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The Crystal Structure of Hexaamminecobalt(III) Tetrachlorozincate(II) Chloride, $[Co(NH_3)_6][ZnCl_4]Cl$

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The crystal structure of hexaamminecobalt(III) tetrachlorozincate(II) chloride, $[Co(NH_3)_6][ZnCl_4]Cl$, has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined by full-matrix least-squares techniques to a final R factor, on F, of 3.4% for the 1329 independent reflections that are above background. The material crystallizes in the orthorhombic space group D_{2h}^{16}-Pnma, with four formula units in a cell of dimensions $a = 21.219$ (9), $b = 7.653$ (4), and $c = 8.106$ (3) Å. The calculated and observed densities are 2.037 and 2.02 ± 0.01 g/cm^3, respectively. Both the cation and the $ZnCl_4^{2-}$ anion are required crystallographically to possess m symmetry. The $Co(NH_3)_6^{3+}$ ion is a slightly distorted octahedron, whereas the structure of the tetrachlorozincate(II) is distorted appreciably from a tetrahedron. The four independent Co–N bond lengths are 1.968 (5), 1.977 (3), 1.953 (3), and 1.974 (5) Å, and the independent Zn–Cl distances are 2.358 (2), 2.269 (1), and 2.223 (2) Å.

Introduction

As the number of authentic five-coordinate complexes increases, it has become apparent that the energy differences between the various pentacoordinate structures are quite small[1] and that subtle changes in the ligand or the metal can dramatically affect the geometry of a given five-coordinate complex.[2] Dynamic vibrational processes quite likely interconvert the various structures in solution.[1] Consequently, we have been interested in definitive structural information on pentacoordinate complexes of simple monodenate ligands where steric or symmetry restrictions on the resulting complexes[3-5] are minimized.

An accurate determination of the crystal structure of $[Cr(NH_3)_6][CuCl_5]$ showed[3] that the $CuCl_5^{3-}$ ion is trigonal bipyramidal and that the equatorial Cu–Cl bonds are 0.095 (2) Å longer than the axial Cu–Cl bonds, in contrast to what is expected on the basis of electrostatic or ligand–ligand repulsion arguments.[1] The shorter axial Cu–Cl bond was attributed to a nonspherical 3d-electron density distribution in a low-spin d^8 or d^9 complex.[3] In order to test this suggestion, *i.e.*, that most of the 3d-electron density of the copper atom is confined to the filled d orbitals in the xy plane, we decided to examine the structure of a simple pentacoordinate d^{10} complex, specifically $ZnCl_5^{3-}$. Zinc(II), cadmium(II), and other d^{10} ions would have a spherical 3d-electron distribution; thus, ligand–ligand interactions in a trigonal bipyramid should make the axial Zn–Cl bonds longer than the equatorial bonds, as is observed in all pentavalent group V molecules.[1]

Although the discrete $ZnCl_5^{3-}$ ion has not been reported, there are numerous five-coordinate zinc(II) complexes which serve as a precedent. For example, $Zn(terpy)Cl_2$ (terpy = 2,2′,2″-terpyridyl),[6,7] bis(N-methylsalicylaldiminato)zinc(II),[8] and $[Zn(acac)_2]_3$[9] (acac = acetylacetonato) all have distorted trigonal-bipyramidal configurations around zinc(II). Using the principle[10] that a large cation of +3 charge should stabilize $ZnCl_5^{3-}$ and the same synthetic procedure[3,11] that readily gives $[Cr(NH_3)_6][CuCl_5]$ and $[Co(NH_3)_6][CuCl_5]$ (both of which contain the trigonal-bipyramidal $CuCl_5^{3-}$ ion),[11,12] we isolated orange crystals of composition $Co(NH_3)_6ZnCl_5$.

This paper reports the determination of the crystal structure of "$Co(NH_3)_6ZnCl_5$." To our disappointment the crystal is a type of double salt with the $ZnCl_4^{2-}$ and Cl^- anions and does not contain the $ZnCl_5^{3-}$ ion.

