# Crystal and Molecular Structure and Vibrational and Nuclear Quadrupole Resonance Spectra of Hexaamminecobalt(III) Pentachloromercurate(II), [Co(NH$_3$)$_6$][HgCl$_5$]

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Hexaamminecobalt(III) pentachloromercurate(II), [Co(NH$_3$)$_6$][HgCl$_5$], has been prepared and its crystal structure determined from three-dimensional X-ray data collected by counter methods. The salt crystallizes in the orthorhombic space group $D_{2h}^{16}$-*Pnma* with 4 formula units in a cell of dimensions $a = 21.033$ (3), $b = 7.591$ (1), and $c = 8.377$ (1) Å. The calculated and observed densities are 2.68 and 2.67 (2) g/cm$^3$, respectively. The structure was solved by a combination of heavy-atom and Fourier synthesis methods. Refinement of 71 parameters by full-matrix least-squares calculations led to a final $R$ factor (on $F$) of 4.8% for 1015 observed reflections for which $|F_o| > 3\sigma(F_o)$. The cation is required crystallographically to possess $m$ symmetry, and it may be described as a slightly distorted octahedron. The average Co–N bond distance is 1.960 (6) Å. The anion is also required crystallographically to possess $m$ symmetry. The mercury atom has five contacts to chlorine atoms at distances which are less than the sum of the van der Waals radii. Three contacts are at normal bond distances of 2.383 (4) and 2.447 (4) Å (twice) to chlorine atoms in nominally equatorial positions. The two remaining contacts are considerably further to axial chlorine atoms at 2.869 (4) and 3.158 (4) Å. The mercury center is 0.18 Å out of the equatorial plane in a direction opposed to the longest Hg–Cl contact. Axial chlorine atoms subtend an angle of 158.8 (1)° at the mercury. The anion geometry is described as a severely distorted trigonal bipyramid. The structural distortion of the anion does not lie along the reaction path of the postulated Berry mechanism. This is an example of a trigonal-bipyramidal complex, albeit distorted, of a d$^{10}$ metal ion in which the axial bonds are longer than the equatorial bonds. The $^{35}$Cl NQR spectrum and the vibrational spectrum were measured to provide additional information about the anionic species present. Four $^{35}$Cl NQR resonances were observed at 20.12, 17.13, 15.52, and 12.30 MHz. The data indicates that the bonding forces operating within the anion are predominantly ionic and that all chlorine atoms are bonded to mercury. Although the [HgCl$_5$]$^{3-}$ ion rigorously possesses only mirror plane symmetry, its vibration spectrum is most readily rationalized in terms of a $C_{3v}$ symmetry model. The low frequencies observed for the deformation modes suggest that the anion should readily undergo distortion.

## Introduction

There are still relatively few examples of compounds containing a metal ion bound to five equivalent unidentate ligands. Such complexes are amenable to spectroscopic and theoretical investigations and present a number of intriguing problems. There is the structural question of whether a trigonal-bipyramidal ($D_{3h}$) or square-pyramidal ($C_{4v}$) geometry will be adopted. These two molecular geometries are readily interconverted[1-6] and the mechanism by which the rearrangement occurs is an interesting problem.[7,8]

Crystal packing effects may be important in deciding the overall geometry of a pentacoordinate complex. Solid-state structures frequently contain ML$_5$ entities which are considerably distorted from an idealized geometry for this reason.[2] In passing from a $D_{3h}$ to a $C_{4v}$ structure along the most symmetrical path, a complex retains $C_{2v}$ symmetry. For the most part, distortions of ML$_5$ structures in the solid state occur along the $C_{2v}$ reaction path that interrelates these two polyhedra.

Examples of pentacoordinate complexes of d$^{10}$ metal ions in which the geometry departs only slightly from a regular square-pyramidal stereochemistry include [InCl$_5$]$^{2-}$ and [TlCl$_5$]$^{2-}$ in their tetraethylammonium salts.[9,10] The anions in [Cr(NH$_3$)$_6$][CuCl$_5$],[11] [Co(NH$_3$)$_6$][CuCl$_5$],[12] [Co(NH$_3$)$_6$][CdCl$_5$],[13,14] and [Cr(NH$_3$)$_6$][HgCl$_5$][15] exist as regular trigonal-bipyramid complexes. These compounds crystallize in the *Fd3c* space group, and the anion has axial bond lengths which are shorter than the equatorial bond lengths. The axial compression is particularly unexpected in the case of the d$^{10}$ metal ions. A filled d shell will have no effect on valency shell electron pairs, and electrostatic or ligand repulsion arguments would predict equatorial bonds to be shorter than axial bonds.

The question concerning the relative strength of axial vs. equatorial bonds in trigonal-bipyramidal complexes has been the subject of several theoretical studies. Early molecular orbital treatments of this problem indicated that for d$^{10}$ systems

either there will be no differences between axial and equatorial bond lengths[16] or longer axial bonds should occur,[17] depending on whether mixing between d and p orbitals is ignored or considered. In a more recent LCAO–MO treatment, it was concluded that under certain conditions the perturbing influence of a $(n - 1)$d$^{10}$ shell is capable of making axial bonds stronger than equatorial bonds.[18] Thus the axial contraction in [CdCl$_5$]$^{3-}$ and [HgCl$_5$]$^{3-}$ might be rationalized in terms of electronic effects.

The structural features of a metal complex will be influenced not only by electronic factors but also by electrostatic, steric,

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and crystal packing effects.[15-17] It remains unclear to what extent crystal symmetry or packing forces contribute to the nonequivalent bond lengths in pentacoordinate complexes of $d^{10}$ metal ions. MO treatments are unable to take these factors into consideration, and at least for $d^{10}$ systems they are probably too important to be neglected. The pentachloromercurate anion in $[Co(NH_3)_6][HgCl_5]$ adopts a trigonal-bipyrammidal geometry, albeit distorted, in which the axial bonds are considerably longer than the equatorial bonds. The results are relevant to the question of relative bond strengths in $ML_5$ complexes and point out the important role played by crystal packing.

