

# Structural Elucidation of tmeda-Solvated Alkali Metal Diphenylamide Complexes

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Lithium, sodium and potassium salts of diphenylamine have been prepared by using a deprotonative route and characterised in both, solid state (by X-ray crystallography) and solution (by NMR spectroscopic studies). In each case the metal atom's coordination sphere is completed by coordination to the synthetically important co-ligand *N,N,N',N'*-tetramethylethylenediamine (tmeda). Complexes **1** and **2** [(tmeda)-M(NPh<sub>2</sub>)<sub>2</sub>] (M = Li for **1**, Na for **2**) can be prepared by treating 1 mol.-equiv. of the parent amine with an equimolar quantity of *n*BuM and tmeda in hexane solution. In the solid state, **1** and **2** are essentially isostructural, being dimeric with a four-atom M–N–M–N framework. The coordination sphere of each M atom is completed by a bidentate tmeda molecule. Complex **3** [(tmeda)<sub>3/2</sub>K(NPh<sub>2</sub>)<sub>2</sub>] has been prepared in a similar way to **1** and **2** except that benzylpotassium has been

utilised as the metallating agent. In addition, 4 mol.-equiv. of tmeda is required to fully solubilise the heavy alkali metal amide mixture. In the solid state, **3** exists as a polymeric array of dinuclear K–N–K–N rings. Akin to **1** and **2**, the K atom is coordinated to a bidentate tmeda molecule; however, each K atom is also bound to another tmeda molecule that acts as a monodentate bridge, thus producing the coordination polymer. Crystalline **1** and **2** are soluble in C<sub>6</sub>D<sub>6</sub>; hence, NMR spectroscopic studies could be performed. These show that the solid-state structure appears to stay intact in arene solution. On the other hand, **3** is not soluble in C<sub>6</sub>D<sub>6</sub>; so solution studies have been performed in [D<sub>8</sub>]thf. These studies reveal that **3** readily loses tmeda during in-vacuo isolation.

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## Introduction

Alkali metal amides and their solvates are continuing to attract a great deal of interest due to their use in alkali metal/hydrogen exchange reactions.<sup>[1–5]</sup> In particular, the metal salts of diisopropylamine [da(H)], 1,1,1,3,3,3-hexamethyldisilazane [hmds(H)] and 2,2,6,6-tetramethylpiperidine [tmp(H)] are widely utilised across synthetic laboratories primarily because of the desirable combination of high Brønsted basicity and low nucleophilicity. Of particular interest in this study, another amido reagent, the thermally highly stable lithium diphenylamide (LiNPh<sub>2</sub>), has shown promise in a range of synthetic transformations. As well as regioselective deprotonation reactions,<sup>[6–10]</sup> it has also been used in catalytic aldol reactions involving silyl enol ethers and aldehydes,<sup>[11,12]</sup> in elimination applications,<sup>[13,14]</sup> in metathetical reactions,<sup>[15–27]</sup> during the preparation of amino-containing carbenes,<sup>[28]</sup> and as an initiator in the polymerisation of methyl methacrylate.<sup>[29]</sup>

Primarily to gain a greater understanding of these synthetic endeavours, the structural chemistry of the alkali metal amides has maintained a high level of interest, since the first reported solid-state structure of an alkali metal amide {that of trimeric [Li(hmds)]<sub>3</sub>} in 1969.<sup>[30,31]</sup> Alkali metal diphenylamide complexes have been extensively studied. The solution structure of LiNPh<sub>2</sub> in thf (in the presence/absence of LiBr) has been comprehensively studied by Collum.<sup>[32,33]</sup> In the solid state, the majority of the complexes reported to date, take the form of solvent-separated alkali metal ate species, whereby the second metal is a transition metal,<sup>[34–38]</sup> lanthanide,<sup>[39–45]</sup> actinide,<sup>[46]</sup> or a group 13 element.<sup>[47,48]</sup> Contacted ate complexes are also prevalent, predominantly with the heavier alkali metals (sodium and potassium) due to their need for further stabilisation by metal–arene  $\pi$ -interactions.<sup>[36,49–54]</sup> Turning to homometallic species, lithium diphenylamide has been shown to form co-complexes with: (i) lithium chloride;<sup>[55]</sup> (ii) *n*-butyllithium and mono-*ortho*-metallated LiNPh<sub>2</sub>;<sup>[56]</sup> and (iii) dilithium diphenylhydrazide.<sup>[57]</sup> But perhaps most pertinent to this study, several alkali metal diphenylamides stabilised by donor ligands (e.g., various ethers<sup>[58–62]</sup> and pyridine<sup>[58]</sup>) have been reported. However, prior to this report surprisingly no homometallic sodium diphenylamide complexes have been reported thus far.

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Over the past few years, we have shown that da, hmds and tmp can be incorporated within heterodimetallic alkali metal/divalent metal ate complexes and utilised in alkali metal mediated metallation (AMMM).<sup>[63,64]</sup> This synergic approach to metal/hydrogen exchange, has enabled the direct and regioselective metallation (sometimes multi-metallation) of several key molecules with “sub-ordinate” metals, that is those normally inert to such reactions.<sup>[65]</sup> We aim to introduce diphenylamide as a newcomer to AMMM, and as a prelude, report here the preparation and structural characterisation of three key monometallic building blocks: namely *N,N,N',N'*-tetramethylethylenediamine (tmeda) adducts of  $\text{MPh}_2$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ). This chemistry is being pursued as tmeda has proved a useful co-ligand in reagents designed for AMMM applications.<sup>[63–65]</sup>

## Results and Discussion

### Preparation and Solution Structures

Complexes **1–3** were prepared by treating the appropriate organo alkali metal reagent with an equimolar quantity of diphenylamine in hexane (Scheme 1). For **1** and **2**, 1 mol-equiv. of tmeda in toluene was required to achieve homogeneity, whereas for **3**, a fourfold excess was required. A similar scenario was encountered during the synthesis of the tmeda adduct of  $\text{K(tmp)}$ .<sup>[66]</sup> X-ray quality crystals of **1–3** precipitated from the respective solutions at ambient temperature in moderate yields (typically 36–48%). The crystals were isolated in vacuo, and in the case of **3**, this resulted in a loss of crystallinity. The excellent solubility of **1** and **2** in arene solvents allowed an NMR spectroscopic study to be conducted. Complex **3** was insoluble in  $\text{C}_6\text{D}_6$  solution, so a  $[\text{D}_8]\text{thf}$  solution was studied. Tables 1 and 2 contain the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data for **1–3** and, for comparison, those for diphenylamine and tmeda.

