Cu-N(2) distance of 1.995 (2) Å is in the range of 1.971-2.032 Å found for copper-amine complexes.[2,30-37] The Cu-Cl(1)′ and Cu-Cl(2) distances of 2.272 (1) and 2.264 (1) Å are also similar to the values reported for terminal Cu-Cl bonds in a variety of complexes.[4,38,39] The out-of-plane Cu-Cl distances of 3.504 (2) and 3.522 (2) Å are longer than any that could be found in the literature; in $Cu(py)_2Cl_2$,[28] $Cu(\alpha\text{-pic})_2Cl_2$,[26] and $KCuCl_3$,[40] for example, this distance is 3.05, 3.37, and 3.113 Å, respectively. They are, however, stronger interactions that the out-of-plane Cu-Br interactions in[8] $Cu(\alpha\text{-pic})_2Br_2$, where the Cu-Br distance is 3.872 (5) Å and yet there is magnetic exchange between adjacent copper atoms.[5] The geometry of the substituted pyridine ring is similar to that reported for other copper complexes of substituted pyridines.[2,7,8,25-29] The ring atoms are roughly coplanar, with no atom deviating from the least-squares plane by more than 0.011 Å.

Registry No. $CuCl_2(C_7H_{10}N_2)$, 38704-59-5.

Acknowledgments. This research was supported by the Materials Research Center of the University of North Carolina through Grant GH 33632 from the National Science Foundation. We are grateful for this continuing support. We are also grateful to Dr. D. Y. Jeter for useful discussions concerning the magnetic properties of this complex.

(28) J. D. Dunitz, *Acta Crystallogr.*, 10, 307 (1957).

(29) G. Davey and F. S. Stephens, *J. Chem. Soc. A*, 2803 (1970).

(30) M. H. Meyer, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Acta Crystallogr., Sect. B*, 28, 1607 (1972).

(31) B. Morosin, *Acta Crystallogr., Sect. B*, 25, 19 (1969).

(32) M. B. Cingi, C. Guastini, A. Musatti, and M. Nardelli, *Acta Crystallogr., Sect. B*, 26, 1836 (1970).

(33) I. Agrell, *Acta Chem. Scand.*, 20, 1281 (1966).

(34) T. Distler and P. A. Vaughan, *Inorg. Chem.*, 6, 126 (1967).

(35) Y. Iitaka, K. Shimizu, and T. Kwan, *Acta Crystallogr.*, 20, 803 (1966).

(36) B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, 17, 254 (1964).

(37) Y. Komiyama and E. C. Lingafelter, *Acta Crystallogr.*, 17, 1145 (1964).

(38) R. S. Sager and W. H. Watson, *Inorg. Chem.*, 7, 2035 (1968).

(39) R. D. Willett and R. E. Rundle, *J. Chem. Phys.*, 40, 838 (1964).

(40) R. D. Willett, C. Dwiggins, Jr., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, 38, 2429 (1963).

Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada

Preparation and Raman Spectra of Compounds of the Hg_3^{2+} Cation. Crystal Structure of Trimercury Bis(hexafluoroarsenate(V)) $Hg_3(AsF_6)_2$

B. D. CUTFORTH, C. G. DAVIES, P. A. W. DEAN, R. J. GILLESPIE,* P. R. IRELAND, and P. K. UMMAT

Received October 26, 1972

The compounds $Hg_3(AsF_6)_2$ and $Hg_3(Sb_2F_{11})_2$ have been prepared by the reaction of mercury with AsF_5 and SbF_5, respectively, in solution in liquid SO_2. The ion Hg_3^{2+} is formed when mercury is dissolved in HSO_3F. The symmetrical stretching mode of the Hg_3^{2+} ion in solution is found at 113 cm^{-1} in the Raman spectrum. The structure of $Hg_3(AsF_6)_2$ has been determined from three-dimensional X-ray data collected by counter methods. The space group was found to be $P2_1/c$ and the cell parameters at 22° are $a = 5.981$ (5), $b = 8.551$ (6), $c = 11.282$ (10) Å, $\beta = 91.16$ (7)°, and $Z = 2$. The structure was solved from the Patterson function and refined by the method of least squares to a discrepancy index of 0.106 for 636 reflections. The crystal contains Hg_3^{2+} cations and octahedral AsF_6^- anions. The Hg_3^{2+} ion is linear and centrosymmetric with an Hg-Hg bond length of 2.552 (4) Å. There is a weak mercury-fluorine bridge between the terminal mercury atoms and a fluorine of neighboring AsF_6^- ions which has a length of 2.38 (5) Å.

