The Dibromine Cation; the Crystal Structure of $[Br_2]^+[Sb_3F_{16}]^-$

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THE blue paramagnetic species formed from iodine in strongly acidic media has been shown[1,2] by cryoscopic, conductimetric, and spectroscopic measurements to be the di-iodine cation, I_2^+. The existence of the dichlorine cation, Cl_2^+, in antimony pentafluoride solution, has recently been reported[3] on the basis of electron paramagnetic resonance measurements. We now report the preparation of the dibromine cation, Br_2^+.

The interaction of antimony pentafluoride, bromine, and bromine pentafluoride produces a scarlet solid, m.p. 69°, with a magnetic moment at room temperature of *ca.* 1·6 B.M. No electron paramagnetic resonance spectrum was observed from the solid at room temperature or at $-196°$. In antimony pentafluoride solution, the compound shows absorption maxima at 12,000 and 33,500 cm.$^{-1}$, with intensities in the approximate ratio 25 : 1. The small peak at 33,500 cm.$^{-1}$ shows fine structure with an average interval of 630 cm.$^{-1}$.

By analogy with the spectrum of the di-iodine cation[2] three absorptions are expected for the transitions $^2\Pi_{3/2}(u)$, $^2\Pi_{1/2}(u) \leftarrow {}^2\Pi_{3/2}(g)$, and $^4\Sigma(u) \leftarrow {}^2\Pi_{3/2}(g)$. The separation of the $^2\Pi_{3/2}(u)$ and $^2\Pi_{1/2}(u)$ states for Br_2^+ in the gas phase is too small to be observed in the photoelectron spectrum,[4] and we therefore consider that transitions to these two states give rise to the large peak at 12,000 cm.$^{-1}$. The Raman spectrum of the solid shows a strong band at 368 cm.$^{-1}$, compared with that for bromine[5] at 317 cm.$^{-1}$.

The scarlet solid formed thin plate-like crystals of approximately hexagonal shape, which gave very poor *X*-ray photographs. During a concurrent investigation of the adduct of bromine pentafluoride and antimony pentafluoride we observed that a scarlet decomposition product[5] of this adduct also formed hexagonal shaped crystals, which were shown by *X*-ray methods to be identical with our original material.

These crystals gave good *X*-ray photographs and our structure determination has shown that the compound corresponds to the formula $Br_2Sb_3F_{16}$. Crystal data were determined from Weissenberg

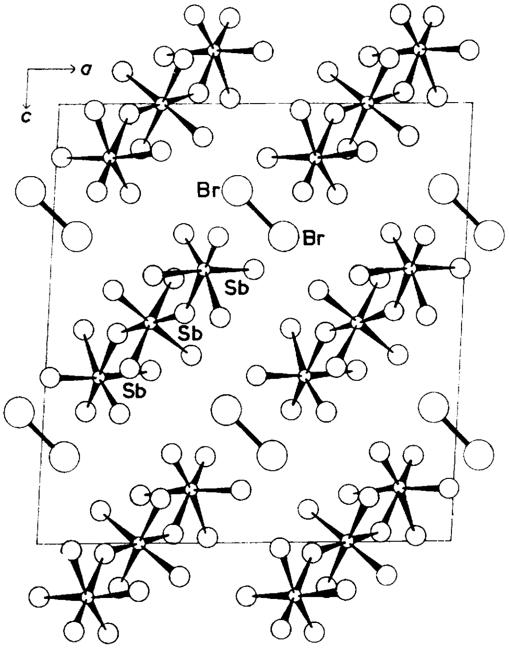

FIGURE. *Projection down* [010].

and precession photographs with Cu-K_α radiation: $Br_2Sb_3F_{16}$, $M = 830$, monoclinic, $a = 13{\cdot}58$, $b = 7{\cdot}71$, $c = 14{\cdot}33$ Å, $\beta = 93{\cdot}7°$, $U = 1497$ Å^3, space group $C2/c$ (C_{2h}^6, No. 15), $Z = 4$. The atom positions were determined from the usual three-dimensional Patterson function and electron density maps. Full-matrix least-squares refinement of positional and isotropic temperature parameters has led to a value of 0·125 for R for 610 independent reflections.

The atomic arrangement is shown in the Figure. The structure consists of separate Br_2^+ and $Sb_3F_{16}^-$ ions. The two bromine atoms are 2·13 Å apart (estimated standard deviation ± 0·01 Å) and have no near fluorine atom neighbours (the closest Br···F contact is 2.85 Å). This Br–Br distance is significantly shorter than the 2·27 Å in the bromine molecule,[7] as expected for the cation.

In the previously unreported anion, the Sb–F(terminal) distances average 1·83 ± 0·07 Å, and the Sb–F(bridge) distances 2·03 ± 0·07 Å. The Sb–F–Sb angle is 147°. Unlike other systems that we have investigated, which contain *cis*-bridging fluorine atoms[8] in octahedral arrangements, the anion has *trans*-bridges at the central antimony atom.

(*Received, October 9th,* 1968; *Com.* 1374.)

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