Because the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data obtained for **1** and **2** suggest that tmeda remains coordinated to the respective alkali metal atom, and only one set of diphenylamido resonances are observed in  $\text{C}_6\text{D}_6$ , it appears that only one oligomer of solvated alkali metal amide [presumably the dimeric solid-state species (vide infra)] exists in solution,<sup>[32]</sup> although there is precedent for other dimeric s-block metal species to slowly convert to other oligomers

Table 1.  $^1\text{H}$  NMR spectroscopic data for **1–3**, diphenylamine and tmeda; spectra acquired at 400.13 MHz, 300 K in  $\text{C}_6\text{D}_6$  ( $[\text{D}_8]\text{thf}$  for **3**).

|                        | $\text{CH}_3$ (tmeda)      | $\text{CH}_2$ (tmeda)      | <i>o</i> -, <i>m</i> -, <i>p</i> -CH                  |
|------------------------|----------------------------|----------------------------|-------------------------------------------------------|
| $\text{Ph}_2\text{NH}$ | –                          | –                          | 6.85, 7.10, 6.83<br>(7.04, 7.16, 6.78) <sup>[a]</sup> |
| tmeda                  | 2.12 (2.15) <sup>[a]</sup> | 2.36 (2.30) <sup>[a]</sup> | –                                                     |
| <b>1</b>               | 1.72                       | 1.75                       | 7.26, 7.26, 6.74                                      |
| <b>2</b>               | 1.68                       | 1.54                       | 7.27, 7.27, 6.69                                      |
| <b>3</b>               | (2.15) <sup>[a]</sup>      | (2.30) <sup>[a]</sup>      | (6.84, 6.84, 6.14) <sup>[a]</sup>                     |

[a] Data in parentheses obtained from  $[\text{D}_8]\text{thf}$  solution of the respective compound.

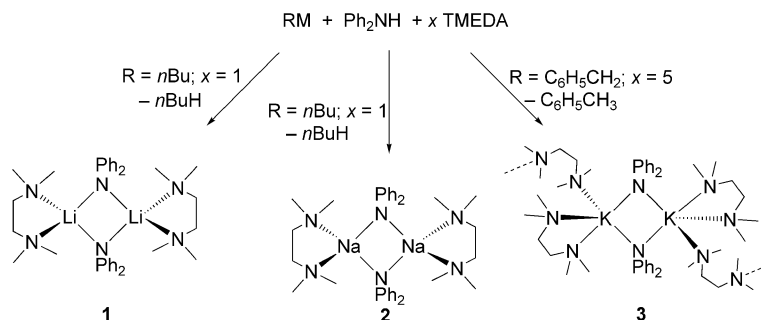
Table 2.  $^{13}\text{C}$  NMR spectroscopic data for **1–3**, diphenylamine and tmeda; spectra acquired at 400.13 MHz, 300 K in  $\text{C}_6\text{D}_6$  or  $[\text{D}_8]\text{thf}$ .<sup>[a]</sup>

|                        | $\text{CH}_3$ (tmeda)      | $\text{CH}_2$ (tmeda)      | <i>i</i> -C and <i>o</i> -, <i>m</i> -, <i>p</i> -CH                      |
|------------------------|----------------------------|----------------------------|---------------------------------------------------------------------------|
| $\text{Ph}_2\text{NH}$ | –                          | –                          | 143.6, 118.2, 129.5, 121.2<br>(145.0, 118.2, 129.7, 120.8) <sup>[a]</sup> |
| tmeda                  | 46.0 (46.3) <sup>[a]</sup> | 58.4 (59.3) <sup>[a]</sup> | –                                                                         |
| <b>1</b>               | 45.7                       | 57.1                       | 158.1, 120.5, 130.1, 116.5                                                |
| <b>2</b>               | 45.1                       | 56.8                       | 158.8, 118.7, 130.2, 114.7                                                |
| <b>3</b>               | (46.3) <sup>[a]</sup>      | (59.3) <sup>[a]</sup>      | (158.1, 118.2, 129.7, 112.6) <sup>[a]</sup>                               |

[a] Data in parentheses obtained from a  $[\text{D}_8]\text{thf}$  solution of the respective compound.

over long periods of time.<sup>[67]</sup> For **1**, its respective  $^7\text{Li}$  NMR spectrum also supports this conclusion as only one resonance ( $\delta = 0.88$  ppm) is observed. Higher oligomeric forms (trimer,<sup>[30,68–72]</sup> tetramer,<sup>[73,74]</sup> hexamer<sup>[75]</sup> and polymer<sup>[76]</sup>) of Li amides are known; however, they tend to exist only in the absence of donor solvents.

Crystalline **3** was insoluble in  $\text{C}_6\text{D}_6$ ; hence, solution studies were conducted by using  $[\text{D}_8]\text{thf}$  solutions. As alluded to earlier, isolation of **3** in vacuo resulted in loss of crystallinity of the sample.  $^1\text{H}$  NMR spectroscopy of this powder revealed that the amide/tmeda ratio was approximately 2:0.66 (based on the solid-state molecular structure it should be 2:3). This data suggests that on isolation a significant quantity of tmeda is removed, reflecting the weakness of its binding to the relatively soft potassium centre. When **3** was isolated without utilising vacuum techniques, the integration values of the  $^1\text{H}$  NMR spectrum corresponded well with the expected values from the solid-state structure. In both scenarios, the chemical shifts of the resonances as-



Scheme 1. Syntheses of **1**, **2**, and **3**.

sociated with the  $\text{NPh}_2$  ligand were identical, and the tmeda resonances corresponded to the free tmeda ligand, hence indicating the formation of a  $[\text{D}_8]\text{thf}$  solvate.