Introduction

It has been known for many years that Hg(I) exists in the form of the stable mercurous ion Hg_2^{2+}. As early as 1932 it was reported by Meyer and Schram[1] that mercury dissolves in fluorosulfuric acid to give a yellow solution. It appears to have been assumed that the color was due to the mercurous ion even though this species normally gives colorless solutions. Probably the first suggestion of the existence of an oxidation state of mercury lower than +1 was obtained by Gut[2] in polarographic studies of mercury in the ternary eutectic $AlCl_3$-NaCl-KCl (60:20:14 mol %). The existence of the Hg_3^{2+} cation was first claimed in two preliminary communications. Torsi and Mamantov[3] reported the preparation of the compound $Hg_3(AlCl_4)_2$ from the reaction of mercury with a molten mixture of $HgCl_2$ and $AlCl_3$, and this was followed by a report from this laboratory[4] of the preparation of $Hg_3(AsF_6)_2$ by the reaction of mercury with AsF_5 in liquid SO_2 as solvent. Preliminary Raman spectral data[4] indicated that Hg_3^{2+} is a linear centrosymmetric ion.

Recently, Torsi, *et al.*,[5] have published the details of their work which shows that the Hg_3^{2+} ion may be obtained in acidic chloroaluminate melts by the oxidation of mercury metal or by the partial reduction of Hg_2^{2+}. The Hg_3^{2+} ion was characterized by absorption spectra and by stoichiometric and electrochemical measurements. They obtained the yellow crystalline compound $Hg_3(AlCl_4)_2$ from the chloroaluminate melts. They accounted for the Raman spectrum of this compound in terms of a slightly bent Hg_3^{2+} ion bridged at each end *via* a chlorine atom to an $AlCl_4^-$ ion. This is the structure that has since been found in a determination of the crystal structure by Ellison, *et al.*,[6] in which it was found that the Hg-Hg-Hg bond angle is 174.4°.

This paper reports the preparation of the compounds $Hg_3(AsF_6)_2$ and $Hg_3(Sb_2F_{11})_2$, the Raman spectra of both com-

(1) J. Meyer and G. Schram, *Z. Anorg. Allg. Chem.*, 206, 24 (1932).

(2) R. Gut, *Helv. Chim. Acta*, 43, 830 (1960).

(3) G. Torsi and G. Mamantov, *Inorg. Nucl. Chem. Lett.*, 6, 843 (1970).

(4) C. G. Davies, P. A. W. Dean, R. J. Gillespie, and P. K. Ummat, *Chem. Commun.*, 782 (1971).

(5) G. Torsi, K. W. Fung, G. H. Begun, and G. Mamantov, *Inorg. Chem.*, 10, 2285 (1971).

(6) R. D. Ellison, H. A. Levy, and K. W. Fung, *Inorg. Chem.*, 11, 833 (1972).

pounds, and the crystal structure of the former. Our results are compared with those of Ellison, *et al.*,[6] and of Torsi, *et al.*[5]

Experimental Section

Reaction of Mercury with Antimony Pentafluoride. In a typical experiment mercury (2.74 g, 0.0137 mol) was stirred with antimony pentafluoride (4.94 g, 0.0228 mol) in sulfur dioxide at −63° and the mixture was allowed to warm to room temperature and then stirred for 24 hr. A very light yellow solution containing a yellow solid was obtained. The yellow solid was extracted with SO_2 until the remaining solid residue was white. This white solid was identified as antimony trifluoride. The sulfur dioxide extract was evaporated under vacuum and a light yellow crystalline solid was obtained. *Anal.* Calcd for $Hg_3(Sb_2F_{11})_2$: Hg, 39.94; Sb, 32.32; F, 27.74. Found: Hg, 39.80; Sb, 32.23; F, 27.92.

Reaction of Mercury with Arsenic Pentafluoride. In a typical experiment, arsenic pentafluoride (0.0164 mol) was condensed onto elemental mercury (0.0164 mol) in sulfur dioxide at −196° and the mixture was allowed to warm to room temperature and then stirred for a few hours. All the mercury reacted to give a light yellow solution. On evaporation of the solvent this solution yielded a yellow crystalline solid. *Anal.* Calcd for $Hg_3(AsF_6)_2$: Hg, 61.43; As, 15.30; F, 23.27. Found: Hg, 61.39; As, 15.28; F, 22.92.

Preparation of $Hg_2(AsF_6)_2$ and Reaction of Mercury with $Hg_3(AsF_6)_2$. In a typical experiment, arsenic pentafluoride (3.37 g, 0.0198 mol) was condensed onto elemental mercury (2.65 g, 0.0132 mol) in sulfur dioxide at −196° and the solution was allowed to warm up to room temperature. After a few hours all the mercury reacted to give a clear solution which yielded a white solid upon removal of volatiles. The compound was identified as $Hg_2(AsF_6)_2$ by the Raman spectrum.

