Deviations from Ideal Trigonal-bipyramidal Geometry in the $[HgCl_5]^{3-}$ Anion: * Crystal Structures of Two Complex Salts

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A rhombohedral modification of $[Cr(NH_3)_6][HgCl_5]$ has been prepared. The space group is $R\bar{3}c$, with a = 7.521(1), c = 46.111(8) Å (hexagonal axes), and Z = 6. On the other hand, $[Co(NH_3)_6][HgCl_5]$ is monoclinic, space group $P2_1/m$, with a = 8.444(1), b = 7.705(1), c = 11.357(2) Å, β = 107.70(1)°, and Z = 2. The crystal structures have been determined from 411 and 1 591 unique diffractometer-measured intensities respectively, and refined to final R indices of 0.041 and 0.049. Both contain mercury atoms in distorted trigonal-bipyramidal co-ordination, with short equatorial Hg–Cl bonds (2.417—2.431 Å) and very long axial Hg–Cl bonds (2.871—3.038 Å).

THE crystal structure of the complex salt $[Cr(NH_3)_6][HgCl_5]$, which contains a regular trigonal-bipyramidal anion with axial Hg–Cl bonds [2.518(4) Å] considerably shorter than the equatorial bonds [2.640(4) Å], was previously reported.[1] In the course of recent development of *X*-ray diffractometer control software,[2] I attempted to repeat the preparation of this salt, for which the cubic symmetry and presence of a heavy atom on a special position provide an excellent test of procedures for unit-cell determination. Despite following the established method,[3,4] two separate attempts both produced thin-plate crystals with uniaxial optical properties. I, therefore, determined the crystal structure of the product and found it to be a second form of $[Cr(NH_3)_6][HgCl_5]$, with very long, weak, axial Hg–Cl and shorter equatorial Hg–Cl bonds. The $[Co(NH_3)_6]^{3+}$ salt was also investigated crystallographically, and found to have essentially the same anion geometry, although the space group and crystal packing are quite different for the two salts.

EXPERIMENTAL

The preparative method for $[Cr(NH_3)_6][HgCl_5]$ has already been described.[3,4] Although this method was followed, thin-plate crystals were obtained. They were washed with methanol, and air-dried at room temperature. Optical examination indicated a uniaxial crystal system, with the unique axis perpendicular to the plate.

Crystals of $[Co(NH_3)_6][HgCl_5]$, prepared in 1975 from $[Co(NH_3)_6]Cl_3$, $HgCl_2$, and hydrochloric acid in aqueous methanol,[4] were supplied by Dr. B. P. Straughan.

Crystal-structure Determination.—Crystals of both samples were examined on a Stoe–Siemens AED diffractometer, with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). All measurements were made at room temperature.

$[Cr(NH_3)_6][HgCl_5]$, (1). A thin-plate crystal was cut to a maximum size of 0.4 mm and sealed in a capillary tube. The unit-cell parameters were determined by automatic procedures, and refined from 2θ values ($20 < 2\theta < 25°$) of 48 centred reflections.

Crystal data. $M = 532.1$, Rhombohedral, space group $R\bar{3}c$, $a = 7.521(1)$, $c = 46.111(8)$ Å on hexagonal axes, U = 2 258.8 Å^3, $Z = 6$, $D_c = 2.347$ g cm^{-3}, $F(000) = 1\,494$, $\mu = 11.77$ mm^{-1}.

Intensity data were collected for all unique reflections with $2\theta < 50°$.[5] Reflections with odd l were considerably weaker on average than those with even l, and were re-measured for an additional, longer time. These reflections, to which the metal atoms make no contribution because of their special positions, are important for the location of the light atoms. Absorption corrections were applied by an empirical method, based on the measurement of sets of equivalent reflections at various azimuthal angles; transmission factors range from 0.086 to 0.553. 411 Reflections with $F > 2\sigma(F)$ were used for structure determination.