### X-ray Crystallography

The molecular structure of **1** was determined by X-ray diffraction studies and is shown in Figure 1 along with its key structural parameters. Complex **1** crystallises as a dimer whereby the molecular framework consists of a planar (sum of endocyclic angles:  $359.98^\circ$ )  $\text{Li}_2\text{N}_2$  ring. The intra-annular Li–N bond lengths show only slight variation [range: 2.137(3)–2.183(3) Å; mean distance: 2.1505 Å] emphasising the minimal distinction between the lithium–anion  $\sigma$  and the lithium–N lone-pair dative interactions. Each of the coordination spheres of the two crystallographically distinct Li centres are completed by binding to a tmeda molecule, resulting in the metal atoms adopting distorted tetrahedral geometries [sum of angles:  $661.64$  and  $659.04^\circ$  for Li(1) and Li(2), respectively]. As expected, in both cases, the greatest cause of the distortion from true tetrahedral geometry is the acute  $\text{N}_{\text{tmeda}}\text{--Li--N}_{\text{tmeda}}$  angle [ $79.08(11)$  and  $84.41(12)^\circ$  for Li(1) and Li(2), respectively]. Presumably due to the steric constraints of the dimeric molecule, the Li– $\text{N}_{\text{tmeda}}$  distances for each Li centre vary slightly (mean: 2.347 and 2.258 Å for Li(1)– $\text{N}_{\text{tmeda}}$  and Li(2)– $\text{N}_{\text{tmeda}}$ , respectively). There are several tmeda adducts of lithium secondary amides known, which adopt subtly different structural motifs (Figure 2).

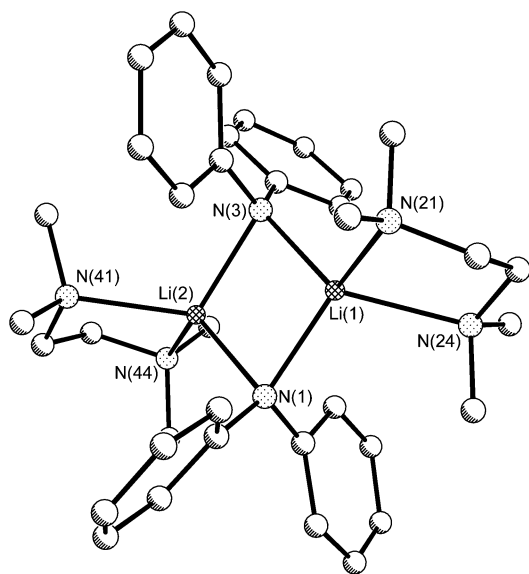


Figure 1. Molecular structure of **1** with selected atom labels. Key bond lengths [Å] and angles [ $^\circ$ ]: Li(1)–N(1) 2.137(3), Li(1)–N(3) 2.183(3), Li(1)–N(21) 2.381(3), Li(1)–N(24) 2.313(4), Li(2)–N(1) 2.142(3), Li(2)–N(3) 2.140(4), Li(2)–N(41) 2.242(4), Li(2)–N(44) 2.273(3), N(1)–Li(1)–N(3) 97.82(14); N(1)–Li(1)–N(21) 131.92(15), N(1)–Li(1)–N(24) 108.66(15), N(3)–Li(1)–N(21) 109.95(14), N(3)–Li(1)–N(24) 134.21(15), N(21)–Li(1)–N(24) 79.08(11), N(1)–Li(2)–N(3) 99.01(14), N(1)–Li(2)–N(41) 124.24(15), N(1)–Li(2)–N(44) 114.13(16), N(3)–Li(2)–N(41) 112.07(16), N(3)–Li(2)–N(44) 125.18(15), N(41)–Li(2)–N(44) 84.41(12), Li(1)–N(1)–Li(2) 82.09(13), Li(1)–N(3)–Li(2) 81.06(13).

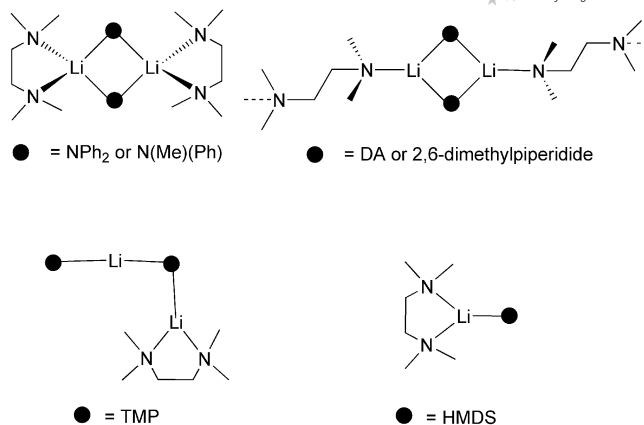


Figure 2. Structural motifs of tmeda solvates of synthetically important lithium amides.

When sterically less demanding amides [e.g.,  $\text{N(Me)(Ph)}$ ]<sup>[77]</sup> are employed, “closed” dimers (akin to **1**) are formed, where the Li centres are formally four-coordinate. By using amides of an intermediate steric bulk (e.g., da<sup>[78]</sup> or 2,6-dimethylpiperidine<sup>[79]</sup>), similar  $\text{Li}_2(\text{N}_{\text{amide}})_2$  four-membered rings are observed; however, in these instances the tmeda ligand binds in a bridging, monodentate manner (hence Li is three-coordinate), producing linear polymeric arrays. By using the sterically most demanding amides (e.g., tmp<sup>[80]</sup>) a closed dimer is not possible. Williard reported the “open” dimeric complex (Figure 2), where one Li centre is formally three-coordinate (bound to one amide group and