When elemental mercury (0.52 g, 0.00258 mol) was treated with $Hg_2(AsF_6)_2$ (2.00 g, 0.00256 mol) in SO_2, a yellow solution was obtained, which yielded the previously identified $Hg_3(AsF_6)_2$ on removal of volatiles.

Materials. Commercially available triply distilled mercury (Shawinigan) was used without further purification. Anhydrous sulfur dioxide (Matheson) was stored as a liquid over P_2O_5 before use. Antimony pentafluoride (Ozark-Mahoning) was distilled several times in moisture-free glass apparatus before use. Arsenic pentafluoride (Ozark-Mahoning) was used without purification after the purity was checked by gas-phase infrared spectroscopy. Fluorosulfuric acid (Allied) was distilled twice in moisture-free glass apparatus.

All compounds were handled in a very good drybox and transfer of solvents was carried out on a vacuum line which had been thoroughly flame-dried before use.

Determination of the Structure of $Hg_3(AsF_6)_2$. Precession photographs showed the systematic absences characteristic of the space group $P2_1/c$ (No. 14, C_{2h}^5). Crystal data for $Hg_3(AsF_6)_2$, mol wt 979.68, are as follows: monoclinic, $a = 5.981$ (5), $b = 8.551$ (6), $c = 11.282$ (10) Å, $\beta = 91.16$ (7)°; $U = 577.1$ Å^3, $Z = 2$, $d_{calcd} = 5.67$ g cm^{-3}. The experimental density was not measured as no satisfactory procedure was evolved for this very hygroscopic material. The unit cell parameters were found by least-squares refinement of the Bragg angle and crystal orientation for 15 reflections in the region $5° < 2\theta < 20°$, measured on a Syntex $P\bar{1}$ four-circle Autodiffractometer using Mo Kα (λ 0.71069 Å) radiation.

The crystals had very poorly defined faces, but an approximately spherical crystal (radius 0.07 mm) was sealed in a thin-walled quartz capillary and used for intensity measurements on the diffractometer. The θ-2θ scan technique was used with scan rates varying from 2 to 24°/min (in 2θ) so that the weaker reflections were examined most slowly to minimize counting errors. Stationary-background counts with a time equal to half the scan time for each reflection were made at each end of the scan range. The scan range varied from 2° at low 2θ to 2.5° for the higher angle data. Two standard reflections were recorded every 100 measurements to monitor the stability of the crystal and its alignment. No distinct time-dependent trend was observed with the maximum intensity variation being of the order of 3%. Reflections within a unique quadrant with $2\theta < 50°$ were measured resulting in 636 reflections with intensities greater than 3 times the standard deviation based on counting statistics. The recorded intensities were corrected for background, Lorentz, and polarization effects. Absorption corrections were made to the data assuming spherical geometry of the crystal. The linear absorption coefficient (μ) is 497 cm^{-1} for Mo Kα radiation and transmission factors varied from 0.017 at $\theta = 0°$ to 0.034 at $\theta = 25°$. Unfortunately, due to the difficulty of adequately defining the crystal shape, a more exact correction could not be applied, but the spherical correction seemed the most appropriate.

Solution and Refinement of the Structure. Due to the imposed molecular symmetry, one mercury atom lies at the origin (0, 0, 0). The positions of four other mercury atoms in the unit cell were found by inspection of the three-dimensional Patterson function.

The mercury positions and estimated isotropic temperature factors were refined by two cycles of full-matrix least squares to give a conventional agreement index R_1 ($=\Sigma\Delta/\Sigma|F_o|$ where $\Delta = ||F_o| - |F_c||$) of 0.32. The 636 reflections were used together with the signs determined from the mercury atoms to calculate a three-dimensional Fourier map which revealed the arsenic and fluorine atoms.

These, when included in another four cycles of least-squares refinement, varying positional coordinates and isotropic temperature factors for the mercury and arsenic atoms reduced R_1 to 0.111, while the weighted agreement index R_2 ($=(\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$) was 0.148 with unit weights. An empirical weighting scheme of the form $\sqrt{w} = (A + BF_o + CF_o^2)^{-1}$ was calculated subject to the condition that $\Sigma w\Delta^2$ be approximately independent of $|F_o|$ and $(\sin\theta)/\lambda$. Least-squares refinement converged at $R_1 = 0.106$ and weighted agreement index R_2 of 0.145. The values of the constants A, B, and C in the weighting expression were respectively 21.11, −0.3043, and 0.0160. A final difference Fourier showed no significant features with the largest peak height being 1.4 e/Å^3. The majority of the highest peaks were concentrated within 2 Å of the mercury atoms.

Errors arising from the absorption correction approximation was probably the main reason that an expected higher precision and lower residual were not obtained.

