The postulated formulation as $[X(SO_3F)_2]^+$ and $[Au(SO_3F)_4]^-$ may however be an oversimplification. Bands in the region of ~1150 cm^{-1} are normally rather characteristic for bidentate bridging fluorosulfate groups,[15] and occurrence of these bands in both the $[Au(SO_3F)_4]^-$ and $[Sn(SO_3F)_6]^{2-}$ derivatives does indicate covalent anion-cation interaction. Such interaction is not really surprising as evidenced by the molecular structures of related interhalogen cation complexes[16] such as BrF_2SbF_6[17] and ICl_2SbCl_6.[18] In these two cases, the short interionic distances suggest the presence of interactions, but not to the extent that the compounds could be classified as being polymeric.

Our preference for an ionic formulation for $[X(SO_3F)_2][Au(SO_3F)_4]$, consistent with the observed vibrational spectra and their similarity to those for the $[Sn(SO_3F)_6]^{2-}$ complexes[13] (here the ^{119}Sn Mössbauer spectrum shows a single line with an isomer shift characteristic for the hexakis(fluorosulfato)stannate(IV) ion), is also based on the solution behavior of the binary fluorosulfates of Au, Br, and I in fluorosulfuric acid. The former is a strong SO_3F^- ion acceptor while the halogen fluorosulfates $I(SO_3F)_3$[19] and $Br(SO_3F)_3$[20] are very weak electrolytes.

The presence of the tetrakis(fluorosulfato)aurate(III) ion in both $Br_5[Au(SO_3F)_4]$ and $Br_3[Au(SO_3F)_4]$ is evident from their vibrational spectra. Differences between the band positions observed for the two compounds are small. Unfortunately a clear identification and subsequent assignment of bands due to the two polybromine cations are rather difficult. A very intense Raman band at ~280 cm^{-1} observed for the $[Au(SO_3F)_4]^-$ ion[1] falls into the same region where the stretching fundamentals for Br_3^+ are expected.[7,10] The 280-cm^{-1} band has only low intensity in the IR spectrum at 80 K, but this region is found on the very end of the working range of our spectrophotometer (Perkin-Elmer 225) and identification is not entirely unambiguous.

The following additional bands, not found for the anion, are observed and may in part be due to the Br_n^+ ion, but the occurrence of lattice modes and of bands due to some covalent anion-cation interaction is possible in this region. For $Br_3[Au(SO_3F)_4]$ these bands are found in the Raman spectrum at 275, 220, 188, and 178 cm^{-1} with a band at 300 cm^{-1} found in the IR spectrum. $Br_5[Au(SO_3F)_4]$ has additional bands at 304, 295, 267, and 205 in the Raman spectrum and at 305, 295, and 260 cm^{-1} in the IR spectrum. It is noteworthy that the Raman spectrum of $Br_5[Au(SO_3F)_4]$ provides no evidence for the presence of free bromine, with ν(Br-Br) expected at 320 cm^{-1}.[10]

Conclusions. The four examples discussed here indicate that unusual cations may be stabilized by the $[Au(SO_3F)_4]^-$ ion, provided suitable synthetic routes can be found. An extension of our synthetic work in this direction is planned.

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Registry No. $Br_3[Au(SO_3F)_4]$, 72030-07-0; $Br_5[Au(SO_3F)_4]$, 72016-94-5; $[Br(SO_3F)_2][Au(SO_3F)_4]$, 72030-08-1; $[I(SO_3F)_2][Au(SO_3F)_4]$, 72016-95-6; $BrSO_3F$, 13997-93-8; $S_2O_6F_2$, 13709-32-5.