The unit-cell parameters are very similar to those of $[Cr(NH_3)_6][ZnCl_4]Cl$,[6] for which the space group is also $R\bar{3}c$. In this complex, the zinc atom is disordered over two sites on either side of the special position $0,0,\frac{1}{4}$. In the case of (1), however, no disorder of the mercury atom could be detected, and a difference synthesis phased by the metal atoms on the positions $0,0,\frac{1}{4}$ (Hg) and 0,0,0 (Cr) revealed the positions of the Cl and N atoms. One of the two independent Cl atoms is disordered. All atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included, with restraints on position (all N–H equal within 0.01 Å, all H ··· H within the NH_3 ligand equal to within 0.01 Å, effectively producing equal H–N–H angles), and with a common isotropic thermal parameter. The N–H bond length refined to 0.87(6) Å, with H–N–H 104(6)°, in agreement with previous observations;[7] U(H) was 0.074(15) Å^2.

The final value of R was 0.041, with $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.054$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$. An isotropic extinction parameter x [$F_c' = F_c/(1 + xF_c^2/\sin^2\theta)^{\frac{1}{4}}$] refined to $6(1) \times 10^{-7}$.

$[Co(NH_3)_6][HgCl_5]$, (2). Crystals were plates of non-uniform thickness, some elongated to form flat needles. A piece *ca.* 0.27 × 0.27 × 0.15 mm was cut from one and sealed in a capillary tube. Unit-cell parameters were refined from 2θ values ($20 < 2\theta < 25°$) of 28 reflections.

Crystal data. $M = 539.0$, Monoclinic, $P2_1/m$, a = 8.444(1), b = 7.705(1), c = 11.357(2) Å, β = 107.70(1)°, U = 703.92 Å^3, $Z = 2$, $D_c = 2.543$ g cm^{-3}, $F(000) = 504$, μ = 13.1 mm^{-1}. The previous report[1] that the space group is $P2_1/c$ was based on a misinterpretation of precession photographs obtained from a poor-quality crystal.

Intensity data were collected for reflections with $2\theta < 55°$ and were corrected empirically for absorption; transmission factors range from 0.356 to 0.890. 1 591 Unique reflections with $F > 4\sigma(F)$ were used for structure determination.

The structure was solved from Patterson and Fourier syntheses in the space group $P2_1/m$. In this space group,

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* Pentachloromercurate(3–).

both metal atoms, together with two Cl and two N atoms, must lie on the mirror plane. Refinement included H atoms, with N–H fixed at 0.87 Å and H–N–H at 109.5°; H atoms were assigned isotropic thermal parameters fixed at 1.2 times the equivalent isotropic values of the corresponding N atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters.

The final values of R and R' were 0.049 and 0.064 respectively, with $w^{-1} = \sigma^2(F) + 0.001F^2$. The refined value of the extinction parameter x was 2.4(2) × 10^{-5}.

For both compounds, attempts to refine the structure in space groups of lower symmetry (*e.g.* $P2_1$ or $R3c$) were unsuccessful.

Atomic co-ordinates and thermal parameters, bond lengths and angles are given in Tables 1—4. Hydrogen-atom parameters and structure-factor lists are available as Supplementary Publication No. SUP 23205 (15 pp.).*

TABLE 1

Atomic co-ordinates (× 10^4) and anisotropic thermal parameters (Å^2 × 10^4) for (1) *

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	0	0	2 500	529(5)	U_{11}	637(7)	0	0	$U_{11}/2$
Cr	0	0	0	342(9)	U_{11}	245(12)	0	0	$U_{11}/2$
Cl(1)	0	0	3 158(1)	484(11)	U_{11}	472(18)	0	0	$U_{11}/2$
Cl(2)	2 756(6)	−766(7)	2 530(1)	719(24)	1 275(54)	446(24)	−239(34)	−137(24)	680(33)
N	1 849(9)	−658(9)	258(1)	473(30)	512(31)	394(30)	49(25)	−17(25)	272(23)

* Parameters without estimated standard deviations are fixed by symmetry constraints. The anisotropic thermal parameter exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$.

