Geometric control of cage architecture; observation of ligand-selective behaviour in the structures of $[\{As_2(NCy)_4\}_2M_4]$ ($M = Na, Cu$; $Cy = C_6H_{11}$)

Alan Bashall,[a] Michael A. Beswick,[b] Eilis A. Harron,[b] Alexander D. Hopkins,[b] Sara J. Kidd,[b] Mary McPartlin,[a] Paul R. Raithby,[b] Alexander Steiner[c] and Dominic S. Wright*[b]

[a] *School of Chemistry, University of North London, London, UK N7 8DB*
[b] *Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: dsw1000@cus.cam.ac.uk*
[c] *Department of Chemistry, Crown Street, Liverpool, UK L69 7ZD*

Received (in Cambridge, UK) 15th April 1999, Accepted 13th May 1999

The structure of $[\{As_2(NCy)_4\}_2Cu_4]$ reveals a dramatic change in the metal coordination mode compared to that found in the Sb analogue $[\{Sb_2(NCy)_4\}_2Cu_4]$, resulting in the distortion of the Cu_4 core from a square-planar to a butterfly shape and providing the first illustration of ligand-selective cage modification in such heterobimetallic species; in contrast the square-planar Na_4 arrangement found in $[\{Sb_2(NCy)_4\}_2M_4]$ ($M = Na, Cu, Ag$) is retained in $[\{As_2(NCy)_4\}_2Na_4]$.

In recent years the synthesis of nitrogen-containing anion ligands of Groups 15 and 16 [such as isoelectronic $S(NR)_3^{2-}$ [1] and $Sb(NR)_3^{3-}$ [2]] has provided new opportunities for the assembly of molecular cages containing a broad spectrum of mixed-element compositions.[3] However, most studies of the coordination chemistry of these and related systems have involved the alkali or alkaline earth metals[3,4] and no studies have so far indicated that changing the Group 15 or 16 elements within a particular family of ligands has any major effect on the coordination behaviour or on the nature of the cage formed for a particular metal. Studies of $[\{Sb_2(NCy)_4\}_2M_4]$ ($M = Li$,[5] Na,[6] Cu, Ag[4a,b]) have shown that the geometries of the supported M_4 cores arise from the compromise between the predominant rigidity of the $[Sb_2(NCy)_4]^{2-}$ ligand and the bonding demands of the coordinated metal ions. These influences are responsible for the switch from a tetrahedral Li_4 core for the Li complex to essentially square-planar M_4 cores in the Na, Cu(I) and Ag(I) complexes, and for the accompanying greater involvement of the μ_2- and exocyclic-N donor centres of the $[Sb_2(NCy)_4]^{2-}$ ligand in the latter. The recent synthesis of $[\{As_2(NCy)_4\}_2Li_4]$,[7,8] a source of the $[As_2(NCy)_4]^{2-}$ ligand, provides the opportunity for assessing the impact of differing geometric demands on cage architecture for a closely related ligand. We report here the first observation of ligand-selective modification for such a heterometallic cage.

In order to provide comparison with the related Sb systems, the Na complex $[\{As(NCy)_4\}_2Na_4]$ **1** and $[\{As_2(NCy)_4\}_2Cu_4]$ **2** were prepared. Complex **1** was obtained from the reaction of $As(NMe_2)_3$ with $CyNH_2$ followed by the addition of CyNHNa. Transmetallation of **1** with CuCl gave **2** (Scheme 1).†

The low-temperature X-ray study of **1**‡ (Fig. 1) shows that the complex has a cage structure consisting of two $[As(NCy)_4]^{2-}$ anions which coordinate four Na^+ cations using a combination of their μ-N and exocyclic-N donor sites. This overall structure and the rhombic arrangement of the Na^+ cations at the centre of the cage is identical to that occurring in the Sb analogue $[\{Sb_2(NCy)_4\}_2Na_4]$[6] and in the Cu and Ag complexes $[Sb_2(NCy)_4]_2M_4$ ($M = Cu, Ag$).[4a,b] However, although still essentially planar and possessing similar Na···Na distances (av. 3.17 Å) the Na_4 core in **1** is significantly more distorted than that in $[\{Sb_2(NCy)_4\}_2Na_4]$ (with alternating Na···Na···Na angles of av. 99.6 and av. 80.4°; *cf.* av. 93.5 and 86.4° [6]).

$$2As(NMe_2)_3 \xrightarrow[\text{ii 2CyNHNa}]{\text{i 2CyNH}_2} \underset{\mathbf{1}}{[\{As(NCy)_4\}_2Na_4]} \xrightarrow{4CuCl} \underset{\mathbf{2}}{[\{As(NCy)_4\}_2Cu_4]}$$

