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Concerning the crystal structure of $BrF_3 \cdot AuF_3$

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Abstract

Crystals of the adduct, $BrF_3 \cdot AuF_3$, are monoclinic, with: $a = 5.356(4)$ Å, $b = 5.766(4)$ Å, $c = 8.649(3)$ Å, $\beta = 101.39(4)°$, $V = 261.8(5)$ Å^3, $z = 2$, $D_c = 4.96$ g/cm^3. An ordered structure in $P2_1$ was found, but is of low precision ($R_1 = 0.082$) because of crystal deformation. The structure has planar BrF_4 units sharing F ligands *cis* with planar AuF_4 groups, each AuF_4 being similarly linked to two BrF_4. This generates a ribbon, creased at the bridging F along *y*, the gold on one side of the crease, the bromine on the other. Such ribbons are stacked parallel along *y*, with nearest neighbors related by twofold screw axes. This sandwiches each AuF_4 strip of a ribbon symmetrically between like strips. These contacts between the Au-strips bring up, to each Au-atom, two "non-bridging Au–F ligands" of each of the two neighboring strips, to give eight coordination in F. The bromine side of the creased ribbon is unsymmetrically sandwiched between a screw-axis related relative, and the edge of a Au-containing strip oriented almost perpendicular to it. This brings two non-bridging F of the nearest-strip BrF_4 and two non-bridging F of the AuF_4 strip into the secondary cordination sphere of the Br atom. Raman spectra of the $BrF_3 \cdot AuF_3$, molecular BrF_3, and polymeric AuF_3 suggest that the Br–F and Au–F stretching vibrations of $BrF_3 \cdot AuF_3$ are shifted slightly from those of the parent BrF_3 and AuF_3, and indicate some $BrF_2^+AuF_4^-$ character. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $BrF_3 \cdot AuF_3$; Synthesis; Vibrational spectroscopy; Crystal structure

1. Introduction

In 1949, Sharpe discovered that gold dissolves in liquid bromine trifluoride at ambient temperatures [1]. From the solution, he obtained a yellow 1:1 adduct

$$2BrF_3 + Au \rightarrow BrF_3 \cdot AuF_3 + \tfrac{1}{2}Br_2$$

The high chemical reactivity of this solid and the ready deformation of the crystals made difficult the task of fixing suitable single crystals in appropriate containers. Room temperature diffraction data were collected on crystals, lodged in thin-walled drawn-down quartz capillaries. Attempts to obtain low temperature data were foiled by the cooled crystals becoming detatched from the capillary wall. Solution of the room temperature structure was achieved in space group $P2_1$, but poor crystal quality (probably deriving from plastic flow of the crystal into the curved surface of the capillary) has diminished the precision with which the atom positions are defined.

Since it seems unlikely that a more precise structure of this compound will be obtained soon, the rough structure, and its probable significance to the acid/base properties of BrF_3 and AuF_3, are given in this paper.

2. Results and discussion

Fig. 1 illustrates the structure. Atomic coordinates are given in Table 1 and chemically significant interatomic distances and angles in Table 2. The structure has planar BrF_4 units sharing F ligands *cis* with planar AuF_4 groups, each AuF_4 being similarly linked to two BrF_4 units. These linked BrF_4 and AuF_4 generate ribbons (see Fig. 1b), creased at the bridging F along *y*, the gold on one side of the crease, the bromine on the other. The ribbons are stacked parallel along *y* with nearest neighbors related by twofold screw axes, as shown in Fig. 1a. This sandwiches each AuF_4 strip of the ribbon symmetrically between like strips. Closest contacts between the Au-strips brings up to each Au atom two sets of "non-bridging Au–F ligands" from the two neighboring strips, giving eight coordination in F. The bromine side of the creased ribbon is unsymmetrically sandwiched between a screw axis related relative and the edge of a Au-containing strip, the latter oriented almost perpendicular to it. This brings two non-bridging F of the