Space Group and Lattice Parameters

Orange crystals of composition $Co(NH_3)_6ZnCl_5$ were prepared from $[Co(NH_3)_6]Cl_3$ and $ZnCl_2$ in an aqueous hydrochloric acid solution according to the procedure of Mori, *et al.*,[11] for the preparation of $[Co(NH_3)_6][CuCl_5]$.[3] *Anal.* Calcd for $H_{18}Cl_5CoN_6Zn$: H, 4.50; N, 20.82; Cl, 43.90. Found: H, 4.62; N, 20.63; Cl, 43.70.

Precession photographs of zero- and upper-level zones taken with Mo Kα radiation indicated orthorhombic symmetry. The systematic absences $0kl$ for $(k + l)$ odd and $hk0$ for h odd are consistent with either of the space groups D_{2h}^{16}-Pnma or C_{2v}^{9}-Pn2_1a. The former space group was chosen initially and this choice was confirmed by the successful solution and refinement of the structure.

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

[2] For example, the tetradentate ligand $P(o\text{-}C_6H_4SCH_3)_3$ forms trigonal-bipyramidal Ni(ligand)X$^+$ complexes [L. P. Haugen and R. Eisenberg, *Inorg. Chem.*, **8**, 1072 (1969)], whereas the analogous tridentate $C_6H_5P(o\text{-}C_6H_4SCH_3)_2$ forms square-pyramidal Ni(ligand)X_2 complexes [D. W. Meek and J. A. Ibers, *ibid.*, **8**, 1915 (1969)].

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

[4] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 1362 (1968).

[5] J. K. Stalick and J. A. Ibers, *ibid.*, **8**, 1084, 1090 (1969).

[6] F. W. B. Einstein and B. R. Penfold, *Acta Cryst.*, **20**, 924 (1966).

[7] D. E. C. Corbridge and E. C. Cox, *J. Chem. Soc.*, 594 (1956).

[8] P. L. Orioli, M. DiVaira, and L. Sacconi, *Inorg. Chem.*, **5**, 400 (1966).

[9] M. J. Bennett, F. A. Cotton, and R. Eiss, *Acta Cryst.*, **B24**, 904 (1968).

[10] W. E. Hatfield, R. Whyman, R. C. Fay, K. N. Raymond, and F. Basolo, *Inorg. Syn.*, **11**, 47 (1968); K. N. Raymond and F. Basolo, *Inorg. Chem.*, **5**, 949 (1966).

[11] M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Japan*, **34**, 295 (1961).

[12] I. Bernal, N. Elliott, R. A. Lalancette, and T. Brennan, "Progress in Coordination Chemistry," Proceedings of the 11th International Conference on Coordination Chemistry, Haifa, Elsevier Publishing Co., New York, N. Y., 1968, p 518.

The lattice constants, obtained by a least-squares procedure described below, are $a = 21.219$ (9), $b = 7.653$ (4), and $c = 8.106$ (3) Å. These parameters were obtained at 22° with Mo Kα_1 radiation (λ 0.70930 Å). For 4 formula units in the cell, the calculated density is 2.037 g/cm^3. This value is in good agreement with the experimental density of 2.02 ± 0.01 g/cm^3 obtained by flotation in carbon tetrachloride–methyl iodide solutions.

The data crystal (dimensions 0.21 × 0.10 × 0.48 mm) was mounted on a glass fiber so that the b axis (the 0.48-mm length) was roughly coincident with the spindle direction of the eucentric goniometer head. Intensity data were collected with a Picker four-circle card-controlled automatic diffractometer, using Mo Kα radiation and a takeoff angle of 1.4°. At this angle the intensity of the diffracted beam was $\sim$85% of the maximum intensity. The mosaicity of the crystal was examined by performing ω scans on several reflections at a takeoff angle of 0.6°; the peaks were very symmetrical and peak widths at half-height were $<0.08°$, which is acceptably low.[13] Ten high-angle ($2\theta > 38°$) reflections from the crystal were accurately centered through a narrow vertical slit at a takeoff angle of 0.5°. These reflections formed the basis for the least-squares refinement of cell parameters and crystal orientation; the refinement was performed in our program PICK as previously described.[14,15]

