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π(Arene) versus donor ligand complexation in the formation of the heterobimetallic lithium–potassium dianion of (S)-N-(α-methylbenzyl)allylamine

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Abstract

Reaction of the chiral amine (S)-N-(α-methylbenzyl)allylamine with n-BuLi in hexane and the subsequent addition of the thus formed lithium amide to n-BuK followed by thf results in the formation and crystallisation of the cyclic heterobimetallic tetramer, $\{[(S)\text{-}\alpha\text{-}(PhC(H)Me)(CH_2CH{=}CHK)N]Li \cdot (thf)\}_4$ (**1**), containing the C-metallated and N-metallated dianion of the chiral amine. The structure reveals a degree of asymmetry derived from competitive binding of K^+ cations to available thf molecules, π(arene) electrons, and deprotonated allylamine moieties. Solution studies indicate very strong agostic interactions with C–H bonds in the allylamine group and retention of the terminal vinylic anion rather than delocalisation.
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Keywords: Lithium; Potassium; Hetrobimetallic; Amide; Chiral; Structure

1. Introduction

Heterobimetallic complexes containing alkali metals can behave with unusual reactivity and selectivity when used either for deprotonation or as ligand transfer agents when compared with that of their independant component parts [1]. Traditional 'superbase' mixtures which are normally composed of two different anions, a carbanion in conjunction with either an alkoxide or amide, and two different metals, normally Li and K, have established themselves as invaluable reagents in reactions requiring electrophilic substitution at positions normally inaccesible due to low relative acidity of the proton at the target site [2]. 'Ate' complexes, such as lithium aluminates and cuprates, are also indespensible in both stereo- and regio-selective synthesis and in asymmetric catalysis [3]. In recent years Mulvey

and coworkers have described the structural chemistry of a family of 'inverse crown' complexes derived from heterobimetallic amides and have demonstrated some remarkable reactivity and selectivity of these complexes towards aromatic substrates arising from a 'synergistic' relationship between the metals themselves, and with the accompanying anions [4]. In all of these areas the characterisation of the heterometallic complexes in the solid state and in solution is key to understanding and expanding our knowledge of their exceptional behaviour. However, there is still a significant paucity of such information across all three areas. In considering the synthetic and structural information that has been accumulated we know that in each of these compound types each metal cation is introduced into the system with an accompanying anionic partner both of which then participate in aggregate formation or in the case of many 'ate' complexes into separated ion pairs.

Recent research in our group has focussed on examining the unusual structures and anion rearrangements

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which can occur when synthesising homochiral alkali metal amides from simple commonly used chiral amines, and as part of this we recently published crystal structures of dilithiated (*S*)-*N*-(α-methylbenzyl)allylamide and the analogous heterobimetallic lithium–sodium structure [5]. The dilithiated complexes were originally described by Yus and co-workers [6] in reactions where electrophilic substitution was targeted at the terminal vinylic carbon resulting in new chiral amines. Our studies confirmed that both in solution and in the solid state metallation does indeed occur both at the N and at the terminal vinylic carbon leading to complex aggregated structures; for example the unsolvated dilithio complex, $\{[(S)\text{-}\alpha\text{-}(PhC(H)Me)(CH_2CH=CHLi)N]Li\}_6$ (**2**), is a cyclic hexamer. The solvent dependant formation of analogous dilithiated dianions based on *N*-(trimethylsilyl)allylamine has also recently been the subject of extensive investigation by Williard and co-workers [7] using both density functional calculations and solution studies to elucidate the mechanism of formation and preferred regiochemistry. Unlike the three structural types of heterobimetallic complexes mentioned above these dilithiated complexes belong to the class of polymetallated anions in which a single organic substrate is metallated at various sites. There are many descriptions of these in the literature as reactive intermediates, and even of their solid state structures, however, being homometallic they tend to be predictable in their synthetic behaviour [8].

