Formation of [M(15-crown-5)₂]₂[Li(NHPy)₃] (M = K or Cs): the first structurally authenticated examples of a monomeric lithium species coordinated by three amide anions

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The title compounds crystallise as solvent-separated ion triplets incorporating the first structurally authenticated examples of a monomeric species with lithium coordinated by three rather than two amide anions; the compounds, products of a heavier alkali metal mediated ligand cleavage reaction, can be viewed as the products of an incomplete metathesis reaction due to their heterobimetallic nature.

Recent times have witnessed enormous interest in the structure and reactivity of alkali metal complexes due to their use as ligand transfer reagents and numerous applications in organic synthesis.[1] Attention has focused on alkyls, imides, alkoxides and, in particular, amides.[2] This research has led to a better understanding of the bonding in such complexes, and the fundamental structural building principles which operate are now well understood and are, to a large extent, predictable.[3] In particular, for lithium amides the principles of ladder formation and the dependence of structure upon the type and presence, or absence, of coordinating solvent is well documented.[2d,4] Within ladder systems the lithium centres are coordinated by three amide anions by virtue of the ladder architecture.[4b–e] However, whilst this coordination mode is mandatory in ladders and is common in lower aggregates, there are, to the best of our knowledge, no examples of a monomeric system containing lithium coordinated to three amide anions. Indeed 'ate' type complexes with nitrogen donors are generally rare.[5] We recently reported as part of a systematic study of Group I amides with crown ethers a complete series (Li to Cs) of complexes of the secondary amide 2-trimethylsilylamidopyridine (tap) incorporating 12-crown-4 ether (12C4).[5a] We repeatedly observed N–Si bond cleavage in the metathesis step with the caesium alkoxide employed, which produced the caesium primary amide [{Cs-(NHPy)(12C4)}∞].[5a] In that case the reaction can be viewed as complete in the sense that the primary amide complex generated is homometallic in nature. We have subsequently found that, when 15-crown-5 ether (15C5) is employed instead of 12C4, a similar N–Si bond cleavage reaction occurs in the metathesis step with BuᵗOK (at elevated temperatures) to produce the title compound [K(15C5)₂]₂[Li(NHPy)₃] **1**. We also find that use of caesium 2-ethylhexoxide at room temperature generates the isostructural title compound [Cs(15C5)₂]₂-[Li(NHPy)₃] **2**. Complexes **1** and **2** are notable for being the first structurally authenticated examples to incorporate a monomeric lithium centre coordinated by three amide anions.

To elaborate, using standard Schlenk techniques, addition of an equimolar quantity of BuᵗOK or caesium 2-ethylhexoxide to a preformed solution of [Li(PyNSiMe₃)(15C5)] in THF (and reflux for potassium) affords faintly cloudy dark orange solutions. Filtering and removal of volatiles yields dark red oils which, when recrystallised from concentrated THF solutions at 5 °C, affords complexes **1** and **2** in 40.2 and 49.8% yield respectively.† These moderate yields, which fall far short of being quantitative, indicate an incomplete reaction, as reflected by the heterobimetallic nature of the products. Use of greater quantities of the potassium or caesium reagent does not significantly

alter the results obtained. It is germane to note that with 12C4 and caesium the reaction proceeds to completion with the generation of the aforementioned homonuclear caesium cluster,[5a] and that with potassium and 12C4 no cleavage reaction occurs, even at elevated temperatures. The implications of this are that the crown ether affects the reactivity of the reaction intermediates; the origins of this may lie in the differing host–guest fit of 12C4 compared to 15C5. With heavier alkali metals the fit is more favourable with 15C5 as reflected by the sandwiched cations found in **1** and **2** (see below). Thus, due to the macro-cyclic effect, these cations are 'trapped' and retained in the heterobimetallic products **1** and **2**, and they are unavailable for further reaction to give homometallic final products. This is perhaps not surprising, given that the solid state structures adopted by alkali metal complexes are intimately dependent upon the co-ligand(s) present.

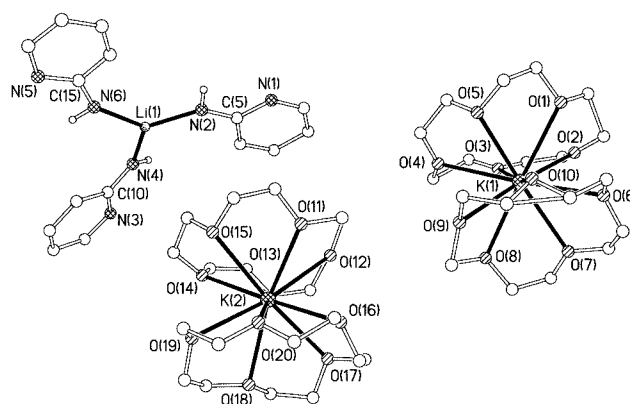The structure of **1** (Fig. 1)‡ consists of a heterobimetallic

