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The Syntheses, Structures, and Laser Raman and Infrared Spectra of $Co(NH_3)_6CuCl_5$, $[Co(NH_3)_5OH_2]CuCl_5$, $Co(NH_3)_6CdCl_5$, $Co(NH_3)_6ZnCl_5$, and $Co(NH_3)_6ZnCl_4(NO_3)$

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The new compounds $Co(NH_3)_6CdCl_5$, $Co(NH_3)_6ZnCl_5$, and $Co(NH_3)_6ZnCl_4(NO_3)$ have been synthesized, and their infrared and laser Raman spectra have been measured, along with that of $Co(NH_3)_6CuCl_5$, in an effort to draw conclusions regarding their structures. The differences observed in the spectra of the isomorphic cadmium and copper salts indicate that the $CdCl_5^{3-}$ ion exists as a trigonal-bipyramidal species in which the axial Cd–Cl bonds are equivalent in length or longer than the equatorial ones. This inference was verified by an X-ray diffraction study, which shows that $r(\text{Cd–Cl}_{ax}) = 2.527$ (5) Å and $r(\text{Cd–Cl}_{eq}) = 2.564$ (5) Å. The observed equivalence in the Cd–Cl_{ax} bonds implies that the axial compression in the $CuCl_5^{3-}$ ion is a manifestation of the electronic structure of the Cu(II) ion, rather than crystalline effects. The spectra of the zinc-containing compounds indicate that the tetrachlorozincate(II) ion is the anionic species in these salts, although both this moiety and the $Co(NH_3)_6^{3+}$ ions appear to be considerably distorted from their ideal symmetries, probably due to hydrogen-bonding effects.

Introduction

Despite an apparent profusion of verifiably pentacoordinate complexes, there are few examples in which the central metal ion is bound to equivalent unidentate ligands. In several respects, the most fascinating of these is the $CuCl_5^{3-}$ ion, which is stabilized in the solid state by precipitation with $Cr(NH_3)_6^{3+}$[2] or $Co(NH_3)_6^{3+}$.[3] For the hexaamminechromium(III) derivatives the structure of the $CuCl_5^{3-}$ moiety is reported to be a trigonal bipyramid in which the $\text{Cu–Cl}_{\text{axial}}$ distances are 2.2964 Å and the $\text{Cu–Cl}_{\text{equatorial}}$ distances are 2.3912 Å. A similar structure for the pentachlorocuprate(II) ion is observed in $Co(NH_3)_6CuCl_5$ in which the Cu–Cl_{ax} distance is 2.295 Å and the Cu–Cl_{eq} distance is 2.392 Å. These experimental observations have been rationalized by invoking substantial d-electron-ligand repulsion effects, which presumably stabilize the actually contracted situation for a d^9 ion, since simple electrostatic or ligand–ligand arguments would predict that the equatorial bonds should be significantly shorter than those which lie on the unique axis.[4]

It remains unclear whether effects associated with crystal symmetry or packing forces markedly contribute to the nonequivalent bond lengths as juxtaposed to distortions which arise from intracomplex electronic stabilizations.[5] To this end, $Co(NH_3)_6ZnCl_5$ and $Co(NH_3)_6CdCl_5$ were synthesized, and percentage elemental analyses are in agreement with these stoichiometric formulations. Potentially, the preparation of these compounds is a signal achievement. Were they to contain discrete pentacoordinate anions, they would be the first zinc or cadmium complexes in which the five-coordination sites are occupied by identical monodentate ligands. Furthermore, there is the intriguing possibility that one or both of these anionic species might adopt a square-pyramidal configuration in preference to the trigonal-bipyramidal geometry exhibited by $CuCl_5^{3-}$, for the energies of these two configurations are, *a priori*, quite similar. During the course of our spectral measurements a report of the crystal structure of $[(C_2H_5)_4N]InCl_5$ appeared[6] which indicated that a tetragonal-pyramidal geometry is adopted by $InCl_5^{2-}$, and a structure which departs only slightly from square-pyramidal stereochemistry is found for $MnCl_5^{2-}$.[3]

The laser Raman and infrared spectroscopic investigations led us to the following conclusions. (a) The $CdCl_5^{3-}$ anion, which also contains a d^{10} central ion, exists as a trigonal bipyramid in which the Cd–Cl_{ax} distances are probably of equivalent length or longer than the Cd–Cl_{eq} distances. (b) The only zinc-containing species in $Co(NH_3)_6ZnCl_5$ is $ZnCl_4^{2-}$, and this compound is more correctly formulated as $Co(NH_3)_6ZnCl_4(Cl)$.[7,8] Additionally, the $Co(NH_3)_6^{3+}$ ion is distorted and its spectrum is compatible with a species obeying D_{4h} selection rules. (c) The compound $Co(NH_3)_6ZnCl_4NO_3$ also contains $ZnCl_4^{-}$ rather than a pentacoordinate ion. (d) The geometry and bond lengths of the anion in $Co(NH_3)_5OH_2CuCl_5$ are similar to those in $Co(NH_3)_6CuCl_5$.

