COMMUNICATION www.rsc.org/chemcomm | ChemComm

Structural variations in bimetallic sodium–magnesium and sodium–zinc ketimides, and a sodium–zinc alkide–alkoxide–amide: connections to ring-stacking, ring-laddering, and inverse crown concepts†

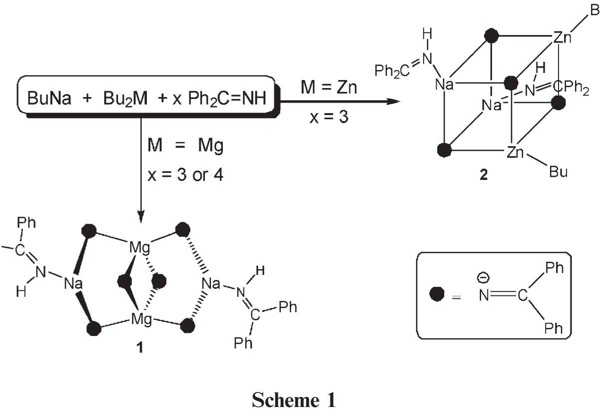
William Clegg,[a] Sophie H. Dale,[a] David V. Graham,[b] Ross W. Harrington,[a] Eva Hevia,[b] Lorna M. Hogg,[b] Alan R. Kennedy[b] and Robert E. Mulvey*[b]

Received (in Cambridge, UK) 20th December 2006, Accepted 16th January 2007
First published as an Advance Article on the web 6th February 2007
DOI: 10.1039/b618609b

The first sodium–magnesium and sodium–zinc ketimido complexes display contrasting inverse crown ring and pseudo-cubane structures respectively, while a sodium–zinc hetero-trianionic alkide–alkoxide–amide adopts a third type of structure with a stepped ladder motif.

Derived from ketimines ($R^1R^2C{=}NH$), ketimido ligands of general formula ($R^1R^2C{=}N^-$) have played a pivotal role in the development of Snaith's ring-stacking principle in organolithium chemistry.[1,2] Due to favourable stereochemical dispositions of 'R' substituents emanating from their C=N bonds, lithium ketimides have small, single $(NLi)_n$ ring units (n is usually 2 or 3) which can maximise their electrostatic (attractive) contacts by aggregating further in face-to-face stacking arrangements. Other common ligands such as amides ($R^1R^2N^-$) are adversaries of ketimino ligands as the stereochemistries of their 'R' substituents are fundamentally different such that ring stacking is prohibited, but where further aggregation is possible it is manifested in ring laddering [lateral, edge-to-edge association of $(NLi)_2$ rings].[1] Able to rationalise numerous aspects of the structural chemistry of lithium, the ring-stacking and ring-laddering concepts have recently been extended by Bond to metal-free ammonium halide salts.[3] A germane example of a lithium ketimide stack is the benzophenone imine derived tetramer $[(Ph_2C{=}NLi{\cdot}NC_5H_5)_4]$,[4] the cubane structure of which may conveniently be regarded as stacked pairs of pyridine-solvated cyclic dimers "$(Ph_2C{=}NLi{\cdot}NC_5H_5)_2$". Mixed alkali metal ketimides have also been synthesised[5] including the tetralithium–disodium example $[\{Ph(Bu^t)C{=}N\}_6Li_4Na_2]$, which exhibits a threefold stack of cyclic dimers. However, to the best of our knowledge, hitherto there have been no reports of mixed alkali metal–magnesium or –zinc ketimides. Given the special synergic chemistry that can result when these divalent metals partner an alkali metal in alkyl- and/or amido-ligand complexes,[6] a complementary mixed-metal ketimido chemistry seems worthy of development, not least to ascertain whether the ring-stacking model has any relevance to the structures found. Thus, herein, we report the first mixed-metal ketimides of this type, both of which are derived from benzophenone imine, and reveal surprising synthetic and structural distinctions between these sodium–magnesium and sodium–zinc systems. In addition, we report another sodium–zinc complex with a heterotrianionic ligand set, that adopts a third type of structure with a ladder framework.