Fig. 1 The molecular structure of **1** with selective labelling; disorder and hydrogen atoms other than amide NH omitted for clarity. The ordered structure of **2** is essentially identical in appearance. Selected bond lengths (Å) and angles (°): K(1)–O(1) 2.904(5), K(1)–O(2) 2.852(7), K(1)–O(3) 3.012(7), K(1)–O(4) 2.955(5), K(1)–O(5) 2.832(5), K(1)–O(6) 2.895(5), K(1)–O(7) 2.870(6), K(1)–O(8) 2.884(5), K(1)–O(9) 2.910(5), K(1)–O(10) 2.877(5), K(2)–O(11) 2.863(3), K(2)–O(12) 2.898(4), K(2)–O(13) 2.924(4), K(2)–O(14) 2.870(4), K(2)–O(15) 2.934(4), K(2)–O(16) 2.836(4), K(2)–O(17) 2.956(4), K(2)–O(18) 2.893(4), K(2)–O(19) 2.882(4), K(2)–O(20) 2.878(4), Li(1)–N(2) 1.968(14), Li(1)–N(4) 1.963(12), Li(1)–N(6) 2.025(15), N(2)–C(5) 1.318(8), N(4)–C(10) 1.325(7), N(6)–C(15) 1.358(9); N(2)–Li(1)–N(4) 118.3(6), N(2)–Li(1)–N(6) 128.1(7), N(4)–Li(1)–N(6) 113.4(7), Li(1)–N(2)–C(5) 140.9(6), Li(1)–N(4)–C(10) 137.5(5), Li(1)–N(6)–C(15) 144.6(10).

solvent-separated ion triplet in which two potassium cations are sandwiched by 15C5 molecules. The anion is a lithium centre coordinated to three amide anions and is without precedent. Turning to the sandwich cations first, there are two crystallographically independent but essentially identical ions in the asymmetric unit exhibiting pseudo-D_{5d} symmetry. The K–O

bond lengths span the range 2.832(5)–3.012(7) Å, in good agreement with previously reported examples of 15C5-sandwiched potassium ions.[6] Consequently, the potassium cations reside an average distance of 1.636 Å from the oxygen mean planes of the crowns and these oxygen mean planes are essentially parallel with a mean dihedral angle of 4.1°. The anionic component consists of a lithium centre coordinated by three monodentate 2-amidopyridine anions. This results in a three-coordinate lithium centre that is essentially trigonal planar [sum of angles = 359.8(2)°]. The Li–N bond lengths span the range 1.963(12)–2.025(15) Å, which is at the shorter end of the range of distances frequently reported for lithium amides.[2c,d] It is a testament to the exceptionally small size of the lithium ion that, despite the use of THF as a solvent, the 'ate' fragment crystallises unsolvated. Presumably coordination by three anions satisfies the coordination demands. Turning to the three ligands, the pyridyl rings each exhibit short N(H)–C_{ipso} bond lengths in the range 1.318(8)–1.358(9) Å indicating bond orders greater than one, and therefore some delocalisation of charge. All three pyridyl rings are tilted out of the (LiN$_3$) plane to varying degrees; two are marginally bent out of the plane by 3.4° [N(1) pyridyl] and 6.7° [N(5) pyridyl], the other [N(3) pyridyl] more so at 29.0°. The fact that this 'ate' fragment exists at all is almost certainly due to the strong driving force of solvation of the potassium cations by 15-crown-5, and also reflects the stronger polarising power of lithium and consequent better matching with the hard amide anions.

In the isostructural compound 2 both caesium-15C5 sandwiches exhibit pseudo-D_{5d} symmetry as in 1. The Cs–O bond lengths span the range 3.058(8)–3.397(13) Å, longer than in 1, reflecting the larger ionic radius of caesium compared to potassium, and agreeing well with other reported examples.[7] Consequently the caesium ions reside a mean distance of 2.035 Å from the oxygen mean planes of the crowns. The sandwiches are slightly bent with a mean dihedral angle of 6.5° for the two oxygen mean planes, a small increase in bending compared to 1, reflecting the greater polarisation with caesium. The 'ate' fragment has again a distorted trigonal planar geometry [sum of angles = 359.4(7)°] and the Li–N and N(H)–C_{ipso} bond lengths show no statistically significant differences from those observed in 1. All three pyridyl rings are tilted out of the (LiN$_3$) plane to varying degrees; one by 10.1° [N(4)], the other two more so at 22.7° [N(6)] and 25.0° [N(2)]. These are larger deviations than in 1 and, given the highly polar nature of the bonding, are likely to be due to crystal packing forces. All intermolecular contacts to Li atoms in both structures are at least 3.45 Å, and there are no unusual interactions among the various ions.

In conclusion, by utilising a larger macrocycle we have isolated the first structurally authenticated examples of a monomeric lithium centre coordinated by three amide anions. Further work will examine the effect other macrocycles have on the products of such metathesis reactions.

