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Crystal structure of a heavier alkali metal diisopropylamide complex: a discrete $(KN)_2$ ring dimer with TMEDA chelation and short intramolecular K···H(C) contacts

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Abstract

Synthesized by treating diisopropylamine with a potassium reagent (the solid isolated from a 1:1 reaction mixture of potassium *t*-butoxide and *n*-butyllithium) in the presence of N,N,N′,N′-tetramethylenediamine (TMEDA), the potassium diisopropylamide complex $[(^iPr_2NK.\ TMEDA)_2]$ has been subjected to a low temperature X-ray diffraction study. This reveals a discrete dimeric arrangement centred on an asymmetrical $(KN)_2$ cyclic ring, with bond lengths of 2.706(2) and 2.837(2) Å and endocyclic bond angles of 100.54(5) and 79.46(5)° (at K and N, respectively). Terminal, chelating TMEDA ligands complete the distorted tetrahedral N_4 primary coordination sphere about the K^+ cations. However, there are several secondary intramolecular K···H(C) contacts involving methyl fragments of the diisopropylamido ligands. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Amide; Crystal structure; Intramolecular bonding; Potassium

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1. Introduction

The diisopropylamido ($^iPr_2N^-$) ligand has a special significance in alkali metal chemistry as lithium diisopropylamide (LDA) is one of the most widely utilized deprotonating agents in modern chemistry. In its pure solvent-free state, solid LDA exists as a single-strand helical polymer composed of near-linear N–Li–N segments [1]. Two simple LDA solvates have also been crystallographically characterized. The degree of aggregation in both is two, taking the form of four-membered $(NLi)_2$ rings, which exist discretely in the 1:1 solvate $[(^iPr_2NLi.THF)_2]$ [2], but link together in an infinite chain in the hemi-solvate $[\{(^iPr_2NLi)_2.TMEDA\}_\infty]$ [3] (THF = tetrahydrofuran; TMEDA = N,N,N′,N′-tetramethylethylenediamine). Other LDA molecules have also been characterized in the solid state as component parts of mixed-anion species. In this category is the solvent-free lithium ketone enolate $[\{^tBuSi(Me)_2OCH_2CH_2C(Me)_2C(=CH_2)OLi\}_2(^iPr_2\ NLi)_2]$ [4], in which the silyl ether oxygen acts as an internal donor atom; there are also two TMEDA-solvated examples in the chloride $[LiCl(^iPr_2NLi)_2.\ (TMEDA)_2]$ [5] and the nitrile $[PhC(H)CNLi(^iPr_2NLi).\ (TMEDA)_2]$ [6]. There is considerably less structural information available on diisopropylamido derivatives of the heavier alkali metals. No structures are known for any of the pure, solvent-free compounds. Moreover, only one crystalline solvate has been structurally elucidated hitherto: the TMEDA-solvated sodium dimer, $[(^iPr_2NNa.\ TMEDA)_2]$ [7]. In this discrete $(NNa)_2$ ring structure, the distorted tetrahedral environment of the Na^+ cation is completed by the didentate coordination of a TMEDA molecule. This paucity of structural information reflects in part the lower stability of the heavier alkali metal organoamides (and organic derivatives generally) compared with their lithium counterparts. How-

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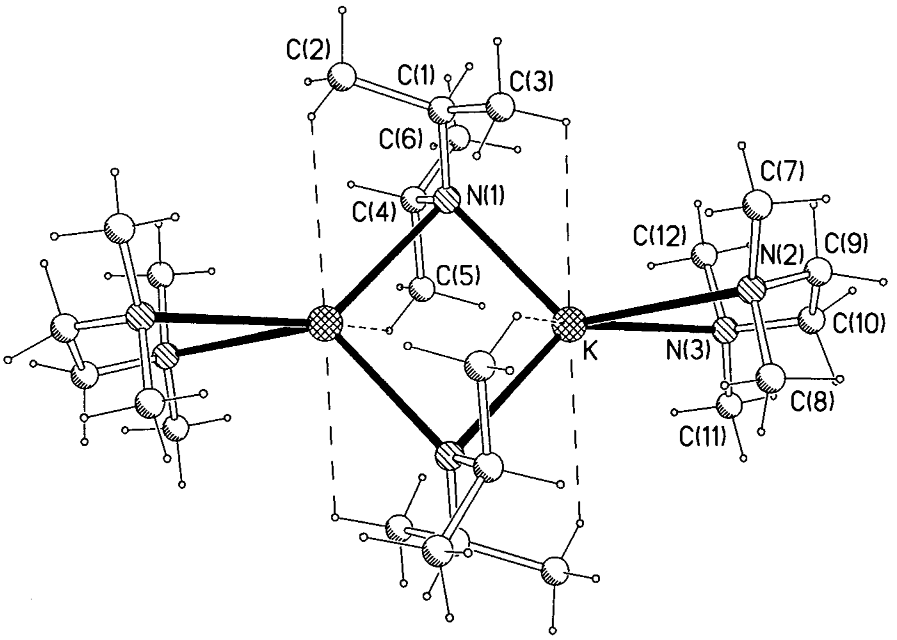

