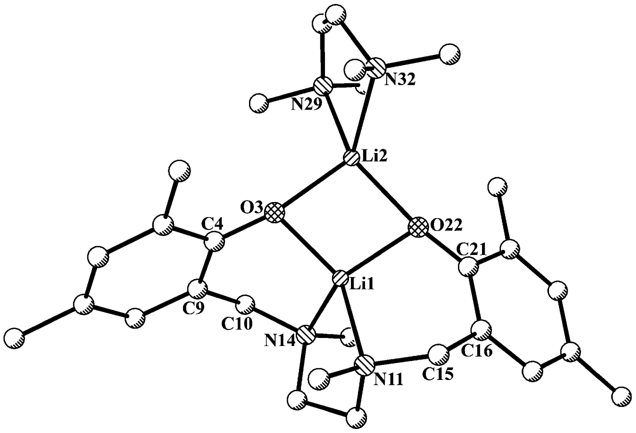


Fig. 6 The molecular structure of [**2**-Na_2·(OEt_2)]$_2$, showing selected atom labelling with hydrogen atoms omitted for clarity. Dashed bonds represent the Na–$O_{(ether)}$ bonding.

Table 4 Crystal data and structure refinement for (**1**-Li_2)$_2$, [**2**-Li_2·(TMEDA)] and [**2**-Na_2·(OEt_2)]$_2$

Compound	(**1**-Li_2)$_2$	[**2**-Li_2·(TMEDA)]	[**2**-Na_2·(OEt_2)]$_2$
Molecular formula	$C_{82}H_{124}Li_4N_4O_4$	$C_{28}H_{46}Li_2N_4O_2$	$C_{52}H_{80}N_4Na_4O_6$
Formula mass	1257.61	484.57	949.16
T/K	123(2)	150(2)	123(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	15.1350(6)	12.151(3)	16.2626(4)
b/Å	16.7141(6)	15.012(3)	16.8683(6)
c/Å	18.3935(7)	16.937(4)	21.4569(5)
α/°	88.527(2)	90	90
β/°	66.122(2)	109.913(3)	111.185(2)
γ/°	69.106(2)	90	90
V/Å^3	3936.4(3)	2904.7(10)	5488.3(3)
Z	2	4	4
D_c/Mg m^{-3}	1.061	1.108	1.149
μ/mm^{-1}	0.063	0.069	0.101
Crystal size/mm	0.28 × 0.10 × 0.06	0.80 × 0.60 × 0.60	0.40 × 0.30 × 0.30
Reflections collected	26003	25601	16661
Independent reflections (R_{int})	13822 (0.0636)	7055 (0.0184)	8619 (0.0757)
Refined parameters	896	412	604
Goodness-of-fit on F^2	1.010	1.039	1.105
R (F, $F^2 > 2\sigma$)	0.0617	0.0460	0.0839
R_w (F^2, all data)	0.1521	0.1375	0.2350
Max, min difference/e Å^{-3})	0.33, −0.30	0.40, −0.42	0.51, −0.42

it appears that [**2**-Na_2·(OEt_2)]$_2$ is the first structurally characterised Na amine bis(phenolate) complex. However, several Na phenolate complexes[9,30–38] adopt structures with a similar cubanoid core to that of [**2**-Na_2·(OEt_2)]$_2$. Perhaps most pertinent to our work is the study of sodium Schiff base complexes presented by Deacon *et al.*[38] Like [**2**-Na_2·(OEt_2)]$_2$, the complexes reported in this study—[Na_2(salpn)(OEt_2)]$_2$ and [Na_2(salpn)(DME)]$_2$ (where salpn is [(*o*-$OC_6H_4CH{=}NCH_2)_2CH_2$] and DME is dimethoxyethane)—have a Na_4O_4 core and two of the Na atoms are solvated by an ethereal solvent molecule. The Na–O bonds in the diethyl ether-solvated Schiff base complex [range of bond distances, 2.235(3)–2.347(3) Å] are similar to those in [**2**-Na_2·(OEt_2)]$_2$ [range of bond distances, 2.235(3)–2.347(3) Å].

Solution structures

Crystalline samples of (**1**-Li_2)$_2$, [**2**-Li_2·(TMEDA)] and [**2**-Na_2·(OEt_2)]$_2$ are soluble in C_6D_6 solution; hence, a NMR spectroscopic study of the complexes was possible.