Recently we showed how the tris(alkyl) 'ate "Bu_3NaMg" could be effective as a deprotonative reagent for preparing mixed sodium–magnesium enolate complexes in reactions with a ketone.[7] Here, preparing the same reagent *in situ* from a 1 : 1 mixture of butylsodium and dibutylmagnesium, and introducing three molar equivalents of benzophenone imine produced the crystalline disodium dimagnesium ketimide–ketimine complex $[(Ph_2C{=}NH)_2(Ph_2C{=}N)_6Na_2Mg_2]$, **1** (Scheme 1).‡ Accounting for the 'extra' ketimine molecules present in **1**, the reaction was repeated using a 1 : 1 : 4 stoichiometry of reactants to give an improved yield of 68%. Characterisation of **1** was completed by NMR spectroscopic and X-ray crystallographic studies (see below). In this reaction "Bu_3NaMg" functions as a tribasic reagent utilising all three of its butyl arms (with concomitant evolution of butane). The same reaction (1 : 1 : 3 stoichiometry) substituting sodium tributylzincate "Bu_3NaZn" for "Bu_3NaMg" produced the crystalline disodium dizinc mixed alkide–ketimide–ketimine complex $[(Ph_2C{=}NH)_2(Ph_2C{=}N)_4(Bu)_2Na_2Zn_2]$, **2** (Scheme 1).‡ This heterobianionic complex was also characterised by NMR spectroscopic and X-ray crystallographic studies (see below). The reluctance of "Bu_3NaZn" to break all of its butyl arms (only two are broken in forming **2**), making it dibasic in contrast to the tribasicity of "Bu_3NaMg", is consistent with the stronger electrophilicity (carbophilicity) of zinc *vs.* magnesium. Even when an excess of ketimine is employed, this butyl-containing product **2** is formed preferentially. In contrast in



Scheme 1

---

[a] *School of Natural Sciences (Chemistry), Newcastle University, Newcastle upon Tyne, UK NE1 7RU*
[b] *WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL. E-mail: r.e.mulvey@strath.ac.uk*

† Electronic supplementary information (ESI) available: Full details of syntheses, spectroscopic characterisation, and ring-stacking bond length analysis. See DOI: 10.1039/b618609b

the Mg case, with a deficiency of ketimine, the all-ketimido product **1** is still obtained, presumably leaving some unreacted "Bu_3NaMg" in solution.

The centrosymmetric molecular structure of **1** (Fig. 1)§ does not fit the ring-stacking model. Instead, it shows an open bicyclic arrangement, centred on a planar (Mg1N4Mg1*N4*) ring, either side of which has an N2Na1N1 bridge linking the Mg atoms together. All of these N atoms belong to ketimido anions. Exocyclic ketimine ligands bind terminally to Na through their (H)N donor atom to complete the structure. Alternatively, **1** could be viewed as an inverse crown structure[8] comprising an eight-membered $[(NaNMgN)_4]^{2+}$ "host" ring and two $Ph_2C{=}N^-$ "guests", which sit above and below the centre of the host ring in bridging the Mg atoms. Resembling a flattened chair, the host ring has a near-planar NMgN···NMgN seat with transoid-disposed Na atoms in the head- and foot-rest positions. The host N atoms (Mg/Na coordinated) form slightly shorter bonds to Mg (mean length, 2.0103 Å) than do the guest N atoms (Mg_2 coordinated; mean length 2.1016 Å) which lie far removed from Na [shortest contact, Na1···N4, 3.1477(14) Å]. The Mg atoms occupy a highly irregular N_4 coordination geometry [range of NMgN bond angles, 89.69(5)–142.49(6)°; mean, 107.43°]. There is little distinction in length between the Na–N(H) dative bond [2.4244(17) Å] and its anionic counterparts (mean, 2.4268 Å). The Na atoms occupy a pyramidal N_3 coordination geometry [range of NNaN bond angles, 100.96(6)–123.15(5)°; mean, 111.36°], but in addition they engage in short contacts with the imido, *ipso* and *ortho* C atoms of one ketimido ligand [lengths, 2.9569(18), 3.0477(18) and 3.082(2) Å, respectively]. Though unique for a ketimide, this inverse crown motif, as discussed elsewhere,[6] is known for other homoanionic and heteroanionic ligand systems. As with many alkali metal-magnesium structures, **1** could also be viewed as an 'ate complex,[6,8] specifically a dimer of "$[(Ph_2C{=}N)_3Mg]^-$" electrostatically attached to ketimine-ligated Na^+ cations. In this alternative description, the N anions interacting with Na/Mg centres [formally terminal in $(R_2MgR_2MgR_2)^{2-}$] will carry a higher negative charge to those interacting with Mg/Mg centres [formally bridging in $(R_2MgR_2MgR_2)^{2-}$], and this fits the pattern of bond lengths observed (*i.e.* former Mg–N bonds are shorter than latter).