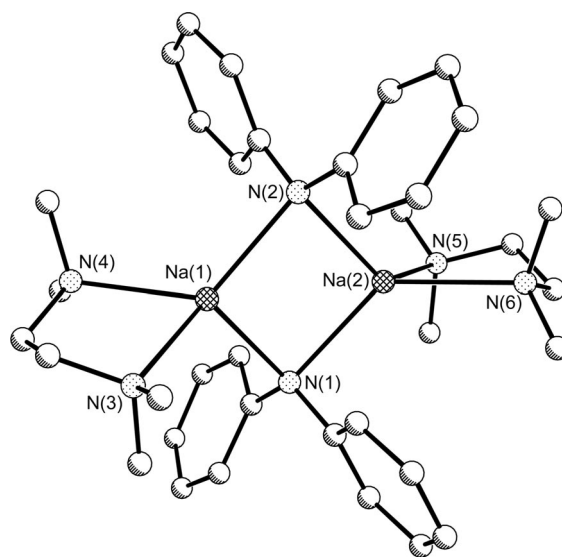


Figure 3. Molecular structure of **2** with selected atom labels. Bond lengths [Å] and angles [ $^\circ$ ]: Na(1)–N(1) 2.422(2), Na(1)–N(2) 2.436(2), Na(1)–N(3) 2.466(2), Na(1)–N(4) 2.460(2), Na(2)–N(1) 2.484(2), Na(2)–N(2) 2.466(2), Na(2)–N(5) 2.479(2), Na(2)–N(6) 2.498(2); N(1)–Na(1)–N(2) 99.43(8), N(1)–Na(1)–N(3) 106.06(8), N(1)–Na(1)–N(4) 123.92(8), N(2)–Na(1)–N(3) 127.86(8), N(2)–Na(1)–N(4) 124.35(8), N(3)–Na(1)–N(4) 75.22(8), N(1)–Na(2)–N(2) 96.96(7), N(1)–Na(2)–N(5) 104.39(8), N(1)–Na(2)–N(6) 133.17(8), N(2)–Na(2)–N(5) 128.46(8), N(2)–Na(2)–N(6) 120.95(8), N(5)–Na(2)–N(6) 74.23(8), Na(1)–N(1)–Na(2) 81.74(7), Na(1)–N(2)–Na(2) 81.81(7).

two tmeda N atoms) and the other is two-coordinate (bound only to two amide N atoms).<sup>[80]</sup> When the silylamide hmds<sup>[81]</sup> is utilised, a monomeric tmeda adduct is isolated.

The molecular structure of **2** is shown in Figure 3 along with its key structural parameters. Its dimeric structural motif is essentially identical to that of **1**, containing an Na<sub>2</sub>N<sub>2</sub> ring which is planar (sum of endocyclic angles: 359.94°). The obtuse internal angles are at the Na atoms and the acute angles are at the N atoms – a common feature in alkali metal amide ring systems. Akin to **1**, little discrimination exists between the distances of the Na–N<sub>amide</sub> bond [range of distances: 2.422(2)–2.484(2) Å; mean distance: 2.457 Å]. As expected, these are slightly shorter than the dative Na–N<sub>tmeda</sub> bonds [2.466(2) and 2.460(2) Å; mean distance: 2.463 Å]. The mean N<sub>tmeda</sub>–M–N<sub>tmeda</sub> bite angle in **2** is 74.725°, which is approximately 7° more acute than the corresponding angle in lithium-containing **1**. To the best

of our knowledge, **2** is surprisingly the first homometallic sodium complex of diphenylamide to be crystallographically characterised.

The molecular structure of centrosymmetric **3** is shown in Figure 4 along with its key bond lengths and angles. Unlike its lithium and sodium analogues, **3** adopts a linear polymeric arrangement. However, its asymmetric unit bears a close resemblance to that of **1** and **2**. It consists of a planar K<sub>2</sub>N<sub>2</sub> ring (sum of endocyclic angles: 360°); however, due to the larger size of potassium, its coordination sphere can accommodate an additional donor atom (hence each K atom is five-coordinate). Supplementary stabilisation by K⋯π-arene interactions appears minimal [shortest K⋯C separations are 3.1936(13) and 3.2407(12) Å for K(1)–C(116A) and K(1)–C(111A), respectively]. One tmeda ligand binds to the metal centre in the usual bidentate fashion, whereas the second tmeda molecule binds in a unidentate manner [K(1)–N(3)]. The K–N bond in the latter [3.2959(13) Å] is considerably longer (and by implication weaker) than that of the bidentate-coordinated ligand (mean distance: 2.922 Å). From a supramolecular perspective, a coordination polymer is constructed whereby the remaining tmeda N atom intermolecularly binds to another K atom (Figure 5). The K atoms are in a distorted square-pyramidal environment (Figure 4 and Scheme 1), where the anionic N atom and an N atom from the bidentate-coordinated tmeda occupy the pseudo-axial positions [N(1A)–K(1)–N(21) 164.66(8)°].

Only three other donor complexes of potassium diphenylamide have been crystallographically characterised, namely the solvent-separated 18-crown-6,<sup>[82]</sup> dimeric thf<sup>[61]</sup> and polymeric dioxane<sup>[62]</sup> solvates (Figure 6). Clear structural similarities exist between **3** and the aforementioned

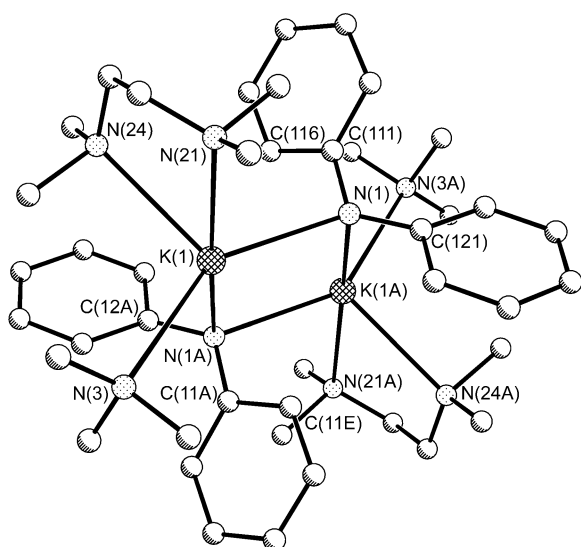


Figure 4. Molecular structure of **3** with selected atom labels. Key bond lengths [Å] and angles [°]: K(1)–N(1) 2.8094(12), K(1)–N(1A) 2.9221(11), K(1)–N(21) 2.950(5), K(1)–N(24) 2.893(4), K(1)–N(3) 3.2959(13), K(1)–C(111A) 3.2407(12), K(1)–C(116A) 3.1936(13); N(1)–K(1)–N(1A) 80.55(3), N(1)–K(1)–N(21) 89.99(7), N(1)–K(1)–N(24) 115.84(8), N(1)–K(1)–N(3) 142.92(3), N(1A)–K(1)–N(21) 164.66(8), N(1A)–K(1)–N(24) 110.10(8), N(1A)–K(1)–N(3) 104.64(3), N(21)–K(1)–N(24) 63.27(12), N(21)–K(1)–N(3) 90.20(7), N(24)–K(1)–N(3) 97.11(8), K(1)–N(1)–K(1A) 99.45(3). Symmetry transformation used to generate equivalent atoms:  $-x + 2, -y + 2, -z$ .