Because the vibrational spectra indicated that a pentacoordinate cadmium complex is formed, while the zinc compounds form only tetracoordinate species, an X-ray crystallographic investigation of $Co(NH_3)_6CdCl_5$ was

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[1] (a) The Pennsylvania State University. (b) Public Health Service Predoctoral Fellow. (c) Brookhaven National Laboratory.

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

[3] I. Bernal, N. Elliott, R. A. Lalancette, and T. Brennan, "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier Publishing Co., Amsterdam, 1968, p 518.

[4] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

[5] Interestingly, the adoption of a flattened tetrahedral structure by the tetrachlorocuprate(II) anion has been successfully rationalized by assuming the primacy of mutual repulsions by negative charges on the chlorine atoms in determining this geometry: G. Felsenfeld, *Proc. Roy. Soc.* (London), **A236**, 506 (1956).

[6] D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*, **8**, 14 (1969).

[7] Subsequent to the conclusion of the analysis reported in this paper, it came to our attention that a single-crystal X-ray diffraction study of $[Co(NH_3)_6ZnCl_4]Cl$ has been completed.[8] The diffraction measurements show that $ZnCl_4^{2-}$ is, indeed, the only zinc-containing species in this crystal. We wish to express our appreciation to Professors Meek and Ibers for providing the structural data on this system prior to publication.

[8] D. W. Meek and J. A. Ibers, *Inorg. Chem.*, **9**, 465 (1970).

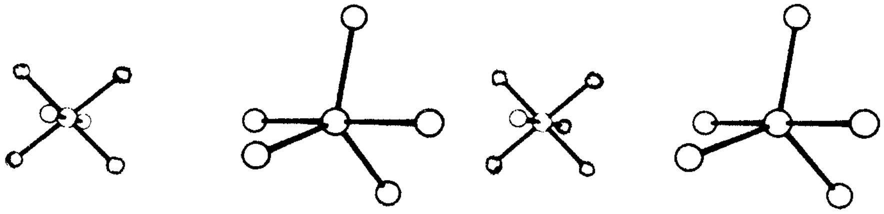

Figure 1.—Stereochemistry of the $Co(NH_3)_6^{3+}$ and $CdCl_5^{3-}$ Ions. The relative orientation of these ions in the lattice has been preserved in this figure. This is a stereopair which can best be appreciated if the observer uses a hand-held stereoviewer.

undertaken, and details of the structure of this compound are given below. Again, it is possible that symmetry or packing factors in the crystal energy term favor the observed stereochemistry. Complementary nuclear quadrupole resonance measurements are in progress on all molecules reported here.[9]

Experimental Section

Syntheses. $Co(NH_3)_6CuCl_5$.—To 20 g of $Co(NH_3)_6(NO_3)_3$ in 600 ml of distilled water 20 g of $CuCl_2 \cdot 2H_2O$ was added, and the solution was heated to 70°. While keeping the solution at this temperature, 200 ml of concentrated HCl was added, slowly, and with continuous stirring. After an induction period of a few seconds, the solution turned cloudy, and a cream-colored solid began to precipitate. The solution was allowed to cool slowly, and pale yellow crystals, seldom larger than 0.1 mm, were formed. The solid was filtered, washed with methanol, and dried at 60°. *Anal.* Calcd for $Co(NH_3)_6CuCl_5$: Cu, 15.81; Co, 14.66; Cl, 44.10; N, 20.91; H, 4.51. Found: Cu, 15.68; Co, 14.59; Cl, 44.07; N, 20.3; H, 4.2.[10]

$Co(NH_3)_6CdCl_5$.—This compound can be prepared by the same procedure as that given for the $CuCl_5^{3-}$ salt. However, since $Co(NH_3)_6CdCl_5$ is considerably less soluble than the copper salt, the amount of HCl necessary to precipitate the $CdCl_5^{3-}$ derivative is quite small. The powder pattern of this substance is identical with that of the $CuCl_5^{3-}$. *Anal.* Calcd for $Co(NH_3)_6CdCl_5$: Co, 13.07; Cl, 39.32. Found: Co, 13.03; Cl, 39.25. This compound can also be made from $Co(NH_3)_6Cl_3$ with identical results. (See the preparation of $ZnCl_5^{3-}$ derivatives for the origin of this remark.)

$[Co(NH_3)_5OH]_2CuCl_5$.—An attempt to make $[Co(NH_3)_5Cl]CuCl_4$ using $[Co(NH_3)_5Cl]Cl_2$ and following the procedure given for the preparation of hexaamminecobalt(III) pentachlorocuprate produced the aquopentaammine derivative of $CuCl_5^{3-}$. This result was verified by the following tests: (a) the optical spectrum of the solid, which can readily distinguish the aquopentaammine cation from the chloropentaammine, shows the presence of $Co(NH_3)_5OH_2^{3+}$, and (b) powder patterns show this substance to be cubic and, except for very minor changes in relative intensities, the powder pattern is superposable on that of the $Co(NH_3)_6CuCl_5$. *Anal.* Calcd for $[Co(NH_3)_5OH_2]CuCl_5$: Co, 14.63; Cu, 15.78; Cl, 44.00. Found: Co, 14.62; Cu, 15.70; Cl, 43.86.