Scheme 1

In view of the similarity between **1** and the analogous Sb complex $[\{Sb_2(NCy)_4\}_2Na_4]$ it was anticipated that the Cu(I) complex $[\{As_2(NCy)_4\}_2Cu_4]$ **2** would exhibit the same overall structure as $[\{Sb_2(NCy)_4\}_2Cu_4]$[2] (in which essentially the same coordination mode as that found in **1** is preserved). However, the low-temperature X-ray study of 2‡ reveals that replacement of the Na^+ cations with Cu^I results in a dramatic change in the cage architecture. Rather than the μ-N and exocyclic-N centres of the two $[As_2(NCy)_4]^{2-}$ ligands bridging the alternate Cu···Cu edges of the Cu_4 core (as occurs in the Sb analogue[2]), the N atoms of each coordinate separate Cu ions in a manner not previously observed. This change in bonding mode results in essentially linear Cu(I) geometries [N–Cu–N 175.4(2)°]. The consequence of the asymmetrical coordination of the Cu centres of **2** [exocyclic-N–Cu 1.854(4), μ-N–Cu 1.949(4) Å] is that the Cu_4 core now has a butterfly-shape (rather than planar) arrangement. The switch from a symmetrical to an asymmetrical coordination mode corresponds to a 45° rotation of the Cu_4 core, a result of which is that the As_2N_2 and Cu_4 rings are now eclipsed.

The structural pattern found in **1** and in the Sb analogue, $[\{Sb_2(NCy)_4\}_2Na_4]$, stems from the presence of essentially ionic metal–ligand interactions which favour a ligand mode that maximises the coordination number of Na^+. In complexes containing Cu^I the preference for an essentially linear geometry can be satisfied by maintaining this same coordination mode (as

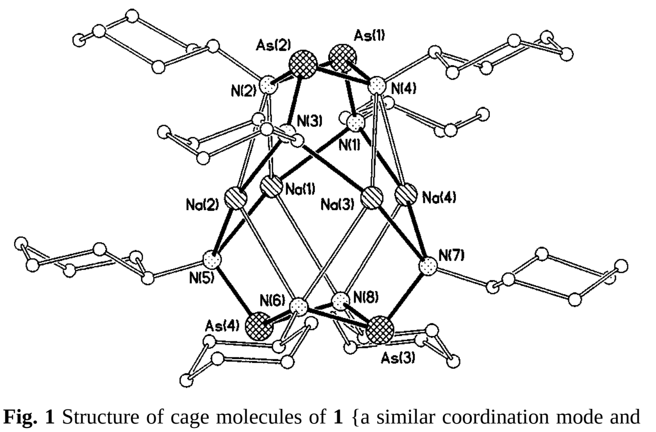

Fig. 1 Structure of cage molecules of **1** {a similar coordination mode and cage arrangement is also found in $[\{As_2(NCy)_4]_2M_4]$ ($M = Na, Cu, Ag$)}. H-atoms have been omitted for clarity. Key bond lengths (Å) and angles (°); As(1)–N(1) 1.80(1), As(1)–N(2) 1.94(1), As(1)–N(4) 1.94(1), As(2)–N(3) 1.80(1), As(2)–N(4) 1.992(1), As(2)–N(2) 1.95(1), As(3)–N(7) 1.78(1), As(3)–N(6) 1.93(1), As(3)–N(8) 1.94(1), As(4)–N(5) 1.78(1), As(4)–N(8) 1.92(1), As(4)–N(6) 1.96(1), range exocyclic-N–Na 2.28(1)–2.37(1), range μ-N–Na 2.68(1)–2.99(1), Na···Na mean 3.17; As–(μ-N)–As means 93.0 (μ-N)–As–(μ-N) mean 78.8, (μ-N)–As–(*exo*-N) mean 103.8, (*exo*-N)–Na–(*exo*-N) mean 156.9, (μ-N)–Na–(μ-N) mean 122.9, Na···Na(2,4)···Na mean 99.6, Na···Na(1,3)···Na mean 80.4.