Intensity data were collected by the θ–2θ technique at a scan rate of 1.0°/min. The scan range was taken from $-0.50°$ from the 2θ value calculated for Kα_1 to $+0.70°$ from the 2θ value calculated for Kα_2. Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan range. The diffracted beam was filtered through 3.0 mils of Nb foil. The scintillation counter was 29 cm from the crystal and had an aperture of 5 × 6 mm; the pulse-height analyzer was set to admit about 90% of the Mo Kα peak. Copper foil attenuators were inserted automatically when the intensity of the diffracted beam exceeded about 7000 counts/sec.

A unique set of reflections with $2\theta \leqslant 56°$ was generated and arranged in an efficient order to minimize slewing time; a total of 1637 independent intensities were recorded. No data were collected at 2θ values $>56°$, since very few reflections were above background beyond this point. Intensities of four strong reflections in diverse regions of reciprocal space were monitored every 12 hr. There was no variation in their intensities beyond that expected from counting statistics ($\leqslant 2\%$).

The data were processed as previously described.[14,15] After initial correction for background, the standard deviation $\sigma(I)$ of the corrected intensity I was estimated using a value of $p = 0.045$.[14] The intensities were next corrected for Lorentz and polarization effects and then for absorption.[16] The absorption coefficient μ of this compound for Mo Kα radiation is 41.51 cm^{-1}; transmission coefficients for the data crystal ranged from 0.45 to 0.74. Of the 1637 reflections, 1487 had $I \geq \sigma(I)$ and 1329 had $I \geq 3\sigma(I)$. The latter 1329 reflections will be referred to as being above background and were used in the refinement.

Solution and Refinement of the Structure

The coordinates of the Co and Zn atoms were obtained from a three-dimensional Patterson function.[16] A structure factor calculation followed by a difference Fourier synthesis phased by the Co and Zn atoms revealed the positions of two chlorine atoms. Full-matrix least-squares refinement of the structure was begun using the 1329 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. Refinement was based on F, with the weights w taken as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors tabulated by Ibers[17] were used for neutral Cl and N, those of Cromer and Waber[18] for neutral Co and Zn, and those of Stewart, *et al.*,[19] for H. The effects of both real and imaginary anomalous scattering by Co, Zn, and Cl were included in F_c;[20] Cromer's[21] values of $\Delta f'$ and $\Delta f''$ for Co, Zn, and Cl were used.

Refinement of atomic coordinates and isotropic thermal parameters for Co, Zn, and two Cl atoms gave values of 0.454 and 0.584 for $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (or weighted R factor) $= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, respectively. A subsequent difference Fourier synthesis revealed the positions of the other chlorine atoms and the four independent nitrogen atoms. Three cycles of least-squares refinement of atomic coordinates and isotropic thermal parameters reduced the values of R_1 and R_2 to 0.082 and 0.109, respectively. At this stage it was obvious that the zinc anion was $ZnCl_4^{2-}$ instead of $ZnCl_5^{3-}$. One cycle of refinement with anisotropic thermal parameters assigned to all ten atoms led to $R_1 = 0.048$ and $R_2 = 0.074$. The raw data were then corrected for absorption,[16] and a subsequent least-squares cycle reduced R_1 to 0.043 and R_2 to 0.071.

A difference Fourier map was calculated and six hydrogen atoms were located. In best agreement with these approximate positions, idealized coordinates for the six hydrogens were computed assuming an N–H bond length of 0.85 Å and an H–N–H angle of 108.0°. The N–H bond length was chosen as an average value of N–H and C–H distances that have been refined from X-ray data.[3,22] One least-squares calculation with fixed hydrogen coordinates and variable isotropic

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[13] T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

[14] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[15] R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

[16] In addition to various local programs for the CDC 6400 computer, local modifications of the following programs were employed: Hamilton's GONO9 absorption program; Zalkin's FORDAP Fourier program; the Busing–Levy ORFLS least-squares and ORFFE error function programs; and Johnson's ORTEP thermal ellipsoid plotting program.