We have been intrigued by the possibility of forming complexes which bring together the various features of polylithiated organic substrates with those of traditional 'superbases' to produce a single heterobimetallated organic moiety which displays diversity in the atoms to which the different metals are bonded. As such, we were fortunate enough in our original studies on (*S*)-*N*-(α-methylbenzyl)allylamine to be able to obtain the crystal structure of the mixed Li/Na complex in relatively high yield by using *n*-BuNa rather than *t*-BuLi as the strong base to metallate at the terminal vinylic carbon thereby producing $\{[(S)\text{-}\alpha\text{-}(PhC(H)Me)\text{-}(CH_2CH=CHNa)N]Li \cdot (thf)\}_4$ (**3**); a cyclic tetramer in which each Na$^+$ cation on the external 'rim' of the bicycle wheel-type structure is coordinated by a single thf molecule [5]. Our prime target, though, was the mixed metal lithium–potassium complex which would more closely resemble typical in-situ generated amide/carbanion 'superbase' complexes. However, this proved to be an extremely difficult target. Finally, after many attempts we have managed to synthesise and characterise, by single crystal X-ray diffraction and solution NMR studies, an example of this rare type of heterobimetallic dianionic complex, $\{[(S)\text{-}\alpha\text{-}(PhC(H)Me)(CH_2\text{-}CH=CHK)N]Li \cdot (thf)\}_4$ (**1**), and it is its synthesis and unusual structural features which we now report here.

2. Results and discussion

2.1. Synthesis

Complex **1** was synthesised by the dropwise addition of the pale yellow hexane solution of the chiral lithium amide $\{[(S)\text{-}\alpha\text{-}(PhC(H)Me)(CH_2CH=CH_2)N]Li\}_n$, pre-prepared by the addition of *n*-BuLi to (*S*)-*N*-(α-methylbenzyl)allylamine, to a hexane suspension of *n*-BuK cooled to −78 °C. To ensure that the reaction was kinetically controlled and that deprotonation occurred at the vinylic carbon without decomposition the heterogenous reaction mixture was stirred at this temperature for 2 h. To increase the chance of solubalisation and deaggregation of any polymeric species due to the high coordinative demands of the larger K$^+$ cation a minimum of 2 equivalents of thf was added before allowing the whole reaction mixture to warm slowly to room temperature. A small crop of dark orange crystals of **1** were obtained over one week at −20 °C after concentration and filtration. While this procedure as described appears straight forward, in reality almost all attempts at preparation, storage and crystallisation led to decomposition, sometimes rapid, and ultimately to either precipitation of a dark brown insoluble solid (which was still highly reactive towards air and water) or to a solution which would only give a thick dark oil on removal of all volatiles. The maximum yield we obtained of crystalline or microcrystalline **1** was 19%. These difficulties came as no real surprise since we have previously documented the ease with which the anion in metallated chiral amides can rearrange or cleave under what is considered typical reaction conditions, particularly in the presence of the heavier alkali metals [9]. The high reactivity of **1** became quite apparent through the rapid decomposition which occurred in deuterated thf solution on preparing samples for variable temperature NMR studies. This supports recent [10] and earlier studies [11] that saturated ethers are extremely vulnerable to highly carbanionic potassium reagents even at very low temperatures, suggesting at least one reason why the crystalline complex was so very difficult to obtain and isolate intact from the reaction mixture.

2.2. Solid state structure

In its gross features the solid state structure of **1**, shown in Fig. 1, resembles that of the Li/Na analogue, **3**. The complex is tetrameric (tetragonal space group $P4(3)2(1)2$) and adopts a similar bicycle wheel-like structure with a cubane core of C–Li bonds and an external 'wheel' rim of N–K bonds. While the cluster in **3** is comprised of four independent monomers (orthorhombic), **1** is constructed across a mirror plane with K2 and K3 lying on the plane itself and K1, the central potassium cation in the asymmetric unit, projected
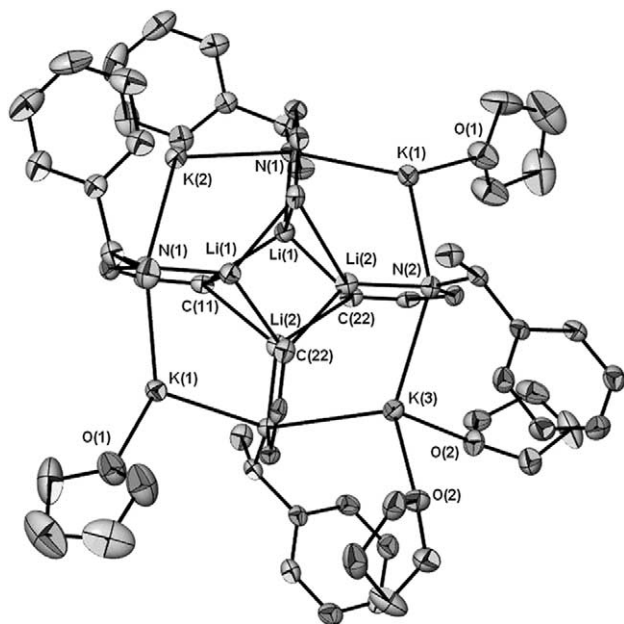
Fig. 1. Molecular structure of {[(S)-α-(PhC(H)Me)(CH₂CH=CHK)-N]Li · (thf)}₄ (**1**). Thermal ellipsoids are shown at 50% probability. All H omitted for clarity. Selected bond lengths and angles are given in Table 1.