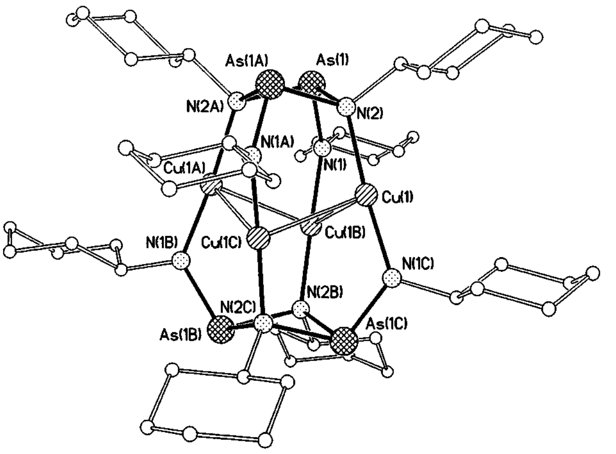

Fig. 2 The unique cage arrangement found in **2**. H-atoms have been omitted for clarity. Key bond lengths (Å) and angles (°); As(1)–N(2) 1.955(4), As(1)–N(2a) 1.949(4), As(10–N(1) 1.767(4), N(1)–Cu(1b) 1.854(4), N(2b)–Cu(1b) 1.927(4), Cu(1)···Cu(1b) 2.692(1); N(2)–As(1)–N(2a) 80.4(2), As(1)–N(2)–As(1a) 94.3(2), N(2)–As(1)–N(1) 104.3(4), N(2a)–As(1)–N(1) 104.0(2), N(1)–Cu(1b)–N(2b) 175.4(2), Cu(1b)···Cu-(1)···Cu(1c) 83.4(2), dihedral angles between the As_2N planes in the As_2N_2 rings 143.2, and the Cu_3 planes of the Cu_4 core 126.0.

occurs in $[\{Sb_2(NCy)_4]_2Cu_4]^2$). This symmetrical arrangement has the advantage that the Cu centres can increase their coordination numbers by additional weak interactions with the μ-N donor sites. However, with the more compact $[As_2(NCy)_4]^{2-}$ ligand adoption of the same mode would presumably destabilise the complex since the consequent compression of the Cu_4 core would lead to unfavourably short Cu···Cu contacts (*ca.* 2.46 Å; *cf.* 2.56 Å in Cu metal).[9] The alternative adopted in **2** gives a release from this effect since the asymmetrical ligand mode results in puckering of the Cu_4 core {with a resulting increase in Cu···Cu separation to 2.692(1);*cf.* 2.57 Å in $[\{Sb_2(NCy)_4\}_2Cu_4]^2$, but still maintains a linear Cu coordination geometry,

This study shows for the first time that geometric changes brought about by substitution of one Group 15 element for another within a particular family of poly-imido ligands can have large effects on the cage produced. This finding has important implications to the targeted design of cages with a particular structure and to the possibility of selective coordination involving ligands based on p block element frameworks.

We gratefully acknowledge the EPSRC (A. D. H., S. J. K., P. R. R., M. McP.), the Leverhulme Trust (M. A. B.) and Electron Industries (A. D. H.) for financial support.

Notes and references

† *Syntheses*: **1**; a mixture of $[PhCH_2Na\}$ (0.46 g, 4 mmol) and $CyNH_2$ (0.46 ml, 4 mmol) in a toluene (10 ml) was heated briefly to reflux, with the formation of a pale yellow precipitate. In a separate Schlenk tube, a mixture of $As(NMe_2)_3$ (2.5 ml, 4.0 mmol) and $CyNH_2$ (0.46 ml, 4 mmol) in toluene (10 ml) was briefly heated to reflux. This solution (cooled to room temperature) was added to the first, with the formation of a clear yellow solution which became orange after bringing to reflux (2 min). A small amount of solid was removed by filtration and careful reduction of the filtrate under vacuum resulted in precipitation of a small amount of white solid. Hexane (1 ml) was added and the precipitate was warmed into solution. Storage at room temp. (72 h) gave small, colourless needles of **1** (0.63 g, 54%). Final decomp. 192 °C. IR (Nujol, NaCl), ν_{max} = 1094m, 1067, 1019m, 798m, 750w. ^1H NMR (+25 °C, d_6-benzene, 250 MHz), δ 3.67 (m 2H, α-C–H Cy), 2.63 (m 2H, α-C–H Cy), 2.20–1.0 (m 40 H, $-CH_2-$ Cy). Satisfactory elemental analysis (C, H, N) was obtained.

2; a mixture of **1** (1.22 g, 1.0 mmol) and CuCl (0.46 g, 4.6 mmol) in toluene (20 ml) was briefly heated to reflux then stirred (3 h). A cloudy grey–green suspension was formed which was filtered off to give a yellow filtrate. The solution was reduced under vacuum until precipitation commenced, this being warmed back into solution. Storage at room temp. (72 h) gave small, colourless needles of **2** (0.07 g, 5% first batch). Decomp. 188 °C. ^1H NMR (+25 °C, d_6-benzene, 250 MHz), δ 3.65 (2H, m α-C–H of Cy), 3.55 (2H, m α-C–H of Cy), 2.7–1.1 (40 H, overlapping m, $-CH_2-$ of Cy). Satisfactory elemental analysis (C, H, N) was obtained.

