Crystal Structure and Vibrational Spectroscopy of Hexa-amminechromium(III) Pentachloromercurate(II)

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Crystals of the title compound are cubic, with a = 22.653 Å, Z = 32, space group $Fd3c$. The structure was solved from 249 counter intensities and refined by least-squares to R 4.46%. The $[HgCl_5]^{3-}$ anion is a regular trigonal bipyramid, with axial bond lengths 2.518(4) and equatorial 2.640(4) Å. The highly significant difference between these values is compared with results for other MX_5 species and with theoretical predictions. Vibrational data are reported also and tentatively assigned.

THERE are very few examples of compounds in which a central metal ion is bound to five equivalent unidentate ligands. Known examples include $[Et_4N]_2[InCl_5]$,[1] $[Et_4N]_2[TlCl_5]$,[2] and the $[CuCl_5]^{3-}$ and $[CdCl_5]^{3-}$ anions,[3,4] which are stabilised in the solid state by precipitation with the large cations $[Cr(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{3+}$. The $[InCl_5]^{2-}$ and $[TlCl_5]^{2-}$ anions adopt a square-based pyramidal structure. In contrast, the copper and cadmium salts belong to the cubic space group $Fd3c$ and the anions exist as regular trigonal bipyramidal species in which the metal–chlorine axial bonds are slightly compressed compared with the equatorial bonds.

Recent MO treatments of trigonal bipyramidal co-ordination have predicted for d^{10} systems either no difference in bond lengths[5] or longer axial bonds,[6] depending on whether mixing between d and p orbitals is ignored or considered. The $[CdCl_5]^{3-}$ anion was noted[6] as being ' an outstanding exception ' where theory and results disagreed.

A new five-co-ordinate anion with the d^{10} configuration would be an important advance both to check the anomalous behaviour of the cadmium salt and to explore the possibility of a square-pyramidal in preference to a trigonal bipyramidal geometry; the energies of both configurations are known to be very similar.

We now report the full characterisation of the pentachloromercurate(II) anion in the compound $[Cr(NH_3)_6][HgCl_5]$. It has a trigonal bipyramidal geometry and the axial bond lengths are found to be significantly shorter than the equatorial.

EXPERIMENTAL

The complex was prepared as reported previously,[7] washed with ethanol, and dried at 60°. The resulting golden-yellow crystals are air-stable.

The % of cation present was checked spectrophotometrically using the visible band at 467 nm for $[Cr(NH_3)_6]^{3+}$ cation in aqueous methanol solution. This calculated value agreed to within 0.5% with that required by the empirical formula for the five-co-ordinate salt.

Vibrational Spectra.—I.r. spectra were recorded in the region 4 000–400 cm^{-1} on a calibrated Perkin-Elmer model 457 grating spectrometer (KBr disc). The 400—40 cm^{-1} region was recorded by use of a Beckmann RIIC 720 Michelson interferometer coupled to an FTC 100 Fourier-transform computer, with sample both as Nujol mull between Polythene plates and as pressed Polythene disc. A spectrum of the disc at *ca.* 100 K, recorded by use of a Beckmann RIIC low-temperature cell, was much better resolved and the frequencies quoted in Table 3 refer to it. The possibility of a phase change occurring at low temperature was checked by X-ray crystallography (see next section). Frequency positions are accurate to ± 2 cm^{-1}.

Raman spectra were obtained on a modified Cary 81 spectrometer, with a Coherent Radiation 52 krypton ion gas laser as the radiation source. The finely powdered sample, examined with 6 471 Å radiation, was prone to scorching and the laser power had to be limited to 5 mW at the sample. The reported Raman frequencies are accurate to within 2 cm^{-1}.

Magnetic Susceptibility Measurements.—These were carried out on a Gouy balance, and they confirmed a d^3 (t_{2g}) spin-state for the $[Cr(NH_3)_6]^{3+}$ cation.

Crystal Structure Determination

Crystal Data.—$[Cr(NH_3)_6][HgCl_5]$, $M = 532.1$, Cubic, $a = 22.653(1)$ Å, $U = 11\,625$ Å^3, $D_c = 2.425$, $Z = 32$, $D_m = 2.44$ (by flotation), $F(000) = 7\,968$. Space group $Fd3c$ (from absences). Mo-K_α radiation, Zr-filtered, $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_\alpha) = 124.3$ cm^{-1}.