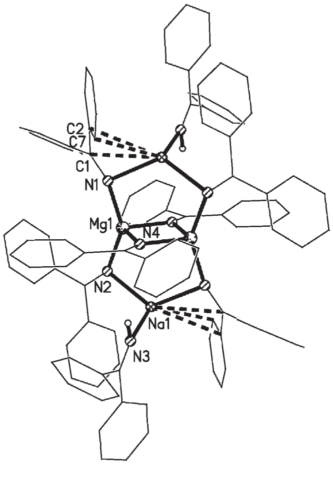


Fig. 1 Molecular structure of **1**. For clarity Ph rings are shown as wire frame, Na–C interactions as dashed lines, and all hydrogen atoms (except N–H) are omitted. Selected bond lengths (Å): Na1–N1* 2.4467(15), Na1–N2 2.4068(15), Na1–N3 2.4424(17), Mg1–N1 1.9864(14), Mg1–N2 2.0343(14), Mg1–N4 2.1134(14).

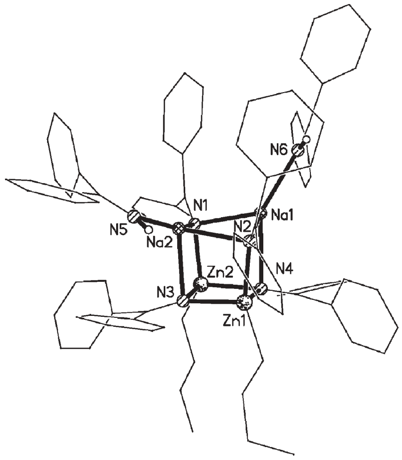


Fig. 2 Molecular structure of **2** with Ph rings shown as wire frame and hydrogen atoms (except N–H) and minor disorder components omitted for clarity. Selected bond lengths (Å): Zn2–N1 2.063(4), Zn1–N2 2.058(4), Na1–N1 2.377(4), Na2–N2 2.398(5), Zn1–N4 2.103(4), 2.111(4), Na1–N2 2.403(4), Na2–N1 2.402(4), Zn1–N3 2.112(4), Zn2–N4 2.139(4), Na1–N4 2.548(4), Na2–N3 2.448(4).

Interestingly, despite its similar composition to **1**, the zinc complex **2** surprisingly adopts a fundamentally different molecular structure (Fig. 2).§ A distorted cubane with alternating imido N and metal (2 × Na; 2 × Zn) corners, the structure is completed by terminal ketimine and butyl ligands on Na and Zn respectively. Empirically, this structure could be said to fit the ring-stacking model as in general cubanes can be regarded as two stacked dimeric (or dinuclear in this case) rings. However, in Snaith's more quantitative analysis of such lithium stacks, there was a definite pattern to the Li–N bond lengths within the cubane. Reproduced for $[(Ph_2C{=}NLi{\cdot}NC_5H_5)_4]$[4] in Fig. 3, this shows that bonds in the stacking direction are of intermediate length, while the constituent dimeric rings have alternating short and long bonds with short superimposed on long between the rings. Considering the relative bond lengths for each metal in **2** separately, a definite though different pattern is discernible (Fig. 3): the dinuclear rings Na1N1Zn2N4 and Na2N3Zn1N2 display short, short, long, long metal–N bonds, while bonds of intermediate length link the two rings in the stacking direction (see legend for Fig. 2). This is one of three possible stacking directions linking $(MN)_2$ faces of the cubane, but the other two have short bonds in the stacking direction which seems less compatible with Snaith's analysis. The constituent dimeric ring therefore appears to be heterometallic (NaNZnN) and not homometallic (NaNNaN and ZnNZnN),

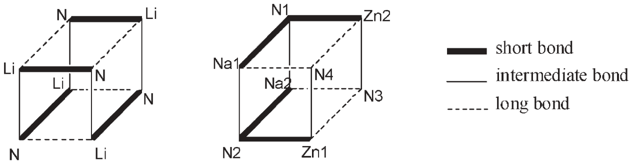


Fig. 3 Cubane frameworks of $[(Ph_2C{=}NLi{\cdot}NC_5H_5)_4]$ (LHS) and **2** (RHS).