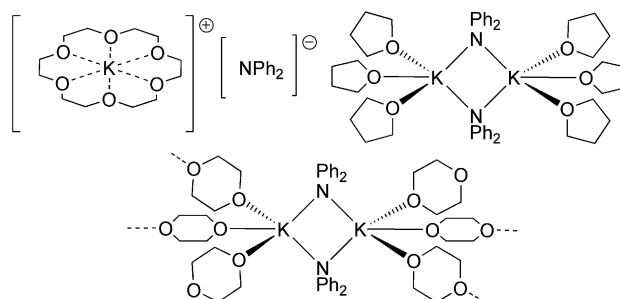


Figure 6. Solvated potassium diphenylamide complexes crystallographically characterised prior to this work.

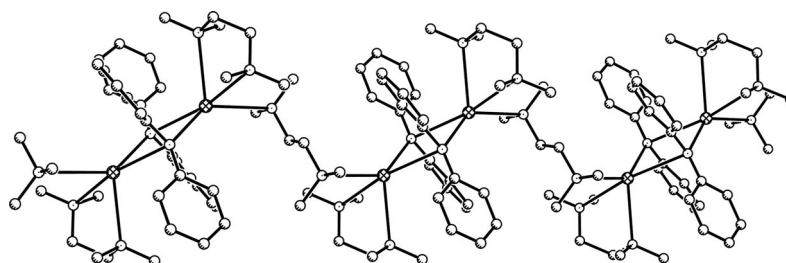


Figure 5. Extended supramolecular view of **3**.

thf and dioxane adducts. In each case, the K centres are five-coordinate (the metal atoms' coordination spheres being composed of two anionic N and three neutral donor centres). Despite the change from O- to N-based ligands, the K–N<sub>amide</sub> bond length remains similar (mean distance: 2.8255, 2.8461 and 2.8658 Å for thf adduct, dioxane adduct and **3**, respectively).

## Conclusions

Three new tmeda complexes of lithium, sodium and potassium diphenylamide have been prepared and characterised in both, solution and solid state. The sodium complex is the first structurally characterised homometallic diphenylamide complex of this particular metal. Future studies will focus on the utilisation of these homometallic reagents in the field of alkali metal magnesiate and zincate chemistry – will the expected lower basicity of diphenylamide (cf., da or tmp) be reversed by synergic mixed-metal effects?

## Experimental Section

**General:** All reactions and manipulations were carried out under dry, pure argon gas by using standard Schlenk protocols. Hexane and toluene were freshly distilled from Na/benzophenone. NMR samples were prepared under a protective gas inside a glovebox by using C<sub>6</sub>D<sub>6</sub> or [D<sub>8</sub>]thf as solvent [which was degassed by using freeze-pump-thaw cycles, and pre-dried with molecular sieves (4 Å)]; tmeda was distilled from CaH<sub>2</sub> and stored over molecular sieves (4 Å). *n*BuLi in the form of a 1.6 M solution in hexane was purchased from Aldrich Chemicals and used as received. *n*-Butyllithium,<sup>[83]</sup> and benzylpotassium<sup>[84]</sup> were prepared according to literature methods. All NMR spectra were measured with a Bruker DPX400 or AMX400 spectrometer. For the X-ray structural determinations, all data were collected with monochromated Mo-*K*<sub>α</sub> radiation ( $\lambda = 0.71073$  Å) at 123 K. Samples **1** and **3** were measured with an Oxford Diffraction Gemini S instrument, and a Nonius

Kappa CCD was used to measure sample **2**. For **3**, the tmeda ligands were found to be disordered. After several trial calculations, each was treated as split over two sites in a 80:20 ratio. All structures were refined<sup>[85]</sup> to convergence against *R*<sup>2</sup>. There was no residual electron density >0.365 e Å<sup>-3</sup>. Selected crystallographic and refinement parameters are given in Table 3. CCDC-742646, -742647, and -742648 contain the supplementary crystallographic data for this paper. These can be obtained free of charge at [www.ccdc.cam.ac.uk/contents/retrieving.html](http://www.ccdc.cam.ac.uk/contents/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

**[[tmeda]Li(NPh<sub>2</sub>)<sub>2</sub>] (**1**):** A flame-dried Schlenk tube was charged with *n*-butyllithium (1.56 mL of 1.6 M solution in hexanes, 2.5 mmol) and hexane (2 mL). Diphenylamine (0.43 g, 2.5 mmol) was then added at ambient temperature to precipitate a white solid; tmeda (0.38 mL, 2.5 mmol) and toluene (1 mL) were added to produce a completely homogeneous solution. After 24 h at ambient temperature, a crop of X-ray quality colourless crystals of **1** [0.35 g, 48% (not optimised)] precipitated from the solution. <sup>1</sup>H NMR (400.13 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 7.26$  (m, 16 H, *o*- and *m*-CH), 6.74 (m, 4 H, *p*-CH), 1.75 (s, 8 H, CH<sub>2</sub>), 1.72 (s, 24 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100.62 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 158.1$  (*i*-C), 130.1 (*m*-C), 120.5 (*o*-C), 116.5 (*p*-C), 57.1 (CH<sub>2</sub>), 45.7 (CH<sub>3</sub>) ppm. <sup>7</sup>Li NMR (155.47 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.88$  ppm.

