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Structural Characterization of Dichloro[2-(2-aminoethyl)pyridine]copper(II)

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The crystal and molecular structure of dichloro[2-(2-aminoethyl)pyridine]copper(II), $CuCl_2(C_7N_2H_{10})$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group $D_{2h}{}^{15}$-*Pbca* of the orthorhombic system with eight formula units in a cell of dimensions $a = 8.791$ (4), $b = 19.533$ (10), and $c = 10.877$ (7) Å. The observed and calculated densities are 1.76 (5) and 1.824 g cm^{-3}, respectively. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.032 for 1957 independent reflections having $F^2 > 3\sigma(F^2)$. The complex has been found to be isomorphous with the bromo analog and consists of infinite Cu-Cl-Cu chains which are joined by doubly bridged Cu-Cl-Cu-Cl linkages. Both types of chlorine bridges are asymmetric, the Cu-Cl separations in the chains being 2.264 (1) and 3.504 (2) Å while those in the pairwise interactions are 2.272 and 3.522 (2) Å. Antiferromagnetic exchange at low temperatures indicates that these weak interactions are significant so that the complex must be viewed as a six-coordinate polymer, and the geometry around the copper is best described as a severely distorted octahedron. The small but significant differences between the structure of this complex and its bromo analog are consistent with the observed low-temperature susceptibility data.

Introduction

Complexes of formulation $Cu(AEP)Cl_2$ and $Cu(AEP)Br_2$, where AEP is 2-(2-aminoethyl)pyridine, were first reported by Uhlig and Maaser,[1] and it was suggested initially that they were halogen-bridged dimers with five-coordinate geometry at copper. We, however, have recently shown[2] that the bromo complex is actually best described as a six-coordinate polymer containing both dimer-type interactions and infinite chains. The low-temperature magnetic susceptibility data of the complexes[3] support this formulation and suggest that there are important differences between the magnetic properties of the chloro and bromo complexes. Hence, we felt that it would be profitable to compare the structures of the two complexes in order to further our studies on the relationship between the structural and magnetic properties of magnetically condensed systems.[2-9] We have, therefore, undertaken a precise three-dimensional structural analysis of the chloro complex, $Cu(AEP)Cl_2$.

Collection and Reduction of the X-Ray Data

Attempts to prepare the complex by the method of Uhlig and Maaser[1] were unsuccessful. The material was prepared by adding a few drops of AEP to a solution of $CuCl_2 \cdot 2H_2O$ in ethanol. Well-formed blue plates crystallized from a green solution. *Anal.* Calcd for $CuCl_2C_7N_2H_{10}$: C, 32.76; H, 3.93; N, 10.92; Cl, 27.63. Found:[10] C, 32.67; H, 3.79; N, 10.88; Cl, 27.87.

On the basis of precession and Weissenberg photography the crystals were assigned to the orthorhombic system. The observed systematic absences are $hk0$ for h odd, $h0l$ for l odd, $0kl$ for k odd, which strongly suggests that the space group is $D_{2h}{}^{15}$-*Pbca*. The cell constants, obtained by the least-squares procedure of Busing and Levy,[11] are $a = 8.791$ (4), $b = 19.533$ (10), $c = 10.877$ (7) Å. A density of 1.824 g cm^{-3} calculated for eight monomeric formula units is in acceptable agreement with the value of 1.76 (5) g cm^{-3} obtained by flotation in dibromoethane-carbon tetrachloride. Hence, no crystallographic symmetry need be imposed on monomeric species in the cell. Moreover, the cell data strongly suggest that the complex is isomorphous with the bromo analog.[2]