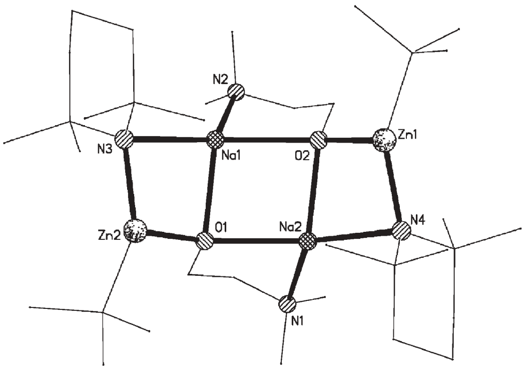


Fig. 4 Molecular structure of **3** with hydrogen atoms omitted for clarity. Selected bond lengths (Å): Zn1–O2 2.025(3), Zn1–N4 1.967(4), Zn1–C5 2.003(5), Zn2–O1 2.036(3), Zn2–N3 1.968(4), Zn2–C1 2.013(5), Na1–O1 2.280(4), Na1–O2 2.328(4), Na1–N2 2.406(5), Na1–N3 2.413(4), Na2–O1 2.309(4), Na2–O2 2.289(4), Na2–N1 2.424(4), Na2–N4 2.436(4).

which is given credence by earlier reports of discrete dinuclear mixed Na–Zn ligand ring systems.[9–11] The beauty of Snaith's ring-stacking principle is that it can be applied to a wide variety of organolithium structures, so several other mixed alkali metal–zinc complexes will need to be structurally characterised and interpreted similarly to this first such complex before any definite conclusions can be reached on the applicability or otherwise of ring-stacking to these mixed valent structures. In that regard, as with **1**, **2** can also be alternatively interpreted as an 'ate, specifically as a dimer of "$[(Ph_2C{=}N)_2(Bu)Zn]^-$" with attached ketimine·Na^+ cations. Again this description fits well with the pattern of Zn–N bond lengths observed [*i.e.* the formally terminal bonds in $(RR'ZnR_2ZnRR')^{2-}$ which interact with 2Na/1Zn centres are shorter than their bridging 1Na/2Zn-coordinated counterparts].

To explain the different structural motifs of **1** and **2**, one must focus on the failure of the Bu ligand in **2** to bridge between metals, a consequence of the selfish carbophilicity of zinc which keeps Bu terminal, whereas both metals share the μ-bonding ketimido ligands in **1** and **2**. Supporting this point, with more electron-rich enolato ligands but significantly also in the absence of Bu ligands, mixed Na–Zn complexes can adopt inverse crown motifs akin to that of **1**.[11]

A link to the ring-laddering principle[1,2,12] has also been established through the synthesis and crystallographic characterisation of the mixed sodium–zinc mixed alkide–alkoxide–amide complex $[\{(Me_2NCH_2CH_2O)(Bu^t)(TMP)NaZn\}_2]$, **3**, prepared from a 2 : 2 : 2 : 1 mixture of butylsodium, TMPH (2,2,6,6-tetramethylpiperidine), di-*tert*-butylzinc and *N*,*N*-dimethylaminoethanol. Its molecular structure (Fig. 4) reveals a step-ladder motif comprising outer amido N–Zn rungs and inner alkoxo O–Na rungs. Completing the structure, along the ladder edge internal Me_2N donor atoms and Bu^t anions ligate to Na and Zn respectively. In a ring-laddering model, **3** could be viewed as two dinuclear (NaOZnN) rings which combine laterally though Na–O edges to generate the tetranuclear ladder. Clearly, the high steric demands of the TMP/Bu^t ligand set rule out the alternative possibilities of ladder formation through combining Zn–N edges or of any type of stacked structure.

Finally, with three distinct structural architectures found in three related complexes, mixed sodium–magnesium/zinc chemistry, and the broader landscape of mixed alkali metal–magnesium/zinc chemistry, would appear to be a fertile area for uncovering further structural types.

We thank the EPSRC (grant award nos. GR/T27228/01 and EP/D076889/1) and the Royal Society (Fellowship to E. H.) for generously sponsoring this research and the referees for their helpful comments.

Notes and references

‡ All reactions were performed under a protective argon atmosphere.

