DALTON
COMMUNICATION

Synthesis and structure of $[\{Sb(NCy)_3\}\{Cd[N(SiMe_3)_2]\}_3]\cdot[Li\{N(SiMe_3)_2\}\cdot thf]_2$, containing a bimetallic $[SbCd_3]$ cage

Allan Bashall,[a] Michael A. Beswick,[b] Christopher N. Harmer,[b] Mary McPartlin,[a]
Michael A. Paver[b] and Dominic S. Wright*[,b]

[a] *School of Applied Chemistry, University of North London, Holloway Road, London, UK N7 8DB*
[b] *Chemistry Department, Cambridge University, Lensfield Road, Cambridge, UK CB2 1EW*

The reaction of $[\{Sb(NCy)_3\}_2Li_6]$ with $[Cd\{N(SiMe_3)_2\}_2]$ (1:6 equivalents) gave the unusual co-complex $[\{Sb(NCy)_3\}\{Cd[N(SiMe_3)_2]\}_3]\cdot[Li\{N(SiMe_3)_2\}\cdot thf]_2$, containing a heterobimetallic $[SbCd_3]$ cage.

Molecules containing a variety of mixed Group 12 (M = Zn or Cd) and 15 (E = P or As) stoichiometries have been the focus of a number of studies in the past,[1,2] as a result of their potential applications as single-source precursors for the deposition of 12/15 (2/5) semi-conductor layers such as Cd_3P_2. Complexes of this type have been most commonly prepared by (*i*) the metallation reactions of Group 12 organometallics with secondary phosphines or arsines or (*ii*) by desilylation reactions of the Group 12 halides with $[E(SiMe_3)_3]$. We have shown[1i,3] that nucleophilic substitution of Group 12 bis(trimethylsilylamides), $[M\{N(SiMe_3)_2\}_2]$, can be employed in the preparation of metalloorganic Group 12 compounds. This strategy, which was originally pioneered by Lappert and co-workers[4] in the synthesis of Group 14 complexes, is of particular value in the formation of Cd compounds for which no commercially available stable organometallic precursor exists, *e.g.* the homoleptic phosphide dianion $[Cd_4(PPh_2)_{10}]^{2-}$.[1i] However, the syntheses and properties of complexes containing the heaviest Group 15 elements (Sb or Bi) have been largely ignored. In view of recent advances made in the assembly of mixed-metal cage complexes utilising imido Sb^{III} anions,[5] we decided to investigate the preparation of complexes containing novel Sb^{III}–Group 12 combinations.

We report here the synthesis and structure of the unusual co-complex $[\{Sb(NCy)_3\}\{Cd[N(SiMe_3)_2]\}_3]\cdot[Li\{N(SiMe_3)_2\}\cdot thf]_2$ **1** ($Cy = C_6H_{11}$), prepared from the reaction of $[\{Sb(NCy)_3\}_2Li_6]$ with $[Cd\{N(SiMe_3)_2\}_2]$ (1:6 equivalents) in thf (Scheme 1).†

$$[\{Sb(NCy)_3\}_2Li_6] + 6[Cd\{N(SiMe_3)_2\}_2] \xrightarrow{(i)} 2[\{Sb(NCy)_3\}\{Cd[N(SiMe_3)_2]\}_3]\bullet[Li\{N(SiMe_3)_2\}\bullet thf]$$