across the plane. The asymmetric unit is shown in Fig. 2 and selected bond lengths and angles are given in Table 1. As can be seen, the K⁺ cations are accompanied by two amine moieties and two thf molecules.
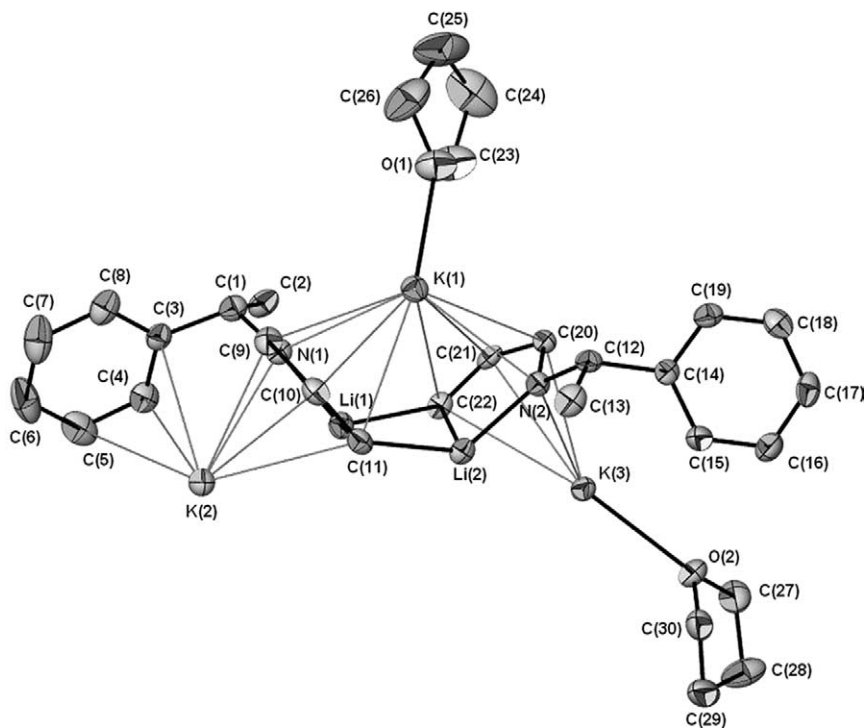
Thus, there is a lower degree of symmetry in **1** than that observed in **3** resulting from the most striking difference between the solid state structures of the two complexes. While the coordination environment of K1 is similar to that found for each Na⁺ cation in **3**, in **1** however, K3 is coordinated by 2 thf molecules while K2 has no coordinated thf molecules but preferentially forms strong compensatory interactions with the π-electrons in the two adjacent Ph groups. Thus, K2 sits directly above C4 at a distance of 3.04 Å and forms close contacts with the neighbouring carbon atoms; C3 at 3.31 Å and C5 at 3.41 Å. The two coordinated thf molecules on K3 mean that the closest contact distance to the nearest Ph group is 3.55 Å (K3–C15) suggesting that the face-on orientation of the two Ph groups to this particular K⁺ cation is a hangover from the strong interactions which would have been present prior to the introduction of thf into the reaction mixture. That K3 is tightly sandwiched is evidenced by the observation that the K2–C4 bond distance is at the short end of the spectrum for such K⁺···π(arene) interactions (normally ca. 3.2–3.3 Å) [12,13] and that the angles at the two contrasting benzylic carbons are substantially different being 110.6° for N1–C1–C3 and 114.1° for N2–C12–C14. The existence of such K⁺···π(arene) bonding and its importance as 'weak' noncovalent interactions alongside traditional hydrogen bonding in biological systems has provoked some interest of late. Various experimental [14] and ab initio ther-

Fig. 2. Asymmetric unit of {[(S)-α-(PhC(H)Me)(CH₂CH=CHK)N]Li · (thf)}₄ (**1**). Thermal ellipsoids are shown at 50% probability. All H atoms omitted for clarity.