The atomic scattering factors for mercury, arsenic, and fluorine with corrections for anomalous dispersion for the mercury and arsenic atoms were taken from ref 7. All calculations were performed on a CDC 6400 computer using the series of programs in the XRAY 71 system[8] and our own programs. The final atomic positional coordinates and temperature factors are given in Table II, while a listing of the observed and calculated structure factors is available.[9]

Results and Discussion

Trimercury Bis(hexafluoroarsenate(V)), $Hg_3(AsF_6)_2$. When mercury is treated with a solution of AsF_5 in liquid sulfur dioxide at room temperature, the liquid mercury rapidly reacts to yield a pale golden crystalline compound with a distinct metallic appearance. This compound was originally believed[10] to have the empirical formula Hg_3AsF_6 but a crystal determination[11] has now shown that it has the composition $Hg_{2.85}AsF_6$ and has a novel structure containing infinite polymeric cationic mercury chains. On further reaction with AsF_5 this gold compound dissolves to give a deep red solution. The nature of this solution is still under investigation. With a further quantity of AsF_5 a yellow solution is finally obtained. On evaporation of the solvent this solution yields a yellow crystalline solid. The weight of the solid obtained corresponded to that required for the reaction $3Hg + 3AsF_5 \rightarrow Hg_3(AsF_6)_2 + AsF_3$, and the elemental analysis of the compound was in good agreement with this formula. The compound was found to be diamagnetic and its formulation as the compound $Hg_3^{2+}(AsF_6^-)_2$ was fully confirmed by the X-ray crystallographic study which was subsequently carried out and which is reported in this paper. If the yellow solution is treated with a further quantity of AsF_5, it becomes colorless and a white crystalline solid is obtained on removal

---

(7) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962.

(8) J. M. Stewart, F. A. Kundell, and J. C. Baldwin, "XRAY 71 System of Crystallographic Programs," Technical Report, University of Maryland, 1971.

(9) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1343.

(10) R. J. Gillespie and P. K. Ummat, *Chem. Commun.*, 1168 (1971).

(11) I. D. Brown, B. D. Cutforth, C. G. Davies, R. J. Gillespie, P. R. Ireland, and J. E. Vekris, to be submitted for publication.

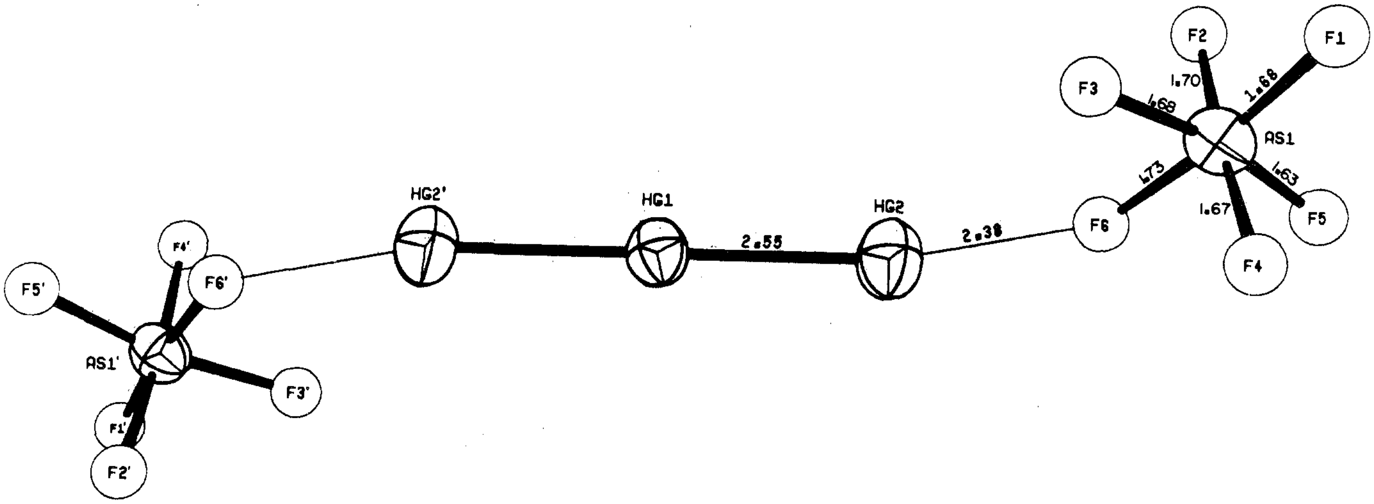


Figure 1. Perspective view of $Hg_3^{2+}(AsF_6^-)_2$. There is a crystallographic center of symmetry at atom Hg(1). Interatomic distances are in angstroms.