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Crystal and Molecular Structure of 2,3-Dimethyl-4,7-dihydroxy-10-bromo-2,3-dicarba-*closo*-undecaborane

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2,3-Dimethyl-4,7-dihydroxy-10-bromo-2,3-dicarba-*closo*-undecaborane, $(CH_3)_2C_2B_9H_6(OH)_2Br$, crystallizes in the space group *Fddd* [D_{2h}^{24}; No. 70, second setting] with a = 21.484 (2) Å, b = 26.252 (5) Å, c = 17.169 (3) Å, V = 9683 Å^3, and Z = 32. Diffraction data were collected with a Picker FACS-I four-circle diffractometer using Zr-filtered Mo Kα radiation. The structure has been refined by full-matrix least-squares methods to residuals R = 0.082 and weighted R = 0.094, for 145 variables and 1459 significant observations. The OH groups are located on adjacent vertex positions B(4, 7) and the bromine at the B(10) position. The configuration of the polyhedral cage is intermediate between the closo C_{2v} structure and nido C_{5v} icosahedral fragment. The distortion from the closo structure toward an approximate nido fragment is attributed to donation of electron density from the lone-pair electrons on the oxygens to the molecular-orbital framework of the polyhedron. This, in effect, increases the skeletal electron count from the closo $n + 1$ pairs of electrons toward the nido $n + 2$, where n = number of vertex positions.

Introduction

In previous papers[2,3] the preparation and chemistry of the bis(B,B'-dihydroxy) derivative of 2,3-dimethyl-2,3-dicarba-*closo*-undecaborane have been described. On the basis of chemical and spectroscopic evidence, the two hydroxy groups were assigned to the B(4, 7) positions. The X-ray structure determination of the bis(B,B'-dihydroxy)-B-bromo derivative[2] reported herein confirms the location of the B-hydroxy groups and also details the distortions of polyhedral geometry in the cage structure. The distortion is attributed to the interaction between the exopolyhedral B-hydroxy groups and polyhedral framework.

Experimental Section

A clear irregular octahedron of $(CH_3)C_2B_9H_6(OH)_2Br$, with approximate maximum dimensions 0.54 × 0.70 × 0.40 mm, was sealed within a thin-walled capillary under inert atmosphere. X-ray diffraction photographs revealed a face-centered orthorhombic lattice ($h + k = 2n + 1$, $k + l = 2n + 1$, $h + l = 2n + 1$ for hkl) with additional systematic extincitions ($h + k = 4n + 1, 2, 3$ for $hk0$, $k + l = 4n + 1, 2, 3$ for $0kl$, $h + l = 4n + 1, 2, 3$ for $h0l$) that uniquely

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Table I. Final Fractional Coordinates and Anisotropic Thermal Parameters[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	−1766.1 (5)	2674.5 (5)	406.1 (7)	10.6 (3)	16.5 (2)	41.7 (6)	−0.3 (2)	−3.1 (3)	−4.2 (3)
B(1)	507 (6)	2673 (5)	181 (7)	13 (3)	13 (2)	24 (5)	0 (2)	−1 (3)	−3 (3)
C(2)	169 (4)	2120 (4)	275 (6)	15 (3)	8 (1)	23 (4)	4 (2)	0 (3)	−2 (2)
C(3)	155 (5)	3259 (4)	217 (6)	14 (3)	11 (2)	32 (5)	2 (2)	1 (3)	−2 (2)
B(4)	−435 (6)	2288 (5)	−182 (7)	18 (3)	10 (2)	24 (5)	−3 (2)	4 (3)	−3 (3)
B(5)	297 (6)	2356 (5)	1136 (7)	16 (3)	14 (2)	18 (4)	−1 (2)	−3 (3)	2 (3)
B(6)	288 (5)	3048 (5)	1085 (8)	11 (3)	16 (2)	28 (5)	1 (2)	4 (3)	−4 (3)
B(7)	−431 (5)	3066 (4)	−208 (7)	11 (3)	11 (2)	20 (5)	0 (2)	1 (3)	0 (2)
B(8)	−461 (6)	2129 (5)	868 (8)	33 (4)	21 (3)	41 (6)	1 (3)	−1 (4)	0 (3)
B(9)	−464 (6)	3265 (5)	803 (7)	14 (3)	12 (2)	20 (5)	−4 (2)	−6 (3)	−2 (3)
B(10)	−850 (5)	2695 (4)	464 (6)	10 (3)	10 (2)	19 (4)	1 (2)	−3 (3)	−2 (3)
B(11)	−407 (6)	2718 (5)	1399 (7)	15 (3)	15 (2)	23 (5)	0 (2)	−4 (3)	−5 (3)
C(12)	510 (6)	1633 (4)	29 (8)	26 (4)	13 (2)	48 (6)	10 (2)	−2 (4)	−6 (3)
C(13)	507 (6)	3728 (5)	−74 (8)	25 (3)	14 (2)	62 (7)	−9 (2)	−2 (4)	9 (3)
O(1)	−654 (4)	3255 (3)	−895 (4)	28 (2)	19 (1)	30 (2)	8 (2)	−5 (2)	2 (2)
O(2)	−647 (3)	2084 (3)	−855 (4)	25 (2)	17 (1)	30 (3)	0 (1)	−8 (2)	−9 (2)