Table I. Positional Parameters for $Cu(C_7N_2H_{10})Cl_2$

	x	y	z
Cu	0.05836 (3)	0.06294 (1)	0.12576 (3)
Cl(1)	−0.00869 (8)	0.04511 (4)	−0.19188 (8)
Cl(2)	−0.19030 (7)	0.09297 (3)	0.13004 (6)
N(1)	0.1257 (2)	0.16178 (10)	0.1240 (2)
N(2)	0.2646 (2)	0.0293 (1)	0.0787 (2)
C(1)	0.2322 (3)	0.1853 (1)	0.0469 (2)
C(2)	0.2773 (3)	0.2534 (1)	0.0513 (3)
C(3)	0.2157 (4)	0.2968 (2)	0.1366 (3)
C(4)	0.1090 (3)	0.2722 (1)	0.2176 (3)
C(5)	0.0674 (3)	0.2045 (1)	0.2077 (3)
C(6)	0.3011 (3)	0.1356 (1)	−0.0415 (3)
C(7)	0.3768 (3)	0.0755 (1)	0.0215 (3)
H(2)	0.355 (4)	0.264 (2)	0.009 (3)
H(3)	0.243 (5)	0.336 (2)	0.138 (3)
H(4)	0.063 (3)	0.300 (2)	0.274 (3)
H(5)	−0.008 (3)	0.189 (1)	0.259 (3)
H(61)	0.228 (3)	0.115 (2)	−0.093 (3)
H(62)	0.377 (4)	0.161 (2)	−0.085 (3)
H(71)	0.435 (4)	0.089 (2)	0.087 (4)
H(72)	0.443 (4)	0.057 (2)	−0.028 (4)
H(N1)	0.298 (4)	0.010 (2)	0.148 (3)
H(N2)	0.243 (4)	−0.004 (2)	0.032 (3)

Diffraction data were collected from a trapezoidal plate crystal with faces (010), ($0\bar{1}0$), ($1\bar{1}\bar{1}$), ($\bar{1}11$), ($\bar{1}0\bar{1}$), (101). The crystal was mounted on a glass fiber roughly parallel to the c axis, and data were collected on a Picker four-circle automatic diffractometer using niobium-filtered (0.0015 in.) Mo Kα radiation in the manner described previously.[4] The data were collected at a scan rate of 1°/min, and the peaks were scanned from 0.5° in 2θ below the calculated Kα_1 peak position to 0.5° above the calculated Kα_2 peak position. Data were collected out to a value of 2θ(Mo Kα_1) = 60°, 3235 independent intensities being recorded; there were very few reflections above background at values of $2\theta > 60°$.

The data were processed by the method of Corfield, Doedens, and Ibers[12] using our program DATPROC.[13] After background corrections were applied the intensities were assigned[14] standard deviations $\sigma(I)$ as

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + p^2I^2]^{1/2}$$

where the symbols have their usual meanings[4,12] and p was chosen as

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Table II. Thermal Parameters for $Cu(C_7N_2H_{10})Cl_2$

	β_{11}[a] or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00867 (4)	0.0012001 (8)	0.00787 (4)	−0.0014 (1)	0.00146 (3)	−0.00017 (1)
Cl(1)	0.01213 (9)	0.00140 (2)	0.01383 (10)	−0.00043 (3)	0.00130 (8)	0.00091 (3)
Cl(2)	0.00889 (7)	0.00184 (2)	0.00768 (6)	0.00024 (3)	0.00142 (5)	−0.00022 (3)
N(1)	0.0084 (2)	0.00137 (5)	0.0059 (2)	−0.00009 (9)	−0.0002 (2)	0.00003 (8)
N(2)	0.0091 (3)	0.00151 (6)	0.0068 (2)	0.00013 (10)	0.0005 (2)	0.00018 (9)
C(1)	0.0083 (3)	0.00153 (6)	0.0051 (2)	−0.0000 (1)	−0.0008 (2)	0.00042 (9)
C(2)	0.0113 (4)	0.00172 (7)	0.0093 (3)	−0.0010 (1)	0.0007 (3)	0.0010 (1)
C(3)	0.0138 (4)	0.00128 (6)	0.0111 (4)	−0.0009 (1)	−0.0021 (3)	0.0008 (1)
C(4)	0.0115 (4)	0.00150 (6)	0.0082 (3)	0.0003 (1)	−0.0019 (3)	−0.0009 (1)
C(5)	0.0108 (4)	0.00145 (6)	0.0062 (2)	0.0001 (1)	0.0004 (2)	−0.0001 (1)
C(6)	0.0109 (3)	0.00202 (7)	0.0058 (2)	−0.0002 (1)	0.0009 (2)	0.0005 (1)
C(7)	0.0080 (3)	0.00211 (8)	0.0073 (3)	0.0004 (1)	0.0010 (2)	−0.0001 (1)
H(2)	5.0 (8)					
H(3)	7 (1)					
H(4)	4.0 (7)					
H(5)	3.4 (6)					
H(61)	3.7 (7)					
H(62)	4.4 (7)					
H(71)	4.4 (8)					
H(72)	6 (1)					
H(N1)	5.7 (9)					
H(N2)	3.5 (7)					