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

K(1)–O(1)	2.765(3)	Li(1)–C(22)	2.245(7)
K(1)–N(1)	2.880(3)	Li(2)–C(22)#2	2.264(7)
K(1)–N(2)	2.937(3)	Li(1)–C(11)	2.314(7)
K(2)–N(1)#2	2.971(3)	Li(1)–C(11)#2	2.287(7)
K(2)–N(1)	2.971(3)	Li(1)–N(1)	1.923(7)
K(3)–N(2)#2	2.998(3)	Li(2)–C(22)	2.298(6)
K(3)–O(2)	2.699(2)	Li(2)–C(11)	2.318(7)
K(3)–N(2)	2.998(3)	Li(2)–N(2)	1.914(6)
N(1)–C(1)	1.460(4)	N(2)–C(12)	1.468(4)
N(1)–C(9)	1.445(4)	N(2)–C(20)	1.429(4)
C(9)–C(10)	1.514(5)	C(20)–C(21)	1.523(5)
(C10)–C(11)	1.339(5)	C(21)–C(22)	1.349(5)
O(1)–K(1)–N(1)	113.44(9)	N(1)–Li(1)–C(22)	123.1(3)
O(1)–K(1)–N(2)	113.16(9)	N(1)–Li(1)–C(11)	83.4(2)
N(1)–K(1)–N(2)	116.56(8)	N(1)–Li(1)–C(11)#2	124.5(3)
N(1)#2–K(2)–N(1)	116.85(11)	C(22)–Li(1)–C(11)	111.4(3)
O(2)–K(3)–O(2)#2	94.02(11)	C(11)#2–Li(1)–C(11)	110.5(3)
O(2)–K(3)–N(2)#2	101.96(7)	N(2)–Li(2)–C(22)	84.6(2)
O(2)–K(3)–N(2)	120.95(7)	N(2)–Li(2)–C(22)#2	127.1(3)
N(2) #2–K(3)–N(2)	116.11(11)	C(22)#2–Li(2)–C(22)	110.5(2)
		N(2)–Li(2)–C(11)	122.6(3)
K(1)–N(1)–K(2)	134.95(10)	C(22)–Li(2)–C(11)	109.4(3)
Li(1)–N(1)–K(1)	79.7(2)		
Li(1)–N(1)–K(2)	76.8(2)	C(21)–C(22)–Li(2)	101.3(3)
K(1)–N(2)–K(3)	134.38(10)	C(21)–C(22)–Li(1)	139.0(3)
Li(2)–N(2)–K(3)	76.5(2)	Li(1)–C(22)–Li(2)	68.2(2)
Li(2)–N(2)–K(1)	79.57(19)	C(21)–C(22)–Li(2)#2	142.3(3)
		Li(1)–C(22)–Li(2)#2	72.6(2)

Symmetry operations: #1 $x - 1/2$, $-y + 1/2$, $-z + 1/4$; #2 $y, x, -z$; #3 $x + 1/2$, $-y + 1/2$, $-z + 1/4$.

modynamic studies [15] have indicated that the energy involved in $M^+ \cdots \pi$(arene) interactions (M = alkali metals) can be comparable with that of typical Lewis donor binding of the M^+ cation. Thus, equilibrium exchange of the cation between π(arene) and Lewis donors can be invoked either as transport mechanisms in biological environments, where water would be the most obvious donor solvent, or in the formation of participatory transition structures in chemical reactions, where metals can form complexes with, for example, ether solvents. The subtle differences in the structures of **1** and **3** seems to imply only a small energy difference is associated with the preference of the M^+ cation for thf molecules or the electron density associated with the Ph groups.

Thus, from the solid state structures we get a glimpse of how the coordination environment of the K^+ cations could subtly change and become a highly attractive and active 'naked' site in the presence of an organic substrate with Lewis basic properties (e.g. carbonyls) in solution.

