The Utility of $(C_5Me_5)_2Sm$ in isolating Crystallographically Characterizable Zintl Ions. X-Ray Crystal Structure of a Complex of $(Sb_3)^{3-}$

William J. Evans,* Shirley L. Gonzales and Joseph W. Ziller

Department of Chemistry, University of California, Irvine, California 92717, USA

$(C_5Me_5)_2Sm$ reacts with $Sb(Bu^n)_3$ in toluene to form $[(C_5Me_5)_2Sm]_3(\mu\text{-}\eta^2:\eta^2:\eta^1\text{-}Sb_3)(thf)$ (thf = tetrahydrofuran), which contains a bent $(Sb_3)^{3-}$ ion [114.5(1)°] with an average Sb–Sb distance of 2.688(1) Å.

Although for over 100 years the main group elements have been known to form a fascinating variety of anions upon reduction with alkali metals in liquid ammonia,[1] definitive characterization of these so-called[2] Zintl[3] ions by X-ray crystallography has proved difficult. The introduction of ethylenediamine and cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) into these systems provided crystallographically characterizable salts of several Zintl ions,[1,4–6] but the structures of many of these species remain unknown.

Recently, we have been able to use the bent metallocene, $(C_5Me_5)_2Sm$,[7] to make crystallographically characterizable complexes of the dianions, $(N_2)^{2-}$ [8] and $(Bi_2)^{2-}$.[9] In efforts to extend this chemistry to the other congeners in main group 15, we have found that $(C_5Me_5)_2Sm$ will form a crystallographically characterizable complex of a triatomic Zintl ion. We

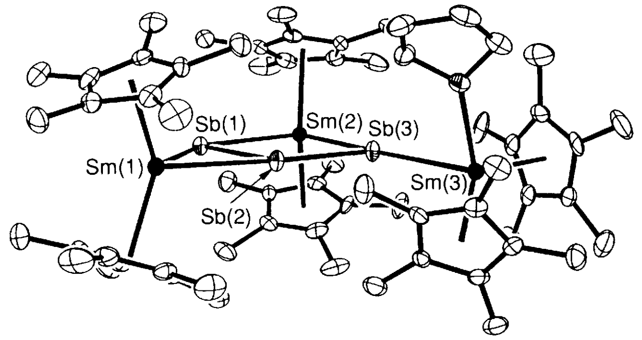

Fig. 1 ORTEP diagram of $[(C_5Me_5)_2Sm]_3(\mu\text{-}\eta^2:\eta^2:\eta^1\text{-}Sb_3)(thf)$, **1**, with probability ellipsoids drawn at the 50% level. Selected bond distances (Å) and angles (°) follow: Sm–C(C_5Me_5) averages: 2.775(14) [Sm(1)], 2.749(19) [Sm(2)], 2.734(19) [Sm(3)]; (ring centroid)–Sm–(ring centroid) angles: 133–136°. Sm(1)–Sb(1), 3.190(1); Sm(1)–Sb(2), 3.182(1): Sm(2)–Sb(1), 3.193(1); Sm(2)–Sb(3), 3.162(1); Sm(3)–Sb(3), 3.205(1); Sm(3)–O(1), 2.492(4); Sb(1)–Sm(1)–Sb(2), 49.9(1); Sb(1)–Sm(2)–Sb(3), 90.7(1); Sb(3)–Sm(3)–O(1), 89.3(1); Sm(1)–Sb(1)–Sm(2), 142.0(1); Sm(1)–Sb(2)–Sb(3), 177.1(1); Sm(2)–Sb(3)–Sm(3); 166.8(1), Sm(2)–Sb(3)–Sb(2), 77.7(1); Sm(3)–Sb(3)–Sb(2), 115.2(1).

report here the isolation and structural details of an $(Sb_3)^{3-}$ complex which demonstrates the potential of the $(C_5Me_5)_2Sm$ unit in developing the chemistry of main group element polyanions.