‡ *Crystal data*: **1**; $C_{48}H_{88}As_4Na_4N_8$, M = 1168.90, orthorhombic, space group *Pbca*, Z = 8, a = 24.883(5), b = 37.424(8), c = 11.980(9) Å, V = 11156(9) Å^3, μ(Mo-Kα) = 2.446 mm^{-1}, T = 180(2) K. Data were collected on an Siemens-Stoe AED diffractometer and corrected for absorption using ψ-scans. Of a total of 9314 reflections collected, 6096 were independent (R_{int} = 0.068). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final $R1$ = 0.105 [$I > 2\sigma(I)$] and $wR2$ = 0.264 (all data).[10] The high R values for **1** are due to poor crystal quality. Maximum peaks in the Fourier synthesis can be assigned to a shadow image of the molecule in the crystal structure. Refinement of these peaks as As and Na positions give an occupation of 8% for the shadow image. However, in the final refinement the shadow image was omitted owing to rather high correlation factors and lack of convergence.

2; $C_{48}H_{88}As_4Cu_4N_8$, M = 1331.10, tetragonal, space group $I4_1/a$, Z = 4, a = 24.046(3), b = 24.046(3), c = 9.941(3) Å, V = 5748(2) Å^3, μ(Mo-Kα) = 3.783 mm^{-1}, T = 223(2) K. Data were collected on a Siemens P4 diffractometer and corrected for absorption using ψ-scans. Of a total of 2653 reflections collected, 2001 were independent (R_{int} = 0.044). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final $R1$ = 0.044 [$I > 2\sigma(I)$] and $wR2$ = 0.076 (all data).[10] CCDC 182/1259. See http://www.rsc.org/suppdata/cc/1999/1145/ for crystallographic files in .cif format for compound **1**.

1 R. Fleischer, S. Freitag, F. Pauer and D. Stalke, *Angew. Chem.*, 1996, **108**, 208; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 204; T. Chivers, X. Gao, M. Parvez and G. Schatte, *Inorg. Chem.*, 1996, **35**, 4094.

2 M. A. Beswick, N. Choi, C. N. Harmer, A. D. Hopkins, M. A. Paver, M. McPartlin, P. R. Raithby, A. Steiner, M. Tombul and D. S. Wright, *Inorg. Chem.*, 1998, **37**, 2177.

3 M. A. Beswick and D. S. Wright, *Coord. Chem. Rev.*, 1998, **176**, 373; M. A. Beswick, M. E. G. Mosquera and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1998, 2437 and references therein.

4 For examples involving other metals, see for example: (*a*) M. A. Beswick, C. A. Harmer, P. A. Paver, P. R. Raithby, A. Steiner and D. S. Wright, *Inorg. Chem.*, 1997, **36**, 1740; (*b*) D. Barr, A. J. Edwards, S. Pullen, M. A. Paver, M.-A. Rennie, P. R. Raithby and D. S. Wright, *Angew. Chem.*, 1994, **106**; 1960; *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1875; (*c*) D. F. Moser, I. Schranz, M. C. Gerrety, L. Stahl and R. J. Staples, *J. Chem. Soc., Dalton Trans.*, 1999, 751.

5 R. A. Alton, D. Barr, A. J. Edwards, M. A. Paver, M.-A. Rennie, C. A. Russell, P. R. Raithby and D. S. Wright, *J. Chem. Soc, Chem. Commun.*, 1994, 1481.

6 A. Bashall, M. A. Beswick, C. N. Harmer, A. D. Hopkins, M. McPartlin, M. A. Paver, P. R. Raithby and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1998, 1389.

7 M. A. Beswick, E. A. Harron, A. D. Hopkins, P. R. Raithby and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1999, 107.

8 See also I. Schranz, L. Stahl and R. J. Staples, *Inorg. Chem.*, 1998, **37**, 1493, for the related $[P_2(NBu^t)_4]^{2-}$ ligand.

9 Assuming that the Cu atoms would be located at the mid-points of N(1)–N(1B), N(1)–N(1C), N(1A)–N(1C), N(1A)–N(1B).

10 SHELXTL PC version 5.03, Siemens Analytical Instruments, Madison, WI, 1994.

Communication 9/03010G