The structural situation for the anion in $[Co(NH_3)_6][HgCl_5]$ is intermediate between that in $Cs_3[HgCl_4]Cl$, where the mercury is tetracoordinate,[19] and $[Cr(NH_3)_6][HgCl_5]$ where it is pentacoordinate.[15] The structural data provided in this investigation could be of use in the interpretation of nucleophilic displacement reactions of tetrahedrally coordinated molecules which involve a trigonal-bipyramidal activated complex. Bürgi has discussed the role of such intermediates using comparable structural data to interpret the detailed geometric pathway of ligand-exchange reactions.[20]

## Experimental Section

**Synthesis.** $[Co(NH_3)_6][HgCl_5]$ was prepared by the method previously used in the synthesis of $[Co(NH_3)_6][ZnCl_4]Cl$.[14] To 10 g of $Co(NH_3)_6Cl_3$ in 100 mL of distilled water heated to 75 °C was added, slowly with stirring, a solution of 9.3 g of $HgCl_2$ in 100 mL of distilled water also warmed to 75 °C. After addition of 20 mL of 12 M HCl, orange crystals formed as the solution cooled to room temperature. The precipitate was washed with several small portions of dilute HCl, ethanol, and ether and dried in vacuo at 60 °C for several hours. The yield was 18 g. Anal. Calcd for $Co(NH_3)_6HgCl_5$: Co, 10.93; Cl, 32.89. Found: Co, 10.78; Cl, 32.82.

The hexaamminecobalt(III) pentachloromercurate(II) salt may also be synthesized with $Co(NH_3)_6(NO_3)_3$ as a starting reagent. By contrast, previous attempts to prepare $Co(NH_3)_6ZnCl_5$ which is isomorphous with the mercury compound from hexaamminecobalt(III) nitrate resulted in the formation of $Co(NH_3)_6ZnCl_4(NO_3)$.[14] Both of the zinc salts have been shown to contain discrete, albeit distorted, tetrachlorozincate(II) ions.[14,21]

Addition of an equivalent amount of $HgCl_2$ in distilled water to an aqueous solution of $Co(NH_3)_6Cl_3$ at room temperature results in a complex salt of stoichiometry $Co(NH_3)_6Hg_2Cl_7$. The intense bands appearing at 303 $cm^{-1}$ in the Raman and at 350 $cm^{-1}$ in the infrared reveal that the additional $HgCl_2$ in this salt can be best viewed as "lattice" mercuric chloride.[22] Prior acidification of both solutions with hydrochloric acid prevents the formation of this compound, and the complex of desired stoichiometry precipitates immediately from solution.

**Infrared Spectra.** The infrared spectra were measured in the 4000–200-$cm^{-1}$ region on a carefully calibrated, air-dried Perkin-Elmer Model 621 grating spectrometer. Samples were run as Nujol mulls supported on cesium iodide plates, and with the exception of broad bands, the frequency placements are accurate to 1 $cm^{-1}$.

**Raman Spectra.** All Raman data were obtained from rotating samples with use of a Spex 1401 spectrometer and a Spectra Physics 164 Model krypton ion laser operating at 647.1 nm. With this technique, no decomposition due to heating in the laser beam occurred with an estimated power at the sample of 0.3 W. With use of conventional 90° viewing geometry, sample decomposition due to heating in the laser beam was observed at ca. 50 mW. An instrumental frequency calibration was effected with use of laser emission lines, and except for broad bands, the observed wave number shifts should be good to about 1 $cm^{-1}$. Depolarization measurements were precluded since the spectra were obtained from multicrystalline samples.

**Crystal Data.** The prismatic crystal used for data collection had an average edge dimension of 0.015 cm. An initial mount afforded

### Table I. Experimental Data for the X-ray Diffraction Study of $[Co(NH_3)_6][HgCl_5]$

#### (A) Crystal Data at 22 °C

| | |
|---|---|
| cryst system: orthorhombic | $V = 1337.5$ (3) $A^3$ |
| space group: *Pnma* | $Z = 4$ |
| $a = 21.0335$ (27) Å | mol wt 538.97 |
| $b = 7.5912$ (14) Å | $\rho$(calcd) = 2.68 g $cm^{-3}$ |
| $c = 8.7377$ (13) Å | $\rho$(obsd) = 2.67 (2) g $cm^{-3}$ |

#### (B) Measurement of Intensity Data

diffractometer: Picker FACS-I
radiation: Mo $K\alpha$ ($\lambda = 0.7107$ Å)
takeoff angle: 4.0°
reflctns measd: *hkl*
$2\theta$ range: 0.5–50°
scan type: coupled $\theta$(cryst)–$2\theta$(counter)
scan speed: 1.0°/min (in $2\theta$)
scan range: 1.6(1 + 0.48 tan $\theta$)° centered on $2\theta$(calcd)
bkgd measurement: 10 s at each extremity of the scan
stds: 2 every 50 reflctns with less than 1% change in intensity
reflctns collected: 1390 total, yielding 1256 symmetry-independent data[a]
absorption coeff: 131.9 $cm^{-1}$
absorption cor: empirical[b]

[a] 1015 of these data had $|F_o| > 3\sigma(F_o)$ and were used in the structural refinement. [b] See text.

precession and cone-axis photographs which indicated an orthorhombic cell with systematic absences ($k + l$ odd for $0kl$ and $h$ odd for $hk0$ reflections) consistent with space groups $Pn2_1a$ or $Pnma$; structure solution showed the latter to be correct. The crystal was remounted and transferred to a Picker FACS-I fully automated diffractometer ($a^*$ axis coincident with $\phi$ axis), and lattice constants were determined from eight intense reflections by a least-squares fit of carefully measured $\pm 2\theta$ values (61° $< 2\theta <$ 72°) for the copper $K\alpha_1$–$K\alpha_2$ doublet ($\lambda$(Cu $K\alpha_1$) = 1.540 50 Å, $\lambda$(Cu $K\alpha_2$) = 1.544 34 Å). Additional information on crystal data, data collection, and structure determination is listed in Table I.