The yellow crystals showed faces of the cubic $\{100\}$ and octahedral $\{111\}$ forms. The space group was deduced from absences on precession photographs, which also gave an initial value for the cell edge.

A crystal of dimensions *ca.* 0.2 mm was chosen for intensity measurements, and sealed in a thin-walled Lindemann glass capillary. The unit cell constant was obtained by a least-squares refinement based on the setting angles of 12 carefully centred reflections (Mo-K_α radiation, $2\theta > 38°$) on a Hilger and Watts Y 290 automatic diffractometer.[8]

Intensities were collected in the θ—2θ scan mode for $2\theta < 50°$. All reflections with $h \geqslant 0$, $k \geqslant h$, and $l \geqslant 0$ were measured, giving three equivalent measurements for most reflections. Each reflection was scanned by 80 steps of 0.01° in θ, with a 4 s count at each step, and 80 s background count at each end of the scanning range. No reflections were sufficiently intense to require the insertion of attenuators into the beam.

Three standard reflections were monitored at frequent intervals during data collection, and their decay (*ca.* 1% by the end) used to bring all the reflections to a common scale. Standard deviations of intensities were estimated, taking

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[2] D. F. Shriver and I. Wharf, *Inorg. Chem.*, 1969, **8**, 2167.

[3] K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1111.

[4] T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernal, *Inorg. Chem.*, 1970, **9**, 459; E. F. Epstein, and I. Bernal, *J. Chem. Soc.* (*A*), 1971, 3628.

[5] J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 931.

[6] A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, 1975, **14**, 365.

[7] S. M. Jörgensen, *J. Prakt. Chem.*, 1884, **30**, 17; 1887, **35**, 417.

[8] W. R. Busing and H. A. Levy, *Acta. Cryst.*, 1967, **22**, 457.

into consideration instrument instability and uncertainty in the scaling.[9] Reflections with $I < 2\sigma(I)$ were rejected as unobserved.

The crystal was measured with a micrometer eyepiece fitted to a precession camera telescope, and absorption corrections applied. Data were then merged to give **249** independent reflections. The predicted value of $R'\{= [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}\}$ was 1.62%, based on the agreement between equivalent reflections, with weights $1/\sigma^2(F_o)$.

Refinement of the structure was by full-matrix least-squares methods. Initial co-ordinates were those for $[Cr(NH_3)_6][CuCl_5]$,[3] omitting hydrogen atoms.

Two cycles of isotropic refinement gave values for R 9.95 and R' 13.52%. Anisotropic temperature factors were introduced, and several cycles gave R 4.74 and R' 3.50%. A difference-Fourier synthesis at this point showed broad features around the nitrogen atom, but no resolved peaks. Hydrogen atoms were introduced at idealised positions, assuming N–H 0.87 Å and H–N–H 107°.[10] Refinement continued with these values fixed, and with the constraint of three-fold symmetry of the hydrogen atoms about the Cr–N bond, but allowing the NH_3 group to rotate freely about this bond. A common isotropic temperature factor was refined for the hydrogen atoms. The final values of R and R' were 4.46 and 1.72%. Complex scattering factors for Cr^{3+}, Hg^{2+}, N, Cl^-, and H were taken from ref. 11. Attempts to interpolate between atomic and ionic scattering factors, with refinement of the interpolation,[3] and to remove the constraints from the hydrogen atoms, gave no significant improvement in the agreement.

TABLE 1

Fractional atomic co-ordinates and anisotropic thermal parameters * (Å^2 × 10^4)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	1/4	1/4	1/4	373(2)	U_{11}	U_{11}	−24(5)	U_{23}	U_{23}
Cl(ax)	0.1858(1)	x	x	441(9)	U_{11}	U_{11}	−19(13)	U_{23}	U_{23}
Cl(eq)	1/4	0.1676(1)	1/2-y	1355(42)	397(13)	U_{22}	0(17)	−179(29)	U_{13}
Cr	0	0	0	276(5)	U_{11}	U_{11}	27(18)	U_{23}	U_{23}
N	0.0715(3)	0.0498(3)	−0.0288(3)	302(47)	329(54)	449(46)	−46(44)	19(37)	−22(45)
H(1)	0.0634 †	0.0874	−0.0293						
H(2)	0.0822	0.0401	−0.0643						
H(3)	0.1021	0.0452	−0.0061						

* In the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$. † Reliable estimates of standard deviations for the hydrogen atom positions cannot be made. Isotropic thermal parameters, U 0.117(31).