$Co(NH_3)_6ZnCl_4(NO_3)$.—In an attempt to prepare $Co(NH_3)_6ZnCl_5$ starting with $Co(NH_3)_6(NO_3)_3$ following the procedure given for the preparation of $Co(NH_3)_6CuCl_5$, a salt was isolated which was found to contain insufficient Cl^-, if it was assumed that the salt was a pentachloride. *Anal.* Calcd for $Co(NH_3)_6ZnCl_4(NO_3)$: Co, 13.82; Zn, 15.33; Cl, 32.33; N, 23.00; H, 4.26. Found: Co, 13.78; Zn, 15.27; Cl, 34.72; N, 21.75; H, 4.34.

$Co(NH_3)_6ZnCl_5$.—In view of the fact that the nitrate of cobalt hexaammine cannot be used to prepare the pentachloride of Zn, the synthetic procedure was modified as follows. Ten grams of $Co(NH_3)_6Cl_3$ in 100 ml of distilled water was heated to 75°. To this solution was added, slowly and with stirring, a solution of 20 g of $ZnCl_2 \cdot H_2O$ in 100 ml of distilled water. Upon addition of 50 ml of 12 *M* HCl to the resulting solution (at 75°, with stirring) a light precipitate began to form, which became very bulky as the solution cooled. The filtered precipitate was washed with methanol and dried at 60°. *Anal.* Calcd for $Co(NH_3)_6ZnCl_5$: Co, 14.60; Zn, 16.19; Cl, 43.90. Found: Co, 14.52; Zn, 16.04; Cl, 43.85. This substance is not isomorphic with the cubic $CuCl_5^{3-}$ and $CdCl_5^{3-}$ derivatives of $Co(NH_3)_6^{3+}$; instead, crystals of this substance have been indexed in the orthorhombic system, which made the existence of trigonal-bipyramidal $ZnCl_5^{3-}$ unlikely.

X-Ray Crystallographic Measurements.—The crystal structure of $Co(NH_3)_6CuCl_5$ has been determined using both X-ray[3] and neutron[11] diffraction techniques. The basic crystallographic parameters are as follows: space group, Fd3c; *d*(measd) = 1.92 g cm^{-3}; a = 22.013 (5) Å; z = 32 molecules/cell. The structure of $Co(NH_3)_6CdCl_5$ is isomorphic with the analogous copper salt, and the relevant crystallographic parameters are: space group, Fd3c; *d*(measd) = 2.10 g cm^{-3}; a = 22.379 (2) Å; z = 32 molecules/cell. Figure 1 shows the structure of the cation and the anion in the relative orientation that they have in the $Co(NH_3)_6CdCl_5$ lattice. This figure shows an octahedral array of six NH_3 ligands around the Co(III) ion, and since the $Co(NH_3)_6^{3+}$ ion lies on a 3 axis, symmetry demands that it contains six identical ligands. The $CdCl_5^{3-}$ anion, on the other hand, lies on a crystallographic site with 32 symmetry. Thus, there are no symmetry constraints on the relation between the axial and equatorial Cd–Cl bond lengths. However, the three equatorial bond lengths must be identical, and the two axial ones must likewise be equivalent. For $CuCl_5^{3-}$ it is found[2,3,11] that the equatorial ligands have longer Cu–Cl bond lengths (2.39 Å) than do the axial (2.29 Å), which is in the opposite sense from the distortions generally observed in octahedral copper complexes. This result is to be contrasted with the Cd–Cl bond lengths in the pentachlorocadmate(II) ion (*vide infra*), where the axial Cd–Cl length is 2.527 (5) Å and the equatorial length is 2.564 (5) Å.

The solubility of $Co(NH_3)_6CdCl_5$ is so slight in hydrochloric acid media that most of it precipitates in a finely divided state immediately upon formation. For this reason, and because of its isomorphism with the copper analog, the crystal structure of $Co(NH_3)_6CdCl_5$ was initially studied by integrated powder techniques. At the conclusion of that study, we reported in the first version of this paper that the Cd–Cl bonds were, within the experimental error, equal in length. Because of an unduly large delay in refereeing this paper, we had the opportunity to grow a single crystal of $Co(NH_3)_6CdCl_5$ by slow (2 months) diffusion of the component ions through silica gel and to collect a set of single-crystal data. In order to minimize multiple scattering problems, a single crystal, a cube 0.25 mm on the side, was oriented in a goniometer head approximately along the (0,1,7) direction. A set of single-crystal data was collected using a four-circle Picker diffractometer equipped with a graphite monochromator and controlled by the Brookhaven Multiple

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[9] D. Scaife, private communication, Commonwealth Scientific and Industrial Research Organization, Chemical Research Laboratories, Port Melbourne, Victoria, Australia.