[17] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

[18] D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

[19] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[20] J. A. Ibers and W C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

[21] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[22] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $[Co(NH_3)_6][ZnCl_4]Cl$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.091878 (28)[b]	$^1/_4$	0.133553 (82)	115 (1)	1046 (12)	806 (11)	0	−14 (3)	0
Co	0.359091 (29)	$^1/_4$	0.116043 (78)	81 (1)	676 (11)	458 (10)	0	−15 (3)	0
Cl(1)	0.057771 (65)	$^1/_4$	0.41035 (18)	136 (3)	1987 (33)	753 (21)	0	75 (6)	0
Cl(2)	0.152589 (46)	0.00606 (13)	0.12585 (11)	179 (2)	1243 (19)	759 (14)	138 (5)	58 (4)	181 (13)
Cl(3)	0.009746 (64)	$^1/_4$	−0.03664 (19)	134 (3)	1345 (27)	1116 (24)	0	−99 (7)	0
Cl(ion)	0.198950 (63)	$^1/_4$	−0.23741 (18)	161 (3)	884 (21)	945 (21)	0	−94 (7)	0
N(1)	0.29970 (22)	$^1/_4$	0.30252 (59)	134 (10)	1576 (100)	656 (71)	0	48 (23)	0
N(2)	0.41010 (13)	0.06721 (42)	0.22482 (40)	132 (6)	909 (54)	831 (51)	35 (16)	−50 (15)	152 (46)
N(3)	0.30813 (13)	0.06973 (41)	0.00970 (39)	125 (7)	882 (53)	713 (46)	−47 (15)	−60 (14)	9 (46)
N(4)	0.41661 (20)	$^1/_4$	−0.07532 (56)	105 (9)	1142 (85)	664 (67)	0	28 (21)	0
N(1)H(1)[c]	0.2621	$^1/_4$	0.2694						
N(1)H(2)	0.3053	0.1602	0.3630						
N(2)H(1)	0.3903	−0.0301	0.2280						
N(2)H(2)	0.4447	0.0510	0.1766						
N(2)H(3)	0.4181	0.0950	0.3255						
N(3)H(1)	0.2735	0.1098	−0.0234						
N(3)H(2)	0.3276	0.0275	−0.0745						
N(3)H(3)	0.3011	−0.0148	0.0750						
N(4)H(1)	0.4105	0.3398	−0.1362						
N(4)H(2)	0.4547	$^1/_4$	−0.0459						

[a] All anisotropic thermal parameters, β, are multiplied by 10^5. The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Figures in parentheses here and elsewhere in this paper are the estimated standard deviations of the least significant digits reported. [c] The designation N(1)H(1) refers to H(1) on N(1); the hydrogen atom coordinate positions were determined as described in the text and were not refined; an isotropic temperature factor of 5.0 Å^2 was assigned to the H atoms.

temperature parameters for the six hydrogen atoms gave $R_1 = 0.039$ and $R_2 = 0.058$. The refined isotropic temperature values were in the range 3.0–6.0 Å^2. Examination of F_c and F_o for the strongest reflections indicated that extinction was important, so an isotropic extinction coefficient was included with the variables.[23] Another difference Fourier synthesis led to approximate positions of the other four hydrogen atoms; idealized coordinates for the hydrogen atoms of each NH_3 group were calculated as above.

For the final least-squares calculation, the ten independent hydrogen atoms were assigned an isotropic thermal parameter of 5.0 Å^2 and their atomic coordinates were not varied. The coordinates and the anisotropic thermal parameters of all the other atoms were varied. The final R_1 and R_2 values are 0.034 and 0.046, respectively, and the absolute value of the extinction coefficient is 2.33 (12) $\times 10^{-6}$ electron^{-2}. The estimated error in an observation of unit weight is 1.58. No parameter shifted more than one-tenth of its standard deviation in the final least-squares cycle.