In a reaction analogous to the synthesis of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}Bi_2)$[9] from $(C_5Me_5)_2Sm$ and $BiPh_3$, $(C_5Me_5)_2Sm$ was treated with $Sb(Bu^n)_3$ in toluene. An immediate colour change from dark green to red–brown was observed. The ^1H NMR spectrum of the crude product obtained by removal of solvent contained numerous overlapping C_5Me_5 resonances in the δ 0.8 to 1.7 region. Despite the complexity of this mixture, dark-red single crystals were obtainable by recrystallization from benzene in the presence of thf. An X-ray diffraction study† showed that the crystals were not the antimony analogue of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}Bi_2)$, but instead the triantimony species $[(C_5Me_5)_2Sm]_3(\mu\text{-}\eta^2:\eta^2:\eta^1\text{-}Sb_3)(thf)$, **1**, Fig. 1.

Although Zintl first proposed the existence of an $(Sb_3)^{3-}$ ion in 1931[1,3] and cryometric data have suggested its existence,[10] its structure was never determined.[1] The most closely related crystallographically characterized solids containing Sb_n fragments are the $(Sb_6)^{8-}$ anions in Eu_2Sb_3[11] and Sr_2Sb_3[12] and the organic derivative $(Sb_3Ph_4)^-$.[13]

The $(Sb_3)^{3-}$ ion in **1** has indistinguishable Sb–Sb distances of 2.689(1) and 2.686(1) Å. These distances are smaller than the Sb–Sb single bond distances in $(Sb_6)^{8-}$ [2.887(4)–3.016(3) Å],[11,12] $(Sb_3Ph_4)^-$ [2.761(1) Å],[13] $Ph_2SbSbPh_2$ [2.837(1) Å],[14] $Me_2SbSbMe_2$ [2.862(2) Å],[15] $(Me_3Si)_2SbSb(SiMe_3)_2$ [2.867(1) Å],[16] and $[(C_5Me_5)Sb]_4$ [2.856(1) Å],[17] but they are longer than the 2.663 Å distance in *trans*-η^2-$[(CO)_5WSb(Ph)Sb(Ph)W(CO)_5]W(CO)_5$[18] for which an Sb–Sb bond order of 1.5 has been described.[13] The Sb–Sb distance in **1** can also be compared to the 2.749(1) and 2.751(1) Å distances in $Sb_4{}^{2-}$ the molecular orbital diagram of which implies an Sb–Sb bond order of 1.25.[19]

Five of the six Sm–Sb distances in **1** fall in the narrow range of 3.162(1)–3.205(1) Å. These Sm–Sb distances are 0.09–0.13 Å shorter than the 3.29(2) Å Sm–Bi average distance in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}Bi_2)$,[9] a range which overlaps the 0.11–0.16 Å difference in radial size of antimony and bismuth.[20] The sixth Sm–Sb distance, the 3.686(1) Å Sm(2)–Sb(2) length, appears to be too long for a significant interaction.[21] Consequently, each samarium atom is formally eight-coordinate. The structural parameters for each of the three unique $(C_5Me_5)_2Sm^{III}$ units in **1** are in the normal range for eight-coordinate trivalent organosamarium species.[8,22] The Sb–Sb–Sb angle of 114.5(1)° in **1** is larger than those in $(Sb_6)^{8-}$, 103.00(8)–108.7(1)°, and $(Sb_3Ph_4)^-$, 88.8(1)°.

Although the synthetic details of this organosamarium main group 15 reaction system have not yet been fully defined, these results clearly show that the $(C_5Me_5)_2Sm$ unit is able to generate and stabilize anions comprised of several main group elements. The range of usefulness of $(C_5Me_5)_2Sm$ in developing polynuclear main group element chemistry is under investigation.

We thank the National Science Foundation for support of this research. Funds for the purchase of the X-ray equipment were made available from NSF grant CHE-85-14495.