Fig. 1. Molecular structure of **1** showing atom labelling scheme. Short, intramolecular K···H(C) contacts are depicted by broken bonds.

ver, the number of crystal structures in this area is expected to rise significantly in the near future as oil drop mounting techniques for handling metastable crystals at low temperature are now well established [8]. We took advantage of this technique in the present study, which reports the first crystal structure of a potassium diisopropylamide complex, $[({}^{i}Pr_2NK.TMEDA)_2]$, **1**, the data for which were collected at 160 K. The basic dimeric skeleton of the structure bears a close resemblance to the sodium analogue described above, but the orientations of the Me (^{i}Pr) groups differ from those in the sodium dimer, and are such that they facilitate several short K···H(C) contacts.

2. Results and discussion

We first synthesized **1** as a colourless, crystalline solid about five years ago, but at that time a proper characterization could not be carried out as it decomposes to a black amorphous state in a matter of hours following isolation from solution. The crystals are easily obtained by metallating diisopropylamine with freshly prepared potassium reagent (from the action of *n*-butyllithium on potassium *t*-butoxide in a 1:1 molar ratio [9]) in cold hexane, then adding sufficient TMEDA to obtain a dark, but homogeneous solution, before finally cooling to about 0°C. To avoid the aforementioned decomposition during the X-ray analysis, crystals of **1** were selected directly from the reaction solution, coated in an inert protective oil, and promptly mounted on the area-detector diffractometer, with which data were collected overnight.

Fig. 1 shows the molecular structure of **1**, while Table 1 lists selected bond lengths and bond angles. A centrosymmetric dimer, its salient feature is a planar $(KN)_2$ ring made possible by the μ_2-bonding of the diisopropylamido anions. Two additional N atoms from the TMEDA molecule contribute to the N_4 distorted tetrahedron surrounding the K^+ cation. Overall, however, the cation occupies a higher coordination environment as there are also three short intramolecular K···H(C) contacts present.

Bonding within the rhomboidal $(KN)_2$ ring is asymmetric with one edge [K(1)–N(1)] 0.131 Å shorter than the other. The asymmetry is also apparent in the endocyclic bond angles: the K corners are 21.1° wider than the N corners. This feature is not characteristic of amide $(KN)_2$ ring dimers in general. Providing the best comparison with **1**, the structure of the solvent-free amide $[\{(Me_3Si)_2NK\}_2]$ [10] displays a more nearly square ring [K–N bond lengths, 2.770(3) and 2.803(3) Å; bond angles at N, 85.53(9)°, at K, 94.47(9)°]. Two

Table 1
Selected bond lengths (Å) and angles (°) for **1**

K–N(1)	2.706(2)	K–N(1′)	2.837(2)
K–N(3)	2.878(2)	K–N(2)	2.894(2)
N(1)–K–N(1′)	100.54(5)	N(1)–K–N(3)	114.36(7)
N(1′)–K–N(3)	137.66(7)	N(1)–K–N(2)	127.05(7)
N(1′)–K–N(2)	114.21(6)	N(3)–K–N(2)	62.56(8)
C(1)–N(1)–C(4)	113.27(19)	C(1)–N(1)–K	118.26(14)
C(4)–N(1)–K	124.37(15)	C(1)–N(1)–K′	108.16(14)
C(4)–N(1)–K′	103.55(13)	K–N(1)–K′	79.46(5)