The second major structural variation across complexes **1**, **2** and **3** is in the relationship of the 'wheel-rim' M^+ cation with the allyl groups. As with **1** and **2**, the solution (see below) and solid state studies on **3** indicate, that the normal allylic bonding pattern is retained. What differs across the three complexes is the gradual move of the metal cation away from a predominantly σ bonding arrangement for Li^+ at the terminal vinylic site in **2**, to a situation in **3** where the Na^+ cation locates itself such that it is primarily sandwiched between the vinylic $C=C^-$ bonds, to the more extreme position in **1** where the K^+ cation bonds with all the available electron density spread across two non-delocalised allylic moieties in a sandwiched η^8-type arrangement. Comparing the longer bond distances from K^+ to the terminal vinylic carbons to the carbons adjacent to the N_{amido} indicates that it is located more over the N^-–C bonds rather than $C=C^-$ bonds. This gradual relocation of the cation, as illustrated in Fig. 3, is also accompanied by a slight but definite widening of the bond angles at the two central carbons of the allylic moieties: for **1**, **2** and **3** respectively these angles are; C20–C21–C22 125.1(3)°, 124.0(2)°, 124.5(3)° and N2–C20–C21 112.3(3)°, 110.49(18)°, 111.6(3)°.

We previously made the observation that from an analysis of the bond lengths in the Na analogue **3** that there was no apparent transmetallation, most likely resulting from the architectural preference for the smaller Li^+ cation to be contained in the middle of the cluster. The bonding pattern in **1** is again consistent with this. The K–N distances range from 2.938–2.997 Å and are slightly longer than those found for typical potassium amides (ca. 2.7–2.8 Å) but are typical of $K \cdots N$ dative bonding [16]. The Li–N bond distances (N1–Li1, 1.923(7); N2–Li2, 1.914(6) Å) are typical for lithium amides [17] while the average Li–C bonds in the central cubane (av. 2.30 Å) are comparable with **2** and **3** and again are only fractionally longer than those in
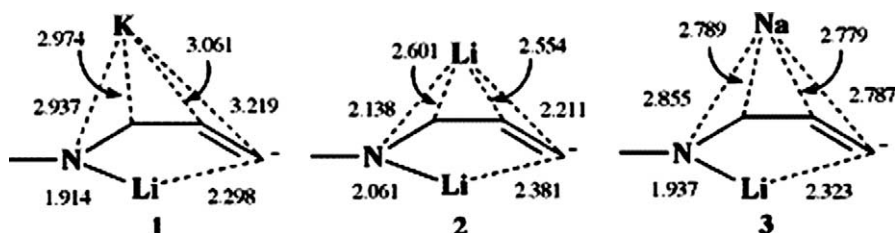

Fig. 3. Comparison of interaction of metal cations in **1**, **2**, and **3** with the allylic moiety. All distances in Å.

analogous lithium alkyl cubane structures (*t*-BuLi, av. 2.24 Å) [18].

2.3. Solution studies

We commented above that attempts to obtain variable temperature NMR spectra in deuterated thf solvent resulted in fast decomposition. Luckily, though, the compound was reasonably soluble in C_6D_6 and was stable long enough for both ^1H and ^{13}C spectra to be obtained. The spectra resemble those obtained from **2** and **3** with no indication of delocalisation of the allyl group. The interesting feature which corroborates the solid state structure of **1** in the relocation of the K^+ cation relative to Li^+ and Na^+ in their relationship with the allylic moiety in **2** and **3** is the chemical shift changes observed for the allylic protons. The large coupling constant associated with the doublet of doublets centred on δ 3.23 ($^1J_{H–K} = 109.2$ Hz), resulting from the diastereotopic protons on the carbon adjacent to the N_{amido}, most likely arises from each individual proton in the CH_2 group forming a strong independent interaction with K^+ cations located on either side of the allyl group and essentially being locked in place. In **2** and **3** the coupling constants are smaller and the doublets shifted to lower frequency [5]. In contrast to the solid state structure of **1** only one signal is observed for the thf molecules in both the ^1H and ^{13}C spectra, indicating an averaged signal or equilibration to a structure similar to **3** in benzene solution at 30 °C. While reaction with the deuterated thf precluded the collection of spectra at lower temperatures, it is possible that variable temperature studies could reveal differing equilibrium environments both for the thf molecules and the Ph groups.