Received, 8th April 1992; Com. 2/01872A

---

† *Crystal data* for **1**: $C_{64}H_{98}OSb_3Sm_3\cdot C_6H_6$, $M = 1777.8$, triclinic space group $P\bar{1}$, $a = 13.475(2)$, $b = 14.987(2)$, $c = 17.916(3)$ Å, $\alpha = 79.780(14)$, $\beta = 78.116(13)$, $\gamma = 84.095(12)$°, $V = 3476.2(9)$ Å^3, $Z = 2$, $D_c = 1.698$ g cm^{-3}. Least-squares refinement of the model based on 8352 reflections $[|F_o| > 2.0\sigma(|F_o|)]$ converged to a final $R_F = 3.3\%$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

References

1 J. D. Corbett, *Chem. Rev.*, 1985, **85**, 383 and references cited therein.
2 J. D. Corbett, D. G. Adolphson, D. J. Merryman, P. A. Edwards and F. J. Armatis, *J. Am. Chem. Soc.*, 1975, **97**, 6267.
3 E. Zintl, J. Goubeau and W. Dullenkopf, *Z. Phys. Chem. Abt. A*, 1931, **154**, 1; E. Zintl, J. Goubeau and W. Dullenkopf, *Z. Phys. Chem., Abt. A*, 1931, **154**, 47.
4 L. Diehl, K. Khodadedeh, D. Kummer and J. Strähle, *Chem. Ber.*, 1976, **109**, 3404; D. G. Adolphson, J. D. Corbett and D. J. Merryman, *J. Am. Chem. Soc.*, 1976, **98**, 7234.
5 M. Björgvinsson, J. F. Sawyer and G. J. Schrobilgen, *Inorg. Chem.*, 1987, **26**, 741; C. Belin and H. Mercier, *J. Chem. Soc., Chem. Commun.*, 1987, 190; V. Angilella, H. Mercier and C. Belin, *J. Chem. Soc., Chem. Commun.*, 1989, 1654.
6 R. G. Teller, L. J. Krause and R. C. Haushalter, *Inorg. Chem.*, 1983, **22**, 1809; R. C. Haushalter, B. W. Eichhorn, A. L. Rheingold and S. J. Geib, *J. Chem. Soc., Chem. Commun.*, 1988, 1027.
7 W. J. Evans, L. A. Hughes and T. P. Hanusa, *J. Am. Chem. Soc.*, 1984, **106**, 4270; W. J. Evans, L. A. Hughes and T. P. Hanusa, *Organometallics*, 1986, **5**, 1285.
8 W. J. Evans, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.*, 1988, **110**, 6877.
9 W. J. Evans, S. L. Gonzales and J. W. Ziller, *J. Am. Chem. Soc.*, 1991, **113**, 9880.
10 M. Okada, R. A. Guidotti and J. D. Corbett, *Inorg. Chem.*, 1968, **7**, 2118.
11 G. Chapuis, F. Hulliger and R. Schmelczer, *J. Solid State Chem.*, 1980, **31**, 59.
12 B. Eisenmann, *Z. Naturforsch, Teil B*, 1979, **34**, 1162.
13 R. A. Bartlett, H. V. R. Dias, H. Hope, B. D. Murray, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1986, **108**, 6921.
14 K. van Deuter and D. Rehder, *Cryst. Struct. Commun.*, 1980, **9**, 167.
15 A. J. Ashe, E. G. Ludwig, J. Oleksyszyn and J. C. Huffman, *Organometallics*, 1980, **3**, 337.
16 G. Becker, H. Freudenblum and C. Witthauer, *Z. Anorg. Allg. Chem.*, 1982, **492**, 37.
17 T. F. Berlitz, H. Sinning, J. Lorberth and U. Muller, *Z. Naturforsch., Teil B*, 1988, **43**, 744.
18 G. Huttner, U. Weber, B. Sigwarth and O. Scheidsteger, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 215; A. H. Cowley, N. C. Norman, M. Pakulski, D. L. Bricker and D. H. Russell, *J. Am. Chem. Soc.*, 1985, **107**, 8211.
19 S. C. Critchlow and J. D. Corbett, *Inorg. Chem.*, 1984, **23**, 770.
20 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
21 W. J. Evans, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.*, 1990, **112**, 219.
22 W. J. Evans and S. E. Foster, *J. Organomet. Chem.*, in the press.