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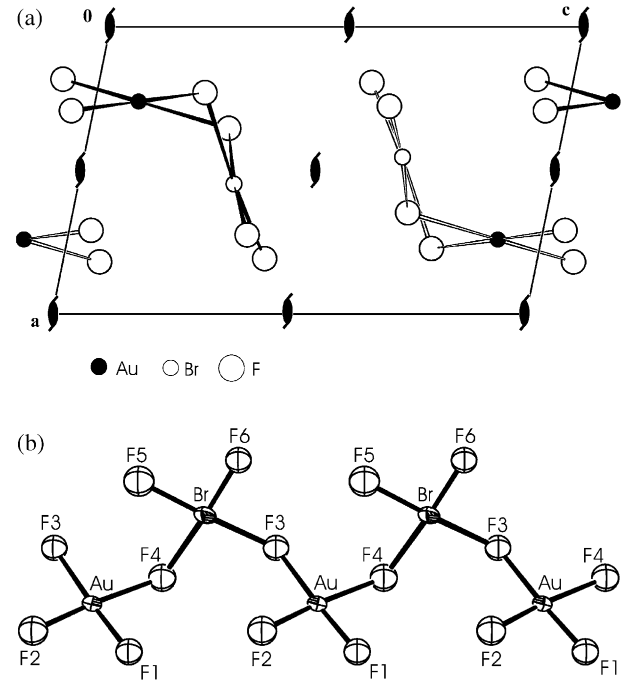

Fig. 1. Structure of $AuF_3 \cdot BrF_3$. ORTEP ellipsoids are drawn at the 50% probability: (a) structure viewed down *b* axis; (b) structure viewed along *b* axis.

nearest-strip BrF_4 and two non-bridging F of the nearest-strip AuF_4 into the secondary cordination sphere of the Br atom.

At ordinary temperatures, AuF_3 is a handed helical polymer containing *cis* bridged planar AuF_4 groups based on a square framework [2]. The bridging F ligand Au–F distance is 1.998(2) Å and the non-bridging 1.876(3) Å. In contrast, BrF_3 is a molecular material with a liquid range roughly that of water. Crystallographic [3] and microwave studies [4] of BrF_3 have been made and the latter shows that it is a T-shaped molecule, the Br–F interatomic distance of the upright (1.721 Å) being shorter than those of the cross-piece (1.810 Å).

Both BrF_3 and AuF_3 accept fluoride ion from good fluorobases to yield, in each case, a square-planar mono-anion. Salts of the same cation are usually isostructural. In typical structures [5,6], the square-planar anions are arranged on edge perpendicular to one another, such that each Br or Au atom is at the center of a roughly cubical arrangement of F ligands formed by the approach to the square-planar EF_4^- by the edges of like anions, along the perpendicular to that plane, above and below it. The Au atom coordination in $BrF_3 \cdot AuF_3$ is related to this. The Br–F distance in EF_4^- is 1.890(3) Å [7] and only marginally shorter than that of Au–F (1.915(3) Å) [8].

Table 1
Atomic coordinates and displacement parameters[a]

Atom	*x*/*a*	*y*/*a*	*z*/*c*	U_{eq}[a] (U_{iso}) (Å^2)
Au	0.2596(3)	0.25000	0.0917(2)	0.028(1)
Br	0.453(1)	0.248(2)	0.6721(5)	0.035(2)
F1[b]	0.182(9)	0.428(9)	0.922(5)	0.045(9)
F2	0.291(10)	0.014(10)	0.954(6)	0.055(11)
F3	0.353(8)	0.061(9)	0.293(5)	0.045(9)
F4	0.228(8)	0.547(9)	0.228(5)	0.051(10)
F5	0.724(9)	0.460(11)	0.377(6)	0.062(13)
F6	0.807(9)	0.902(8)	0.424(5)	0.044(9)

[a] U_{eq} is defined as one-third of the trace of the U_{ij} tensor.

[b] Fluorine atoms were refined with isotropic displacement parameter only.

Table 2
Selected interatomic distances and angles[a]

Distances (Å)		Angles (°)	
Au–F1	1.77(5)	F1–Au–F2	86(2)
Au–F2	1.84(5)	F1–Au–F3	177(2)
Au–F3	2.03(4)	F1–Au–F4	88(2)
Au–F4	2.10(5)	F2–Au–F3	97(2)
Br–F3	2.08(5)	F2–Au–F4	173(2)
Br–F4	2.11(5)	F3–Au–F4	89(2)
Br–F5	1.92(6)	F3–Br–F4	94(2)
Br–F6	1.72(5)	F3–Br–F5	176(2)
		F3–Br–F6	88(2)
Au–F1′	2.99(5)	F4–Br–F5	86(2)
Au–F2′	3.27(5)	F4–Br–F6	175(2)
Au′–F1	3.54(5)	F5–Br–F6	91(2)
Au′–F2	2.94(5)	Au–F3–Br	128(2)
Br–F1′	3.02(5)	Au–F4–Br	122(2)
Br–F2′	3.06(5)		
Br–F3′	3.39(4)		
Br–F5′	3.40(5)		

[a] Symmetry codes used: ′, $(-x, y+1/2, -z)$.