A final difference Fourier map calculated from all 1329 reflections with $F_o^2 \geqslant 3\sigma(F_o^2)$ is flat and shows peaks in the range -0.5 to $+0.5$ e$^-$/Å^3; on the same scale, an average nitrogen atom shows an electron density of 6.1 e$^-$/Å^3.

The positional and thermal parameters derived from the last cycle of least-squares refinement are presented in Table I, along with the associated standard deviations in these parameters as estimated from the inverse matrix. The final values of $10|F_o|$ (corrected for extinction) and $10|F_c|$ (in electrons) are given in Table II for the 1329 reflections used in the refinements. Of the 308 reflections that were omitted from the refinement because $F_o^2 < 3\sigma(F_o^2)$, 303 had $|F_o^2 - F_c^2| < 2\sigma(F_o^2)$ and all had $|F_o^2 - F_c^2| < 3.1\sigma(F_o^2)$. These data are accordingly omitted from Table II.

Discussion of the Structure

The crystal structure contains discrete $Co(NH_3)_6^{3+}$, $ZnCl_4^{2-}$, and Cl^- ions. Figure 1 is a stereoscopic view of the unit cell and Figures 2 and 3 show the structures of the $Co(NH_3)_6^{3+}$ and $ZnCl_4^{2-}$ ions. The site symmetry of both of these ions is m. It can be seen that the inner-coordination geometry about the cobalt atom is a slightly distorted octahedron, whereas the tetrachlorozincate(II) ion is distorted appreciably from a tetrahedron. All interionic contacts, except those involving N(3)H(3), N(3)H(2), N(3)H(1), N(2)H(1), and N(4)H(2) in hydrogen bonding, exceed those predicted from van der Waals radii. In particular, the $ZnCl_4^{2-}$ and Cl^- ions are separated by van der Waals contacts and there is no basis for describing the zinc species as a severely distorted $ZnCl_5^{3-}$ ion.

Principal interatomic distances and angles and their standard deviations as computed from the final parameters and the correlation matrix are given in Table III. The root-mean-square amplitudes of vibration of the atoms are listed in Table IV. The orientations of the thermal ellipsoids may be discerned from the figures.

Since there are some surprising distortions of the ions in this structure, it is appropriate to discuss the evidence in favor of the centrosymmetric space group Pnma assumed here, rather than the noncentrosymmetric space group $Pn2_1a$, which is also consistent with the X-ray extinctions. The very low R factor, the detectability of hydrogen atoms on difference Fourier maps, and the very clean final difference Fourier map all are evidence that the correct space group has been used. Moreover, if the correct space group were

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(23) W. H. Zachariasen, *Acta Cryst.*, **A24**, 212 (1968). In applying this correction the term T was assumed to be unity for all reflections.

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (IN ELECTRONS × 10) FOR $[Co(NH_3)_6][ZnCl_4]Cl$

L	H	FO	FC

Pn2₁a, then one would expect to observe excessive thermal motion perpendicular to the imposed mirror plane in Pnma for those atoms assumed to lie on that mirror plane. That this is not the case may be discerned from the figures. Finally we note that the polar dispersion error[24] that would result if the space group were Pn2₁a and if we had assumed the wrong enantiomorph is far smaller than the observed distortions.

Accepting then the space group to be correct, one may ask two further questions: (1) Are those apparent distortions the result of the effects of thermal motion? (2) Have the standard deviations on bond distances been underestimated so that the significance of the distortions has been overemphasized? The bond distances of Table III can be corrected for ther motion if one assumes specific models for this mot for example, the "riding" or "independent" model Busing and Levy.[25] The corrected distances are course, somewhat longer than those presented in T III, but the relative differences among the various b lengths remain essentially the same when either of tl corrections is made. Thus the distortions are n(manifestation of the effects of thermal motion. four independent Co–N bond distances range f 1.953 (3) to 1.977 (3) Å and average 1.968 Å, and standard deviation of a single observation is 0.01: on the assumption that the four distances are from same population. This standard deviation is thre

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(24) T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Cryst.*, **20**, 836 (1966).