[10] All elemental analyses reported here are the average values of at least two independent runs. Analyses were performed at BNL by Miss B. J. Nine.

[11] A neutron diffraction study of $Co(NH_3)_6CuCl_5$ has been carried out by I. Bernal at BNL. The refinement of this structure is currently under way, and it shows that the NH_3 groups are not freely rotating. This corroborates the same, tentative, conclusion reached in the X-ray study of this substance.[3]

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $Co(NH_3)_6CdCl_5$

	x	y	z	B, Å^2
Co	0	0	0	1.18 (20)
Cd	$^1/_4$	$^1/_4$	$^1/_4$	1.51 (4)
Cl_{ax}	0.1848 (2)	x	x	1.57 (20)
Cl_{eq}	$^1/_4$	0.0810 (3)	$-y$	3.04 (21)
N	0.0706 (7)	0.0470 (6)	−0.0278 (6)	0.30 (32)

Spectrometer System. The low-angle data (up to $d^* = 1.0$) have been refined using isotropic thermal parameters for the atoms to $R_1(F) = 9.0\%$ and $R_2(F) = 11.7\%$. At this stage of the refinement, the lengths of the axial and equatorial Cd–Cl bonds are 2.527 (5) and 2.564 (5) Å, respectively.

The ratio of $Cu–Cl_{eq}/Cu–Cl_{ax} = 1.041$ while the same quantity for the $CdCl_5^{3-}$ ion is 1.015. This net expansion of the Cd–Cl bonds in the axial direction is amply evident in the ir and Raman spectra. The positions and thermal parameters from the final cycle of refinement[12] are given in Table I. The details of the full structural refinement will be given in a subsequent publication.

A powder pattern obtained from a sample of $[Co(NH_3)_5OH_2]CuCl_5$ was compared with one obtained in the same instrument for a sample of $Co(NH_3)_6CuCl_5$ and the results are given in Table II. The intensities quoted are peak heights taken from the recorder chart. Since the shapes and widths of the peaks are approximately equivalent in both samples, the intensities are proportional to the peak heights. On the basis of the agreement obtained, one concludes that the structures are virtually identical. Of course, the aquopentaamminecobalt(III) cation must have the water molecule disordered over the six equivalent positions of the $\bar{3}$ site in the lattice.

TABLE II

PRINCIPAL PEAKS IN THE POWDER DIFFRACTION SPECTRUM OF $[Co(NH_3)_5OH_2]CuCl_5$ (I) AND $[Co(NH_3)_6]CuCl_5$ (II)

hkl	I^a	II
400	Off scale^b	90
440	22	28
531	11	18
444	Off scale	Off scale
137, 355	10	20
800	5	6
820, 644	27	30
844	14	48
666, 10,2,2	68	51
880	7	20
12,00, 884	32	57
888	68	54
16,0,0	6	15

^{a} Intensity scale: number of chart divisions. ^{b} Pen zero for I, 15 chart divisions; for II, 10 chart divisions.

A single crystal of $Co(NH_3)_6ZnCl_4(NO_3)$ was mounted on a Weissenberg camera with c as the rotation axis and the $hk0$, $hk1$, and $hk2$ reciprocal zones were photographed. From the systematic absences ($0kl$ when $k + l \pm 2n$; $h0l$ when $h + l \neq 2n$) the indicated space groups are Pnn2 or Pnnm. On the basis of piezoelectric measurements, the centric space group seems to be the correct one. The cell properties are $a = 13.76$ Å, $b = 27.43$ Å, $c = 7.63$ Å, d(measd) = 1.83 g cm^{-3}, d(calcd) = 1.85 g cm^{-3}, and $z = 8$ molecules/cell. Since the three fragments (*i.e.*, $Co(NH_3)_6^{3+}$, $ZnCl_4^{2-}$, and NO_3^-) lie in general positions for either choice of the space group, a statement cannot be made about the geometry of these fragments from space group symmetry considerations alone. In particular, the question as to whether the NO_3^- group is attached to the $ZnCl_4^{2-}$ fragment, thus creating a pentacoordinated species $ZnCl_4(NO_3)^{3-}$, remains unanswered by these preliminary crystallographic considerations.

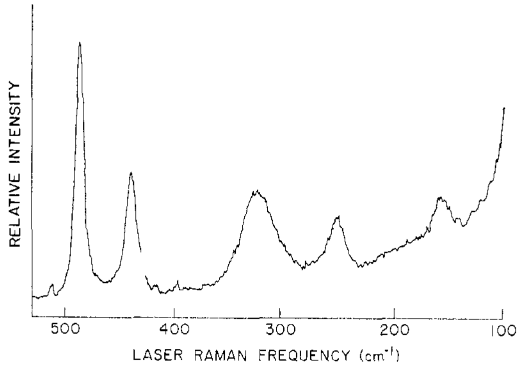

Figure 2.—A portion of the Raman spectrum of $Co(NH_3)_6CdCl_5$. The quality of the spectrum is typical of the spectra recorded for this series of salts. The intensity scale is arbitrary.