**[[tmeda]Na(NPh<sub>2</sub>)<sub>2</sub>] (**2**):** A flame-dried Schlenk tube was charged with *n*-butyllithium (0.20 g, 2.5 mmol) in a glovebox, after which hexane (5 mL) was added. Diphenylamine (0.43 g, 2.5 mmol) was then added at ambient temperature to precipitate a large quantity of white solid; tmeda (0.38 mL, 2.5 mmol) and toluene (3 mL) were added to produce a completely homogeneous solution. After 1 h at ambient temperature, a crop of X-ray quality colourless crystals of **2** [0.28 g, 36% (not optimised)] precipitated from the solution. <sup>1</sup>H NMR (400.13 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 7.27$  (m, 16 H, *o*- and *m*-CH), 6.69 (m, 4 H, *p*-CH), 1.68 (s, 24 H, CH<sub>3</sub>), 1.54 (s, 8 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (100.62 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 158.8$  (*i*-C), 130.2 (*m*-C), 118.7 (*o*-C), 114.7 (*p*-C), 56.8 (CH<sub>2</sub>), 45.1 (CH<sub>3</sub>) ppm.

**[[tmeda]<sub>3</sub>K(NPh<sub>2</sub>)<sub>2</sub>] (**3**):** A flame-dried Schlenk tube was charged with benzylpotassium (0.33 g, 2.5 mmol) in a glovebox, after which hexane (5 mL) was added. Diphenylamine (0.43 g, 2.5 mmol) was then added to the red suspension at ambient temperature. A red to pink colour change was observed along with the precipitation of a large quantity of white solid; tmeda (1.51 mL, 10 mmol) was added to produce a completely homogeneous solution. After 48 h at –28 °C, a crop of X-ray quality colourless crystals of **3** [0.36 g, 47% (not optimised)] precipitated from the solution. By using standard Schlenk in vacuo isolation techniques, **3** visibly lost crystallinity, and NMR spectral analysis showed a diminished tmeda/NPh<sub>2</sub> ratio with respect to the solid-state structure. Isolation of **3** without the use of vacuum techniques resulted in the expected tmeda/NPh<sub>2</sub> (3:2) ratio. <sup>1</sup>H NMR (400.13 MHz, 300 K, [D<sub>8</sub>]thf):  $\delta = 6.84$  (m, 16 H, *o*- and *m*-CH), 6.14 (m, 4 H, *p*-CH), 2.30 (s, 12 H, CH<sub>2</sub>), 2.15 (s, 36 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100.62 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>):  $\delta = 158.1$  (*i*-C), 129.7 (*m*-C), 118.2 (*o*-C), 112.6 (*p*-C), 59.3 (CH<sub>2</sub>), 46.3 (CH<sub>3</sub>) ppm.

**Supporting Information** (see footnote on the first page of this article): NMR spectra for **1**–**3**.

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Table 3. Selected crystallographic and refinement parameters.

|                                                 | <b>1</b>                                                       | <b>2</b>                                                       | <b>3</b>                                                      |
|-------------------------------------------------|----------------------------------------------------------------|----------------------------------------------------------------|---------------------------------------------------------------|
| Empirical formula                               | C <sub>36</sub> H <sub>52</sub> Li <sub>2</sub> N <sub>6</sub> | C <sub>36</sub> H <sub>52</sub> Na <sub>2</sub> N <sub>6</sub> | C <sub>42</sub> H <sub>68</sub> K <sub>2</sub> N <sub>8</sub> |
| Formula mass                                    | 582.72                                                         | 614.82                                                         | 763.24                                                        |
| Crystal system                                  | monoclinic                                                     | monoclinic                                                     | triclinic                                                     |
| Space group                                     | <i>P</i> 2 <sub>1</sub> / <i>n</i>                             | <i>P</i> 2 <sub>1</sub> / <i>n</i>                             | <i>P</i> 1                                                    |
| <i>a</i> [Å]                                    | 10.894(3)                                                      | 9.4833(2)                                                      | 10.9581(11)                                                   |
| <i>b</i> [Å]                                    | 18.465(4)                                                      | 19.8108(5)                                                     | 11.2224(9)                                                    |
| <i>c</i> [Å]                                    | 17.264(4)                                                      | 19.6247(6)                                                     | 11.7229(13)                                                   |
| $\alpha$ [°]                                    | 90                                                             | 90                                                             | 63.275(10)                                                    |
| $\beta$ [°]                                     | 91.174(19)                                                     | 103.849(1)                                                     | 66.062(10)                                                    |
| $\gamma$ [°]                                    | 90                                                             | 90                                                             | 62.674(9)                                                     |
| <i>V</i> [Å <sup>3</sup> ]                      | 3471.9(14)                                                     | 3579.75(16)                                                    | 1107.27(19)                                                   |
| <i>Z</i>                                        | 4                                                              | 4                                                              | 1                                                             |
| Max. $2\theta$ [°]                              | 54.0                                                           | 48.0                                                           | 56.0                                                          |
| Refls. collected                                | 21818                                                          | 31758                                                          | 16157                                                         |
| Refls. unique                                   | 7551                                                           | 5555                                                           | 5330                                                          |
| Refls. obsd.                                    | 4889                                                           | 3637                                                           | 4476                                                          |
| <i>R</i> <sub>int</sub>                         | 0.0968                                                         | 0.105                                                          | 0.0245                                                        |
| Goodness of fit                                 | 1.035                                                          | 1.060                                                          | 1.106                                                         |
| <i>R</i> [ <i>I</i> > 2σ( <i>I</i> )], <i>F</i> | 0.0600                                                         | 0.0538                                                         | 0.0352                                                        |
| <i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> ) | 0.1814                                                         | 0.1144                                                         | 0.0929                                                        |