(25) W. R. Busing and H. A. Levy, *ibid.*, **17**, 142 (1964).

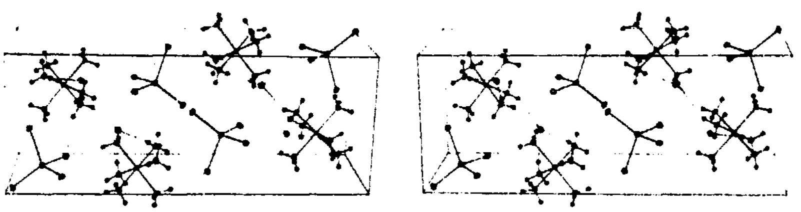

Figure 1.—A stereoscopic view of the unit cell of $[Co(NH_3)_6][ZnCl_4]Cl$. In this view the *a* axis goes from left to right, the *c* axis goes from bottom to top, and the view is nearly along the *b* axis. For the sake of clarity the thermal parameters of all H atoms have been set at 1 Å². For the other atoms the 50% probability ellipsoids are shown. The light lines illustrate the hydrogen bonds (Table V) within the cell.

TABLE III

SELECTED INTERATOMIC DISTANCES AND ANGLES

Distance, Å

Bonding		Nonbonding	
Zn–Cl(1) [1][a]	2.358 (2)	Zn–Cl(ion)	3.769 (2)
Zn–Cl(2) [2]	2.269 (1)	Cl(1)–Cl(ion)	4.139 (2)
Zn–Cl(3) [1]	2.223 (2)	Cl(2)–Cl(ion) [2]	3.623 (2)
Co–N(1) [1]	1.968 (5)	Cl(3)–Cl(ion)	4.332 (3)
Co–N(2) [2]	1.977 (3)	Co–Cl(ion)	4.445 (2)
Co–N(3) [2]	1.953 (3)	Co–Zn	5.672 (3)
Co–N(4) [1]	1.974 (5)		

Angle, deg

Cl(1)–Zn–Cl(2) [2]	101.56 (4)	N(2)–Co–N(3)	90.02 (13)
Cl(1)–Zn–Cl(3)	110.49 (6)	N(2)–Co–N(4)	90.70 (13)
Cl(2)–Zn–Cl(3)	115.35 (4)	N(3)–Co–N(4)	89.73 (14)
Cl(2)–Zn–Cl(2′)[b]	110.72 (7)	N(2)–Co–N(2′)[a]	90.09 (19)
N(1)–Co–N(2)	90.44 (14)	N(3)–Co–N(3′)	89.86 (19)
N(1)–Co–N(3)	89.12 (14)	N(2)–Co–N(3′)	179.55 (13)
N(1)–Co–N(4)	178.38 (19)		

[a] The number of bonds or angles of this type is shown in brackets. [b] Primed atoms are related to the corresponding unprimed atoms through the crystallographic mirror plane.

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION[a] ALONG PRINCIPAL AXES OF THERMAL VIBRATION (IN Å)

Atom	Min	Intermed	Max
Zn	0.159 (1)	0.167 (1)	0.176 (1)
Co	0.122 (1)	0.138 (1)	0.142 (1)
Cl(1)	0.144 (2)	0.188 (2)	0.243 (2)
Cl(2)	0.151 (2)	0.166 (2)	0.229 (1)
Cl(3)	0.157 (2)	0.200 (2)	0.208 (2)
Cl(ion)	0.159 (2)	0.162 (2)	0.207 (2)
N(1)	0.142 (8)	0.180 (7)	0.216 (7)
N(2)	0.141 (5)	0.176 (5)	0.184 (5)
N(3)	0.140 (5)	0.158 (5)	0.184 (5)
N(4)	0.143 (8)	0.160 (7)	0.184 (7)

[a] The figures provide an indication of the directions of the vibrations.