**Treatment of Data and Structure Determination.** Intensities were corrected for absorption as follows: the intensity of the 400 reflection ($\chi = 90°$) was measured as a function of the $\phi$ angle and the resulting intensity profile used to generate an absorption correction for each reflection based on its $\phi$ angle setting. The ratio of observed intensities (max/min) in the 400 reflection profile was 1.3, compared to a 1.6 transmission factor ratio calculated for similar cylindrical crystals. Intensities were also corrected for Lorentz and polarization effects in the usual manner and converted to structure amplitudes.

The structure was solved by a combination of heavy-atom and Fourier synthesis methods and refined by full-matrix least-squares calculations which minimized the function $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2$ and $\sigma^2(F_o) = [|F_o|/2I_n]^2[I_s + (t_s/t_b)^2I_b + (0.05I_n)^2]$ where $I_s$, $I_b$, and $I_n$ are scan, background, and net intensities, and $t_s$ and $t_b$ are scan and background times. Scattering factors for nonhydrogen atoms were taken from tabulations of Cromer and Waber[23] and from Stewart, Davidson, and Simpson[24] for the hydrogen atoms; values for mercury, cobalt, and chlorine were corrected for both real and imaginary anomalous dispersion effects.[25] The $R$ value after all anisotropic nonhydrogen atoms were varied was 0.053. As a check on the correctness of the space group selection, refinement of the structure was also attempted in space group $Pn2_1a$. This resulted in unacceptably large correlation matrix elements for atom pairs previously related by $m$ symmetry; the distribution of intensities also favored a centrosymmetric space group. A difference Fourier electron density map yielded several hydrogen atom coordinates which were given idealized tetrahedral positions at N–H distances of 0.87 Å;[26] remaining hydrogen atom positions were calculated. All hydrogen atoms were assigned an isotropic thermal parameter of 4.0 $Å^2$ and held fixed.

Refinement of 71 parameters (including an isotropic extinction parameter) resulted in a final $R_F = 0.048$ and $R_{wF} = 0.065$ where $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$, and in a goodness of fit of 1.25.

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**Table II.** Final Positional Parameters[a]

| atom | x | y | z | B(EQ) |
|------|-----|-----|-----|-------|
| Hg | 0.09857 (3) | 0.2500 | 0.08966 (9) | 3.3 |
| Co | 0.36354 (9) | 0.2500 | 0.11583 (22) | 1.7 |
| Cl(1) | −0.0007 (2) | 0.2500 | −0.0474 (5) | 3.6 |
| Cl(2) | 0.1614 (1) | −0.0160 (4) | 0.1378 (3) | 3.3 |
| Cl(3) | 0.0608 (2) | 0.2500 | 0.4188 (5) | 3.2 |
| Cl(4) | 0.1895 (2) | 0.2500 | −0.2105 (5) | 2.7 |
| N(1) | 0.3055 (7) | 0.2500 | 0.2992 (14) | 3.3 |
| N(2) | 0.4170 (4) | 0.0683 (12) | 0.2160 (11) | 3.0 |
| N(3) | 0.3112 (4) | 0.0668 (11) | 0.0171 (11) | 2.7 |
| N(4) | 0.4188 (6) | 0.2500 | −0.0729 (15) | 2.8 |

[a] Estimated standard deviations are in parentheses. B(EQ) is the equivalent isotropic thermal parameter in $\text{Å}^2$ units.

**Table III.** Selected Interatomic Distances and Angles

Distances, Å

| Co–N(1) | 1.959 (13) | Co–N(3) | 1.953 (9) |
|---------|------------|---------|-----------|
| Co–N(2) | 1.967 (9) | Co–N(4) | 1.961 (13) |

Angles, Deg

| N(1)–Co–N(2) | 91.1 (4) | N(3)–Co–N(4) | 89.6 (4) |
|--------------|----------|--------------|----------|
| N(1)–Co–N(3) | 89.0 (4) | N(2)–Co–N(2') | 88.9 (5) |
| N(1)–Co–N(4) | 178.1 (6) | N(3)–Co–N(3') | 90.4 (5) |
| N(2)–Co–N(3) | 90.4 (4) | N(2)–Co–N(3') | 179.2 (4) |
| N(2)–Co–N(4) | 90.3 (4) | | |
| Cl(1)–Cl(2) | 123.6 (2) | Cl(2)–Cl(3) | 89.5 |
| Cl(2)–Cl(2') | 111.2 | Cl(2)–Cl(4) | 78.7 |
| Cl(1)–Cl(3) | 102.7 | Cl(3)–Cl(4) | 158.8 |
| Cl(1)–Cl(4) | 98.4 | | |

**Table IV.** Interatomic Distances and Angles Involved in Hydrogen Bonding[a]

| atoms involved | | Cl–N, Å | Cl–H,[b] Å | Cl–H– N,[b] deg | symmetry position of H |
|----------------|------|---------|---------|---------|------------------------|
| Cl | H(N) | | | | |
| Cl(2) | H'(N3) | 3.253 | 2.392 | 171 | $1/2 - x, -y, 1/2 + z$ |
| Cl(2) | H(N3) | 3.369 | 2.589 | 149 | $x, y, z$ |
| Cl(3) | H(N4) | 3.253 | 2.390 | 171 | $x - 1/2, 1/2 - y, 1/2 - z$ |
| Cl(4) | H(N2) | 3.352 | 2.494 | 169 | $1/2 - x, -y, z - 1/2$ |
| Cl(4) | H''(N3) | 3.314 | 2.552 | 148 | $1/2 - x, -y, z - 1/2$ |
| Cl(4) | H(N2) | 3.352 | 2.494 | 169 | $1/2 - x, 1/2 + y, z - 1/2$ |
| Cl(4) | H''(N3) | 3.314 | 2.552 | 148 | $1/2 - x, 1/2 + y, z - 1/2$ |

[a] Only Cl–N distances less than 3.4 Å are considered to be significantly involved in hydrogen bonding.[21]  [b] These distances and angles are calculated from the ideal hydrogen positions.