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Internuclear Distances and Angles in $Cu(C_7N_2H_{10})X_2$ (X = Cl or Br)[a]

	Distance, Å			Angle, deg	
Atoms	Br[2]	Cl	Atoms	Br[2]	Cl
Cu–Cu′	4.006 (3)	3.819 (2)	X(1)′–Cu–X(1)	101.33 (4)	100.75 (3)
Cu–X(1)	2.413 (2)	2.272 (1)	X(1′)–Cu–X(2)	92.55 (5)	92.78 (3)
Cu–X(1)′	3.706 (3)	3.522 (2)	X(1)′–Cu–X(2)″	90.22 (5)	92.11 (3)
Cu–X(2)	2.388 (2)	2.264 (1)	X(1)′–Cu–N(1)	160.3 (2)	161.33 (7)
Cu–X(2)″	3.569 (2)	3.504 (2)	X(1)′–Cu–N(2)	87.5 (2)	87.12 (7)
Cu–N(1)	2.021 (5)	2.019 (2)	X(2)–Cu–X(2)″	122.29 (5)	123.36 (3)
Cu–N(2)	1.989 (6)	1.995 (2)	X(2)–Cu–X(1)	82.46 (3)	83.35 (2)
N(1)–C(1)	1.328 (9)	1.338 (3)	X(2)–Cu–N(1)	92.5 (2)	92.03 (6)
C(1)–C(2)	1.379 (10)	1.390 (4)	X(2)–Cu–N(2)	163.4 (2)	165.47 (7)
C(2)–C(3)	1.379 (12)	1.369 (5)	X(1)–Cu–X(2)″	152.47 (4)	149.94 (2)
C(3)–C(4)	1.357 (12)	1.373 (4)	X(1)–Cu–N(1)	98.2 (2)	97.73 (6)
C(4)–C(5)	1.366 (10)	1.377 (4)	X(1)–Cu–N(2)	81.3 (2)	82.40 (8)
C(5)–N(1)	1.342 (9)	1.336 (3)	X(2)″–Cu–N(1)	71.1 (2)	70.26 (6)
C(1)–C(6)	1.508 (10)	1.494 (4)	X(2)″–Cu–N(2)	74.3 (2)	71.14 (8)
C(6)–C(7)	1.508 (11)	1.515 (4)	N(1)–Cu–N(2)	93.0 (2)	92.66 (9)
C(7)–N(2)	1.455 (10)	1.475 (3)	C(1)–N(1)–C(5)	118.6 (6)	118.8 (2)
C(2)–H(2)	1.17 (10)	0.85 (3)	N(1)–C(1)–C(2)	121.0 (7)	120.4 (2)
C(3)–H(3)	0.80 (14)	0.80 (5)	N(1)–C(1)–C(6)	117.6 (6)	117.7 (2)
C(4)–H(4)	0.88 (8)	0.91 (3)	C(2)–C(1)–C(6)	121.4 (7)	121.9 (2)
C(5)–H(5)	0.94 (7)	0.92 (3)	C(1)–C(2)–C(3)	120.0 (7)	120.2 (3)
C(6)–H(61)	1.10 (8)	0.94 (3)	C(2)–C(3)–C(4)	118.6 (7)	119.2 (3)
C(6)–H(62)	0.99 (11)	0.95 (4)	C(3)–C(4)–C(5)	119.0 (8)	117.9 (3)
C(6)–C(71)	0.91 (11)	0.91 (4)	C(4)–C(5)–N(1)	122.8 (7)	123.5 (3)
C(7)–H(72)	0.97 (11)	0.87 (4)	C(1)–C(6)–C(7)	112.3 (6)	113.0 (2)
N(2)–H(N1)	0.89 (7)	0.89 (3)	C(6)–C(7)–N(2)	111.9 (6)	111.8 (2)
N(2)–H(N2)	0.87 (11)	0.85 (3)			

[a] Atoms designated with a single prime are related to the reference atom by the inversion center; doubly primed atoms are related to the reference atom by the a glide perpendicular to *c*.