Table I. Raman Spectra of Mercury Cations

$Hg_2(AsF_6)_2$	$Hg_3(AsF_6)_2$ Soln	$Hg_3(AsF_6)_2$ Solid	Assignment
180 vs	113 vs	79 s 138 vs	ν_1
375 w		371 w	ν_5 AsF_6^-
575 w			ν_2 AsF_6^-
680 vs		675 vs	ν_1 AsF_6^-
	$Hg_3(Sb_2F_{11})_2$ Soln	$Hg_3(Sb_2F_{11})_2$ Solid	Assignment
	113 vs	94 s 141 vs	ν_1
		291 s 544 w 630 w 644 vs 683 w	$Sb_2F_{11}^-$
$Hg_3(SO_3F)_2$ soln in HSO_3F			Assignment
113 vs[a]			ν_1

[a] Plus previously reported bands for HSO_3F and SO_3F^-.

Table II. Structural Parameters[a] for $Hg_3(AsF_6)_2$

Parameter $\times 10^4$	Hg(1)	Hg(2)	As(1)
x	0	2395 (5)	2997 (10)
y	0	2302 (3)	6431 (6)
z	0	705 (3)	1722 (5)
U_{11}	441 (17)	567 (16)	492 (29)
U_{22}	514 (18)	671 (17)	497 (31)
U_{33}	588 (19)	791 (18)	513 (29)
U_{12}	−30 (13)	−110 (12)	−3 (23)
U_{13}	62 (13)	15 (12)	112 (22)
U_{23}	−24 (13)	−93 (13)	48 (22)

	10^3x	10^3y	10^3z	10^3B, Å^2
F(1)	169 (8)	806 (6)	216 (4)	98 (13)
F(2)	316 (7)	722 (5)	34 (3)	78 (10)
F(3)	55 (15)	551 (10)	146 (7)	171 (28)
F(4)	306 (10)	575 (7)	311 (4)	115 (16)
F(5)	556 (9)	696 (6)	203 (4)	98 (13)
F(6)	412 (9)	474 (6)	114 (4)	102 (14)

[a] x, y, and z are fractional atomic coordinates. The isotropic temperature factor B is from the expression $\exp[-B(\sin^2\theta/\lambda^2]$ and the form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$. Least-squares-estimated standard errors in the least significant digits are given in parentheses.

of volatiles. The weight of the solid corresponded to the formation of mercury(I) hexafluoroarsenate, $Hg_2(AsF_6)_2$, according to the equation $2Hg + 3AsF_5 \rightarrow Hg_2(AsF_6)_2 + AsF_3$, and the elemental analysis of the compound was in good agreement with this formula.

Treatment of $Hg_2(AsF_6)_2$ with an equimolar amount of mercury in liquid SO_2 yields a yellow solution from which $Hg_3(AsF_6)_2$ can be obtained: $Hg_2(AsF_6)_2 + Hg \rightarrow Hg_3(AsF_6)_2$.

The AsF_6^- ion in $Hg_3(AsF_6)_2$ was characterized by the observation of the 1:1:1:1 quartet of AsF_6^- in the ^{19}F spectrum of a solution in acetone with which some reaction occurs, by the observation of the strong ν_3 vibration of AsF_6^- at 639 cm^{-1} in the infrared spectrum, and by the observation of the characteristic ν_1, ν_2, and ν_5 bands in the Raman spectrum of the solid (Table I).

Trimercury Bis[μ-fluoro-bis(pentafluoroantimonate(V))], $Hg_3(Sb_2F_{11})_2$. The reaction of mercury with antimony pentafluoride in liquid sulfur dioxide in the mole ratio Hg:SbF_5 = 3:5 proceeds according to the equation $3Hg + 5SbF_5 \rightarrow Hg_3(Sb_2F_{11})_2 + SbF_3$. The product is somewhat less soluble in SO_2 than the hexafluoroarsenate but it can be separated from the insoluble antimony trifluoride by repeated extraction with SO_2. Removal of the solvent yielded a pale yellow crystalline solid, for which the elemental analysis was in excellent agreement with the formulation $Hg_3(Sb_2F_{11})_2$. The Raman spectrum of a solution of the compound in SO_2 or HSO_3F showed the characteristic frequencies of $Sb_2F_{11}^-$ (Table I).

Solutions of both $Hg_3(AsF_6)_2$ and $Hg_3(Sb_2F_{11})_2$ in SO_2 or HSO_3F are yellow and have a characteristic absorption band at 325 nm and a characteristic strong Raman band at 113 cm^{-1} in addition to the lines due to the solvent and the anion. This Raman frequency is assigned as the symmetrical stretch of a linear Hg_3^{2+} cation.

Reaction of Mercury with Fluorosulfuric Acid. It was reported as early as 1932 that fluorosulfuric acid reacts with mercury to give a yellow solution.[1] The absorption spectrum of this solution has the characteristic band of Hg_3^{2+} at 325 nm and the Raman spectrum has the characteristic strong Raman frequency of 113 cm^{-1}. The color of the solution slowly diminishes on standing at room temperature, the 325-nm band diminishes in intensity and the solution becomes colorless after several days. It is clear that mercury is initially oxidized by fluorosulfuric acid to the Hg_3^{2+} cation which is slowly further oxidized to Hg_2^{2+}.