A single crystal of $Co(NH_3)_6ZnCl_5$ was mounted on a Weissenberg camera and it was found that these crystals belong to the orthorhombic system. The cell parameters are as follows: space group, Pnma; $a = 21.233$ (15) Å; $b = 7.651$ (5) Å; $c = 8.096$ (6) Å; d(measd) = 1.92 g cm^{-3}; $z = 4$ molecules/cell. Piezoelectric tests indicate that the cell is centric; however, negative piezoelectric tests are not conclusive.

Laser Raman and Infrared Spectra.—The laser Raman spectra were measured on a module instrument that has as its major components a Spex Model 1400-11 double monochromator, a Spectra-Physics Model 112 helium–neon laser (monitored power level at 6328 Å, 26 mW), an ITT-FW-130 photomultiplier with an S-20 coating, and a dc amplifier. The spectrum of each of the samples was measured at a variety of spectral resolutions from *ca.* 2.5 to *ca.* 10 cm^{-1}, except in the N–H stretching region where the spectrum could be accurately observed only with 10-cm^{-1} slit widths. An instrumental frequency calibration was effected using certain neon lines and known frequencies for CCl_4, CH_2Cl_2, and CH_3NO_2. Except for broad bands the reported Raman frequencies are accurate to within 2 cm^{-1}. Depolarization measurements were precluded, since the spectra were obtained from multicrystalline pressed pellets mounted on a goniometer head at an angle of 20° to the incident laser beam.

The infrared spectra were measured in the region 4000–200 cm^{-1} on a carefully calibrated, air dried Perkin-Elmer Model 621 grating infrared spectrometer. Spectra of the salts were obtained both in cesium iodide pellets and in Nujol mulls supported on cesium iodide plates, and the higher quality mull spectra are reported. With the exception of broad peaks, the frequency placements are accurate to 1 cm^{-1}.

Vibrational Results and Discussion

$Co(NH_3)_6CuCl_5$, $Co(NH_3)_6CdCl_5$, and $Co(NH_3)_5OH_2CuCl_5$.—Spectra of the hexaamminecobalt(III) compounds are given in Table III. The laser Raman spectrum of $Co(NH_3)_6CdCl_5$ in the region 600–100 cm^{-1} is shown in Figure 2, and the quality of this spectrum is representative of those reported herein. Frequencies attributable to the $Co(NH_3)_6^{3+}$ ions in these two compounds are remarkably similar, indicating close structural resemblance. This finding is in agreement with the diffraction data which show that the structures of the anhydrous cadmium and copper salts are isomorphic. The vibrations attributable to motions within the NH_3 ligand and to infrared-active Co–N modes are assigned congruent with those of Shimanouchi and Nakagawa.[13] The large number of modes observed in the N–H stretching, NH_3 degenerate deformation,

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[12] Refinement was carried out using LINUS, which is Brookhaven's least-squares refinement program.

[13] T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta*, **18**, 89 (1962).

TABLE III

LASER RAMAN AND INFRARED SPECTRA[a,b]

$Co(NH_3)_6CuCl_5$		$Co(NH_3)_6CdCl_5$		
Infrared	Raman	Infrared	Raman	Assignments[c]
	3280 vw, br		3275 w, br	NH str
3240 s, br	3235 vw, br	3235 s, br	3230 w, br	
	3210 vw, br		3205 mw, br	
3150 sh		3150 sh	3165 w, br	
1690 w		1692 w		NH_3 degen def
1639 mw, br, sh		1645 mw, br, sh		
1600 m		1604 m		
1560 mw, br, sh		1565 mw, br, sh		
1329 ms		1332 s		NH_2 sym def
	1324 m		1327 s	
969 vw		968 vw		$2\nu_3$ (Co–N asym str)
851 s		851 s		NH_3 rock
	490 vs		488 vs	ν_1 (Co–N sym str, A_{1g})
480 mw		479 w		ν_3 (Co–N asym str, F_{1u})
	441 ms		441 s	ν_2 (Co–N str, E_g)
331 s		331 s		ν_4 (N–Co–N def, F_{1u})
	327 m		323 s	ν_5 (N–Co–N def, F_{2g})
268 m				ν_3* (Cu–Cl str, A_2'')
	260 vs			ν_1* (Cu–Cl str, A_1')
			251 mw	ν_1* (Cd–Cl str, A_1')
		236 w		ν_3* (Cd–Cl str, A_2'')
	170 w			ν_7* (Cl–Cu–Cl bend E′) or ν_5* (Cu–Cl str, E′)
			157 w	ν_7* (Cl–Cd–Cl bend, E′) or ν_5* (Cd–Cl str, E′)
			98 vw(?)	ν_6* or ν_8* ($CdCl_5^{3-}$ def, E′)
	95 vw (?)			ν_6* or ν_8* ($CuCl_5^{3-}$ def, E′)