Positional and thermal parameter shifts in the last least-squares cycle were less than 10 and 20% of their estimated errors, respectively. The final difference map contained a maximum peak of 1.0 e $\text{Å}^{-3}$ located near the mercury atom and several other peaks which were less than 10% the peak height of an average nitrogen atom. Positional parameters are given in Table II, and Table III lists distances and angles between atoms.

## Results and Discussion

**Crystal and Molecular Structure.** The structure of this compound consists of discrete slightly distorted octahedral $[Co(NH_3)_6]^{3+}$ cations and severely distorted trigonal-bipyramidal $[HgCl_5]^{3-}$ anions. Both cation and anion are required crystallographically to posses *m* symmetry. Cobalt and two trans-coordinated nitrogen atoms lie in the mirror plane. The four remaining cobalt coordination sites are occupied by two nitrogen atoms and their symmetry-equivalent atoms which lie off the plane. The average cobalt–nitrogen bond distance is 1.960 (6) Å, and each bond length is within 1σ of the average. This value is comparable to the average Co–N distances of 1.960 (6) and 1.968 (11) Å reported for other structures containing this cation.[13,21] Since all N–Co–N bond angles are within 3σ of being right or linear, it is appropriate to describe the cation as a slightly distorted octahedron.

The anion moiety shown in Figure 1 consists of a mercury atom in contact with five chlorine atoms over a considerable range of distances. All five mercury–chlorine contacts are less than the sum of the mercury and chlorine van der Waals radii.[27–29] Thus the
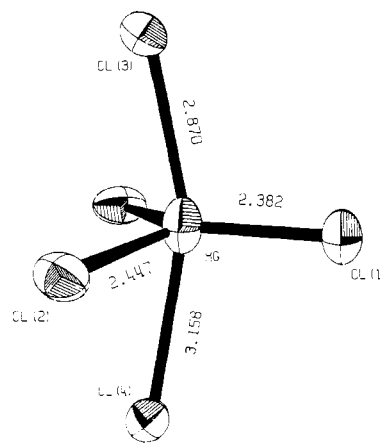


**Figure 1.** Perspective drawing of the $[HgCl_5]^{3-}$ ion. The 50% probability ellipsoids are shown.

**Table V.** NQR Frequencies, Calculated Degree of Covalency, and Fractional Bond Order

| $^{35}Cl\ \nu_q$, MHz | $\sigma^a$ | d(Hg–Cl), Å | $n^b$ |
|------------------------|------------|-------------|-------|
| 20.12 | 0.367 | 2.383 | 0.70 |
| 17.13 | 0.312 | 2.447 | 0.55 |
| 15.52 | 0.283 | 2.869 | 0.11 |
| 12.30 | 0.224 | 3.158 | 0.04 |

[a] Degree of covalency calculated from $\sigma = \nu_q/54.873$.  [b] Fractional bond order calculated from Pauling's relationship $d(n) = d(1) - 0.60 \log n$ with $d(1) = 2.29$ Å.[27,36]

effective coordination number for mercury is 5.[30]

In the anion, three chlorine atoms and the mercury atom are located in a mirror plane. The two remaining chlorine atoms, Cl(2) and its symmetry equivalent, lie off this plane. There are four independent mercury–chlorine distances. Three chlorine atoms at normal bonding distances of 2.383 (4) and 2.477 (3) Å (twice) form the equatorial plane of a severely distorted trigonal bipyramid. These are strongly bonded to the mercury atom which lies 0.18 Å above this plane. Chlorine atoms Cl(3) and Cl(4) occupy axial positions located 2.869 (4) and 3.158 (4) Å from mercury, respectively. Both distances are greater than the normal Hg–Cl single-bond length (ca. 2.5 Å) characteristic of mercury with an effective coordination number of 4[31] and suggest weak bonding interactions. These separations are significantly greater than the axial Hg–Cl bond distance of 2.518 (4) Å observed in $[Cr(NH_3)_6][HgCl_5]$ where the anion adopts a regular trigonal-bipyramidal geometry.[15] These findings are relevant to the question of relative bond strengths in trigonal-bipyramidally coordinated metal ions[16–18] and provide the first example of a simple $d^{10}$ metal complex, albeit distorted, in which nominally axial bonds are longer than the equatorial bonds.

The reason for the reversal of the relative bond lengths in $[HgCl_5]^{3-}$ when crystallized with $[Co(NH_3)_6]^{3+}$ as compared to $[Cr(NH_3)_6]^{3+}$ may be due to the low bond energies between mercury and a fourth and fifth ligand. It has been noted that the high promotional energy of $6s^2 \rightarrow 6s6p$ for mercury (524 kJ/mol) involved in the formation of two covalent bonds is probably the main reason that two-coordination is common for mercury.[32] This has the consequence that further ligands can be added to mercury only with difficulty. In solution, for example, even at high chloride to mercury concentration ratios, the highest chloromercury complex present appears to be the

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(29) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.
(30) The term effective coordination number has been suggested to indicate the number of atoms that, in the solid state, approach mercury at distances less than the sum of the van der Waals radii.[27] The term is quite useful since frequently large variations in Hg–L distances are found within a compound.
(31) Dean, P. A. W. *Prog. Inorg. Chem.* **1978**, *24*, 109.
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$[HgCl_4]^{2-}$ anion.[33,34] If approach of the axial ligands is a low-energy process, the mercury–chlorine bond distances should be determined predominantly by crystal forces and should show wide variations. Burdett has calculated the stabilization energies of square-planar, square-pyramidal, and octahedral $d^8$ and $d^9$ complexes, and the wide variations observed in axial bond length for Cu(II) and low-spin Ni(II) complexes have been rationalized in these terms.[35]