[a] All values in the table are multiplied by 10^4. The form of the anisotropic thermal parameter is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Estimated standard deviations in parentheses correspond to the last significant digit.

determine the space group *Fddd* (D_{2h}^{24}, No. 70, second setting). Lattice parameters a = 21.484 (2) Å, b = 26.252 (5) Å, and c = 17.169 (3) Å were obtained from least-squares refinement of 32 reflections with $2\theta \geq 40°$ for Mo Kα radiation which were automatically centered on a Picker FACS-I four-circle diffractometer at 20 °C. With $Z = 32$, the calculated density is D_x = 1.49 g cm^{-3}, with a formula weight of 271.36 and a cell volume of 9683 Å^3.

Diffracted intensities were measured for a total of 2780 reflections with $(\sin\theta)/\lambda \leq 0.6496$ by using the diffractometer in θ–2θ scan mode with Zr-filtered Mo Kα radiation (λ = 0.710 69 Å) incident at a takeoff angle of 2.5°. Each scan was done at a rate of 1° of 2θ/min and over a range of 1.5° in 2θ at minimum, plus a systematic allowance for spectral dispersion; 40-s background counts were taken at each end of the scan. Of the 1849 reflections found to be independent and not systematically absent, 1459 were regarded as objectively observed with $|F_o| \geq 1.58\sigma_F$, where $|F_o| = [k(C - tB)/Lp]^{1/2}$ and $\sigma_F = k[(C + t^2B)^{1/2}/(2|F_o|Lp) + 0.02|F_o|]$; C is the total count recorded during the scan, t is the ratio of the scanning time to the total time for the background B, and L and p are the Lorentz and polarization corrections, respectively. Correction for adsorption of X-rays was made through the value of k, which was computed for each reflection by using a value of μ = 3.56 mm^{-1} by an algorithm[4,5] for a crystal of arbitrary shape bounded by plane faces. Three standard reflections were periodically monitored with each 50 data throughout the 15 days, and the average standard deviation of these intensity measurements was about 2.5%. Corrections for extinction of X-rays were not applied to the data.

Structure Determination and Refinement

The position of the bromine atom was located in a Patterson synthesis, and subsequent Fourier syntheses revealed the remaining nonhydrogen atoms. Full-matrix least-squares refinement of coordinates and isotropic-temperature factors lessened the residual to ~0.17, and thereafter anisotropic temperature factors were applied to all 16 atoms until convergence. A difference Fourier synthesis computed at this point revealed the positions of some hydrogen atoms, but subsequent syntheses calculated with these peaks included failed to significantly affect the residual nor yield any further information. Therefore, only the nonhydrogen atoms were retained in the final refinement. The total number of parameters thus varied was 145, including a scale factor.

The quantity minimized in the least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$ with σ defined above. Scattering factors were those of Cromer and Mann,[6] and the anomalous dispersion correction applied to the bromine form factor was that of Cromer.[7] The final conventional residual was R_1 = 0.082, and the weighted residual, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, was 0.094 with a data-to-parameter ratio of 10.0 to 1. The final difference Fourier synthesis displayed a maximum residual density of 0.75 e Å^{-3} at a position consistent with a hydrogen atom of the molecule. The final structural parameters are listed in Table I.