[a] Frequencies in units of cm^{-1}. [b] Abbreviations: s, strong; m, medium; w, weak; br, broad; sh, shoulder; v, very. [c] Frequency numbering for the $Co(NH_3)_6^{3+}$ skeletal modes corresponds to that given by T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta*, **18**, 89 (1962). For $CuCl_5^{3-}$ and $CdCl_5^{3-}$ the frequency description is taken from K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963, p 116. These frequencies are starred only in order to distinguish them from the $Co(NH_3)_6^{3+}$ modes.

and NH_3 symmetric deformation regions may arise from crystal field splittings. The Raman-active low-frequency modes of the $Co-N_6$ skeleton are assigned on the basis of a thorough examination of the laser Raman spectra of cobalt hexaammines, pentaammines, and tetraammines in the solid state and in aqueous solution.[14] The appearance of the strong Raman line at *ca.* 490 cm^{-1} (ν_1) for this moiety indicates that the asymmetric Co–N stretching mode (ν_3) is correctly assigned to the weak absorption at *ca.* 480 cm^{-1} [13,15] rather than to the stronger band at *ca.* 330 cm^{-1}, as had been suggested.[16] A fragmentary report of the laser-excited spectrum of $Co(NH_3)_6^{3+}$ is available,[15] but ν_5 and the Raman spectrum of the ammine groups are reported here for the first time.

After discrimination of those frequencies associated with the internal motions of the $Co(NH_3)_6^{3+}$ cation, one infrared and two, perhaps three, Raman bands are apparent in the measured region for both the copper and the cadmium salts. For the trigonal-bipyramidal geometry (D_{3h}) which $CuCl_5^{3-}$ is known to possess in this crystal, six Raman-active (2 A_1', 3 E′, and E″) and five infrared-active (2 A_2'' and 3 E′) vibrations are predicted. A numbering and illustrations of these normal modes have been given previously.[17] For the pentachlorocuprate(II) ion, the intense Raman shift at 260 cm^{-1} almost certainly arises from the $\nu_1(A_1')$ symmetric breathing mode of the chlorides in the equatorial plane. While it is possible that other modes (*e.g.*, $\nu_2(A_1')$, symmetric breathing mode involving the axial ligands) are accidentally degenerate with this band, none was resolved with moderately narrow slits. The single infrared band at 268 cm^{-1} has been previously assigned to an E′ mode (ν_5),[18] but the alternative assignment to an asymmetric stretching motion involving the axial chlorides, $\nu_3(A_2'')$, was not considered. Since an E′ mode would also be expected to be active in the Raman effect, and no band in this position is distinguished, we favor an assignment in which this absorption is ascribed to $\nu_3(A_2'')$. Of course, this designation must remain problematical because of the incomplete nature of the spectra, but some experimental support is mustered from the behavior of this frequency on going to the cadmium complex. Again, an accidental coincidence may occur. An examination of the spectra of other pentacoordinate molecules[17] indicates that the Raman line measured at 170 cm^{-1} in $Co(NH_3)_6CuCl_5$ is probably too high in energy to be either $\nu_6(E')$ or $\nu_8(E')$ and perhaps too low to be $\nu_5(E')$. It is tempting to identify it instead with the Cl–Cu–Cl bending mode involving the axial chloride ions, $\nu_7(E')$, since a frequency displacement of -90 cm^{-1} from ν_1 (A_1') is not unreasonable. A very weak feature at 95 cm^{-1} may be either ν_6 or ν_8.

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(14) T. V. Long, J. Zinich, and T. M. Loehr, to be submitted for publication.

(15) T. E. Haas and J. R. Hall, *Spectrochim. Acta*, **22**, 988 (1966).

(16) G. M. Barrow, R. H. Krueger, and F. Basolo, *J. Inorg. Nucl. Chem.*, **2**, 340 (1956).

(17) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963, p 116.

(18) G. C. Allen and N. S. Hush, *Inorg. Chem.*, **6**, 4 (1967).

TABLE IV

LASER RAMAN AND INFRARED SPECTRA OF $Co(NH_3)_6ZnCl_5$[a]

Infrared[b]	Raman[b]	Assignments[c]
	3305 w, br	
3240 s, br	3255 w, br	
	3205 mw, br	NH str
3160 s, br	3160 w, br	
3060 s, br	3090 vw	
1700 v br, sh		NH_3 degen def
1583 m, vbr		
	1416 w	
1352 ms	1355 m, br	
1330 m	1327 s	NH_3 sym def
1321 w, sh		
1312 m	1316 m	
1298 mw	1302 w	
970 vw		$2\nu_3$ (Co–N asym str)
888 w, sh		
862 ms		
841 ms, sh		NH_2 rock
784 vw, sh		
	508 s	ν_1 (Co–N_{ax} sym str, A_{1g})
490 vw		ν_3 (Co–N_{ax} asym str, A_{2u})
	486 vs	ν_2 (Co–N_{eq} str, A_{1g})
471 vw		ν_g (Co–N_{eq} str, E_u)
	443 s	ν_5 (Co–N_{eq} str, B_{1g})
	355 mw, br	ν_8 (N_{ax}–Co–N_{eq} def, E_g)
351 w, sh		ν_{10} (N_{ax}–Co–N_{eq} def, E_u)
323 s		ν_4 (N_{ax}–Co–N_{eq} def, A_{2u})
	317 ms, br	ν_6 (N_{eq}–Co–N_{eq} def, B_{2g})
	290 m	ν_1* (Zn–Cl sym str, A_1)
279 ms	290 m	ν_3* (Zn–Cl asym str, F_2)
233 mw		ν_{11} (N_{eq}–Co–N_{eq} def, E_u)
	140 w, br	ν_4* (Zn–Cl def, F_2)
	112 w	ν_2* (Zn–Cl def, E)

