Synthesis and Structure of the First 20-Bi-9 System:[1] A Discrete Nine-Coordinate 20-Electron Bismuth

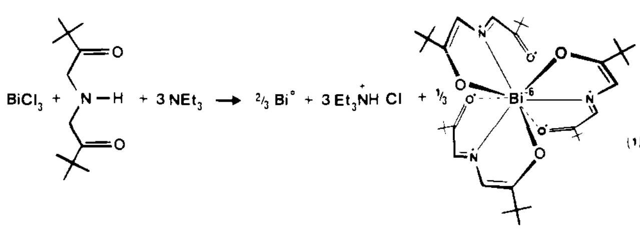
Constantine A. Stewart, Joseph C. Calabrese, and Anthony J. Arduengo, III*

Contribution No. 3697, Central Research & Development Department, Experimental Station E. I. du Pont de Nemours & Co. Wilmington, Delaware 19898

Received February 1, 1985

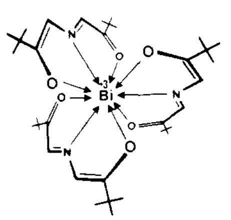
We report the synthesis of the first discrete, nine-coordinate, 20-electron bismuth species. The transargononic[2] 20-Bi-9 system [tris(4-aza-1,7-dioxa-2,6-di-*tert*-butylhepta-2,5-dien-1,4,7-triyl)-bismuth **2**] represents the greatest electron count and highest coordination number exhibited by a p-block element.[3]

The reaction of the secondary amine **1** with $BiCl_3$ in THF at −78 °C in the presence of triethylamine affords **2**[4] in greater than 90% yield. The mass balance (eq 1) indicates that $BiCl_3$ acts both as an oxidant and substrate for **1**.

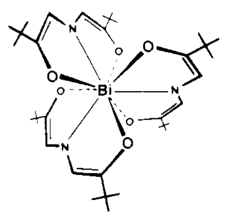


1 2

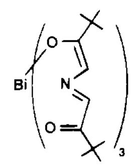
Three types of bonding descriptions can be formulated for **2**. Structure **3** represents a bismuth +3 ion solvated by three mo-



3



4

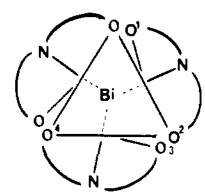


5

noanionic tridentate ligands. This totally ionic structure can be ruled out on the basis of the similarity of the ^1H and ^{13}C NMR spectra of **2** to those of the previously reported 10-Pn-3 ADPnO systems (Pn = pnictogen: P[5], As[6], Sb[7]). This similarity of NMR shifts suggests the same charge distribution in the ligand backbone of the 20-Bi-9 and 10-Pn-3 systems and not a delocalized mononanion as **3** requires. In addition, **2** is not ionized in strongly polar solvents (e.g., Me_2SO, CH_3CN). The inability to observe ^{17}O and ^{15}N resonances suggests strong Bi–O and Bi–N interactions which results in rapid relaxation of these nuclei by the bismuth nucleus.[8] Structure **4** is readily dismissed since it would require a +9 valence state for bismuth (bismuth has only five valence electrons). NMR spectra of **2** eliminate structure **5** as a possibility. The temperature independence (−90 → 40 °C) and resemblance of the ^1H and ^{13}C NMR spectrum of **2** to 10-Pn-3 systems implies a similar symmetrically situated ligand. In addition, the solid-state ^{13}C NMR spectrum of **2** shows virtually identical resonances with its solution spectra.

Verification of structure **2** was carried out by X-ray diffraction.[9] The crystallographic unit contains two unique molecules, one more symmetric than the other.[10] Figure 1 illustrates the face-capped twisted trigonal-prismatic geometry[11] observed for **2**. The bismuth center is enclosed by a trio of ligands which form a propeller arrangement (D_3). Each 20-Bi-9 system is thus chiral with both enantiomers present in the crystal by virture of crystal symmetry. Table I gives the representative bond lengths and angles observed in the 20-Bi-9 system. It is interesting to note that the Bi–O and

Table I. Bond Lengths and Angles in 20-Bi-9 System[a]



bond lengths, pm		bond angles,[b] deg			
Bi–O	251 (3)	O^1–Bi–O^2	128.0 (0.3)	N–C–C	117.8 (2.5)
Bi–N	254 (3)	O^1–Bi–O^3	75.4 (1.0)	C–C–O	121.7 (1.1)
C–O	125 (1)	O^1–Bi–O^4	149.8 (1.5)	C–O–Bi	118.7 (1.7)
N–C	133 (4)	O^2–Bi–O^3	91.4 (1.1)	C–N–Bi	116.7 (1.6)
C–C	140 (5)	N–Bi–N	120.0 (4.1)	C–N–C	126.0 (2.2)

[a] These numbers are averages from the most symmetric structure with standard deviations. [b] Twist between ligand planes and trigonal prism axis, 53.

(1) The N–X–L system has previously been described: Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. N valence electrons about a central atom X, with L ligands.

(2) The term "transargononic" is derived from the name "argonon" which refers to the noble gas family. Here we mean to imply an electron count beyond the normal octet about some central atom (Bi). See: Pauling, L. "General Chemistry", 3rd ed.; W. H. Freeman and Co.: San Francisco, 1970; p 194.

(3) There are other reports of nine-coordinate bismuth systems, but they occur as nondiscrete polymeric crystalline solids and show sets of long and short bonds rather than symmetric environments. Udovenko, A. A.; Volkova, L. M.; Sergienko, S. S.; Davidovich, R. L.; Shevechenko, V. Ya. *Koord. Khim.* **1983**, *9*, 711–713. Ferrari, M. B.; Capacchi, L. C.; Cavalca, L.; Gasparri, G. F. *Acta. Crystallogr., Sect. B* **1972**, *B28*, 1169.