- [1] M. F. Lappert, A. V. Protchenko, P. P. Power, A. Seeber, *Metal Amide Chemistry*, John Wiley & Sons, Chichester, **2009**.
- [2] J. K. Crandall, M. Apparu, *Org. React.* **1983**, 29, 345.
- [3] P. O'Brien, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1439.
- [4] T. Satoh, *Chem. Rev.* **1996**, 96, 3303.
- [5] C. H. Heathcock in *Comprehensive Organic Synthesis*, vol. 2 (Eds.: B. M. Trost, I. Fleming), Pergamon, New York, **1991**, chapter 1.6.
- [6] M. E. Jung, T.-H. Zhang, *Org. Lett.* **2008**, 10, 137.
- [7] X.-X. Yan, C.-G. Liang, Y. Zhang, W. Hong, B.-X. Cao, L.-X. Dai, X. L. Hou, *Angew. Chem. Int. Ed.* **2005**, 44, 6544.
- [8] L. Xie, K. Vanlandeghem, K. M. Isenberger, C. Bernier, *J. Org. Chem.* **2003**, 68, 641.
- [9] L. Xie, K. M. Isenberger, G. Held, L. M. Dahl, *J. Org. Chem.* **1997**, 62, 7516.
- [10] T. Abe, C. Sato, H. Ushirogouchi, K. Sato, T. Takasaki, T. Isoda, A. Mihira, I. Yamamura, K. Hayashi, T. Kumagai, S. Tamai, M. Shiro, A. M. Venkatesan, T. S. Mansour, *J. Org. Chem.* **2004**, 69, 5820.
- [11] H. Fujisawa, T. Mukaiyama, *Chem. Lett.* **2002**, 182.
- [12] T. Mukaiyama, H. Fujisawa, T. Nakagawa, *Helv. Chim. Acta* **2002**, 85, 4518.
- [13] T. Satoh, T. Kawashima, S. Takahashi, K. Sakai, *Tetrahedron* **2003**, 14, 9599.
- [14] T. Satoh, M. Yoshida, Y. Takahashi, H. Ota, *Tetrahedron: Asymmetry* **2003**, 14, 281.
- [15] Z. J. Tonzetich, Y. C. Lam, P. Müller, R. R. Schrock, *Organometallics* **2007**, 26, 475.
- [16] M. A. Antunes, M. Dias, B. Monteiro, Â. Domingos, I. C. Santos, N. Marques, *Dalton Trans.* **2006**, 3368.
- [17] M. Silva, M. Augusta Antunes, M. Dias, Â. Domingos, I. Cordeiro dos Santos, J. Marçalo, N. Marques, *Dalton Trans.* **2005**, 3353.
- [18] A. Sinha, R. R. Schrock, P. Müller, A. H. Hoveyda, *Organometallics* **2006**, 25, 4621.
- [19] Y. Yao, Y. Zhang, Q. Shen, K. Yu, *Organometallics* **2002**, 21, 819.
- [20] M. Xue, Y. Yao, Q. Shen, Y. Zhang, *J. Organomet. Chem.* **2005**, 690, 4685.
- [21] A. Friedrich, U. Radius, *Eur. J. Inorg. Chem.* **2004**, 4300.
- [22] F. Amor, J. Sánchez-Nieves, P. Royo, H. Jacobsen, O. Blaque, H. Berke, M. Lanfranchi, M. A. Pellinghelli, A. Tiripicchio, *Eur. J. Inorg. Chem.* **2002**, 2810.
- [23] G. Mund, D. Vidovic, R. J. Batchelor, J. F. Britten, R. D. Sharma, C. H. W. Jones, D. B. Leznoff, *Chem. Eur. J.* **2003**, 9, 4757.
- [24] T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2004**, 126, 6252.
- [25] H. Link, P. Reiss, S. Chitsaz, H. Pfister, D. Fenske, *Z. Anorg. Allg. Chem.* **2003**, 629, 755.
- [26] F. Preuss, M. Vogel, U. Fischbeck, J. Perner, G. Overhoff, E. Fuchslocher, F. Tabellion, B. Geiger, G. Wolmershäuser, *Z. Naturforsch., Teil B* **2001**, 56, 1100.
- [27] Z. Gebeyehu, F. Weller, B. Neumuller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1991**, 593, 99.
- [28] S. Conejero, Y. Canac, F. S. Tham, G. Bertrand, *Angew. Chem. Int. Ed.* **2004**, 43, 4089.
- [29] E. Ihara, T. Todaka, K. Inoue, *J. Polym. Sci., Part A* **2004**, 42, 31.
- [30] D. Mootz, A. Zinnius, B. Böttcher, *Angew. Chem. Int. Ed. Engl.* **1969**, 8, 378.
- [31] R. D. Rodgers, J. L. Atwood, R. Grüning, *J. Organomet. Chem.* **1978**, 157, 229.
- [32] J. S. DePue, D. B. Collum, *J. Am. Chem. Soc.* **1988**, 110, 5518.
- [33] J. S. DePue, D. B. Collum, *J. Am. Chem. Soc.* **1988**, 110, 5524.
- [34] J. Guan, S. Jin, Y. Lin, Q. Shen, *Organometallics* **1992**, 11, 2483.
- [35] H. Hope, M. M. Olmstead, B. D. Murray, P. P. Power, *J. Am. Chem. Soc.* **1985**, 107, 712.
- [36] J.-I. Song, S. Gambarotta, *Chem. Eur. J.* **1996**, 2, 1258.
- [37] M. Tayebani, S. Gambarotta, G. Yap, *Organometallics* **1998**, 17, 3639.
- [38] Y. Yao, X. Lu, Q. Shen, K. Yu, *J. Chem. Crystallogr.* **2004**, 34, 275.
- [39] J. Guan, Q. Shen, S. Jin, Y. Lin, *Polyhedron* **1994**, 13, 1695.
- [40] L. Mao, Q. Shen, S. Jin, *Polyhedron* **1994**, 13, 1023.
- [41] L. Mao, Q. Shen, Y.-H. Lin, *Chin. J. Org. Chem.* **1994**, 14, 215.
- [42] H. Schumann, E. Palamidis, J. Loebel, *J. Organomet. Chem.* **1990**, 390, 45.
- [43] M. L. Sheng, S. Qi, L. Y. Hua, *Chin. J. Struct. Chem.* **1998**, 17, 65.
- [44] W.-K. Wong, L. Zhang, F. Xue, T. C. W. Mak, *Polyhedron* **1997**, 16, 345.
- [45] W.-K. Wong, L. Zhang, F. Xue, T. C. W. Mak, *Polyhedron* **1997**, 16, 2013.
- [46] J. G. Reynolds, A. Zalkin, D. H. Templeton, N. M. Edelstein, *Inorg. Chem.* **1977**, 16, 1090.
- [47] J. Kim, S. G. Bott, D. M. Hoffman, *Inorg. Chem.* **1998**, 37, 3835.
- [48] J. Pauls, B. Neumuller, *Inorg. Chem.* **2001**, 40, 121.
- [49] R. K. Minhas, Y. Ma, J.-I. Song, S. Gambarotta, *Inorg. Chem.* **1996**, 35, 1866.
- [50] M. Karl, A. Dashti-Mommertz, B. Neumuller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1998**, 624, 355.
- [51] M. Karl, K. Harms, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1999**, 625, 1774.
- [52] Y. Wang, Q. Shen, F. Xue, K. Yu, *Organometallics* **2000**, 19, 357.
- [53] M. T. Garner, P. W. Roesky, *Inorg. Chem.* **2005**, 44, 5963.
- [54] P. Reiss, D. Fenske, *Z. Anorg. Allg. Chem.* **2000**, 626, 1317.
- [55] W. Clegg, A. J. Edwards, F. S. Mair, P. M. Nolan, *Chem. Commun.* **1998**, 23.
- [56] R. P. Davies, P. R. Raithby, R. Snaith, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 1215.
- [57] B. Gemund, H. Nöth, H. Sachdev, M. Schmidt, *Chem. Ber.* **1996**, 129, 1335.
- [58] U. Braun, T. Haberer, H. Nöth, J. Piotrowski, M. Warchold, *Eur. J. Inorg. Chem.* **2002**, 1132.
- [59] R. A. Bartlett, H. V. R. Dias, H. Hope, B. D. Murray, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1986**, 108, 6921.
- [60] F. Becke, F. W. Heinemann, T. Ruffer, P. Wiegeleben, R. Boese, D. Blaaser, D. Steinborn, *J. Organomet. Chem.* **1997**, 548, 205.
- [61] M. Gärtner, H. Görls, M. Westerhausen, *Acta Crystallogr., Sect. E* **2007**, 63, m2289.
- [62] M. Gärtner, H. Görls, M. Westerhausen, *Acta Crystallogr., Sect. E* **2007**, 63, m2287.
- [63] R. E. Mulvey, *Acc. Chem. Res.* **2009**, 42, 743.
- [64] R. E. Mulvey, *Organometallics* **2006**, 25, 1060.
- [65] R. E. Mulvey, F. Mongin, M. Uchiyama, Y. Kondo, *Angew. Chem. Int. Ed.* **2007**, 46, 3802.
- [66] D. R. Armstrong, D. V. Graham, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, *Chem. Eur. J.* **2008**, 14, 8025.
- [67] E. R. Hurley, X. He, S. N. Brown, K. W. Henderson, *J. Am. Chem. Soc.* **2009**, 131, 6056.
- [68] R. D. Rogers, J. L. Atwood, R. Grüning, *J. Organomet. Chem.* **1978**, 157, 229.
- [69] D. Barr, W. Clegg, R. E. Mulvey, R. Snaith, *J. Chem. Soc., Chem. Commun.* **1984**, 285.
- [70] D. R. Armstrong, D. R. Baker, F. J. Craig, R. E. Mulvey, W. Clegg, L. Horsburgh, *Polyhedron* **1996**, 15, 3533.
- [71] D. R. Armstrong, K. W. Henderson, A. R. Kennedy, W. J. Kerr, F. S. Mair, J. H. Moir, P. H. Moran, R. Snaith, *J. Chem. Soc., Dalton Trans.* **1999**, 4063.
- [72] B. Wrackmeyer, B. Schwarze, J. Weidinger, W. Milius, *Z. Naturforsch., Teil B* **1992**, 52, 431.
- [73] M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers, R. Shakir, *J. Am. Chem. Soc.* **1983**, 105, 302.
- [74] J. Jubbs, P. Berno, S. Hao, *Inorg. Chem.* **1995**, 34, 3563.