The weakness of the axial bonds is evident from the fraction bond orders calculated from Pauling's empirical relationship $d(n) = d(1) - 0.60 \log n$, where $d(n)$ is the bond distance for fractional bond order $n$ and $d(1)$ is the single-bond distance.[36,37] The values obtained using $d(1) = 2.29$ Å are listed in Table V.[27] The two axial Hg–Cl distances correspond to only 0.11 and 0.04 of a single Hg–Cl bond order, while the two independent equatorial distances correspond to a bond order of 0.70 and 0.55. By comparison in $[Cr(NH_3)_6][HgCl_5]$ the values are 0.42 and 0.26 for the axial and equatorial bonds, respectively. On the basis of these considerations as well as the NQR and vibrational results, the anionic portion of the structure is best described in terms of a $[HgCl_5]^{3-}$ ion with three normal equatorial and two weaker axial bonds.

It is reasonable to ask if the structural situation might be described as a distorted tetrahedral anion and ionic chloride. This is the case in $Cs_3[HgCl_4]Cl$ and $[Co(NH_3)_6][ZnCl_4]Cl$ where the fifth chloride is significantly more distant from the metal atom than the sum of the van der Waals radii. Both crystallize in the *Pnma* space group and contain anions which are considerably distorted from a regular tetrahedral geometry.[19,21] In $[Co(NH_3)_6][HgCl_5]$ the fifth chloride is within the sum of the van der Waals radii, and the Cl–Hg–Cl bond angles deviate markedly from ideal tetrahedral values. Mercury is nearly planar with the three closest chlorine atoms, and the HgCl(3) bond vector forms an 81.5° angle with this plane. An out of plane displacement of 0.82 Å is expected for mercury in a regular tetrahedral $[HgCl_4]^{2-}$ unit with Hg–Cl bond distances of 2.46 Å, and the bond vector would be perpendicular to the plane. By comparison, in $Cs_3[HgCl_4]Cl$, mercury is 0.85 Å about this plane, and the corresponding angle is 87.2°.[19] Thus, there is little support for describing the anion in the present compound as a distorted tetrahedron.

There are a number of features which contribute to the departure of the anion from a regular trigonal-bipyramidal coordination geometry. However, the distortion is not along the Berry reaction coordinate toward a square pyramid. The $C_2$ axis necessary to interconvert a trigonal bipyramid to a square pyramid along the most symmetrical path is not present. Furthermore, the axial and equatorial bond vectors are bending in the same direction, *not* in opposite directions as required in the postulated Berry mechanism.[7]

The increasing departure from $D_{3h}$ symmetry about mercury in passing from $[Cr(NH_3)_6][HgCl_5]$ to $Cs_3[HgCl_4]Cl$ to $[Co(NH_3)_6][HgCl_5]$ is so evident that an analysis of the type employed by Burgi for distorted five-coordinate $XCdS_3Y$ complexes was conducted.[20] Although the major trends noted in Burgi's study were observed, the agreement between calculated and observed displacements is quite poor for the mercury complexes. This suggests that the mercury anions in these three compounds are not related members in a series of reaction intermediates which mark the course of a nucleophilic displacement reaction of tetrahedrally coordinated mercury complexes.

The positions of the chlorine atoms appear to be determined primarily by the competition between interactions with mercury and optimal packing forces. Mercury–chlorine distances decrease in a systematic way depending upon the strength of the interaction and the number of hydrogen bonds to the chlorine atom: Cl(1) which is closest to mercury does not participate in hydrogen bonding, Cl(2) participates in one weak and one strong hydrogen bond, Cl(3) forms one strong hydrogen bond, and Cl(4) is involved in four weak hydrogen bonds. The hydrogen bonding scheme is very similar to that in the isomorphous zinc compound.[21] Information on hydrogen bonding is contained in Table IV.

The crystal structure of $[Co(NH_3)_6][HgCl_5]$ is much like that of the zinc compound.[21] While the two compounds are not isostructural,

they have similar cell parameters, cell contents, atomic coordinates; and therefore crystal packing forces must be quite similar. Cobalt, nitrogen, and chlorine atoms are nearly in the same positions in the two structures. The axial chlorine atoms are 5.92 Å apart and subtend an angle of 158.8° at mercury in the present case. In the zinc structure, the separation and the corresponding angle are nearly the same, i.e., 6.05 Å and 160.8°, respectively. This seems to support the view that packing forces play a significant role in determining the axial bond distances in pentacoordinate complexes of $d^{10}$ metal ions. The most significant difference between the zinc and mercury structure is the location of the metal atom. Mercury is nearly planar with the three closest chlorine atoms, while zinc lies 0.6 Å above this plane and it is clearly tetracoordinate. The distances between the equatorial chlorine atoms are 4.038 and 4.226 Å (twice) in the mercury compound, and the corresponding chlorines are 3.734 and 3.796 Å (twice) apart in the zinc structure. The structures exhibited by two related complexes, $[TlCl_5]^{2-}$ and $[TlBr_5]^{2-}$, also appear to be sensitive to their environment. The various geometries adopted by these anions in different salts have also been attributed to crystal packing effects.[38]