From the crystal structure of (**1**-Li_2)$_2$, it is evident that, if the solid-state structure is maintained in solution, two chemically distinct phenoxide groups (pertaining to μ_2-O and μ_3-O bonding modes), should be observed in the ^{1}H NMR spectrum. In practice, only one type of phenoxide is observed in C_6D_6 solution at concentrations of 5 mg l^{-1} and 15 mg l^{-1} (only two aromatic *H* resonances are seen, *c.f.* the ^{1}H NMR spectrum for **1**-H_2). This observation is consistent with the dimeric (tetranuclear) solid-state structure deaggregating in solution to give monomeric (dinuclear) oligomers which may be C_6D_6-solvated (Fig. 7). In D_8-toluene solution at 228 K, the ^{1}H NMR spectrum revealed that there were still only two aryl resonances corresponding to the complex; hence, these data suggest that the ladder undergoes dissociation in solution rather than being subject to rapid intramolecular dynamic exchange. Alkali metal–π interactions like those alluded to here have recently been subject to considerable research[39–41] and their importance has been realised in fields as diverse as zeolite-supported processes,[42] in the interaction of alkali metal cations with aromatic side chains of proteins,[43–46] and in the selectivity of superbases,[47] *via* coordination of an arene molecule to a Group 1 metal centre. In (**1**-Li_2)$_2$ the ligand has two sets of diastereotopic CH_2 groups (Fig. 1). In the ^{1}H NMR spectrum of (**1**-Li_2)$_2$ four distinct CH_2 resonances can be observed. This appears to indicate that the Li–O bonding in the solution oligomers is strong, resulting in a fixed stereochemistry of the ligand and hence the appearance of the diastereotopic H atoms in the NMR spectrum. These data are in agreement with those obtained by Kerton *et al.* for (**1**-Li_2)$_2$ in D_5-pyridine.[14]

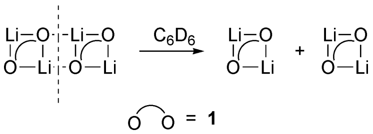


Fig. 7 Proposed symmetrical deaggregation of (**1**-Li_2)$_2$ in C_6D_6 solution.

The ^{1}H NMR spectrum of crystalline [**2**-Li_2·(TMEDA)] in C_6D_6 was found to be extremely complex (due to the large number of overlapping signals in both the aromatic and aliphatic regions of the spectrum—see supporting information§) and no useful data could be extrapolated from the spectrum. The aryl regions of such spectra normally give an indication of the purity of the complex (because of the generally low number and good separation of the resonances). This complexity presumably arises due to a high degree of dynamic transformations in solution, and/or the existence of multiple solution oligomers being present. In an effort to simplify the spectrum, the experiment was repeated using the strong σ-donating solvent D_5-pyridine. The spectrum obtained was significantly simplified. As well as uncoordinated TMEDA, it appears that the only lithium phenolate complex present is a pyridine-solvated dinuclear monomer [other than the residual pyridine signals, only two resonances in the aryl region of the spectrum (7.07 and 6.90 ppm) were observed]. The CH_2 resonances in the ^{1}H spectrum appeared broad. Likewise, their respective resonances in the $^{13}C\{^1H\}$ NMR spectrum are also broad.

The ^{1}H NMR spectrum obtained for [**2**-Na_2·(OEt_2)]$_2$ shows that no diethyl ether was lost on isolation despite the crystals being subjected to vacuum during the process. In contrast to the NMR spectra of the previous compounds reported here, it appears that the cuboidal framework of [**2**-Na_2·(OEt_2)]$_2$ remains intact in solution. O(4) and O(6) are in significantly different chemical environments from O(3) and O(5) (Fig. 8); therefore, the associated benzene rings are different, giving rise to four resonances in the aryl region of the ^{1}H spectrum. However, the entire structure does not stay intact in C_6D_6 solution—the chemical shifts for diethyl ether molecules are identical to those of uncoordinated solvent, indicating that it is probably labile in C_6D_6. Due to the complication that there are two distinct phenolate environments present in the solution structure of [**2**-Na_2·(OEt_2)]$_2$ this should result in the appearance of eight diastereotopic CH_2 resonances—a similar scenario was noticed in the solution structure of (**1**-Mg)$_2$[10] and in a dimeric calcium bis(phenolate) complex reported by Bochmann *et al.*[48] However, presumably due to dynamic behaviour within the ligand framework, no obvious C*H* resonances could be observed in the ^{1}H spectrum of [**2**-Na_2·(OEt_2)]$_2$; instead a broad region (from 4.2 to 1.8 ppm) just above the spectrum's baseline is observed. This type of dynamic behaviour has previously been noted for (**1**-Ba)$_3$·(THF)$_2$.[11]