0.05. An absorption correction was applied to the data;[15] the linear absorption coefficient μ for these atoms and Mo Kα radiation is 29.4 cm^{-1}, and for the sample used the transmission coefficients were found to lie in the range 0.263–0.727. Of the 3235 independent intensities, 1957 were greater than 3 times their assigned standard deviations.

Solution and Refinement of Structure

All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c the atomic scattering factors for Cu were taken from Cromer and Waber,[16] that for H was taken from Stewart, Davidson, and Simpson,[17] and those for C, N, and Cl were taken from Ibers.[18] The effects of anomalous dispersion were included in calculations of F_c,[19] the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.[20] Only the 1957 independent intensities which were greater than 3 times their estimated standard deviations were used for the refinement of the structure.

Initial values for the atomic coordinates were taken from the isomorphous bromo structure[2] with chlorine atoms assigned the positions of the bromine atoms. After an absorption correction had been applied, two cycles of least-squares calculations in which all nonhydrogen atoms were assigned variable anisotropic thermal parameters were run. The usual agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma(F_o)$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2)^{1/2}$ were 0.049 and 0.072, respectively. The ten hydrogen atoms were unambiguously

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located in a difference Fourier map computed at this stage, and two further least-squares cycles were calculated in which the nonhydrogen atoms were assigned anisotropic thermal parameters and hydrogen atoms were assigned isotropic thermal parameters; all positional and thermal parameters (including the hydrogen parameters) were refined. The final values of R_1 and R_2 were 0.032 and 0.039, respectively.

A final difference Fourier map was featureless, with no peak higher than 0.4 e Å^{-3}; the peak height of a typical carbon atom in this analysis was about 4 e Å^{-3}. Examination of the data suggested to us that no correction for secondary extinction was necessary. In the final cycle of least-squares refinement, no parameter experienced a shift greater than half of its estimated standard deviation, which was taken as evidence that the refinement had converged. The value of R_2 showed no dependence on $|F_o|$ or on sin θ, which suggests that our weighting scheme was appropriate.

The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix are presented in Tables I and II. A table of observed and calculated structure amplitudes is available.[21]

Description of the Structure

The structure of the complex is very similar to that of the corresponding bromo complex,[2] consisting of infinite Cu-Cl(2)-Cu-Cl(2) chains joined by doubly bridged Cu-Cl(1)-Cu-Cl(1) linkages. The polymeric nature of the complex is depicted in Figure 1, and a view of the coordination geometry around one copper center is shown in Figure 2. The coordination polyhedron around the copper atom is a severely distorted octahedron, with a basal "plane" formed by two cis nitrogen and two chlorine atoms and the axial positions being occupied at much greater distances by two further chlorine atoms. As was also seen in the bromo analog, the four "in-plane" ligands deviate markedly from coplanarity; Cl(1)′ and N(1), which are trans to each other, lie 0.29 and 0.32 Å, respectively, below the least-squares plane through these atoms, while Cl(2) and N(2) are 0.27 and 0.33 Å, respectively, above it. The internuclear distances and angles in the chloro complex are compared with those found in the bromo complex in Table III. While the out-of-plane Cu–Cl distances of 3.504 (2) and 3.522 (2) Å are very long, the observation of antiferromagnetic exchange[3] at low temperatures indicates that these weak interactions are significant and that the complex must be viewed as a six-coordinate polymer rather than a four-coordinate monomer.