§ *Crystal data* for **1**: $C_{104}H_{82}Mg_2N_8Na_2$, $M = 1538.4$, triclinic, space group $P\bar{1}$, $a = 12.9334(3)$, $b = 13.9081(4)$, $c = 14.1940(4)$ Å, $\alpha = 65.832(1)$, $\beta = 85.235(2)$, $\gamma = 65.586(1)^\circ$, $V = 2109.69(10)$ Å^3, $Z = 1$, $D_c = 1.211$ g cm^{-3}, $\mu = 0.09$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$ Å), $T = 123$ K; 36668 reflections measured ($\theta < 27.1^\circ$), 9261 unique, $R_{int} = 0.045$, R (F, $F^2 > 2\sigma$) = 0.035, R_w (F^2, all data) = 0.103, goodness of fit on $F^2 = 1.02$, 527 refined parameters, constrained riding H atoms except for NH, final difference map within ± 0.20 e Å^{-3}. *Crystal data* for **2**: $C_{86}H_{80}N_6Na_2Zn_2$, $M = 1374.3$, monoclinic, space group $P2_1/n$, $a = 13.2031(12)$, $b = 27.339(3)$, $c = 20.0914(18)$ Å, $\beta = 92.909(2)^\circ$, $V = 7242.8(11)$ Å^3, $Z = 4$, $D_c = 1.260$ g cm^{-3}, $\mu = 0.72$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$ Å), $T = 150$ K; 63519 reflections measured ($\theta < 27.5^\circ$), 16561 unique, $R_{int} = 0.029$, R (F, $F^2 > 2\sigma$) = 0.078, R_w (F^2, all data) = 0.185, goodness of fit on $F^2 = 1.33$, 976 refined parameters, 551 restraints on geometry and displacement parameters to assist refinement of disordered ligands, constrained riding H atoms except for NH, final difference map within ± 1.00 e Å^{-3}. *Crystal data* for **3**: $C_{34}H_{74}N_4Na_2O_2Zn_2$, $M = 747.7$, orthorhombic, space group $P2_12_12_1$, $a = 10.380(2)$, $b = 17.783(3)$, $c = 22.035(4)$ Å, $V = 4067.2(14)$ Å^3, $Z = 4$, $D_c = 1.221$ g cm^{-3}, $\mu = 1.23$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$ Å), $T = 150$ K; 28407 reflections measured ($\theta < 25.0^\circ$), 7155 unique, $R_{int} = 0.069$, R (F, $F^2 > 2\sigma$) = 0.049, R_w (F^2, all data) = 0.113, goodness of fit on $F^2 = 1.15$, 416 refined parameters, constrained riding H atoms, final difference map within ± 1.05 e Å^{-3}. CCDC 631656–631658. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618609b

1 K. Gregory, P. v. R. Schleyer and R. Snaith, *Adv. Inorg. Chem.*, 1991, **37**, 47.
2 R. E. Mulvey, *Chem. Soc. Rev.*, 1991, **20**, 167.
3 (*a*) A. D. Bond, *Coord. Chem. Rev.*, 2005, **249**, 2035; (*b*) A. D. Bond, *Cryst. Growth Des.*, 2005, **5**, 755.
4 D. Barr, R. Snaith, W. Clegg, R. E. Mulvey and K. Wade, *J. Chem. Soc., Dalton Trans.*, 1987, 2141.
5 R. E. Mulvey, *Chem. Soc. Rev.*, 1998, **27**, 339.
6 R. E. Mulvey, *Organometallics*, 2006, **25**, 1060.
7 E. Hevia, K. W. Henderson, A. R. Kennedy and R. E. Mulvey, *Organometallics*, 2006, **25**, 1778.
8 R. E. Mulvey, *Chem. Commun.*, 2001, 1049.
9 P. C. Andrikopoulos, D. R. Armstrong, H. R. L. Barley, W. Clegg, S. H. Dale, E. Hevia, G. W. Honeyman, A. R. Kennedy and R. E. Mulvey, *J. Am. Chem. Soc.*, 2005, **127**, 6184.
10 D. R. Armstrong, W. Clegg, S. H. Dale, E. Hevia, L. M. Hogg, G. W. Honeyman and R. E. Mulvey, *Angew. Chem., Int. Ed.*, 2006, **45**, 3775.
11 S. E. Baillie, E. Hevia, A. R. Kennedy and R. E. Mulvey, *Organometallics*, 2007, **26**, 204.
12 For a microreview of ring laddering in lithium heterocarboxylates, see: A. Downard and T. Chivers, *Eur. J. Inorg. Chem.*, 2001, 2193.