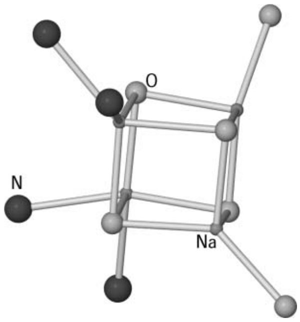


Fig. 8 View of [**2**-Na_2·(OEt_2)]$_2$ cubane showing the different connectivities of the phenoxide ligands. (For clarity all C and H atoms have been omitted.)

Conclusions

Three new alkali metal diamine bis(phenolate) complexes have been prepared and characterised. In the solid state, the donor-free Li complex (**1**-Li_2)$_2$ is dimeric (hence tetranuclear) and adopts a 'ladder-like' arrangement; in C_6D_6 solution, the dimer appears to deaggregate. [**2**-Li_2·(TMEDA)] is monomeric in the solid state. Perhaps surprisingly, in C_6D_6 solution the complex is subject to a high degree of dynamic activity, which can be suppressed by using a more polar solvent such as D_5-pyridine. Finally, [**2**-Na_2·(OEt_2)]$_2$ is dimeric (tetranuclear) in the solid state, but unlike (**1**-Li_2)$_2$ it adopts a cubanoid arrangement. ^{1}H NMR spectroscopy appears to indicate that the cubanoid core remains intact in C_6D_6.

Experimental

Materials and methods

All experimental manipulations (except ligand preparations) were performed under an atmosphere of dry, oxygen-free argon, using standard Schlenk techniques and a glovebox. 1.6 M *n*-Butylithium in hexane was purchased from Aldrich. *n*-Butylsodium was prepared using previously published methods.[49] Diethyl ether, hexane and toluene were freshly distilled from sodium benzophenone ketyl, and TMEDA was distilled from CaH_2 prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 400.13 MHz and 100.06 MHz respectively using a Bruker AMX400 or DPX400. The chemical shifts for residual ^{1}H and ^{13}C resonances of the C_6D_6 solvent were referenced to 7.16 and 128.0 ppm respectively.

X-Ray crystallography

Crystal data and other information on the structure refinements are given in Table 4. Data for (**1**-Li_2)$_2$ and [**2**-Na_2·(OEt_2)]$_2$ were collected on a Nonius KappaCCD diffractometer, and those for [**2**-Li_2·(TMEDA)] on a Bruker SMART 1K diffractometer, all with Mo-Kα radiation ($\lambda = 0.71073$ Å), using standard procedures and software.[50,51] The structures were solved by direct methods and refinement was on F^2 values for all unique data in each case.[52]

Preparation of *N*,*N*′-bis(2-hydroxy-3,5-*tert*-butyl)-*N*,*N*′-dimethylethane-1,2-diamine (1-H_2)

1-H_2 was prepared using a modified Mannich reaction[53,54] by combining *N,N*′-dimethylethylenediamine (5.32 mL, 50 mmol), formaldehyde solution (38 wt% in H_2O) (8.7 mL, 110 mmol), and 2,4-di-*tert*-butylphenol (20.6 g, 100 mmol) in methanol.[53] The resultant mixture was heated to reflux for 18 h, and **1**-H_2 was collected by filtration and washed with cold methanol. Typical yield: 20.3 g (77%). ^{1}H NMR (400.13 MHz, C_6D_6, 300 K): δ 10.77 (br s, 2H, OH), 7.50 (d, 2H, J_{HH} = 2.5 Hz, Ar–H), 6.88 (d, 2H, J_{HH} = 2.5 Hz, Ar–H), 3.26 (s, 4H, ArCH_2N), 2.12 [br s, 4H, N(CH_2)$_2$], 1.78 (s, 6H, N–CH_3), 1.70 [s, 18H, C(CH_3)$_3$], 1.36 [s, 18H, C(CH_3)$_3$]. ^{13}C NMR (100.63 MHz, C_6D_6, 298 K): δ 155.4 [$C_{(aryl)}$–OH], 141.2 [$C_{(aryl)}$–^{t}Bu], 136.6 [$C_{(aryl)}$–^{t}Bu], 124.0 [$C_{(aryl)}$–H], 123.7 [$C_{(aryl)}$–H], 122.0 [$C_{(aryl)}$–CH_2], 63.2 (N$C$$H_2$$CH_2$), 54.0 (N$C$$H_2$–Ar), 41.4 (N–$C$$H_3$), 35.7 [Ar–$C$($CH_3$)$_3$], 34.7 [Ar–$C$($CH_3$)$_3$], 32.4 [Ar–C($C$$H_3$)$_3$], 30.4 [Ar–C($C$$H_3$)$_3$]. Mass spectroscopic data: (FAB positive mode) *m*/*z*, 524.7 (M^+, 100%), 261.7 (37%), 218.7 (83%), 202.7 (11%).