Scheme 1 (*i*) thf, $-2[Li\{N(SiMe_3)_2\}]$

The low-temperature X-ray structure of **1** ‡ shows it to consist of two chemically distinct molecular units resulting from the co-crystallisation of the product of the reaction, $[\{Sb(NCy)_3\}\{Cd[N(SiMe_3)_2]\}_3]$ (Fig. 1), with the by-product, $[Li\{N(SiMe_3)_2\}\cdot thf]_2$. The crystal structure of the thf monosolvate of (trimethylsilylamido)lithium has previously been reported[6] and the structure and arrangement of the dimeric molecular unit in **1** is identical within crystallographic error. The heterobimetallic Sb^{III}–Cd cage $[\{Sb(NCy)_3\}\{Cd[N(SiMe_3)_2]\}_3]$ results from the nucleophilic substitution of only one of the $N(SiMe_3)_2$ groups of each $[Cd\{N(SiMe_3)_2\}_2]$ by the $[Sb(NCy)_3]^{3-}$ trianions of $[\{Sb(NCy)_3\}_2Li_6]$, with the elimination of $[Li\{N(SiMe_3)_2\}]$. The

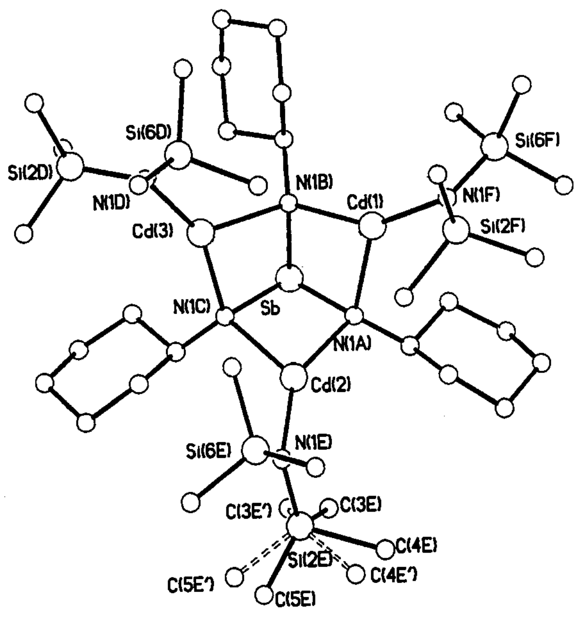

Fig. 1 Molecular structure of complex **1**. Hydrogen atoms and the $[Li\{N(SiMe_3)_2\}\cdot thf]_2$ dimer units (one per formula unit) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sb(1)–N(1A) 2.04(1), Sb(1)–N(1B) 2.054(9), Sb(1)–N(1C) 2.056(9), Cd(1)–N(1A) 2.299(9), Cd(1)–N(1B) 2.193(9), Cd(2)–N(1A) 2.21(1), Cd(2)–N(1C) 2.31(1), Cd(3)–N(1B) 2.328(9), Cd(3)–N(1C) 2.20(1), average Cd–N $(SiMe_3)_2$ 2.08; average N–Sb–N 87.9, average Cd–N–Sb 95.8, average N–Cd–N 78.1, average Cd–N (Cy)–Cd 112.5

---

† Synthesis of complex **1**. To a solution of $[\{Sb(NCy)_3\}_2Li_6]$ (1.08 g, 1.25 mmol) in thf (10 ml) was added $[Cd\{N(SiMe_3)_2\}_2]$ (1.5 ml, 3.75 mmol). The reaction mixture was briefly heated to reflux, with a faint yellow solution resulting. The thf was removed under vacuum, giving a colourless solid which was dissolved in a minimum volume of hexane (4 ml). Storage at 25 °C (one week) gave large colourless needles of **1** (0.85 g, 40%); m.p. *ca.* 60 °C; IR (Nujol), ν_{max}/cm^{-1} major bands at 1010s (br), 940s, 850s, 810vs (br); ^1H NMR (250 MHz, +25 °C, C_6D_6), 3.61 (m, 8 H, thf), 2.30–1.00 (m, 33 H, NCy), 1.25 (m, 8 H, thf), 0.38 {s, 36 H, $Li[N(SiMe_3)_2]$}, 0.36 {s, 54 H, $Cd[N(SiMe_3)_2]$} (Found: C, 39.2; H, 8.2; N, 6.6. Calc. for $C_{44}H_{113}Cd_3LiN_7OSbSi_8$: C, 39.3; H, 8.1; N, 6.6%).