TABLE 2

Bond lengths (Å) and angles (°)

Hg–Cl(ax)	2.518(4)
Hg–Cl(eq)	2.640(4)
Cr–N	2.079(8)
N–Cr–N	89.5(3)

TABLE 3

Comparison of bond lengths (Å) in related structures

Anion	M–Cl(eq)	M–Cl(ax)	Difference
$[CuCl_5]^{3-}$ [a]	2.3912(13)	2.2964(12)	0.0948(14)
$[CdCl_5]^{3-}$ [b]	2.561(2)	2.526(1)	0.036(1)
$[HgCl_5]^{3-}$ [c]	2.640(4)	2.518(4)	0.122(6)

[a] Ref. 3. [b] Ref. 4. [c] Present work.

An analysis of the variance as a function of sin θ, F_o, indices, and parity subgroups shows no systematic trends.

In order to check for a possible phase change between room and liquid-nitrogen temperatures (see earlier), powder photographs were taken on an adapted Weissenberg camera (*a*) at room temperature, and (*b*) with the same specimen cooled in a stream of dry nitrogen just above its boiling point. The only significant change observed was an increase in the relative intensities of the higher-angle lines, caused by reduced thermal vibration. There was no evidence for a change in structure.

RESULTS AND DISCUSSION

Results are summarised in Tables 1—4. Atomic co-ordinates and temperature factors are given in Table 1 and bond lengths and angles in Table 2, with estimated standard deviations in parentheses. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21 519 (4 pp., 1 microfiche).*

The cation geometry (see Figure 1) is similar to that in related salts. The site symmetry is $\bar{3}$ (S_6), but the angular distortion from octahedral at the chromium atom is insignificant.

TABLE 4

Vibrational frequencies (cm^{-1}) and assignments for some $MCl_5{}^{3-}$ anions belonging to point group D_3

$[CuCl_5]^{3-}$ [a]		$[CdCl_5]^{3-}$ [a]		$[HgCl_5]^{3-}$		
I.r.	Raman	I.r.	Raman	I.r.	Raman	Assignments
	260vs		251mw		269vs	ν_1 and ν_2 (A_1)
268m		236w		(263) [b]		ν_3 (A_2)
				240msh	237m	ν_5 (E)
				141s		ν_4 (A_2)
				156s	*ca.* 160w	ν_6 (E)
				102w		ν_7 (E)
				185mwsh	*ca.* 190w	ν_8 (E)

[a] Taken from ref. 4. [b] Frequency taken from i.r. spectrum of $[Co(NH_3)_6][HgCl_5]$; vs = very strong, m = medium, w = weak, mw = medium weak, sh = shoulder.

The anion (Figure 2) is a regular trigonal bipyramid. There are only two independent bond lengths, the equatorial being significantly longer than the axial. This difference is in the same direction as for the $[CdCl_5]^{3-}$ anion,[4] but rather larger. Bond lengths in the copper, cadmium, and mercury anions are compared in Table 3.

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

[9] L. E. McCandlish, G. H. Stout, and L. C. Andrews, *Acta Cryst.*, 1975, **A31**, 245.

[10] M. R. Churchill, *Inorg. Chem.*, 1973, **12**, 1213.

[11] D. T. Cromer and J. T. Waber, 'International Tables for X-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974, pp. 99–102, 149–150.

Thermal parameters and non-bonded distances are similar to those for the copper and cadmium complexes, and require no further comment.

The vibrational frequencies for the pentachloromercurate(II) anion together with the published frequencies for $[CuCl_5]^{3-}$ and $[CdCl_5]^{3-}$ are given in Table 4. $[Cr(NH_3)_6][HgCl_5]$ belongs to the same cubic space group as $[Co(NH_3)_6][CuCl_5]$ and $[Co(NH_3)_6][CdCl_5]$ and the frequencies of the anions can therefore be compared directly. We have also prepared the complex $[Co(NH_3)_6][HgCl_5]$ but since it belongs to space group $P2_1/c$ (monoclinic) it will not be considered in detail here.

