Selective oxygen capture in lithium zincate chemistry: the syntheses and solid-state structures of (μ-O)Zn_4[N(2-C_5H_4N)Bz]$_6$ and Bu^t(μ_3-O)Li_3(μ_6-O)Zn_3[N(2-C_5H_4N)Me]$_6$ (Bz = benzyl)

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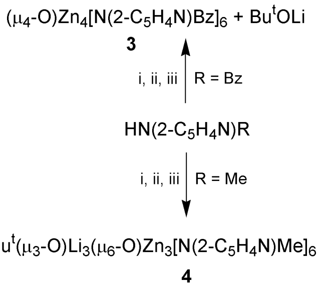
Received (in Cambridge) 29th June 2000, Accepted 17th August 2000

Sequential reaction of $ZnMe_2$ with the (2-pyridyl)amines HN(2-C_5H_4N)R (R = Bz = benzyl 1, Me 2), Bu^{t}Li and oxygen affords species which demonstrate oxo-encapsulation {(μ_4-O)Zn_4[N(2-C_5H_4N)Bz]$_6$ 3}, and both encapsulation and insertion into a C–Li bond {Bu^t(μ_3-O)Li_3(μ_6-O)Zn_3[N(2-C_5H_4N)Me]$_6$ 4}; in the solid-state 4 has a new type of *fac*-isomeric (μ_6-O)$M_3M'_3$ octahedral core.

Current interest in the properties of lithium containing heterobimetallic species derives from their ability to effect organic transformations whose selectivity differs from those afforded by homometallic organolithium compounds. Hence, whereas organolithium reagents perform 1,2-addition across α,β-unsaturated ketones,[1] it has been reported lately that in the presence of group 13 Lewis acids 1,4-addition is preferred,[2] with the formation of a lithium aluminate recently being implicated in this process.[3] Also of use in such conjugate additions,[4] lithium organozincates find extensive employment in synthetic chemistry.[5] In spite of this utility, lithium zincate structural chemistry is not well understood, and of the few known structures two classes dominate. Ion-separated species are favoured by the presence of strongly coordinating Lewis bases[6] whereas in their absence ion-associated [Li(μ_2-C)$_2$]$_n$Zn (n = 1, 2)[7] motifs prevail. In the light of advances in the controlled oxygenation of heterobimetallic compounds[8] we report here on the incorporation of oxygen by mixed Li–Zn systems and detail the variable reactivity towards oxygen of the products afforded by sequentially treating (2-pyridyl)amines with organozinc and organolithium reagents (Scheme 1).

The reaction of a non-donor solution of HN(2-C_5H_4N)R (R = Bz = benzyl **1**) with $ZnMe_2$ and Bu^{t}Li was followed by treatment with air (pre-dried over P_2O_5) until the evolution of fumes subsided. Storage of the resultant solution afforded two crystalline compounds.‡ The characterisation of both species was made possible by their mechanical separation, with ^{1}H NMR spectroscopy verifying that one of these products was Bu^{t}OLi. The remaining compound was shown by X-ray crystallography§ to be the trigonal pyramidal complex (μ_4-O)Zn_4[N(2-C_5H_4N)Bz]$_6$ **3** [Fig. 1(a)] for which formulation there is a toluene molecule in the lattice. Of the two types of Zn centre in this species, three describe the pyramid base [Zn1A···Zn1B 3.130(2) Å] each non-bonding edge of which is spanned by a [N(2-C_5H_4N)Bz]$^-$ ligand [Zn–N(2-C_5H_4N) 2.069(7) Å, Zn–NBz 1.984(7) Å]. The final metal centre (Zn2) occupies the C_{3v} cluster apex and is stabilised by the pyridyl N-centres of the remaining three organic residues [Zn2–N(2-C_5H_4N) 2.045(7) Å], each of which spans one non-bonding Zn1···Zn2 [3.089(2) Å] pyramid edge [Zn1–NBz 2.002(7) Å]. At the core of the C_{3v} cluster is a nearly tetrahedral O^{2-} centre (mean Zn–O 1.903 Å, mean Zn–O–Zn 108.9°). It is noteworthy that previous examples of oxo-encapsulation by Zn_4-tetrahedra have resulted from the deliberate introduction of water[9,10] or



Scheme 1 *Reagents and conditions*: i, $ZnMe_2$; ii, Bu^{t}Li; iii, O_2.