‡ Crystal data for complex **1**. $C_{44}H_{113}Cd_3LiN_7OSbSi_8$, $M = 1471.04$, triclinic, space group $P\bar{1}$, $a = 9.4399(8)$, $b = 20.378(3)$, $c = 21.150(3)$ Å, $\alpha = 63.209(8)$, $\beta = 83.853(8)$, $\gamma = 88.427(8)°$, $U = 3610.0(7)$ Å^3, $Z = 2$, $T = 198(2)$ K, μ(Mo-Kα) = 1.408 mm^{-1}. 12 991 Data were collected which were merged giving 12 182 unique reflections ($R_{int} = 0.0485$). Some components of the anisotropic thermal parameters of the silyl groups Cd–Sb unit were high, indicating rotational disorder. The disorder could only be resolved for one of the Me_3Si groups, with two orientations [C(3E), C(4E), C(5E) and C(3E′), C(4E′), C(5E′)] with 50:50 occupancy. The $[LiN(SiMe_3)_2\cdot thf]_2$ unit lies on an inversion centre. The high anisotropic thermal parameters for the $N(SiMe_3)_2$ groups are consistent with rotational disorder, but this was not resolved. CCDC reference number 186/851.

remaining $N(SiMe_3)_2$ groups of the Cd–Sb cage resist substitution by a further $[\{Sb(NCy)_3\}]^{3-}$ trianion, and the 1 : 3 reaction yields the same product. This reactivity pattern is very different to that observed in the reaction of $[\{Sb(NCy)_3\}_2Li_6]$ with $[PbCp_2]$ ($Cp = C_5H_5$) which results in disubstitution of the Pb^{II} precursor, giving the polyhedral cage $[\{Sb(NCy)_3\}_2Pb_3]$.[5b]

Comparison of the Sb geometry found in the $[\{Sb(NCy)_3\}\{Cd[N(SiMe_3)_2]\}_3]$ unit of **1** with the Me_2NH complex of the Sb–Li precursor $[\{Sb(NCy)_3\}_2Li_6{\cdot}2HNMe_2]$ indicates that there is considerable strain induced by the accommodation of three Cd^{2+} ions into the cage arrangement. Although the Sb atom retains a broadly similar pyramidal geometry to that present in $[\{Sb(NCy)_3\}_2Li_6{\cdot}2HNMe_2]$ and the Sb–N bond lengths (average 2.05 Å) are almost unaltered, there is a large reduction in the N–Sb–N angles from those present in the Li precursor (average 87.9° in **1**; *cf.* average 93.4°). This compression in the N–Sb–N angles has the effect of reducing the steric confrontation between the Cy groups of the $[Sb(NCy)_3]^{3-}$ trianion and the Cd-attached $N(SiMe_3)_2$ groups, and results (geometrically) in extremely acute internal N–Cd–N co-ordination angles (average 78.1°). Highly irregular trigonal-planar geometries are therefore adopted by the three Cd^{2+} ions (sum of angles 359.5°), which are co-ordinated asymmetrically by two imido N centres of the Sb^{III} trianion and by a terminal $N(SiMe_3)_2$ group. Although the shorter Cd–N bond lengths within the Cd_3N_3 ring of **1** (average 2.20 Å) are similar to those found in other amido Cd complexes,[3] the longer Cd–N bonds (average 2.31 Å) are well outside the expected range for three-co-ordinate Cd and are best formulated as co-ordinative interactions (*cf.* typical Cd–N bond lengths of *ca.* 2.37–2.57 Å in Lewis-base adducts).[3,7] In order to compensate for the generally poor co-ordination of the imido-N groups to the Cd^{2+} cations the bonding to the terminal $N(SiMe_3)_2$ groups is enhanced, leading to unusually short Cd–N bonds {average 2.08 Å; *cf.* 2.136(7) Å for the terminal Cd–N bonds in $[\{(Me_3Si)_2N\}Cd\{(2,4,6\text{-}Me_3C_6H_2)_2PO\}_2Li{\cdot}2thf]$[8]}.