The reasons why the *Pnma* space group is adopted by $[Co(NH_3)_6][HgCl_5]$ and not the *Fd3c* space group as in the chromium salt[15] are not clear. It has been reported that salts of empirical formula $[M(NH_3)_6][M'Cl_5]$ with M = Cr and Co are not necessarily isostructural,[39] although they are when M' = Cu.[11,12] Our own observations reveal that the stoichiometry of the solid isolated from solutions containing $Co(NH_3)_6Cl_3$ and $HgCl_2$ is highly dependent upon the chloride ion concentration. At low chloride ion concentrations, $Co(NH_3)_6Hg_2Cl_7$, rather than the title compound was obtained. It is not uncommon for mercuric chloride to form complexes with excess "lattice" $HgCl_2$ present.[31] The intense bands appearing at 303 cm$^{-1}$ in the Raman spectrum and at 350 cm$^{-1}$ in the infrared spectrum of the heptachloro compound indicate that the additional $HgCl_2$ is "lattice" mercuric chloride.[22] A large excess of chloride ion, added as aqueous hydrochloric acid, prevents the formation of this material. It may be that solution pH, chloride ion concentration, and temperature also play a role in determining the space group of the material which is isolated. If this is the case, one might anticipate that $[Co(NH_3)_6][HgCl_5]$ would crystallize in other space groups. In fact, it has been reported to also crystallize in the space group $P2_1/c$ (monoclinic), but preparative and structural details are not given.[15]

**Nuclear Quadrupole Resonance Spectrum.** The $^{35}Cl$ NQR spectrum of $[Co(NH_3)_6][HgCl_5]$ was measured to obtain additional information about the anionic species in this compound.[40] Since different field gradients commonly exist for nonequivalent nuclei, a different resonance frequency is expected for each type of nuclear environment. Consistent with the X-ray structural results, four $^{35}Cl$ NQR frequencies were observed at 20.12, 17.13, 15.52, and 12.30 MHz. The resonance frequency for a chlorine bonded to mercury occurs in the range from about 8 MHz to somewhat more than 23 MHz.[37] Since the observed resonances fall in this range and a thorough search below 7 MHz yielded no additional signals, all five chlorine atoms are considered to be bonded to mercury.

The signal to noise ratio for the transitions was not much greater than unity, and the estimated experimental uncertainty in their frequency is ±0.05 MHz. The NQR frequencies were measured under a variety of experimental conditions.[40] Consequently, the relative signal to noise ratio for the transitions varied. In any case, line intensities are of little help in assigning frequencies to a specific atom since NQR sensitivity is highly dependent upon line width, transition frequency, and experimental conditions.

A correlation between NQR frequency and bond distance has been reported for mercury–chloride complexes.[37] In general, the shorter the Hg–Cl distance the higher the $^{35}Cl$ NQR frequency. While the data for $[Co(NH_3)_6][HgCl_5]$ falls significantly off the curve reported for axially symmetric bonding situations,[37] assigning the NQR frequencies in order, i.e., the lowest frequency to the chlorine at the greatest distances from mercury and so on, reveals an approximately linear relationshiop between the four separate resonances.

Assuming that this assignment is correct, it is reasonable to inquire about the information on bonding which can be derived from the NQR frequencies. A number of approaches have been used to obtain

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**Table VI.** Vibrational Frequencies and Assignments for the Chloromercurate Anion in $[Co(NH_3)_6][HgCl_5]$ and Related Compounds[a,b]

| [Cr(NH₃)₆][HgCl₅][c] | | | [(CH₃)₄N][HgCl₃][d] | [Co(NH₃)₆][HgCl₅][e] | | |
|---|---|---|---|---|---|---|
| Raman | infrared | | Raman | Raman | infrared[f] | assignts[e] |
| 269 vs | | $(\nu_1 \text{ and } \nu_2(A_1'))$ | 274 vs $(\nu_1(A_1))$ | 271 vs, br | 276 w, sh | $\nu_1(A_1)$, HgCl₃ eq sym str |
| | (263)[g] | $(\nu_3(A_2''))$ | | | 260 m | $\nu_3(A_1)$ or $\nu_2(A_1)$, HgCl₂ ax str |
| 237 m | 240 m, sh | $(\nu_5(E'))$ | 244 w, br $(\nu_3(E))$ | 234 w | 232 m[h] | $\nu_5(E)$, HgCl₃ eq asy str |
| 190 w | 185 mw, sh | $(\nu_8(E''))$ | | 125 s, br | | $\nu_8(E)$, HgCl₂ ax def, rocking |
| 160 w | 156 s | $(\nu_6(E'))$ | 90 s, br $(\nu_2(A_1))$ | 91 s, br | | $\nu_4(A_1)$, HgCl₃ eq out-of-plane bending |
| | 141 s | $(\nu_4(A_2''))$ | 74 s $(\nu_4(E))$ | 72 m | | $\nu_6(E)$, HgCl₃ eq def |
| | 102 w | $(\nu_7(E'))$ | 56 s (lattice) | 52 m | | $\nu_7(E)$, HgCl₂ ax def |

[a] Frequencies in units of cm⁻¹. [b] Abbreviations: s, strong; m, medium; w, weak; br, broad; sh, shoulder; v, very; eq, equatorial; ax, axial; sym, symmetric; asy, asymmetric; str, stretch; def, deformation. [c] From ref 15. Assignments in parentheses are for a ML₅ species of $D_{3h}$ symmetry. [d] From ref 48. Assignments in parentheses are for a pyramidal HgCl₃⁻ ion of $C_{3v}$ symmetry. [e] For HgCl₅³⁻ in the Co(NH₃)₆³⁺ salt the assignment is based on a $C_{3v}$ symmetry model. The numbering scheme and approximate modal description are taken from: Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1963; p 116. The designation of the irreducible representation associated with each vibrational mode reflects the correlation between the $D_{3h}$ and $C_{3v}$ point groups. [f] The infrared spectrum was not measured below 200 cm⁻¹. [g] Frequency taken from the infrared spectrum of $[Co(NH_3)_6][HgCl_5]$. [h] This band is believed to be of complex origin with intensity contributions from both the cation and the anion. See text for explanation.

information about bonding in inorganic systems.[41] For ³⁵Cl with $I = {}^3/_2$, the nuclear quadrupole coupling constant $(eQq)$ may be calculated from $eQq = 2\nu_q/(1 + {}^1/_3\eta^2)$, where $\nu_q$ is the observed frequency and $\eta$ the asymmetry parameter. Since the NQR measurements were conducted on a powder sample, no experimental information about the value of the asymmetry parameter is available. It has been shown that assuming that $\eta$ is equal to zero introduces only small errors in calculated coupling constants for chloromercurate complexes.[42] With this assumption the expression for the coupling constant simplifies to $eQq = 2\nu_q$.