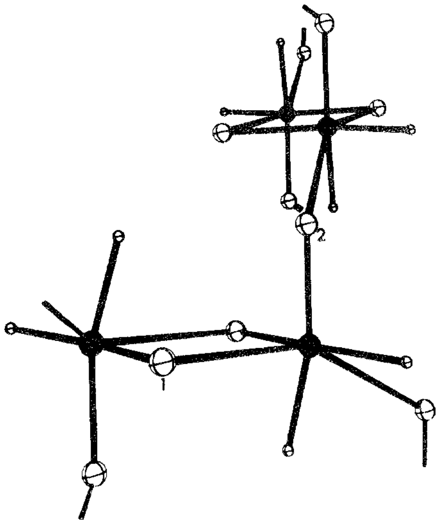

Figure 1. View of the polymeric nature of Cu(AEP)Cl_2. Cu atoms are shown as solid circles, N atoms as small open circles, and Cl atoms as large open circles. Chlorines of the type labeled 1 are Cl(1) and those of the type labeled 2 are Cl(2). The C and H atoms are omitted for clarity.

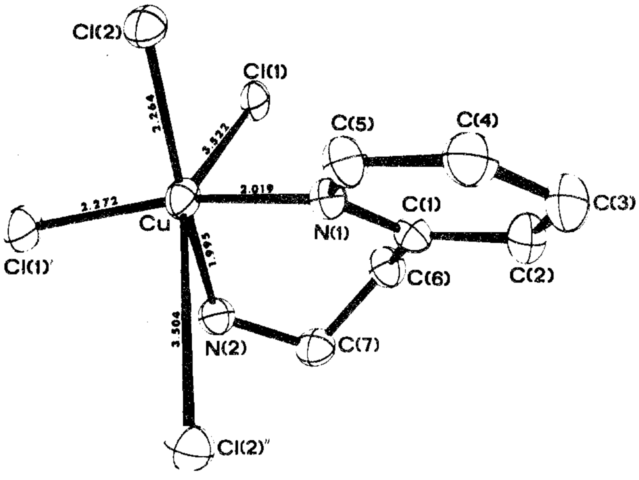

Figure 2. View of the coordination around one Cu in Cu(AEP)Cl_2. Atom Cl(1)′ is related to Cl(1) by the inversion center; atom Cl(2)″ is related to Cl(2) by the *a* glide. The H atoms are omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

While the overall geometry of the complex is very similar to that of the bromo analog, there are magnetically significant differences between the two structures. The pairwise out-of-plane interaction in the chloro complex appears to be significantly stronger than that in the bromo complex, since the Cu-Cl(1) distance of 3.522 (2) Å is 0.19 Å shorter than the corresponding Cu-Br(1) distance while the covalent radius of Cl is only 0.15 Å less than that of Br.[22] The chain interactions, however, show the reverse trend, since the Cu-Cl(2)″ distance of 3.504 (2) Å is only 0.065 Å less than the Cu-Br(2)″ separation. Hence, an examination of these two structures leads to an expectation that if the magnetic behavior of the complexes were dominated by the pairwise (dimeric) interactions the chloro complex should show a stronger interaction than the bromo, while the reverse would be true if the chain interaction were dominant. The observed low-temperature susceptibility data demonstrate that while both exchange pathways are significant, the data more closely obey the Van Vleck equation[23] for exchange-coupled copper dimers than the Fisher equation[24] for linear chains and that the magnitude of $2J$ (the singlet-triplet splitting) is greater for the chloro complex ($2J = -5.7$ cm^{-1}) than for the bromo complex ($2J = -3.6$ cm^{-1}).[3] Hence, we again demonstrate the strong correlation between the magnetic and structural properties of magnetically condensed complexes.

As can be seen in Table III, the Cu-N bond lengths are consistent with those found in related systems. The Cu-N(1) distance of 2.019 (2) Å does not differ significantly from that of 2.021 (5) Å in the bromo complex and lies in the range of 1.98-2.16 Å reported for several other copper complexes of substituted pyridines.[2,7,8,25-29] Similarly, the

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(21) A listing of 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-73-1340.

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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)$_2$Cl$_2$,[28] Cu(α-pic)$_2$Cl$_2$,[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(α-pic)$_2$Br$_2$, 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$_7$H$_{10}$N$_2$), 38704-59-5.

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

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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-

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