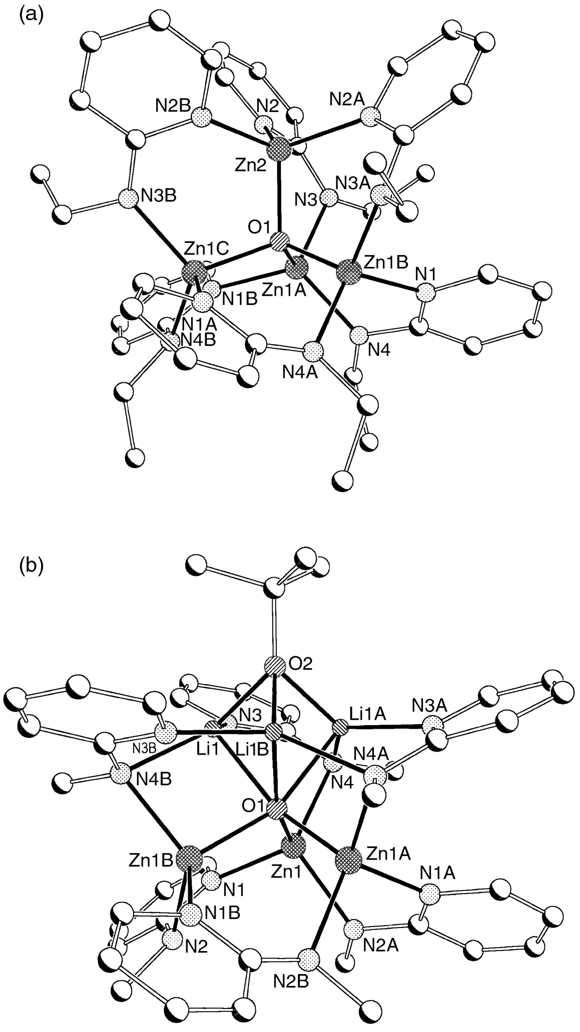


Fig. 1 (a) Molecular structure of **3**; hydrogen atoms and lattice toluene molecule omitted and only the *ipso*-C of Ph shown. (b) Molecular structure of **4**; hydrogen atoms and lattice thf molecule omitted.

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† Deceased.

DOI: 10.1039/b005238h

carbon dioxide[11] whereas **3** is afforded by exposure to oxygen.