If the electric field gradient at a given nucleus arises solely from the bonding and charges within the complex ion, the unbalance in the p-electron population on chlorine is defined as $U_p = eQq/(eQq)_{atom} = \nu_q/54.873$, where $(eQq)_{atom}$ is 109.476 MHz for ³⁵Cl. Using the Townes–Dailey approximation[42] leads to $U_p = 1 - s^2 + d^2 - I - \pi + I(s^2 + d^2)$, where $s^2$ is the degree of s hybridization, $d^2$ the degree of d hybridization, $\pi$ is the degree of $\pi$ bonding, and $I$ is the degree of ionic character in the bond. If $s^2$, $d^2$, and $\pi$ are assumed to be small and set equal to zero, setting $I = 1 - \sigma$ where $\sigma$ is the degree of $p_\sigma$ covalent bonding leads to $\sigma = \nu_q/54.873$.

The calculated values of $\sigma$ with assigned Hg–Cl distances are contained in Table V. The interpretation of the results is complicated somewhat by crystal and hydrogen bonding effects which may affect the chlorine directly or modify the mercury–chlorine covalent bond.[43] These have been neglected in the present analysis. It should be noted that while this could introduce large uncertainty in the actual values for $\sigma$, the degree of covalence determined by this approach should still be useful for comparison purposes.

The calculated values of $\sigma$ plotted against the assigned Hg–Cl distance are quite far removed from the curve reported for the variation of $p_\sigma$ covalency for axially symmetric bonding situations.[37] However, an approximately linear relationship exists between the four separate points as shown in Figure 2. While one should not place too much significance on the actual values calculated for the degree of covalence, the values are useful for assessing the *relative* degree of covalency of the bonds. Two features are evident from the data: the degree of covalency calculated for each mercury–chlorine bond is less than 0.40 and there is a range of covalency exhibited, i.e., from 37 to 22%. To a large extent, then, the bonding forces operating within the anion are ionic. While the range of covalencies is not as great as might have been expected on the basis of the bond order calculations, significant differences do exist.

**Vibrational Spectrum.** The vibrational spectrum of [Co(N-H₃)₆][HgCl₅] was investigated, and the region above 600 cm⁻¹ is similar to that of [Co(NH₃)₆]Cl₃. This has been discussed previously[44] and is not repeated here. The spectrum of the cation below 600 cm⁻¹, where Co–N₆ skeletal vibrations occur, is reminiscent of the results for [Co(NH₃)₆][ZnCl₄]Cl and is indicative of an anisotropic envi-
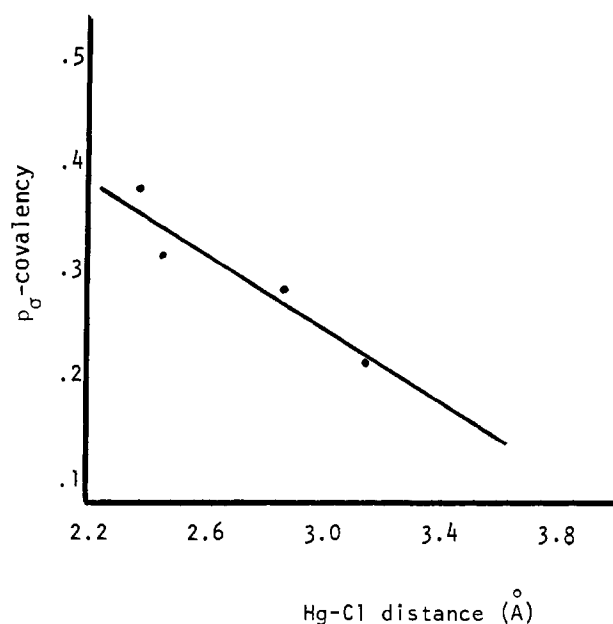


**Figure 2.** Variation of $\sigma$ covalency with mercury–chlorine distance.

ronment.[14] The vibrational data for [Co(NH₃)₆]³⁺ is compatible with $D_{4h}$ symmetry. Three Raman bands are observed in the cobalt–nitrogen stretching region at 500, 481, and 439 cm⁻¹. The Raman-active deformation modes appear as two closely spaced bands at 339 and 315 cm⁻¹. In the infrared spectrum three weak bands at 490, 477, and 436 cm⁻¹ are components of the asymmetric cobalt–nitrogen stretching mode. The infrared-active deformation modes appear as a strong broad band at 329 cm⁻¹ and a band of medium intensity at 232 cm⁻¹. The 232-cm⁻¹ band is believed to be of complex origin with intensity contributions from both a deformation mode of the cation and a stretching mode of the anion (vide infra).

A $C_s$ symmetry model for the anion predicts 12 vibrational modes which should be both infrared and Raman active. After discrimination of frequencies associated with the cation, three infrared and six Raman bands are apparent in the measured region of the spectrum.[45] The $C_s$ model, then, predicts a greater number of lines than are actually observed. In some cases the vibrational spectrum may be insensitive to the reduced symmetry of a species; and if spectral bands are broad or vibrational modes are nearly degenerate and of low intensity, not all formally allowed modes are observed. This is true for the isomorphous zinc compound where even though the anion is considerably distorted no removal of modal degeneracies was evident.[14]

Although the anion possesses only mirror plane symmetry, the vibrational data is most readily rationalized in terms of a $C_{3v}$ symmetry

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(45) The infrared spectrum was investigated only in the region above 200 cm⁻¹ as far-infrared instrumentation was not available.

model. A $ML_5$ species of $C_{3v}$ symmetry has eight fundamental vibrational modes; and the total vibrational representation is $\Gamma_v = 4 A_1 + 4 E$. Of these, 3 $A_1$ and 1 E modes represent stretching motions and the remainder are deformations. All modes are infrared and Raman active and should be coincident. The normal modes of a trigonal-bipyramidal species of $C_{3v}$ symmetry would be similar to those of one of $D_{3h}$ symmetry. Only infrared and Raman activity and the designation of the irreducible representations are different. In going from $D_{3h}$ to $C_{3v}$ symmetry, the irreducible representations correlate as $A_1' \rightarrow A_1$, $A_2'' \rightarrow A_1$, $E' \rightarrow E$, and $E'' \rightarrow E$. A numbering and illustrations of the normal modes for the $D_{3h}$ case have been given previously.[46,47] The vibrations should also be divisible into a higher frequency group containing lines attributable to stretching modes and a lower frequency group containing lines assignable as deformation modes.