Symmetry transformation used to generate primed atoms: $-x$, $-y+2$, $-z$.

other examples, the anilinopyridine [{Ph(2-Pyr)NK. TMEDA}$_2$] [11], and the silylamide [{[^{t}Bu$_2$(F)Si]N-(^{t}Bu)K. (THF)$_2$}$_2$] [12], each have almost equivalent lengths for their distinct K–(amido)N bonds [i.e. 2.805(2)/2.805(3) and 2.958(5)/2.961(5) Å, respectively]. Furthermore, there is little variation in the lengths of the corresponding Na–N bonds in [(^{i}Pr$_2$NNa. TMEDA)$_2$] [range, 2.441(2)–2.453(2) Å], which, on average, are 0.324 Å shorter than their K counterparts in **1** in keeping with the smaller radius of Na. In this sodium dimer the geminal ^{i}Pr groups on the μ-N atom adopt essentially equivalent orientations on either side of the central (NaN)$_2$ ring. Herein lies the major difference with the structure of **1**, as its geminal ^{i}Pr groups take up distinct orientations such that two H atoms on one group (H2C on C2, H3C on C3) but only one H atom on the other (H5C on C5) interact with the K$^+$ cation. These K···H(C) contacts are depicted as dashed lines in the view of the structure (Fig. 1). Significantly shorter than the sum of the van der Waals radius for hydrogen and the covalent radius of K (3.1 Å), the distances involved are 2.895, 2.952, and 2.816 Å, respectively [for these calculations, the H atoms have been moved outward along the C–H bonds from the 0.98 Å appropriate to X-ray diffraction, to 1.08 Å]. All other K···H distances in **1** are greater than 3.1 Å. This includes the three H atoms on C6, none of which interact with the alkali metal cation. It is presumably this asymmetrical bridging of the geminal ^{i}Pr groups which exacerbates the asymmetry in the (KN)$_2$ ring bonding. The structure of [{(Me$_3$Si)$_2$NK}$_2$] alluded to earlier also exhibits short K···H(C) contacts (lengths, 2.96 and 3.16 Å) to compensate for the extremely low formal coordination number of the metal (i.e. 2, to N atoms), but significantly these contacts are more symmetrical involving one H$_3$(C) unit from each Me$_3$Si constituent; hence, the reason for the more nearly square (KN)$_2$ ring. In this silylamide structure the K···C contacts (shortest, 3.34 and 3.47 Å) were also deemed to be important since the sum of the van der Waals radius of CH$_3$ and the covalent radius of K is significantly longer (3.94 Å). The shortest K(1)···C contacts in **1** (ignoring the TMEDA ligand) involve C(3) at 3.389 Å [complementing the short K···H(3C) distance] and C4′ at 3.471 Å (the one attached hydrogen atom of which does not lie close to the metal centre but is 3.358 Å away). On the other hand, the two other C(H) units involved in short K···H contacts have decidedly longer K···C separation distances, i.e. K···C2′, 3.557 Å, K···C5′, 3.583 Å. Clearly it would be wrong to divorce the carbon atoms from their hydrogen partners (and vice versa) when considering the possible interaction of a C–H unit with a highly electropositive s-block metal such as potassium. Some contacts are a necessary geometrical consequence of others, and thus metal coordination numbers are not always well-defined in such structures. These K···H(C) contacts are best regarded as two-component interactions. First, the more covalent contribution would be envisaged as a donor-acceptor interaction between a two-electron bond (i.e. the C–H bond) and an electron-deficient metal centre. The second component would be purely electrostatic in nature involving the attraction of a (C–H)$^-$ unit and K$^+$, though it should be recognized that this metal is much ‘softer’ and therefore less charge localizing that the smaller Li cation. Obviously, the degree of charge localized on the C–H unit will depend on the overall chemical environment, and it should be remembered that either one or both of these atoms could actually carry a positive charge. This concept of pseudo-agostic interactions as distinct from the clear-cut agostic interactions found in transition metal systems [13] has recently been discussed with reference to a series of alkali metal hypersilanides [14].