Structure of $Hg_3(AsF_6)_2$. The structural parameters determined by a single-crystal X-ray study of this compound are listed in Table II. Figure 1 shows the configuration of the $Hg_3^{2+}(AsF_6^-)_2$ unit and Table III lists the bond lengths and angles. The packing of the ions is shown in Figure 2.

To a first approximation the structure may be described as consisting of discrete linear symmetrical Hg_3^{2+} ions and octahedral AsF_6^- ions. The Hg-Hg bond length is 2.552 Å which agrees well with the value of 2.56 Å reported for $Hg_3(AlCl_4)_2$[6] and is somewhat larger than those in the range 2.49-2.54 Å reported for mercurous halides.[12] The central Hg of the Hg_3^{2+} ion lies on a twofold axis and the Hg_3 group must therefore be linear and symmetrical. In $Hg_3(AlCl_4)_2$ the Hg_3 group however appears to deviate slightly from linearity and to have a bond angle of 174.4°. The mercury-fluorine distance is 2.38 Å which is intermediate between approximate values of 2.10 and 2.46 Å which may be estimated for a covalent and an ionic bond, respectively, from covalent and ionic radii. This indicates that the mercury-fluorine bond has some covalent character. The Hg-Hg---F bond angle of 170° is also consistent with the idea that the terminal mercury atoms are forming two bonds with more or less covalent character—one to the central mercury and the other to a fluorine of an AsF_6^- group as such covalent bonds on mercury are expected to have an ideal bond angle of 180°. This Hg-F bridge slightly distorts the AsF_6^- ion and the As-F(6) distance is 1.73 Å, whereas the average of the remaining distances is 1.67 Å, the same as the mean As-F distance reported previously[13] for AsF_6^-. It is noteworthy also that the average bond angle between F(6) and its neighbors is 87.8° whereas the average bond angle between F(1) and its neighbors is 92.5°. It is reasonable to suppose that because a lone pair on F(6) is used to form a bond with the neighboring mercury, this As-F bond becomes more polar; *i.e.*, the bonding electron pair moves further away from the arsenic and the bond angles around arsenic then adjust themselves so as to minimize bond-bond repulsions.

Raman Spectra. The Raman spectra of crystalline $Hg_2(AsF_6)_2$ shows in addition to the characteristic frequencies of AsF_6^- a single intense band at 182 cm^{-1} which can be reasonably assigned to the Hg-Hg stretch in the Hg_2^{2+} ion.

In solution in SO_2 or HSO_3F both $Hg_3(AsF_6)_2$ and $Hg_3(Sb_2F_{11})_2$ gave, in addition to the solvent lines and the expected anion frequencies, a single strong polarized line at 113 cm^{-1} which may be assigned as the symmetric stretch of the linear Hg_3^{2+} ion. The same strong band at 113 cm^{-1} is also observed in the yellow solution obtained when mercury dissolves in HSO_3F. This band is at a much lower frequency than observed for Hg_2^{2+} in the hexafluoroarsenate but it is noteworthy that the Hg-Hg frequency in Hg(I) compounds varies over a wide range from 185 cm^{-1} for Hg_2F_2[14] to 113 cm^{-1} for Hg_2I_2.[15] The Raman spectra of the solid compounds $Hg_3(AsF_6)_2$ and $Hg_3(Sb_2F_{11})_2$ are surprisingly different from the spectra of their solutions. Instead of the single line at 113 cm^{-1} attributed to the Hg_3^{2+} symmetrical stretch they show lines at 79 and 138 cm^{-1} for $Hg_3(AsF_6)_2$ and at 94 and 141 cm^{-1} for $Hg_3(Sb_2F_{11})_2$. The mean frequency of the two lines for $Hg_3(AsF_6)_2$ is 108 cm^{-1} and for $Hg_3(Sb_2F_{11})_2$ is 118 cm^{-1}, which are close to the value observed in solution. In the spectrum of polycrystalline $Hg_3(AlCl_4)_2$ Torsi, *et al.*,[5] also observed two strong Raman frequencies at 93 and 123 cm^{-1} that they assigned as symmetric and asymmetric stretching modes of a nonlinear Hg_3^{2+} ion. However, as the Hg_3^{2+} ion is almost linear in this compound, the asymmetric stretching mode would be expected to be extremely weak and it seems unlikely that their assignment is correct.