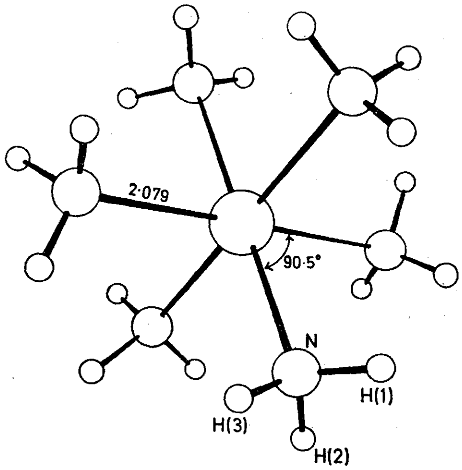

FIGURE 1 A perspective view of the cation along the $\bar{3}$ axis

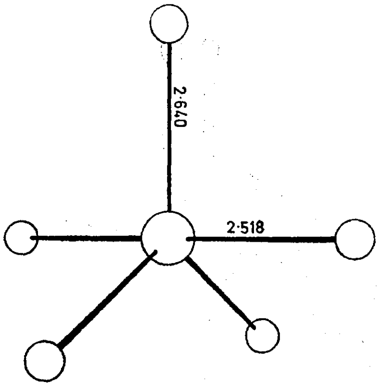

FIGURE 2 A perspective view of the $[HgCl_5]^{3-}$ anion

The vibrational bands >300 cm^{-1} are all associated with cation vibrations and these have been assigned previously.[12] Our data are consistent with the published results.

The point group of the trigonal bipyramidal anions in these $Fd3c$ crystal structures is D_3 (32); six Raman-active ($2A_1 + 4E$) and six i.r.-active ($2A_2 + 4E$) vibrations are predicted (see Table 4). Depolarization measurements were precluded, since the spectra were obtained from a multicrystalline powder.

The $[HgCl_5]^{3-}$ anion exhibits a strong Raman line at 269 cm^{-1} which can be assigned to the ν_1 and ν_2 symmetric breathing modes of the chlorine atoms in the equatorial and axial planes. It was not possible to resolve the Raman band into two components, which is rather surprising but a similar problem is reported in the Raman spectra of the copper and cadmium salts.[4] The i.r. spectrum shows an absorption band at *ca.* 240 cm^{-1} (which is present also as a weak band in the Raman spectrum) and may be assigned to the ν_5 (E) mode. The position of the ν_3 (A_2) antisymmetrical axial stretch is either coincident with ν_5 or, more likely, it is masked by the N–Cr–N deformation mode of the cation which occurs at 276 cm^{-1}. {A second i.r.-active Hg–X stretching mode is observed for the analogous complexes $[Co(NH_3)_6][HgCl_5]$, $[Cr(NH_3)_6][HgBr_5]$, and $[Co(NH_3)_6][HgBr_5]$ but since these three compounds all belong to non-cubic space groups, the detailed results are not considered here.}

The assignment of the Hg–Cl bending modes must remain problematical because of the incomplete nature of the Raman spectrum, which suffers from a high background <200 cm^{-1}, and because of the likely occurrence of lattice modes.

The significant conclusion from the X-ray structure is that the axial Hg–Cl bonds are shorter than the equatorial (see Table 3). Assuming that the vibrational assignments are correct for the three anions, it is interesting to note the relatively high frequencies for ν_1, ν_2 (and possibly ν_3) for $[HgCl_5]^{3-}$ compared with the copper and cadmium analogues. Taking into account both the difference in the atomic weights of cadmium and mercury and the difference in their ionic radii (0.97 and 1.10 Å) it seems likely that the high frequencies reflect the stronger axial and equatorial bonds compared with the strengths of the corresponding Cd–Cl bonds.

In the light of these results, the relative bond lengths in the $[CdCl_5]^{3-}$ anion should not be considered anomalous. This and the $[HgCl_5]^{3-}$ anion are the only d^{10} trigonal bipyramidal structures known, in which all five ligands are the same, and neither fits in with the theoretical predictions. MO theories applied to five-co-ordination have made incorrect predictions about the d^{10} case because of their inability to take into consideration factors such as electrostatic, steric, and crystal packing effects. Clearly, for d^{10} systems at least, these factors are too important to be neglected.

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[5/1173 *Received*, 16*th June*, 1975]

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