There is nothing remarkable about the K-TMEDA chelation in **1**: the mean K–N bond length is 2.886 Å, and the N–K–N ‘bite’ angle is 62.56(8)°. This compares with corresponding values of 2.866 Å and 64.4(1)° in the anilinopyridine [{Ph(2-Pyr)NK. TMEDA}$_2$]. It is worth mentioning that the K$^+$ cations in this latter structure are also each coordinated by two pyridyl-N internal donor atoms [at distances of 2.841(2) and 2.877(3) Å], making them overall six-coordinate. The presence of these additional coordinations (not possible in **1**) provides perhaps the best qualitative guide to the importance of the K···H(C) interactions in **1**, as otherwise the K centres in both structures have approximately equivalent coordination spheres (i.e. made up of two K-amido and two K-TMEDA bonds) of similar dimensions. Thus, in effect, the K···H(C) interactions in **1** mimic the stabilizing role of the K-(pyridyl) dative bonds in the other structure.

3. Experimental

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. A ^{1}H NMR spectrum was recorded on a Bruker AMX400 MHz spectrometer in deuteropyridine solution at 25°C. Elemental analyses were determined on a Perkin–Elmer 2400 elemental analyser; potassium analysis was performed by atomic absorption on a PU 9100 Philips spectrometer.

3.1. Synthesis of **1**

Freshly prepared ‘*n*-butylpotassium’ [9] was suspended in hexane solvent and stirred for 10 min in an ultrasonic bath. The suspension was surrounded by liquid nitrogen coolant at which stage diisopropylamine (10 mmol) was added. After allowing the mixture to warm up to room temperature, an excess of TMEDA (40 mmol) was introduced. Subsequently, the mixture was stirred for 4 h and then filtered through Celite to remove fine solids (trace). Cooling the filtrate in a refrigerator at about −5°C for 48 h produced a large crop of colourless crystals of **1** (yield of first batch, 58%); m.p. 94–96°C; ^{1}H NMR: δ 1.01 (d, 12H, CH(CH_3)$_2$), 2.17 (s,12H, CH$_3$-TMEDA), 2.39 (s, 4H, CH$_2$-TMEDA), 2.86 (septet, 2H, CH (CH$_3$)$_2$). Anal. Calcd. for $C_{12}H_{30}KN_3$: C, 56.5, H, 11.8, K, 15.3, N, 16.5. Found: C, 55.8, H, 11.4, K, 15.6, N, 15.9%.

3.2. Crystal structure determination

Crystal data for **1**; $C_{24}H_{60}K_2N_6$, $M = 511.0$, monoclinic, space group $P2_1/n$, $a = 8.5421(12)$, $b = 19.247(3)$, $c = 10.7848(15)$ Å, $\beta = 109.357(3)°$, $V = 1672.9(4)$ Å^3, $Z = 2$, $D_c = 1.014$ g cm^{-3}, $\mu = 0.30$ mm^{-1} for MoKα radiation ($\lambda = 0.71073$ Å), $F(000) = 568$, $T = 160$ K. Unit cell parameters were refined from all strong reflections in the complete data set, which was collected by several series of 0.3° ω-rotation frames on a Siemens SMART CCD diffractometer; 2θ max = 56.7°, 10361 reflections measured, 3853 unique, $R_{int} = 0.0327$; crystal size $0.34 \times 0.30 \times 0.16$ mm, no absorption correction [15].

The structure was determined by direct methods [16] and refined on F^2 values for all measured data, with weighting $w^{-1} = \sigma^2(F_o^2) + (0.0653P)^2 + 0.6267P$, where $P = (F_o^2 + 2F_c^2)/3$. Isotropic hydrogen atoms were constrained with a riding model, other atoms were refined with anisotropic displacement parameters. An isotropic extinction parameter x was refined to 0.0052(18), whereby F_c is multiplied by $(1 + 0.001xF_c^2\lambda^3/\sin 2\theta)^{-1/4}$. For all reflections, $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2} = 0.1481$, conventional $R = 0.0550$ on F values of 2579 reflections having $F_o^2 > 2\sigma(F_o^2)$, goodness of fit = 1.049 for all F^2 values and 153 refined parameters. Final difference map extremes were +0.61 and −0.48 eÅ^{-3}.

Atomic coordinates, displacement parameters, and complete bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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