[a] Stoichiometric formula. [b] Frequencies in cm^{-1} units. Intensity designations as in Table I. [c] Assignments for $Co(NH_3)_6^{3+}$ were made by analogy to those for $Co(NH_3)_4X_2^+$ in ref 13, with the assumption that the Co–N_6 skeleton is an axially distorted octahedron. The frequencies assigned to $ZnCl_4^{2-}$ are analogous to those of ref 19. The Zn–Cl frequencies have been starred only to distinguish them from those of $Co(NH_3)_6^{3+}$. While this empirical assignment procedure is believed to be accurate for the cobalt–nitrogen stretching modes and for the bending modes labeled ν_4 and ν_6, the assignments of the weaker bands to the specific vibrations ν_8, ν_{10}, and ν_{11} is tenuous.

The isomorphism of the cadmium and copper salts and the convincing similarity of their spectra permit analogous assignments for the $CdCl_5^{3-}$ spectrum on the basis of D_{3h} symmetry. Juxtaposing the spectra of the pentacoordinated copper and cadmium ions, one finds that the Raman-active equatorial breathing mode, ν_1, is only 9 cm^{-1} lower in the cadmium salt, concomitant with the slightly weaker chlorine–cadmium bonding. However, there is a shift (32 cm^{-1}) to 236 cm^{-1} for ν_3, the infrared stretch which involves motions of the axial chlorides and the metal ion. This strongly suggests a weakened metal–Cl_{ax} bond in the cadmate compound. To the extent that an inverse correlation exists between bond length and bond strength, one would predict that the Cd–Cl_{ax} bonds are elongated relative to the Cd–Cl_{eq} bonds. This prediction has been verified by the X-ray diffraction analysis of both structures. The ratio of Cu–Cl_{eq}/Cu–Cl_{ax} = 1.041 compares with a value of 1.015 for the similar bonds in the cadmium compound. Arguing that to at least the first order the effect of crystalline forces on anionic structural parameters must be equal in these isomorphic solids, it would seem likely that the shortness of Cu–Cl_{ax} bonds (relative to the Cu–Cl_{eq} bonds) must be intimately dependent on the electronic configuration of the cupric ion in the D_{3h} ligand field.

In the measurements on $Co(NH_3)_5OH_2CuCl_5$, bands ascribable to motions of the $Co(NH_3)_5OH_2^{3+}$ cation appear in the infrared spectrum at 493, 475, 417, and 326 cm^{-1} and in the Raman spectrum at 513, 486, 446, 427, 336, and 310 cm^{-1}.[14] The bands arising from the $CuCl_5^{3-}$ anion are but slightly shifted in frequency from their positions in the $Co(NH_3)_6CuCl_5$ spectra, with a strong Raman band at 262 cm^{-1}, a considerably weaker shift at 175 cm^{-1}, and an infrared-active mode at 256 cm^{-1}. Significant lengthening of the Cu–Cl_{ax} bonds in this compound compared to those in $Co(NH_3)_6CuCl_5$ is not anticipated.

$Co(NH_3)_6ZnCl_5$ and $Co(NH_3)_6ZnCl_4(NO_3)$.—A crystalline solid with the stoichiometric formulation $Co(NH_3)_6ZnCl_5$ formed under the conditions given above, and preliminary single-crystal X-ray measurements showed that this zinc compound is not isomorphic with the pentacoordinate copper and cadmium salts (*vide supra*).

From Table IV, it is seen that in the region between 300 and 100 cm^{-1}, where vibrations attributable to the zinc–chloride complex should occur, the only pattern of lines is one identical with that of the $ZnCl_4^{2-}$ ion in its cesium salt.[19] This is clearly diagnostic of the presence of tetrachlorozincate(II) as the principal zinc-containing species. Although ν_1 and ν_3 could not be resolved in the Raman spectrum, ν_3 is quite plainly measured in the infrared spectrum, where ν_1 is forbidden. This is in agreement with the initial nuclear quadrupole resonance results[9] which exhibit a single chloride resonance at 8.684 MHz (77°K), found also in $(NH_4)_2ZnCl_4$ and Cs_2ZnCl_4. The excellent agreement between measured and theoretical elemental analyses for this complex permits only two alternatives for the additional chloride ion. Either this chloride is purely ionic, in which case the structure is that of an unusual double salt, or $ZnCl_6^{4-}$ must be contained in equimolar quantities with the $ZnCl_4^{2-}$. Little credence can be afforded the second possibility, because no Raman lines due to a second zinc complex are observed in the zinc–chloride stretching region, and the large ionic charge also argues against this. The correct formulation is thus $Co(NH_3)_6ZnCl_4(Cl)$.[7,8]