(4) Compound **2** is isolated by extraction from Bi metal and $Et_3N{\cdot}HCl$ in pentane. Two crystallizations from pentane at −28 °C afford dark red crystals of **2** in good yield, mp 202 °C dec. ^1H NMR (CD_2Cl_2) δ 1.18 (s, 18 H), 8.13 (s, 2 H). The proton decoupled ^{13}C NMR (CD_2Cl_2) δ 26.5 (CH_3), 40.5 ($C(CH_3)_3$), 122.4 (CH), 197.5 (CO). Satisfactory analyses were obtained (CHN).

(5) Culley, S. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1984**, *106*, 1164.

(6) Culley, S. A.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1985**, *107*, 1089.

(7) Stewart, C. A.; Harlow, R. L.; Arduengo, A. J., III, unpublished results.

(8) We have obtained ^{17}O and ^{15}N NMR data on ADPO, ADAsO, and ADSbO. 10-P-3 ADPO: ^{17}O (CD_2Cl_2) δ 324; ^{15}N (CD_2Cl_2) δ −126 (d, J_{P-N} = 80 Hz). 10-As-3 ADAsO: ^{17}O (CD_2Cl_2) δ 330; ^{15}N (CD_2Cl_2) δ −96. 10-Sb-3 ADSbO: ^{17}O (CD_2Cl_2) δ 305; ^{15}N (CD_2Cl_2) δ −90 (^{15}N resonance relative to $^{15}NO_3^-$ and ^{17}O relative to $D_2{}^{17}O$). Presumably the P, As, and Sb nuclei are not as effective at relaxing the ^{17}O and ^{15}N nuclei as is ^{209}Bi.

(9) With some difficulty X-ray crystals of **2** could be grown from isopropyl alcohol at room temperature. The crystal data (−100 °C) were as follows: $C_{36}H_{60}N_3O_6Bi$, monoclinic-b, space group $P2_1/n$, a = 2593.7 (6) pm, b = 1758.6 (4) pm, c = 1856.5 (4) pm, β = 101.87 (2)°, Z = 8, D_c = 1.346 g/cm³, crystal size 0.29 × 0.06 × 0.44 mm. With 4829 unique absorption corrected (μ = 42.80 cm⁻¹) reflections of intensity greater than 3.0σ, the structure was solved by automated Patterson analysis (PHASE). The final R factors were R = 0.054 and R_w = 0.049.

(10) The distortion is clearly the result of crystal packing forces. The distorted molecule contains two trigonal faces. One face contains a set of long Bi–O bonds (261.6 (2.1) pm) while the other face is comprised of short Bi–O bonds (240.6 (3.2) pm). Each ligand thus makes a long and a short Bi–O bond. For detailed explanation and illustrations, see the supplemental material.

(11) A representation of the view down the three-fold axis is presented in Table I. The spheres in Figure 1 are scaled to 1.5× covalent radii of the elements since a space-filling model drawn with van der Waals radii completely obscure the bismuth.

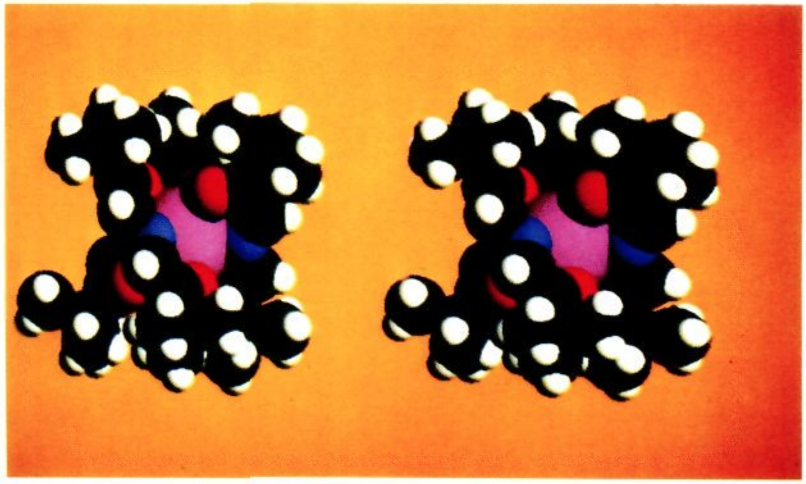


Figure 1. Stereoview of 20-Bi-9 system.

Bi–N bonds are about 36 and 48 pm longer than the Sb–O and Sb–N bonds in 10-Sb-3 ADSbO[12] and the covalent radius of bismuth is about 15 pm[13] greater than that of antimony. These lengths are consistent with the hypervalent nature of the bonding in the 20-Bi-9 system. The extreme crowding about the bismuth center results in unusual chemical stability. The 20-Bi-9 system is unaffected by O_2 and is more resistant to hydrolysis than the 10-Pn-3 systems.

(12) The bond lengths and angles for the ADSbO system. Sb–O, 215 pm; Sb–N, 206 pm; O–Sb–O, 149.6°.

(13) Slater, J. C. *J. Chem. Phys.* **1964**, *41*, 3199.

Work is currently in progress to explore the nature of the bonding in the unusual 20-Bi-9 system as well as resolve the racemate and explore its chemistry.

Acknowledgment is made to Dr. T. Fukunaga for helpful discussions and Dr. D. Ovenall, F. Davidson, and Dr. R. Farlee for the work on the ^{17}O, ^{15}N, and solid-state ^{13}C NMR, respectively.

Supplementary Material Available: A complete description of the X-ray crystallographic structure determination of the 20-Bi-9 system and tables of positional and thermal parameters (9 pages). Ordering information is given on any current masthead page.