TABLE 2

Atomic co-ordinates (× 10^4) and anisotropic thermal parameters (Å^2 × 10^4) for (2)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	2 101(1)	2 500	2 173(1)	493(3)	385(3)	416(3)	0	167(2)	0
Co	2 582(1)	2 500	7 443(1)	247(5)	249(6)	215(6)	0	109(4)	0
Cl(1)	−379(3)	2 500	3 630(2)	382(11)	332(12)	379(13)	0	166(10)	0
Cl(2)	4 894(3)	2 500	1 231(2)	393(11)	536(15)	313(12)	0	163(10)	0
Cl(3)	−141(3)	2 500	248(3)	448(13)	596(18)	377(14)	0	169(11)	0
Cl(4)	3 066(4)	−150(5)	3 331(4)	1 119(23)	903(22)	1 553(33)	795(24)	1 112(25)	690(20)
N(1)	2 248(11)	718(9)	8 567(7)	864(53)	286(32)	549(43)	32(31)	503(42)	4(34)
N(2)	2 899(11)	740(11)	6 303(8)	707(47)	501(44)	637(49)	−300(40)	480(42)	−273(38)
N(3)	4 974(10)	2 500	8 329(9)	241(36)	1 054(94)	291(46)	0	97(35)	0
N(4)	210(12)	2 500	6 562(12)	249(45)	2 368(225)	401(61)	0	132(44)	0

TABLE 3

Bond lengths (Å) and angles (°) for (1) *

Hg–Cl(1)	3.035(4)	Hg–Cl(2)	2.417(5)
Cr–N	2.070(8)		
Cl(1)–Hg–Cl(2)	86.7(1)	Cl(2)–Hg–Cl(2′)	119.7(1)
Cl(1)–Hg–Cl(1′)	180	N–Cr–N′	89.2(2)

* A prime denotes a symmetry-equivalent atom.

TABLE 4

Bond lengths (Å) and angles (°) for (2)

Hg–Cl(1)	3.038(3)	Co–N(1)	1.953(8)
Hg–Cl(2)	2.871(3)	Co–N(2)	1.948(9)
Hg–Cl(3)	2.418(3)	Co–N(3)	1.964(8)
Hg–Cl(4)	2.431(4)	Co–N(4)	1.948(10)
Cl(1)–Hg–Cl(2)	169.5(1)	N(1)–Co–N(2)	91.2(4)
Cl(1)–Hg–Cl(3)	90.7(1)	N(1)–Co–N(3)	89.7(3)
Cl(1)–Hg–Cl(4)	83.0(1)	N(1)–Co–N(4)	90.3(4)
Cl(2)–Hg–Cl(3)	99.7(1)	N(2)–Co–N(3)	90.7(3)
Cl(2)–Hg–Cl(4)	91.3(1)	N(2)–Co–N(4)	89.2(4)
Cl(3)–Hg–Cl(4)	122.0(1)	N(1)–Co–N(1′)	89.4(5)
Cl(4)–Hg–Cl(4′)	114.3(2)	N(2)–Co–N(2′)	88.2(5)
		N(1)–Co–N(2′)	179.3(3)
		N(3)–Co–N(4)	180.0(6)

RESULTS AND DISCUSSION

In both of the determined crystal structures, the co-ordination of mercury can best be described as distorted trigonal bipyramidal (Figures 1 and 2), with axial Hg–Cl bonds much longer than equatorial Hg–Cl. The distortion is greater for (2), in which the Cl(ax)–Hg–Cl(ax) angle deviates markedly from 180°. The Hg–Cl(ax) distances, although very long, are still shorter than the sum of the van der Waals radii for Cl and Hg (3.3 Å),[8] and must be considered to represent bonding interactions, albeit weak. Very similar co-ordination geometries have been observed for the chloromercury complexes $[S(CH_3)_3][HgCl_3]$,[9] $[S_4N_3][HgCl_3]$,[10] $[N(C_2H_5)_4][HgCl_3]$,[11] and bis(L-tryptophanium) trichloromercurate.[12] These, however, are all formally complexes of the $[HgCl_3]^-$ anion, and five-co-ordination of mercury is achieved by sharing of chloride ligands by adjacent mercury atoms,