While $\nu_1(A_1)$ appears at 288 cm^{-1} in Cs_2ZnCl_4 and at 290 cm^{-1} in the present compound, there is a dramatic shift in the infrared-active stretch $\nu_3(F_2)$ from 298 cm^{-1} in the cesium salt to 279 cm^{-1} in $[Co(NH_3)_6ZnCl_4]Cl$. The increases in $\nu_2(E)$, 4 cm^{-1}, and $\nu_4(F_2)$, 10 cm^{-1}, are not so marked. The single-crystal X-ray results[8] show that the point group symmetry of the $ZnCl_4^-$ ion in the cobalt species is not T_d, but m. Despite the considerable distortion of the $ZnCl_4^{2-}$ group, no removal of modal degeneracies is observed,

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(19) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **5**, 2232 (1966).

and the sensitivity of ν_3 remains the primary manifestation of the symmetry reduction.

The complex spectrum associated with the $Co(NH_3)_6^{3+}$ cation suggests an anisotropic environment for this ion. Upon comparing Tables III and IV, it is evident that new lines are measured for $Co(NH_3)_6ZnCl_4(Cl)$ at frequencies that are close to those of the octahedral Co–N_6 skeleton in $Co(NH_3)_6CdCl_5$ and $Co(NH_3)_6CuCl_5$, and relatively intense bands occur at 355 cm^{-1} in the Raman scattering and at 233 cm^{-1} in the infrared region. Reasoning inductively, one may propose that there is a distortion of the $Co(NH_3)_6^{3+}$ ion in the zinc compound, so that the six cobalt–nitrogen bonds are not equivalent. The highest possible *symmetry* which could be exhibited by a distorted Co–N_6 skeleton is D_{4h}. All ten modes that would be allowed for a tetragonally distorted octahedron of D_{4h} symmetry are observed, and all lines appear at frequencies corresponding to those anticipated from comparison with the spectra of the *trans*-dihalotetraamminecobalt(III) salts.[13,20,21] Thus, the vibrational measurements are compatible with D_{4h} symmetry, though lower symmetries cannot be excluded on the basis of these data. The single-crystal diffraction measurements[3] show that the cation is a slightly distorted octahedron located on a site of m symmetry.

Except for nitrate vibrations, the spectra of $Co(NH_3)_6ZnCl_4(NO_3)$ resemble those of the copper and cadmium salts in the region above 850 cm^{-1}. The Raman spectrum of this compound contains shifts at 501, 491, 452, 346, and 315 cm^{-1} of the same relative intensities as ν_1, ν_2, ν_5, ν_8, and ν_6, respectively, of the $Co(NH_3)_6^{3+}$ in $Co(NH_3)_6ZnCl_4(Cl)$ and they must arise from analogous normal modes. Infrared absorptions occur at 488 and 328 cm^{-1}, correlating with ν_3 and ν_4, and bands also appear at 436 (m, sh) and 206 cm^{-1} (vw) in the Raman spectrum and at 441 cm^{-1} (vvw) in the infrared. This suggests a point symmetry for the Co–N_6 skeleton that is lower than that observed in the chloride salt, but these features could evolve from site-group effects. The Raman spectrum in the region below 300 cm^{-1} is otherwise identical with that of the $ZnCl_4^{2-}$ ion with shifts at 292 (ν_1, ν_3), 143 (ν_4), and 117 cm^{-1} (ν_2). On this basis, the formation of a pentacoordinate $ZnCl_4ONO_2^{3-}$ anion seems precluded. In the infrared spectrum, the asymmetric frequency ν_3 appears at 272 cm^{-1}, and this larger shift from the Cs_2ZnCl_4 probably indicates that the distortion of this ion is larger than in the $Co(NH_3)_6ZnCl_4(Cl)$ salt. Additionally, a splitting of this line is observed with a weak shoulder appearing at 249 cm^{-1}, and ν_1 is measured in the infrared spectrum as a medium strong line at 295 cm^{-1}. The vibrational spectra of the nitrate ion conform generally to that of a slightly perturbed species, and the large splittings, characteristic of bonded nitrate in the solid state,[22] do not occur. Totally, the structural conclusions regarding this compound are similar to those of the corresponding chloride salt, and it is probably best formulated as $Co(NH_3)_6ZnCl_4(NO_3)$.

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(20) Factor-group effects are apparently unimportant. An analysis carried out for the D_{2h}^{16} factor group (Pnma) using the method of White and De Angelis[21] shows that 60 internal modes could arise from the Co–N_6 skeleton, and only 10 are possibly observed.

(21) W. B. White and B. A. De Angelis, *Spectrochim. Acta*, **23A**, 985 (1967).

(22) C. C. Addison, D. W. Amos, D. Sutton, and W. H. H. Hoyle, *J. Chem. Soc., A*, 808 (1967).