- [75] R. Snaith, D. Barr, D. S. Wright, W. Clegg, S. M. Hodgson, G. R. Lamming, A. J. Scott, R. E. Mulvey, *Angew. Chem. Int. Ed. Engl.* **1989**, 28, 1241.
- [76] N. D. R. Barnett, R. E. Mulvey, W. Clegg, P. A. O'Neil, *J. Am. Chem. Soc.* **1991**, 113, 8187.
- [77] D. Barr, W. Clegg, R. E. Mulvey, R. Snaith, D. S. Wright, *J. Chem. Soc., Chem. Commun.* **1987**, 716.
- [78] M. P. Bernstein, F. E. Romesberg, D. J. Fuller, A. T. Harrison, D. B. Collum, Q.-Y. Liu, P. G. Williard, *J. Am. Chem. Soc.* **1992**, 114, 5100.
- [79] W. Clegg, L. Horsburgh, S. A. Couper, R. E. Mulvey, *Acta Crystallogr., Sect. C* **1999**, 55, 867.
- [80] P. G. Williard, Q.-Y. Liu, *J. Am. Chem. Soc.* **1993**, 115, 3380.
- [81] K. W. Henderson, A. E. Dorigo, Q.-L. Liu, P. G. Williard, *J. Am. Chem. Soc.* **1997**, 119, 11855.
- [82] P. B. Hitchcock, A. V. Khvostov, M. F. Lappert, A. V. Protchenko, *J. Organomet. Chem.* **2002**, 647, 198.
- [83] C. Schade, W. Bauer, P. v. R. Schleyer, *J. Organomet. Chem.* **1985**, 295, C25.
- [84] D. M. Hoffman, W. Bauer, F. Hampel, N. J. R. van Eikema Hommes, P. v. R. Schleyer, P. Otto, U. Pieper, D. Stalke, D. S. Wright, R. Snaith, *J. Am. Chem. Soc.* **1994**, 116, 528.
- [85] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, 64, A112.

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