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Notes and references

† Synthesis of 1: Bu^{n}Li (1.13 mL, 2.83 mmol) was added dropwise to a solution of 2-trimethylsilylaminopyridine (0.47 g, 2.83 mmol) and 15-crown-5 (0.56 mL, 2.83 mmol) in THF (40 mL). Addition of this solution to Bu^{t}OK (0.32 g, 2.83 mmol) and refluxing for 30 minutes gave a cloudy deep orange solution. Hot filtration and removal of volatiles from the filtrate *in vacuo* yielded a viscous red oil. Recrystallisation from THF at 5 °C gave crystals of 1 suitable for an X-ray study (0.47 g, 40.2%). ^{1}H NMR (298 K, 200.1 MHz, [^{2}H]$_8$-THF) δ = 3.69 (80 H, s, 15C5), 5.47 (3 H, s, br, N–H), 5.90 (3 H, t, β-H–Py), 6.15 (3 H, d, β'-H–Py), 6.93 (3 H, t, γ-H–Py) and 7.72 (3 H, d, α-H–Py). ^{13}C NMR (298 K, 50.3 MHz, [^{2}H]$_8$-THF) δ = 70.38 (15C5), 107.08 (β-C–Py), 110.62 (β'-C–Py), 135.72 (γ-C–Py), 149.16 (α-C–Py) and 172.94 (α'-C–Py). ^{7}Li NMR (298 K, 116.6 MHz, [^{2}H]$_8$-THF) δ = 1.31

(s). Anal. Found: C, 52.30; H, 8.05; N, 6.52. Calc.: C, 53.04; H, 7.69; N, 6.75%.

Synthesis of 2: Bu^{n}Li (1.68 mL, 4.21 mmol) was added dropwise to a solution of 2-trimethylsilylaminopyridine (0.70 g, 4.21 mmol) and 15-crown-5 (0.84 mL, 4.21 mmol) in THF (40 mL). Addition of this solution to caesium-2-ethylhexoxide (0.66 g, 2.53 mmol) with stirring overnight afforded a dark orange solution. Removal of volatiles *in vacuo* yielded a viscous red oil. Recrystallisation from THF at 5 °C gave crystals of 2 suitable for an X-ray study (1.00 g, 49.8%). ^{1}H NMR (298 K, 200.1 MHz, [^{2}H]$_8$-THF) δ = 3.66 (80 H, s, 15C5), 4.54 (3 H, s, N–H), 5.62 (3 H, t, β-H–Py), 5.93 (3 H, d, β'-H–Py), 6.74 (3 H, t, γ-H–Py) and 7.64 (3 H, d, α-H–Py). ^{13}C NMR (298 K, 50.3 MHz, [^{2}H]$_8$-THF) δ = 70.99 (15C5), 102.22 (β-C–Py), 112.67 (β'-C–Py), 134.95 (γ-C–Py), 149.21 (α-C–Py) and 171.31 (α'-C–Py). ^{7}Li NMR (298 K, 116.6 MHz, [^{2}H]$_8$-THF) δ = 1.36 (s). ^{133}Cs NMR (298 K, 39.4 MHz, [^{2}H]$_8$-THF) δ = 33.93 (s). Anal. Found: C, 45.38; H, 6.81; N, 5.66. Calc.: C, 46.09; H, 6.68; N, 5.86%.

‡ Crystal data for 1: $C_{55}H_{95}N_6O_{20}LiK_2$, M = 1245.5, triclinic, space group $P\bar{1}$, a = 13.5783(10), b = 15.1526(11), c = 17.5303(13) Å, α = 76.265(2), β = 75.313(2), γ = 69.484(2)°, U = 3223.4(4) Å^3, Z = 2, D_c = 1.283 g cm^{-1}, μ = 0.22 mm^{-1}, (Mo-Kα, λ = 0.71073 Å), T = 160 K, $R(F^2 > 2\sigma)$ = 0.0899, R_w (F^2, all data) = 0.2941 for all 11246 unique data (23277 measured, R_{int} = 0.0433, $2\theta < 50°$, CCD diffractometer) and 809 refined parameters.

For 2: $C_{55}H_{95}N_6O_{20}LiCs_2$, M = 1433.1, triclinic, space group $P\bar{1}$, a = 14.2706(9), b = 14.6824(9), c = 18.2599(11) Å, α = 77.781(2), β = 71.818(2), γ = 68.921(2)°, U = 3370.3(4) Å^3, Z = 2, D_c = 1.412 g cm^{-3}, μ = 1.15 mm^{-1}, (Mo-Kα, λ = 0.71073 Å), T = 220 K, $R(F^2 > 2\sigma)$ = 0.0651, R_w (F^2, all data) = 0.2108 for all 15450 unique data (29613 measured, R_{int} = 0.0237, $2\theta < 57°$, CCD diffractometer) and 766 refined parameters. Two-fold disorder was resolved and refined for three crown ether ethylene bridges in 1. Programs: standard Bruker AXS control and integration software and SHELXTL.[8] CCDC reference numbers 170594 and 170595. See http://www.rsc.org/suppdata/dt/b1/b109903p/ for crystallographic data in CIF or other electronic format.

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