The observed frequencies for the pentachloromercurate(II) anion in $[Co(NH_3)_6][HgCl_5]$, and the anions in $[Cr(NH_3)_6][HgCl_5]$ and $[(CH_3)_4N][HgCl_3]$ are reported in Table VI. Assignments for $[HgCl_5]^{3-}$ were made empirically by comparison with these two compounds and with a variety of related pentacoordinate species.[46] In the mercury–chlorine stretching region, the vibrational spectrum of $[Co(NH_3)_6][HgCl_5]$ is remarkably similar to that reported for $[Cr(NH_3)_6][HgCl_5]$.[15] In view of the lower symmetry and significantly different Hg–Cl bond length for the anion, one would expect the Hg–Cl stretching frequencies in the two compounds to be quite different. Apparently the vibrational modes in this spectral region are unexpectedly insensitive to the differences in bond lengths. There are, however, substantial differences in spectrum in the frequency region below 200 cm$^{-1}$ where mercury–chlorine bending modes appear.

In the Raman spectrum, an intense band centered at 271 cm$^{-1}$ almost certainly arises from $\nu_1(A_1)$, the symmetric breathing mode of the equatorial chlorines. This mode is infrared active for a $ML_5$ species of $C_{3v}$ or lower symmetry, and a weak shoulder is observed at 276 cm$^{-1}$ in the infrared spectrum. An infrared band of medium intensity at 260 cm$^{-1}$ is assigned as $\nu_3(A_1)$, the axial out-of-phase stretching mode. In the Raman spectrum, $\nu_3$ was not resolved even under conditions of high spectral resolution because of its proximity to $\nu_1$ and the broadness of this latter band. A similar situation was encountered with the $[Cr(NH_3)_6]^{3+}$ salt.[15] The remaining infrared band in the mercury–chlorine stretching region at 232 cm$^{-1}$ is within experimental error of being coincident with a weak Raman band at 234 cm$^{-1}$, and this is assigned as $\nu_5(E)$, an equatorial stretching mode. A band at this frequency in the infrared spectrum of $[Co(NH_3)_6]$-$[ZnCl_4]Cl$ was previously assigned to a deformation mode of the cation, but no corresponding Raman band was observed.[14] For $[Cr(NH_3)_6][HgCl_5]$, where interference from the $[Co(NH_3)_6]^{3+}$ cation is not a problem, $\nu_5$ was observed at 237 cm$^{-1}$. In view of these observations, a dual assignment of the 232-cm$^{-1}$ band to $\nu_5$ annd a cation deformation mode is not unreasonable. The assignment of $\nu_2(A_1)$ is

uncertain since no unique frequency to which it can be readily ascribed was observed. The Raman line measured at 125 cm$^{-1}$ is probably too low in energy to be this mode. More likely, $\nu_2$ is coincident with one of the other stretching modes, possibly $\nu_3$, or it is simply too low in intensity to be observed. Bending forces which determine the frequency of the deformation modes are related to the ionicity of a bond. Since ionic bonds are nondirectional, they undergo deformation more readily than directional covalent bonds.[52] The NQR results for $[Co(NH_3)_6][HgCl_5]$ indicate that the bonding forces operating with the anion are predominantly ionic. Consequently, the anion should readily undergo angular distortions and deformation modes would be expected to occur at low energies. The Raman line measured at 125 cm$^{-1}$ is assigned as $\nu_8(E)$, the Cl–Hg–Cl deformation mode involving the axial chlorine atoms, and the 52-cm$^{-1}$ band is probably $\nu_7(E)$, the other $HgCl_2$ axial deformation mode.[46] The assignment of the two remaining Raman lines at 91 and 72 cm$^{-1}$ is problematical because of the lack of polarization data. In $[Cr(NH_3)_6][HgCl_5]$, $\nu_6$ is reported to be at a higher frequency than $\nu_4$,[15] but because of our findings with the $[HgCl_3]^-$ ion,[48] we prefer the reverse assignment.

Experimental support for the assignments is found in the spectral results for $[(CH_3)_4N][HgCl_3]$.[49] The spectrum of the anion in this compound is consistent with that of an isolated pyramidal ion of $C_{3v}$ symmetry.[48,49] Consequently, the normal modes and the corresponding frequencies might be expected to be similar to those involving the equatorial chlorine atoms in the $[HgCl_5]^{3-}$ complex. It is apparent from the data in Table VI that this is indeed the case. Except for the Raman line at 125 cm$^{-1}$, the spectra of the two anions are s·:kingly similar. The absence of spectral features in the 200–100-cm$^{-1}$ region for $[(CH_3)_4N][HgCl_3]$ supports the assignment of the 125-cm$^{-1}$ band as an axial deformation mode.

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(49) The $[(CH_3)_4N][HgCl_3]$ compound is isomorphous with the corresponding bromide salt in which the mercury atom lies above the plane formed by the three bromine atoms and there are halogen bridging interactions between adjacent anionic species.[50] The $HgCl_3^-$ ion in the tetramethylammonium salt similarly would be expected to be distorted from a planar geometry and exhibit a pyramidal structure. Its spectrum has been interpreted in terms of essentially monomeric anionic units.[48,51]

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