A significant feature demonstrated for the first time in this study is the ability of the $[Sb(NCy)_3]^{3-}$ ligand to alter its geometry in order to satisfy the geometric and steric demands of the co-ordinated metal ions. This contrasts with the rigid arrangements present in related Si^{IV} ligands {such as $[MeSi(NBu^t)_3]^{3-}$} [9] in which the constrained (sp^3) bridgehead is largely unaffected by interchanging the co-ordinated metal ion, *e.g.* in the structurally related complex $[\{MeSi(NBu^t)_3\}\{Mg[N(SiMe_3)_2]\}_3]$[10] obtained by deprotonation of $MeSi(NHBu^t)_3$ with $[Mg\{N(SiMe_3)_2\}_2]$. Although the geometric arrangement of the $[\{Sb(NCy)_3\}\{Cd[N(SiMe_3)_2]\}_3]$ cage is not unprecedented, almost all the structurally characterised complexes reported containing Group 12–Group 15 combinations are arsenides[11] and, to our knowledge, the only structurally characterised molecular complex containing a Group 12 (Zn–Hg)/Sb or Bi mixed-metal composition is the simple adduct $Sb_2Et_4{\cdot}2CdI_2$.[12] Complex **1** is also the only example of a Cd imido compound so far characterised. As demonstrated by the synthesis of **1**, transmetallation of Group 12 metal sources with a pre-formed Group 15 anion ligand arrangement provides a useful route to these potentially valuable precursor materials.[13]

Acknowledgements

We gratefully acknowledge the EPSRC (M. A. B., C. N. H. and M. M.), Jesus College Cambridge (fellowship to M. A. P.) and the Royal Society (D. S. W.) for financial support.

References

1 Zn and Cd phosphides: (*a*) A. M. Arif, A. H. Cowley, R. A. Jones and S. U. Koschmieder, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 1319; (*b*) B. L. Benac, A. H. Cowley, R. A. Jones, C. M. Nunn and T. C. Wright, *J. Am. Chem. Soc.*, 1989, **111**, 4986; (*c*) S. C. Goel, M. Y. Chaing, D. J. Rauscher and W. E. Buhro, *J. Am. Chem. Soc.*, 1990, **112**, 5636; (*d*) S. C. Goel, M. Y. Chaing, D. J. Rauscher and W. E. Buhro, *J. Am. Chem. Soc.*, 1993, **115**, 160; (*e*) A. Eichöfer, J. Eisenmann, D. Fenske and F. Simon, *Z. Anorg. Allg. Chem.*, 1993, **619**, 4986; (*f*) A. J. Edwards, M. A. Paver, P. R. Raithby, C. A. Russell and D. S. Wright, *Organometallics*, 1993, **12**, 4687; (*g*) M. A. Machett, M. Y. Chaing and W. E. Buhro, *Inorg. Chem.*, 1994, **33**, 1109; (*h*) M. G. Davidson, A. J. Edwards, P. R. Raithby, M. A. Paver, M.-A. Rennie, C. A. Russell, A. Steiner, K. L. Verhorevoort and D. S. Wright, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1989; (*i*) M. A. Beswick, M.-A. Rennie, C. A. Russell, P. R. Raithby, A. Steiner, K. L. Verhorevoort and D. S. Wright, *Angew. Chem.*, 1995, **34**, 2891; *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 2662.

2 For selected applications of Zn and Cd/Group 16 precursors, see, M. L. Steigerwald and C. R. Sprinkle, *J. Am. Chem. Soc.*, 1987, **109**, 792; M. L. Steigerwald and C. R. Sprinkle, *Organometallics*, 1988, **7**, 245; M. L. Steigerwald and L. Brus, *Acc. Chem. Res.*, 1990, **23**, 183; M. Bochmann, K. J. Webb, J. E. Hails and D. Wolverson, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 155; J. Arnold, J. M. Walker, K. M. Yu, P. J. Bonasia, A. L. Seligson and E. D. Bourret, *J. Cryst. Growth*, 1992, **124**, 647.