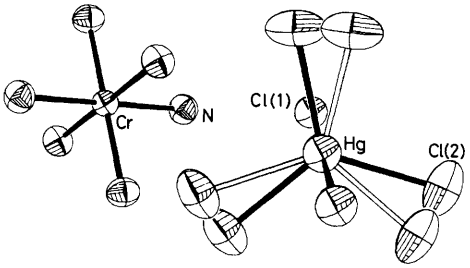

FIGURE 1 The cation and anion in (1). Thermal motion is depicted as 50% probability ellipsoids. Both components of the disorder of Cl(2) are shown

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

producing infinite chains of bridged anions. In (1) and (2), all chloride ligands are terminal; the closest interionic contacts are with ammonia ligands of the cations, so that the structure, in common with others composed of hexa-amminemetal cations and complex chlorometallate anions, contains a network of weak N–H···Cl hydrogen bonds.[1,6,13-15]

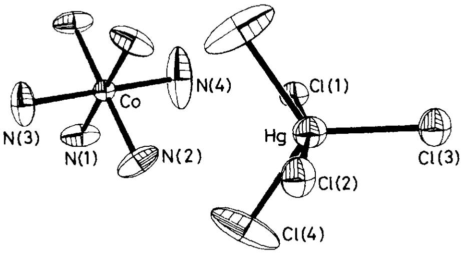

FIGURE 2 The cation and anion in (2)

The disorder in (1) is in the equatorial belt only (Figure 1), and consists of a 1 : 1 distribution over two possible orientations. For each component, the mercury atom lies 0.137 Å out of the plane of the equatorial ligands; in (2) the deviation of the mercury atom from the corresponding plane is 0.181 Å.

The mercury co-ordination contrasts strongly with that in the cubic form of $[Cr(NH_3)_6][HgCl_5]$,[1] for which axial Hg–Cl bonds are 0.122 Å *shorter* than equatorial Hg–Cl. Earlier theoretical treatments of trigonal-bipyramidal co-ordination had predicted for d^{10} systems either no difference in these bond lengths,[16] or longer axial bonds,[17,18] depending on the degree of sophistication of the calculations, although the observed differences for $[HgCl_5]^{3-}$ and for $[CdCl_5]^{3-}$, in which shorter axial bonds have also been observed,[15] could subsequently be rationalised by a different theoretical approach.[19] The observed structures of (1) and (2) demonstrate that the $[HgCl_3]^{3-}$ system is by no means as simple as it had appeared. I venture no explanation for the appearance of $[Cr(NH_3)_6][HgCl_5]$ in two markedly different forms.*

Computer programs were written by W. C. and by Professor G. M. Sheldrick, for a Data General Eclipse S250 mini-computer. I thank the Verband der Chemischen Industrie for financial support, and Dr. B. P. Straughan for supplying crystals of (2).

[1/1320 *Received, 17th August,* 1981]

* *Note added at proof:* The salt $[Co(NH_3)_6][HgCl_5]$ has also been obtained in an orthorhombic modification, and the crystal structure determined (A. W. Herlinger, J. N. Brown, M. A. Dwyer, and S. F. Pavkovic, *Inorg. Chem.*, 1981, **20**, 2366). The co-ordination geometry is very similar to that in the monoclinic form (2) reported here. The precise nature of the product when complex chloromercury anions are precipitated as salts from solution seems to depend critically not only on the reagents, but also on the reaction conditions.

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