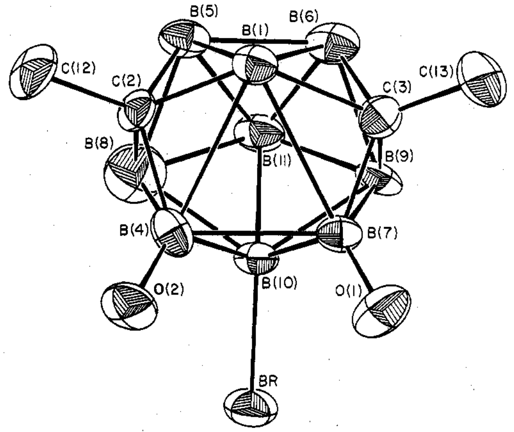

Figure 1. A perspective view of the molecule.

Table II. Interatomic Distances[a]

B(1)–C(2)	1.63 (2)	B(5)–B(6)	1.82 (2)
C(3)	1.71 (2)	B(8)	1.79 (2)
B(4)	2.35 (2)	B(11)	1.84 (2)
B(5)	1.89 (2)		
B(6)	1.90 (2)	B(6)–B(9)	1.78 (2)
B(7)	2 36 (2)	B(11)	1.81 (2)
C(2)–B(4)	1.58 (2)	B(7)–B(9)	1.81 (2)
B(5)	1.63 (2)	B(10)	1.76 (2)
B(8)	1.69 (2)	O(1)	1.37 (1)
C(12)	1.53 (1)	B(8)–B(10)	1.84 (2)
C(3)–B(6)	1.61 (2)	B(11)	1.80 (2)
B(7)	1.54 (2)		
B(9)	1.67 (2)	B(9)–B(10)	1.81 (2)
C(13)	1.53 (1)	B(11)	1.77 (2)
B(4)–B(7)	2.04 (2)	B(10)–B(11)	1.87 (2)
B(8)	1.85 (2)	Br	1.97 (1)
B(10)	1.78 (2)		
O(2)	1.35 (1)		

[a] All distances are in angstroms. Estimated standard deviations in parentheses refer to the last significant digit.

Results and Discussion

The perspective view of the molecule shown in Figure 1 illustrates both the deviation from ideal geometry of the polyhedron and the location of the *B*-hydroxy groups and the bromine atom. The two hydroxy groups are bonded to vicinal boron atoms, B(4, 7), adjacent to the unique seven-coordinate boron atom, which bonds to both hydroxy-substituted borons. Thus, all three substituents lie on the same side of a potential symmetry plane (vide infra) defined by the cage carbon atoms

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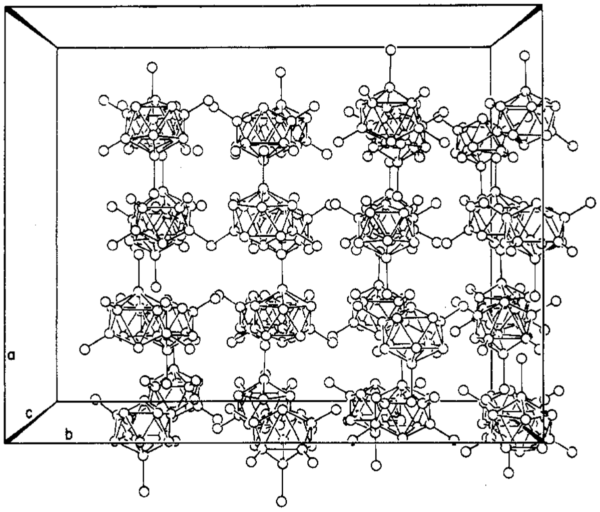

Figure 2. Packing of molecules in the unit cell as viewed down the *c* axis.

and the B(8,9) boron atoms. Examination of the interatomic distances listed in Table II reveals an interesting pattern of distortion in the polyhedral structure, which results from the interaction of these substituents with the boron atoms of the polyhedron.