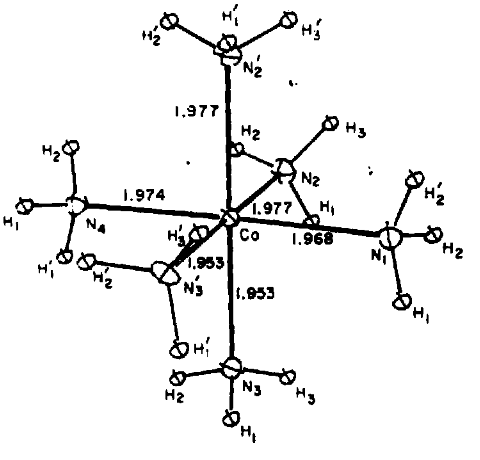

Figure 2.—A perspective drawing of the $Co(NH_3)_6^{3+}$ ion. Here and in Figure 3 the primed atoms are related to the corresponding unprimed atoms through the imposed crystallographic mirror plane. Except for hydrogen atoms, which have been made artificially small for the sake of clarity, the 50% probability ellipsoids are shown.

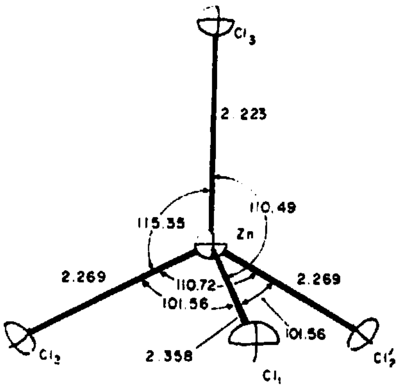

Figure 3.—A perspective drawing of the $ZnCl_4^{2-}$ ion.

four times that of an individual Co–N distance as estimated from the inverse matrix. Hence there are either residual, systematic errors in the data that make the estimates from the inverse matrix unreliable (and optimistic) or significant differences among the independent Co–N distances. However, even if the former is assumed and the standard deviations are increased by a factor of 3, the distortions in the $ZnCl_4^{2-}$ ion, with Zn–Cl distances ranging from 2.223 to 2.358 Å, remain highly significant. Since the $ZnCl_4^{2-}$ ion is distorted, there is no reason to assume that the $Co(NH_3)_6^{3+}$ ion is perfectly symmetric and that the standard deviations are overly optimistic. Incidentally, the average Co–N distance of 1.968 (11) Å is in excellent agreement with the values of 1.968 (10) and 1.968 (8) Å found in $[Co(NH_3)_5Cl]Cl_2$[26] and $[Co(NH_3)_5N_3](N_3)_2$[27] and these values are all somewhat longer than that of 1.936 (15) Å found in $[Co(NH_3)_6]I_3$.[28]

It would be reasonable to attempt to discuss the observed distortions of the ions in terms of hydrogen bonding. The $Co(NH_3)_6^{3+}$, $ZnCl_4^{2-}$, and Cl^- ions are all

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(26) G. G. Messmer and E. L. Amma, *Acta Cryst.*, **B24**, 417 (1968).

(27) G. J. Palenik, *ibid.*, **17**, 360 (1964).

(28) N. E. Kime and J. A. Ibers, *ibid.*, **B25**, 168 (1969).

interconnected by hydrogen bonding from the ammine groups. The $Co(NH_3)_6^{3+}$ ions surround the ionic chloride to form chains diagonally through the crystal along the *b* axis. The shortest N···Cl contact (3.196 Å) involves the N(3)H(3)···Cl(ion) hydrogen bond (Table V). The orientation of the $Co(NH_3)_6^{3+}$ ions is such that each Cl(ion) is surrounded almost trigonally by six hydrogen atoms: two moderately close (N(3)H(3) at 2.356 Å) and four at longer distances N(2)H(1) at 2.549 Å, N(3)H(1) at 2.581 Å) involving only weak hydrogen bonding (Figure 1). The $Co(NH_3)_6^{3+}$ and $ZnCl_4^{2-}$ ions are linked together along the *a* axis *via* the two weak hydrogen bonds N(3)-H(2)···Cl(2) and N(4)H(2)···Cl(1) (Figure 1). Thus, five hydrogen atoms, N(3)H(1), N(3)H(2), N(3)H(3), N(2)H(1), and N(4)H(2), are involved in connecting the $Co(NH_3)_6^{3+}$ cation to both anions in the crystal.