Significant structural modification was observed in the product of the analogous reaction for which R was the less sterically demanding Me group (**2**), this process affording **4**.‡ X-Ray crystallography§ reveals **4** to be the unique distorted octahedral oxo-encapsulation complex $Bu^t(\mu_3\text{-O})Li_3(\mu_6\text{-O})Zn_3[N(2\text{-}C_5H_4N)Me]_6$ [Fig. 1(b)] for which formulation there is one thf molecule in the lattice. That the Li_3 face is μ_3-capped by an OBu^t group points to an oxygen atom having inserted into a Li–C(Bu^t) bond [Li–O2 1.849(14) Å, Li–O2–Li 83.7(7)°].[12] The three lithium centres are less strongly bonded to the encapsulated μ_6-O centre [Li–O1 2.074(13) Å, Li–O1–Li 73.0(6)°] which in turn interacts with the three Zn centres [Zn–O1 1.944(4) Å, Zn–O1–Zn 101.4(3)°]. The result—a molecular *fac*-isomeric $(\mu_6\text{-O})M_3M'_3$ octahedron—has not been seen before. Instead, existing examples of molecular μ_6-O hetero-bimetallic octahedra have either (MM'_5)[13] or $(M_2M'_4)$[14] formulations. The only previous report of a lithium containing heterobimetallic μ_6-O octahedral complex is that of $[RuH(SiHPh_2)(CO)X_2]_2\cdot[Li_2Ru_4OCl_8X_4]$ (X = $PBu^t{}_2Me$), which has a *trans*-isomeric $(\mu_6\text{-O})Li_2Ru_4$ core;[15] all other examples of lithium containing μ_6-O octahedra have been homometallic.[16] The coordination spheres of both Li and Zn centres in **4** are completed by $[N(2\text{-}C_5H_4N)Me]^-$ ligands. Three of these residues span the 3.007(2) Å Zn···Zn non-bonding distances in the lower tier of the cluster [Zn–N1 2.038(7) Å, Zn–N2 2.050(7) Å]. The remaining organic residues circumscribe the non-bonding Li_3 [Li···Li 2.47(2) Å] upper tier but are orientated such that their N-pyridyl centres are precisely in the Li_3 plane while their NMe-groups span non-bonding heterobimetallic [Li···Zn 2.75(1) Å] octahedron edges [Zn1–N4 2.065(7) Å]. The sp^2-orbital on their deprotonated N-centres almost bisects the Li–N(Me)–Zn bond angle [N3–C11–N4–M torsional angles = 42.8° (M = Li1A), 45.4° (M = Zn1)] with the consequent mismatch in orientation of the NMe-centred lone-pairs with the Li^+ ions in the upper tier probably being responsible for the respective Li–N($2\text{-}C_5H_4N$) and Li–NMe bond lengths of 2.071(14) and 2.160(13) Å. This variability in ligand coordination contrasts with the uniformly μ_2- or μ_3-bridging modes adopted by ligand heteroatoms in previously reported μ_6-O molecular heterobimetallic octahedra.[14]

Compounds **3** and **4** both incorporate six-membered MO-M′NCN rings by virtue of $[N(2\text{-}C_5H_4N)R]^-$ coordination [M = M′ = Zn (**3**); both M = M′ = Zn/Li and M = Li, M′ = Zn (**4**)]. Further, both species show almost identical $Zn_3[N(2\text{-}C_5H_4N)R]_3$ basal tiers [Fig. 1(a) and (b)], whilst the remaining three amide ligands exhibit significant variability between **3** and **4**. The orientation which they adopt in **3** results in their pyridyl N-centres bonding only to Zn2 which they render approximately tetrahedral, their deprotonated N-centres bonding only to Zn1. Conversely, in **4** the upper tier ligands are orientated such that the pyridyl N-centres lie in the Li_3 plane with the concomitant stabilisation of adjacent Li centres (by NMe groups) being accompanied by bridging to basal Zn atoms. Thus, **3** and **4** can be viewed as empirically incorporating a $\{(\mu_3\text{-O})Zn_3[N(2\text{-}C_5H_4N)R]_6\}^{2-}$ ligand which is capable of acting either as a heptadentate donor to a C_{3v} cation $[(Bu^tOLi_3)]^{2+}$ in **4**] or as a tetradentate donor to an R_3 cation (Zn^{2+} in **3**) by virtue of flexibility in the orientations demonstrated by the upper tier of $[N(2\text{-}C_5H_4N)R]^-$ ligands.

Attempts to elucidate the structural characteristics of the precursors to **3** and **4** are ongoing, as are studies into the nature of the competition between oxo-insertion (*cf.* the Bu^tO fragment in **4**) and oxo-encapsulation [*cf.* **3** and the $(\mu_6\text{-O})Li_3Zn_3$ fragment in **4**]. Finally, the integrity of the $\{(\mu_3\text{-O})Zn_3[(2\text{-}C_5H_4N)NR]_6\}^{2-}$ ligand is being investigated (by attempting to effect substitution reactions, *e.g.* the conversion of **4** to **3** by reaction with $ZnCl_2$).

We thank the UK EPSRC (D. J. L.) for a Studentship and St. Catharine's (R. P. D.) and Gonville & Caius (A. E. H. W.) Colleges for Research Fellowships.