An X-ray structural analysis[8,9] of a related dimethyl B_9C_2 cage compound, *closo*-2,3-$(CH_3C)_2B_9H_9$, indicates that this parent molecule maintains quasi-C_{2v} symmetry in the crystalline state. The molecule closely approximates mirror symmetry across one plane through atoms B(1, 10, 11) and has a crystallographically required plane through the carbon atoms, C(2, 3) and C(12, 13), and the boron atoms B(1, 8, 9). The pattern of substitution for the molecule in the present study conforms to this first quasi-mirror, and, indeed, the structure of the molecule under study mirrored across this plane may be superimposed[10] upon itself with an average deviation of 0.03 Å. Fourteen pairs of interatomic distances in the structure reported herein may be compared via this quasi-mirror. The distances in only one pair [B(1)–C(2) and B(1)–C(3)] differ by more than 2 esds (Δ = 0.09 (3) Å).

In contrast to this, the potential second mirror plane of the molecule under study is well-preserved only for the cage atoms B(10) and B(11), with the geometry about B(10) largely unaffected by the presence of the bromine atom. While the B(5)–B(6) distance agrees well with that found in the parent molecule, the B(4)–B(7) interatomic distance has increased 0.22 Å. Furthermore, in the structure reported herein, the unique boron atom B(1) is displaced 0.3 Å from the least-squares plane of the atoms C(2, 3) and B(8, 9), toward the B(5, 6) atoms and away from the hydroxy-substituted cage atoms.

These results suggest that the distortion of the cage from C_{2v} symmetry is localized in the region of the B(1)–B(4)–B(7) triangular array of boron atoms. While the remaining cage atoms and the exopolyhedral methyl groups may be superimposed[10] upon their counterparts in the parent molecule, 2,3-$(CH_3C)_2B_9H_9$, with an average deviation of 0.045 Å, the boron atoms bound to the exopolyhedral hydroxy groups lie more than 0.10 Å from their counterparts and the respective seven-coordinate B(1) atoms are more than 0.30 Å apart. As a result of these distortions, evidently induced by the presence of the *B*-hydroxy groups, the B(1)–B(4) and B(1)–B(7) interatomic distances are lengthened (2.36 Å), in comparison to those in the parent molecule (2.04 Å), and the configuration of this polyhedral cage is intermediate between the closo C_{2v} polyhedron and the nido C_{5v} icosahedral fragment.[11,12]

The conversion of closo-polyhedral to nido-polyhedral fragments involves the formal addition of two electrons to the molecular orbital framework.[13] In this example, the probable source of electrons is the lone pairs of the oxygen atoms. Back-donation of these electron pairs to the molecular-orbital framework of the closo polyhedron would result in the conversion of the electron framework count from $n + 1$ pairs of electrons, where n = number of vertex positions, to nearly $n + 2$, with the resultant distortion toward the nido configuration. It is interesting to note, however, that the donation of charge density does not seem to occur in a selenium analogue of this compound. Todd et al. have determined the structure of the isoelectronic $B_{11}H_9Se_3^{2-}$ anion, wherein a three selenium atom chain bridges the B(4) and B(7) positions of the cage.[14] The selenium structure shows no deviation from C_{2v} symmetry and, except for differences in atomic distances associated with the replacement of boron for carbon in the cage, can be closely superimposed upon the unsubstituted *closo*-2,3-$(CH_3C)_2B_9H_9$ structure.[14]

Figure 2 details the simple packing array of molecules in the cell as viewed down the *c* axis. The closest intermolecular contacts are between oxygen atoms (2.84, 2.87, 2.92 Å) and are in the range of known hydrogen bond lengths. While the possibility of an interamolecular hydrogen bond exists, the distance (3.08 Å) and geometry indicate that such a bond is unlikely, and careful examination of the final difference-Fourier synthesis revealed no evidence of distinct hydrogen atom positions.

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Registry No. $(CH_3)_2C_2B_9H_6(OH)_2Br$, 69461-72-9.

Supplementary Material Available: Listings of the interatomic angles and the observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(10) Orientation of one rigid body upon another by least-squares minimization of interatomic distances between the bodies.

(11) *nido*-C_2B_9 may possess C_{5v} symmetry only if carbon and boron atoms are considered equivalent.

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