3. Experimental

Compound manipulations were carried out under strict inert atmosphere and dry conditions using a vacuum/argon line, Schlenk techniques and a high purity argon gas recirculating dry box. Prior to use, solvents were dried by reflux over Na/K alloy and stored over molecular sieves 4 Å. (*S*)-N-(α-methylbenzyl)allylamine was prepared by a literature procedure [6]. *n*-BuK was prepared from the metathesis reaction of *n*-BuLi and *t*-BuOK in hexane and stored as a solid. (*Note.* This solid is extremely pyrophoric and extreme care should be taken when handling and transferring.) *n*-BuLi was purchased from Aldrich (1.6 M solution in hexanes). NMR spectra were obtained on Bruker DRX-400 spectrometer with chemical shifts referenced to the appropriate deuterated solvent. Elemental analyses were carried out by CMAS, Australia.

3.1. Synthesis of {[(S)-α-(PhC(H)Me)(CH₂CH=CHK)N]Li · (thf)}₄ (**1**)

n-BuLi (5 mmol, 3.13 ml) was added dropwise to a clear solution of (*S*)-N-(α-methylbenzyl)allylamine (5 mmol, 0.81 g) in hexane (10 ml) at −78 °C. On warming to −20 °C the pale yellow solution was transferred via cannula into a pre-cooled dark brown suspension of *n*-BuK (0.48 g, 5 mmol) in hexane (20 ml) at −78 °C. The reaction mixture was stirred at this temperature for 2 h at which time two equivalents of thf (0.82 ml, 10 mmol) were added and the reaction mixture allowed to warm slowly to ambient temperature. Subsequent in vacuo removal of approximately 50% of the solvent and filtration left a dark brown solution. This was stored at −20 °C for one week during which the solution produced a small crop of dark orange crystals which were identified as {[(*S*)-α-(PhC(H)Me)(CH₂-CH=CHK)N]Li · (thf)}₄.

Yield: 0.23 g (19%, not maximised), m.p. 128–130 °C, darkening to deep red from ca. 85 °C. ^1H NMR (400 MHz, C_6D_6, 30 °C): δ 1.41 (m, 4H, thf), 1.64 (d, $J = 6.7$ Hz, 3H, CH_3), 3.23 (dd, $^1J_{H–K} = 109.2$ Hz, $^2J_{H–H} = 21.5$ Hz, 2H, NCH_2), 3.39 (q, 1H, PhCH-(CH₃)), 3.55 (m, 4H, thf), 6.82 (t, $J = 7.3$ Hz, 1H, NCH₂CH), 7.08 (t, $J = 7.5$ Hz, 2H, *p*CH), 7.25 (d, $J = 7.9$ Hz, 2H, *m*CH), 7.52 (d, $J = 7.1$ Hz, 1H, *o*CH), 7.82 (d, $J = 16.7$ Hz, 1H, CH=CHM). ^{13}C NMR (100.5 MHz, C_6D_6, 30 °C): δ 25.5 (thf), 25.8 (CH₃), 65.4 (NCH₂), 66.2 (MeC(H)), 67.8 (thf), 124.5 (*p*-C), 126.5 (*m*-C), 127.5 (*o*-C), 148.9 (CH), 152.4 (*i*-C). Anal. Calc. for $C_{60}H_{84}N_4Li_4K_4O_4$: C, 64.1; H, 7.5; N, 6.2. Found: C, 62.8; H, 7.3; N, 5.1%.

4. Crystallography

A single crystal of **1** was coated in oil under argon in a dry box, mounted on a fibre [19] and data collected on an Enraf Nonius KappaCCD at 123 K with MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved using direct methods (SHELXS97) [20] and refined by full matrix least-squares on F^2. All H were placed in calculated positions (C–H 0.95 Å) and included in the final least squares refinement. All other atoms were located and refined anisotropically. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 273808. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Crystallographic data for compound **1**: $C_{60}H_{84}N_4$-$O_4Li_4K_4$, M_w, 1109.47, tetragonal, $P4(3)2(1)2$, $a = b = 14.579(2)$ Å, $c = 29.094(6)$ Å, $\alpha = \beta = \gamma = 90°$,

$V = 6184.2(18)$ Å^3, it $Z = 4$, $2\theta_{max} = 56.8°$, $D_{calc} = 1.192$ g cm^{-3}, $\mu = 0.334$ mm^{-1}, $F(0\,0\,0) = 2368$, $T = 123$ K, $N_{ind} = 7582$, R_w, 0.1510, $R_1[I > 2(I)]$, 0.0604, GoF, 0.950.

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