Many complexes of BrF_3 have been reported with strong fluoride-ion acceptors. Although those of SbF_5 and GeF_4 were formulated [9] by Woolf and Emeléus as $BrF_2^+SbF_6^-$ and $(BrF_2^+)_2GeF_6^{2-}$, such formulations have occasionally been questioned. A structure determination by Edwards and Jones [10] for the fluoro-antimonate has demonstrated, however, that although there are short interactions between the BrF_2 and SbF_6 species, the structure does approach the arrangement anticipated for $BrF_2^+SbF_6^-$. The Br–F distance in that cation is 1.69(2) Å and the bond angle 93.5(2.1)°. The closest approach of an anion F to the Br is 2.29(2) Å. There has been no confirmation that AuF_3 can be similarly effective as a fluorobase although red complex salts of composition $AuF_3 \cdot 2SbF_5$, prepared in these laboratories could possibly be $AuF_2^+Sb_2F_{11}^-$, at least approximately.

The existence of salts, such as $Ag^{2+}[AuF_4^-]_2$ [2,11–13], and the absence of bromine relatives, suggests that AuF_3 monomer is a stronger F^- acceptor than BrF_3. As befits a hypervalent molecule, BrF_3 may be a better F^- donor than an isolated AuF_3 molecule, but the monomeric nature of BrF_3 indicates that this is not great enough to make up for its weak acidity. The polymeric form of AuF_3 would seem to be a consequence of high Lewis acidity at the Au^{III} center, combined with some F^-donor capability. Incidentally, the creased ribbon-like structure of the $Ag^{2+}[AuF_4^-]_2$ type compounds can be roughly viewed as a doubled version of the $BrF_3{\cdot}AuF_3$ structure.

If the monomeric nature of BrF_3 derives largely from the poorer Lewis acid character of Br^{III}, this probably comes from the screening effect that the non-bonding valence s electron pair has on the Br-atom nuclear charge. The similarly-sized Au^{III} has no such s valence-electron pair. That the well ordered 1:1 complex is preferred, over separated polymeric AuF_3 and molecular BrF_3, may be a consequence of the greater F^- donor character of BrF_3, compared with AuF_3. The structural findings are not sufficiently precise to establish a tendency towards $BrF_2^+AuF_4^-$ but the Raman spectra give a hint of it.

Raman spectra of the adduct, and polymeric AuF_3 are shown in Fig. 2. The Raman stretching frequencies reported by Selig et al. [14] for BrF_3 are 675 cm^{-1} (s); 552 cm^{-1} (vs); 612 cm^{-1} (vvw). The adduct band at 559 cm^{-1} is probably related to the strongest band in the BrF_3 spectrum. The highest frequency Raman band in $BrF_3{\cdot}AuF_3$, that can be attributed to Br–F stretching is the highest observed band at 666 cm^{-1}. Stretching vibrations associated with the distinct cation BrF_2^+ would have to be at higher frequency, since in $BrF_2^+SbF_6^-$ the stretching frequencies for the cation are [15] at 705 cm^{-1} (symmetrical) and 702 cm^{-1} (antisymmetrical). On the other hand, the similarity of the local structure of the AuF_4 units in the adduct and polymeric AuF_3 lead one to expect similar vibrational features in the two materials The adduct Raman bands at 611 and 599 cm^{-1} may, therefore, be the counterparts of the 655 and 631 cm^{-1} bands of AuF_3. This marks a significant reduction in stretching frequencies for the AuF_4 units of the adduct, given that these units in the adduct are linked to less massive units (BrF_4) than in the AuF_3 polymer (other AuF_4). Raman active stretching modes in AuF_4^- salts range (for ν_1) from 582 cm^{-1} in the XeF_5^+ salt [16], to 588 cm^{-1} in the Cs^+ salt [17], and (for ν_2) from 552 cm^{-1} in the former to 561 cm^{-1} in the latter. The AuF_4 unit in the adduct does, therefore, appear to be more AuF_4^- like than that unit in AuF_3 polymer. Nevertheless, it is apparent from this vibrational basis, that the adduct is still much removed from $BrF_2^+AuF_4^-$.