Notes and references

‡ **3**: $ZnMe_2$ (0.5 ml, 1 mmol, 2 M in toluene) was added to a stirred −78 °C solution of 2-(benzylamino)pyridine (0.18 g, 1 mmol) in toluene (5 ml). After 30 min the mixture was warmed to −40 °C and Bu^tLi (0.59 ml, 1 mmol, 1.7 M in pentane) was added. Treatment of the room-temperature mixture with (P_2O_5) dry air (until observable reaction ceased after *ca.* 1 min) was followed by reflux and by storage at ambient temperature for 24 h whereupon needles of Bu^tOLi (by ^1H NMR) and blocks of **3** formed. Mechanical separation allowed the characterisation of **3**. Yield 42% (by **1** consumed), mp 140 °C (decomp.). Found: C, 64.96; H, 5.16; N, 11.34. Calc. for $C_{79}H_{74}N_{12}OZn_4$: C 64.53, H 5.04,N 11.44%. δ_H(500 MHz, CD_3CN), 7.40–6.46 (m, 20H, Ar + *Ph*Me), 4.56 (s, 4H, CH_2), 2.33 (s, 1H, Ph*Me*). **4**: $ZnMe_2$ (0.5 ml, 1 mmol, 2 M in toluene) was added to a stirred −78 °C solution of 2-(methylamino)pyridine (0.11 g, 1 mmol) in hexane (1 ml). After 30 min Bu^tLi (0.59 ml, 1 mmol, 1.7 M in pentane) was added. Treatment of the room-temperature mixture with (P_2O_5) dry air (until observable reaction ceased after *ca.* 1 min) and the addition of thf (0.08 ml) was followed by storage at room temperature for 1 week whereupon blocks of **4** formed. Yield 32% (by **2** consumed), mp >300 °C. Found: C, 50.68; H, 6.48; N, 12.64. Calc. for $C_{44}H_{59}Li_3N_{12}O_3Zn_3$: C, 51.69; H, 6.45; N, 13.45%. δ_H(500 MHz, $[^2H_8]$thf), 8.00–6.01 (m, 24H, Ar), 3.65 (m, 4H, thf), 2.81 (s, 9H, NMe), 2.53 (br m, 9H, NMe), 1.80 (m, 4H, thf), 1.12 (s, 9H, Bu^t).

§ *Crystal data*: for **3**: $C_{79}H_{74}N_{12}OZn_4$; M = 1468.98, cubic, space group $Ia3$, a = 30.8060(7) Å, U = 29235.2(12) Å^3, Z = 16, D_c = 1.335 g cm^{-3}, Mo-Kα (λ = 0.71073 Å), μ = 1.350 mm^{-1}, T = 180(2) K. 8240 reflections (4297 unique, $\theta < 25.02°$, R_{int} = 0.0886), data were collected. Refinement on F^2 values of all data gave $wR2$ = 0.1987, conventional R = 0.0849 on F values of all reflections with $F^2 > 2\sigma(F^2)$, 276 parameters. Residual electron density within ±1.45 e Å^{-3}.

4: $C_{11}H_{14.75}Li_{0.75}N_3O_{0.75}Zn_{0.75}$; M = 255.24, cubic, space group $P2_13$, a = 16.694(10) Å, U = 4882.0(10) Å^3, Z = 4, D_c = 1.389 g cm^{-3}, Mo-Kα (λ = 0.71073 Å), μ = 1.513 mm^{-1}, T = 180(2) K. 20356 reflections (2128 unique, $\theta < 22.44°$, R_{int} = 0.0744), data collected. Refinement on F^2 values of all data gave $wR2$ = 0.2093, conventional R = 0.0744 on F values of all reflections with $F^2 > 2\sigma(F^2)$, 205 parameters. Residual electron density within ±1.02 e Å^{-3}.

CCDC 182/1748. See http://www.rsc.org/suppdata/cc/b0/b005238h/ for crystallographic files in .cif format.

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Typeset and printed by Black Bear Press Limited, Cambridge, England