Preparation of *N*,*N*′-bis(2-hydroxy-3,5-methyl)-*N*,*N*′-dimethylethane-1,2-diamine (2-H_2)

2-H_2 was prepared using a modified Mannich reaction[53,54] by combining *N*,*N*′-dimethylethylenediamine (5.32 mL, 50 mmol), formaldehyde solution (38 wt% in H_2O) (8.7 mL, 110 mmol), and 2,4-dimethylphenol (12.2 g, 100 mmol) in methanol.[53] The resultant mixture was heated to reflux for 18 h, and **2**-H_2 was collected by filtration and washed with cold methanol. Typical yield: 14.8 g (83%). ^{1}H NMR (400.13 MHz, C_6D_6, 300 K): δ 10.39 (br s, 2H, OH), 6.87 (d, 2H, J_{HH} = 2.4 Hz, Ar–H), 6.54 (d, 2H, J_{HH} = 2.4 Hz, Ar–H), 3.24 (s, 4H, ArCH_2N), 2.42 (s, 6H, Ar–CH_3), 2.20 [br s, 4H, N(CH_2)$_2$], 2.15 (s, 6H, Ar–CH_3), 1.80 (s, 6H, N–CH_3). ^{1}H NMR (400.13 MHz, D_5-pyridine, 300 K): δ 10.76 (br s, 2H, OH), 6.93 (d, 2H, Ar–H), 6.72 (d, 2H, Ar–H), 3.60 (s, 4H, ArCH_2N), 2.55 (s, 6H, Ar–CH_3), 2.36 [br s, 4H, N(CH_2)$_2$], 2.23 (s, 6H, Ar–CH_3), 2.13 (s, 6H, N–CH_3). ^{13}C NMR (100.63 MHz, C_6D_6, 300K): δ 154.4 [$C_{(aryl)}$–OH], 131.2 [$C_{(aryl)}$–Me], 127.4 [$C_{(aryl)}$–H], 127.0 [$C_{(aryl)}$–Me], 125.1 [$C_{(aryl)}$–H], 121.1 [$C_{(aryl)}$–CH_2], 61.9 (N$C$$H_2$$CH_2$), 54.0 (N$C$$H_2$–Ar), 41.2 (N–$C$$H_3$), 20.6 (Ar–$C$$H_3$), 16.0 (Ar–$C$$H_3$).

Preparation of (1-Li_2)$_2$

A flame-dried Schlenk tube was charged with **1**-H_2 (0.53 g, 1 mmol) and dissolved in 5 mL of toluene. Two molar equivalents of *n*-butyllithium solution (1.25 mL of 1.6 M solution in hexanes, 2 mmol) were added to the colourless solution. The reaction mixture was stirred for 30 minutes, then approximately 50% of the solution was removed *in-vacuo*. On cooling the solution to −27 °C for 15 h, a crop of large, colourless, block-shaped crystals of **1**-Li_2 were obtained (unoptimised yield: 0.23 g, 42%). ^{1}H NMR (400.13 MHz, C_6D_6, 296.2 K): δ 7.45 (d, 2H, J_{HH} = 2.4 Hz, Ar–H), 6.95 (d, 2H, J_{HH} = 2.4 Hz, Ar–H), 3.97 (d, 2H, J_{HH} = 11.6 Hz, Ar–CH_2), 2.76 (d, 2H, J_{HH} = 11.6 Hz, Ar–CH_2), 2.63 (d, 2H, J_{HH} = 8.9 Hz, Ar–CH_2–N–CH_2), 1.60 (s, 6H, N–CH_3), 1.44 [s, 18H, Ar–C(CH_3)$_3$], 1.41 [s, 18H, Ar–C(CH_3)$_3$], 1.28 (d, 2H, J_{HH} = 11.6 Hz, Ar–CH_2). ^{13}C NMR (100.63 MHz, C_6D_6, 300 K): δ 161.6 [$C_{(aryl)}$–O], 138.5 [$C_{(aryl)}$–^{t}Bu], 136.8 [$C_{(aryl)}$–^{t}Bu], 128.0 [$C_{(aryl)}$–H, observed using HSQC experiment], 126.4 [$C_{(aryl)}$–CH_2], 124.4 [$C_{(aryl)}$–H], 63.2 (N$C$$H_2$–Ar), 50.3 (N$C$$H_2$$CH_2$), 42.6 (N–$C$$H_3$), 35.3 [Ar–$C$($CH_3$)$_3$], 34.1 [Ar–$C$($CH_3$)$_3$], 32.1 [Ar–C($C$$H_3$)$_3$], 30.5 [Ar–C($C$$H_3$)$_3$].