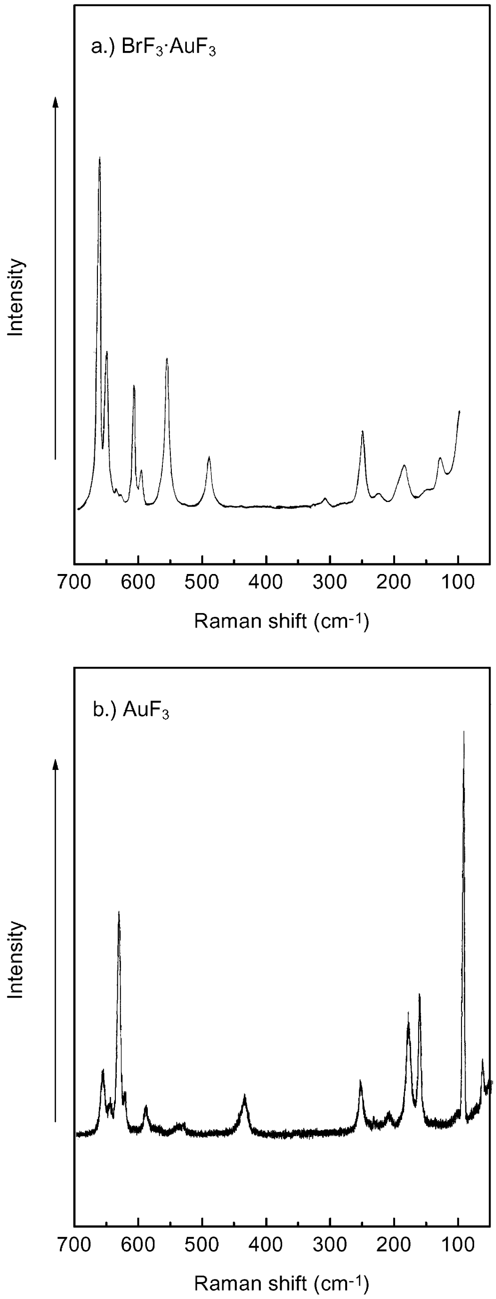

Fig. 2. Raman spectra of (a) microcrystalline $BrF_3{\cdot}AuF_3$; (b) microcrystalline AuF_3.

3. Experimental

Finely divided gold was prepared by reduction of an aqueous auric chloride solution at ~100°C, using oxalic acid in a standard procedure [18]. The thoroughly washed and dried metal was dissolved in bromine trifluoride within a fused silica container. The BrF_3 (supplied by the Matheson Co., East Rutherford, NJ) was subjected to trap to trap distillation to remove bromine and other volatile impurities prior to its use in the preparation and re-crystallization. Interaction of the gold (~1 g) with the BrF_3 (~3 ml) was signaled by evolution of bromine as the bromine trifluoride melted (~282 K). To ensure complete conversion of the gold to $BrF_3{\cdot}AuF_3$, the contents of the vessel were brought to ~300 K for ~15 min. Bromine was removed from the mixture to leave a clear bright yellow solution, from which well formed golden yellow crystals of $BrF_3{\cdot}AuF_3$ separated when the solution was cooled. A second crop of smaller crystals formed as the solvent was removed under dynamic vacuum. The crystals were manipulated in the dry nitrogen atmosphere of a Vacuum Atmospheres Corp. "Drilab" and were wedged in drawn-down thin-walled, 0.5 mm diameter, quartz capillaries (Charles Supper, Natick, MA). Crystals were initially inspected for single crystal character with the aid of a polarizing microscope, then checked by omega scan for acceptable mosaic spread. None of the single crystals of suitable size (~0.1 mm diameter) was of regular shape and absorption corrections were made empirically from $\chi = 90°$ scans of reflection intensity. A set of precession photographs indicated the possible space group $P2_1/m$ or $P2_1$. Accurate cell dimensions, data collection and the structural analysis were obtained using the University of California Chemistry X-ray Crystallographic Facility.[1] Further refinement was completed at the Institute Jožef Stefan.

4. Crystal data

$BrAuF_6$, $M = 390.86$, monoclinic, $a = 5.356(4)$ Å, $b = 5.766(4)$ Å, $c = 8.649(3)$ Å, $\beta = 101.39(4)°$, $V = 261.8(5)$ Å^3, $z = 2$, $D_c = 4.957$ g/cm^3, space group $P2_1$ (no. 4) [19].

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[1] Instrumentation at the University of California, Berkeley, College of Chemistry X-ray Crystallographic Facility (CHEXRAY) consisted of two Enraf-Nonius CAD-4 diffractometers, each equipped with nitogen-flow low temperature apparatus and controlled by a micro VAX II computer. Both used Enraf-Nonius softwares described in the CAD4 Operational Manual, Enraf-Nonius, Delft, November 1977 and updated thereafter.