TABLE V

INTERATOMIC DISTANCES AND ANGLES INVOLVED IN HYDROGEN BONDING[a]

Atom involved					
Cl	H	N	Cl–N, Å	Cl–H, Å[c]	Cl–H–N, deg[c]
Ion	3	3[b]	3.196	2.356	170
2	2	3	3.273	2.478	154
1	2	4	3.280	2.447	170
Ion	1	3[b]	3.359	2.581	154
Ion	1	2[b]	3.368	2.549	161

[a] Only Cl–N distances less than 3.4 Å are considered to be significantly involved in hydrogen bonding.[22] [b] There are two such interactions. [c] These are calculated from the idealized hydrogen positions.

Yet this reasonable hydrogen-bonding scheme does not account for the observed distortions. The strongest N–H···Cl bond is N(3)–H(3)···Cl(ion) (Table V). We would thus expect that the Co–N(3) bond would be lengthened as a result of the hydrogen bonding, perhaps not detectably. In fact, it is detectably the shortest Co–N length. Even more dramatically the $ZnCl_4^{2-}$ ion is severely distorted and yet it is involved in only two weak hydrogen bonds (N(4)···Cl(1) and N(3)···Cl(2)). One might have anticipated some angular distortion as a result of this hydrogen bonding, but it would seem that the energies involved in such bonding are too small to account for the differences observed in the Zn–Cl bond lengths. Although the geometry of the $ZnCl_4^{2-}$ ion approximates T_d symmetry in several other salts,[3,29,30] there are examples where the ion is distorted. Thus in β-[Co(en)(dpt)Cl][$ZnCl_4$][31] (en = ethylenediamine, dpt = dipropylenetriamine) the Cl–Zn–Cl angles range from 104.5 (3) to 118.0 (3)° and the Zn–Cl distances range from 2.254 (8) to 2.286 (8) Å. There are no N–H···Cl bonds in this structure.

A sample of $[Co(NH_3)_6][ZnCl_4]Cl$ was prepared independently and it has been examined recently by infrared and laser-Raman techniques.[32] Long, *et al.*,[32] concluded correctly from the spectral results that the material did not contain $ZnCl_5^{3-}$ and that the symmetries of the $Co(NH_3)_6^{3+}$ and $ZnCl_4^{2-}$ ions were lower than O_h and T_d, respectively, as we have shown. The vibrational spectra of the cation were assigned[32] in terms of D_{4h} symmetry on the basis of the similarity of the $Co(NH_3)_6^{3+}$ frequencies to those of other D_{4h} cobalt(III)–ammine complexes, but such assignments are not too sensitive to the reduced symmetry.

Concerning our original purpose in preparing $[Co(NH_3)_6][ZnCl_4]Cl$, Long, *et al.*,[32] recently prepared the cadmium salt of identical composition and have deduced an approximate structure by X-ray and neutron powder methods. The material is isomorphous with $[Cr(NH_3)_6][CuCl_5]$ and does contain the trigonal-bipyramidal $CdCl_5^{3-}$ ion. In fact, the axial Cd–Cl bond lengths (2.45 Å) appear to be longer than the equatorial Cd–Cl lengths (2.41 Å) although no error estimates are given. Thus, the structure of the $CdCl_5^{3-}$ ion provides confirmation of our original suggestion[3] that the shorter axial Cu–Cl bond lengths in $CuCl_5^{3-}$ are due to the nonspherical nature of the electron density around the cupric ion.

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