Preparation of [2-Li_2·(TMEDA)]

A flame-dried Schlenk tube was charged with **2**-H_2 (0.36 g, 1 mmol) and dissolved in 3 mL of hexane. Two molar equivalents of *n*-butyllithium solution (1.25 mL of 1.6 M solution in hexanes, 2 mmol) were added to the colourless solution. The reaction mixture was stirred for 2 h. TMEDA (0.31 mL, 2 mmol) was added to the mixture to produce a thick white suspension before the majority of the volatiles were removed *in-vacuo*. Toluene (5 mL) was added and the suspension was strongly heated to produce a colourless homogeneous solution. The solution was cooled slowly in a Dewar flask filled with hot water. After 15 h, large, colourless, block-shaped crystals of [**2**-Li_2·(TMEDA)] were obtained (unoptimised yield: 0.23 g, 48%). ^{1}H NMR (400.13 MHz, D_5-pyridine, 300 K): δ 7.07 (br s, 2H, Ar–H), 6.90 (br s, 2H, Ar–H), 2.90–2.68 (br, 2H, CH), 2.49 (br, 2H, CH), 2.40 (s, 4H, CH_2, TMEDA), 2.34 (s, 6H, Ar–CH_3), 2.29 (br, 2H, CH), 2.21 (s, 6H, Ar–CH_3), 2.19 (s, 12H, N–CH_3, TMEDA), 2.10 (s, 6H, N–CH_3), 2.03 (br, 2H, CH). ^{13}C NMR (100.63 MHz, D_5-pyridine, 300 K): δ 165.6 [$C_{(aryl)}$–O], 136.0 [$C_{(aryl)}$–Me], 131.7 [$C_{(aryl)}$–H], 130.7 [$C_{(aryl)}$–H], 126.4 [$C_{(aryl)}$–Me], 118.5 [$C_{(aryl)}$–CH_2], 61.7 ($C$$H_2$), 58.5 ($C$$H_2$,

TMEDA), 55.8 (CH_2), 46.2, 42.5 (CH_3, TMEDA), 21.1 (Ar–CH_3), 19.0 (Ar–CH_3).

Preparation of [2-Na_2·(OEt_2)]$_2$

A flame-dried Schlenk tube was charged with freshly prepared BuNa (0.16 g, 2 mmol), **2**-H_2 (0.36 g, 1 mmol) and hexane (3 mL). The resultant suspension was cooled to −78 °C, prior to the addition of diethyl ether (2 mL). This solution was allowed to stir for 2 h at ambient temperature. Small colourless crystals were deposited (unoptimised yield: 0.33 g, 34%) after allowing the solution to stand for 15 h. ^{1}H NMR (400.13 MHz, C_6D_6, 296.2 K): δ 7.08 (br s, 2H, Ar–H), 7.02 (br s, 2H, Ar–H), 6.85 (br s, 2H, Ar–H), 6.83 (br s, 2H, Ar–H), broad region above baseline 4.2–1.8, 3.19 [q, 8H, OCH_2CH_3 (diethyl ether)], 2.37 [s, 6H, Ar–CH_3], 2.31 [s, 6H, Ar–CH_3], 2.11, 2.02 (s, 6H, Ar–CH_3), 1.95 (s, 6H, Ar–CH_3), 1.93 (s, 6H, N–CH_3), 1.80 (s, 6H, N–CH_3), 1.57, 1.02 [t, 12H, OCH_2CH_3 (diethyl ether)]. Due to a high degree of solution dynamics, the CH_2 resonances could not be unequivocally assigned.

Acknowledgements

The authors thank the University of Strathclyde (GG, CMT) for funding this work.

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