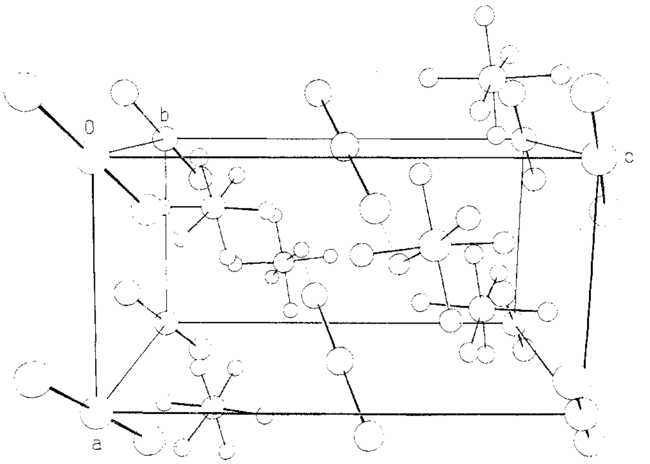


Figure 2. A perspective illustration of the packing of ions in $Hg_3^{2+}(AsF_6^-)_2$ as viewed down the *b* axis of the unit cell.

Table III. Bond Distances and Bond Angles in $Hg_3(AsF_6)_2$

	Distances, Å		
Hg(1)-Hg(2)	2.552 (5)	As(1)-F(1)	1.68 (5)
Hg(2)-F(6)	2.38 (5)	As(1)-F(2)	1.70 (4)
Hg(1)-F(4)	2.91 (9)	As(1)-F(3)	1.68 (8)
Hg(2)-F(2)	2.96 (7)	As(1)-F(4)	1.67 (5)
Hg(2)-F(5)	2.83 (8)	As(1)-F(5)	1.63 (6)
		As(1)-F(6)	1.73 (5)
	Angles Subtended at Hg(2), Deg		
Hg(1)-F(6)	168.9 (1.2)		
	Angles Subtended at Arsenic, Deg		
F(6)-F(1)	173.7 (2.3)	F(1)-F(5)	98.6 (2.4)
F(6)-F(4)	93.6 (2.6)	F(4)-F(2)	174.6 (2.5)
F(6)-F(2)	87.5 (2.1)	F(4)-F(3)	90.4 (3.6)
F(6)-F(3)	83.5 (3.4)	F(4)-F(5)	83.9 (2.6)
F(6)-F(5)	86.4 (2.5)	F(2)-F(3)	95.0 (3.1)
F(1)-F(4)	90.8 (2.5)	F(2)-F(5)	90.9 (2.2)
F(1)-F(2)	88.6 (2.1)	F(3)-F(5)	168.1 (3.4)
F(1)-F(3)	91.8 (3.4)		

Because there are two formula units per unit cell ($Z = 2$) in $Hg_3(AsF_6)_2$ a factor group splitting of the Hg_3^{2+} symmetrical stretch is expected and this probably accounts for the observed splitting of this band although the magnitude of the splitting is rather large and implies unexpectedly strong coupling between the Hg_3^{2+} ions.

A possible alternative explanation of the solid-state splitting is that it arises from Fermi resonance between ν_1 and the first overtone of the bending mode ν_2. This would require that $2\nu_2$ is close to ν_1 and although this is not unreasonable this explanation must be regarded as purely speculative as ν_2 is not known at present as it is not active in the Raman spectrum.

Absorption Spectra. The absorption spectra of $Hg_3(AsF_6)_2$ and $Hg_3(Sb_2F_{11})_2$ in HSO_3F and SO_2 show a single strong peak at 325 nm with an approximate extinction coefficient of 10^4. Torsi and Mamantov also found an absorption peak at 325 nm for $Hg_3(AlCl_4)_2$. The colorless solution of $Hg_2(AsF_6)_2$ in HSO_3F has an absorption band at 248 nm. The yellow solution obtained when mercury dissolves in HSO_3F shows the characteristic band at 325 nm associated with the

---

(12) E. Dorm, *Chem. Commun.*, 466 (1971).

(13) F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. DeBoer, and A. Zalkin, *Chem. Commun.*, 1048 (1968).

(14) H. Stammreich and T. Teixeira, *J. Mol. Struct.*, 1, 55 (1967).

(15) J. R. Durig, K. K. Law, G. Nagarajan, M. Walker, and J. Bragin, *J. Chem. Phys.*, **50**, 2130 (1969).

Hg_3^{2+} cation but this peak rapidly diminishes and is replaced by peaks at 248 and 280 nm. The peak at 248 nm is due to the Hg_2^{2+} ion while the peak at 280 nm is due to the SO_2 formed as the reduction product of HSO_3F.

Registry No. Hg, 7439-97-6; SbF_5, 7783-70-2; AsF_5, 7784-36-3; HSO_3F, 7789-21-1; $Hg_2(AsF_6)_2$, 38832-78-9; $Hg_3(Sb_2F_{11})_2$, 38832-79-0; $Hg_3(AsF_6)_2$, 34738-00-6; $Hg_3(SO_3F)_2$, 38768-48-8.