3 D. Barr, A. J. Edwards, P. R. Raithby, M.-A. Rennie, K. L. Verhorevoort and D. S. Wright, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1627; A. J. Edwards, A. Fallaize, P. R. Raithby, M.-A. Rennie, A. Steiner, K. L. Verhorevoort and D. S. Wright, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 133.

4 See, for example, D. E. Goldberg, D. H. Harris, M. F. Lappert and K. M. Thomas, *J. Chem. Soc.*, *Chem. Commun.*, 1976, 261.

5 (*a*) M. A. Paver, C. A. Russell, D. S. Wright, *Angew. Chem.*, 1995, **107**, 1077; *Angew. Chem.*, *Int. Ed. Engl.*, 1995, **34**, 1545; (*b*) M. A. Beswick, C. N. Harmer, M. A. Paver, P. R. Raithby, A. Steiner and D. S. Wright, *Inorg. Chem.*, 1997, **36**, 1740.

6 L. M. Englehardt, B. S. Jolly, P. C. Junk, C. L. Raston, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1986, **39**, 1337.

7 See, for example, J. Boersma, B. Fischer, W. J. J. Smeets, A. L. Spek and G. P. M. van Meer, *J. Organomet. Chem.*, 1979, **322**, C37; A. L. Spek, *Cryst. Struct. Commun.*, 1982, **11**, 1621; P. O'Brien, M. B. Hursthouse, A. C. Jones, M. Motevalli and J. R. Walsh, *J. Organomet. Chem.*, 1993, **449**, 1; D. Barr, A. J. Edwards, P. R. Raithby, M.-A. Rennie, K. L. Verhorevoort and D. S. Wright, *J. Organomet. Chem.*, 1995, **493**, 175.

8 M. A. Beswick, N. L. Cromhout, C. N. Harmer, J. S. Palmer, P. R. Raithby, A. Steiner, K. L. Verhorevoort and D. S. Wright, *J. Chem. Soc.*, *Chem. Commun.*, 1997, 583.

9 M. Veith, *Adv. Organomet. Chem.*, 1990, **31**, 269; *Chem. Rev.*, 1990, **90**, 3.

10 M. Veith, A. Spaniol, J. Pöhlmann, F. Gross and V. Huch, *Chem. Ber.*, 1993, **126**, 2625.

11 C.-I. Branden, *Acta Chem. Scand.*, 1963, **17**, 1363; *Ark. Kemi*, 1964, **22**, 485; G. Dyer, D. C. Goodall, R. H. B. Mais, H. M. Powell and L. M. Venanzi, *J. Chem. Soc. A*, 1966, 1110; J. Hubert, A. L. Beachamp and R. Rivest, *Can. J. Chem.*, 1975, **53**, 3383; S. Hunter, G. H. Rodley and K. Emerson, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 113; A. L. Balch, M. M. Olmstead and S. P. Rouley, *Inorg. Chem.*, 1988, **27**, 2275; U. Wirringa, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Angew. Chem.*, 1993, **105**, 1680; *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 1628; T. J. Groshens, K. T. Higa and R. J. Butcher, *J. Organomet. Chem.*, 1993, **463**, 97; B. Rademacher, W. Schwarz and M. Westerhausen, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1439.

12 R. S. Dickson, K. D. Heazle, G. N. Pain, G. B. Deacon, B. O. West, G. D. Fallon, R. S. Rowe, P. W. Leech and M. Faith, *J. Organomet. Chem.*, 1993, **449**, 131.

13 A. H. Summer, *Photoemission Materials*, R. E. Kruger Publishing Co., 1968.

Received 30*th October* 1997; *Communication* 7/07816A