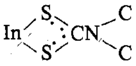
Contribution from the Department of Chemistry,
North Carolina State University, Raleigh, North Carolina 27607

Preparation and Crystal and Molecular Structure of Tris(pentamethylenedithiocarbamato)indium(III), $In(pmtc)_3$

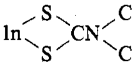
P. J. HAUSER, J. BORDNER, and A. F. SCHREINER*

Received August 3, 1972

The three-dimensional X-ray crystal structure determination of tris(pentamethylenedithiocarbamato)indium(III), $In(pmtc)_3$ or $In(S_2CNC_5H_{10})_3$, was carried out, and relationships of these crystallographic data to other electronic structural features of the $M^{III}S_6$ chromophore are pointed out. The following conclusions are reached: (1) the pair of carbon-sulfur p_π electrons of carbamate in



are delocalized; (2) the nitrogen atom π bonds significantly with carbon of (S_2CN), since this C-N distance is significantly (0.15 Å) shorter than the N-C distance involving the six-membered organic ring carbon atoms; (3) the last mentioned C-N distance of 1.33 Å is also 0.07 Å shorter than the sum of radii of an sp^2 carbon and a saturated amine nitrogen; (4) the seven-atom group



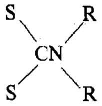
is planar; (5) the three organic rings have the chair conformation; (6) the S-In-S chelate angle is only 69°; (7) the chelate projection angle, ϕ, or (propeller) pitch angle, is only 25°, bringing the structure *closer to a trigonal prism* ($\phi = 0°$) *than an octahedron* ($\phi = 60°$); (8) trigonal crystal field Hamiltonians should be allowed to depend on two independent angles, the polar angle θ and chelate projection angle ϕ, so as to retain general applicability.

Introduction

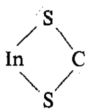
Compounds containing metal-sulfur bonds have occupied a position of special interest from several points of view, *e.g.*, their biochemistry,[1] inorganic chemistry,[2] synthetic chemistry,[2,3] spectroscopy,[2-8] and theoretical features.[3,8] The early works of Kida and Yoneda[9] and Jorgensen[2,10] are especially noteworthy, and the latter author is largely responsible for stimulating a number of more recent detailed investigations.[2-5,8] Some of these more interesting recent questions have dealt with both static structural details and electronic structure problems of electronic ground and excited states. This study will be concerned primarily with the complexed ligand pentamethylenedithiocarbamate, pmtc$^-$, as found in the tris-bidentate chelate complex $In(pmtc)_3$. This complex and the chromium(III) analog, $Cr(pmtc)_3$ (Figure 1), were first prepared by Schreiner and Hauser.[3] Partly due to the interesting nature of the magnetic circular dichroism spectra of $M(tc)_3$[3,8] and because of the interest in the structural details of intraligand chelate angle ζ (Figure 2), chelate projection angle ϕ (Figure 3), and trigonal polar angle θ (Figures 2 and 3), the present study of $In(pmtc)_3$ was undertaken. The relationship of these parameters, their relationship to formulating six-coordinate trigonal crystal field Hamiltonians, and several other electronic structural problems will be discussed.

Discussion

From Figure 4, which shows several averaged interatomic distances and bond angles, it is immediately interesting to point to several features. First, the In-S bond distances in any one [In(pmtc)] moiety are equal (2.59 Å), and this holds for each of the three moieties. This result is entirely consistent with the view that the pair of S-C π electrons of



are completely delocalized in the four-member ring



when the ligand coordinates to the metal. This result is in

---

[1] S. Livingstone and A. E. Mihkelson, *Inorg. Chem.*, **9**, 2545 (1970).
[2] C. K. Jorgensen, *Inorg. Chim. Acta Rev.*, **2**, 65 (1968).
[3] P. J. Hauser, A. F. Schreiner, J. D. Gunter, W. J. Mitchell, and M. K. DeArmond, *Theor. Chim. Acta*, **24**, 78 (1972).
[4] J. D. Lebedda and R. A. Palmer, *Inorg. Chem.*, **10**, 2704 (1971).
[5] J. D. Lebedda and R. A. Palmer, *Inorg. Chem.*, **11**, 484 (1972).
[6] A. A. G. Tomlinson, *J. Chem. Soc. A*, 1409 (1971).
[7] J. R. Wasson, S. J. Wasson, and G. M. Woltermann, *Inorg. Chem.*, **9**, 1576 (1970).
[8] A. F. Schreiner and P. J. Hauser, *Inorg. Chem.*, **11**, 2706 (1972).
[9] S. Kida and H. Yoneda, *J. Chem. Soc. Jap.*, **76**, 1059 (1955).
[10] C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).