The six nitrogens are bonded to the cobalt in the expected octahedral arrangement; the angular distortions from ideality do not seem to follow any particular pattern. The molecule is the meridial (mer) isomer,[15] as previously reported by Tanito, *et al.*[2] All intramolecular nonbonded separations are normal, ranging upward from 2.70 Å (Table III, Figure 1). Nitro group O(1)–N(1)–O(2) is twisted 80° from the plane of N(1)–Co–N(3)–N(2)–N(4), while nitro group O(3)–N(2)–O(4) is twisted 34° and nitro group O(5)–N(3)–O(6) is twisted 52° from this plane. The planes of nitro groups O(3)–N(2)–O(4) and O(5)–N(3)–O(6) thus make an angle of 86° with each other.

The molecules are involved in a complicated three-dimensional network of hydrogen bonds, with intermolecular ammine N to nitro O distances ranging between 2.95 and 3.16 Å (Figure 3, Table V). There are also several O···O and nitro N···O contacts of about 3 Å, which share in making it a very closely packed and compact structure.

Comments on the Two Incorrect Methods

It is of interest (and rather sobering!) to find that two incorrect structures could have seemingly correct bond lengths and angles, reasonable looking Fourier maps, and relatively low values for R. In fact, consideration of nonbonded distances between atoms shows immediately that the structures must be incorrect in spite of apparently satisfactory bond lengths and angles[2] or a reasonably low R.[3]

The Tanito model gives rise to impossibly short intramolecular ammonia N···O separations of 2.20 and 2.09 Å, while there are four other intramolecular contacts about 0.3 Å shorter than is usual.[16] The relatively short intermolecular ammonia N···nitro O separations of 2.74 and 2.78 Å and especially an O···O separation of 2.76 Å mentioned in ref 2 hint that the structure may be incorrect. (A three-dimensional Fourier map, using the new observed data, and phased on the Tanito model, shows a number of spurious peaks and deep negative "holes" as well as ghost peaks in what eventually proved to be the correct positions for the oxygen atoms. R for this calculation was 0.35.)

In the Baines model,[3] an intermolecular O···O separation of 2.44 Å shows conclusively that the model was incorrect and this conclusion is confirmed by two impossibly short intramolecular nonbonded N···O and O···O separations of 2.53 and 2.09 Å, respectively, and the generally rather poor bond lengths and angles.

Recent work[17] confirms the existence of the two isomers of $Co(NO_2)_3(NH_3)_3$ and in fact the assignment of the mer stereochemistry to the product prepared by the method of Jorgensen[18] was made on the basis of the structure determination by Tanito, *et al.*[2] Fortunately, the redetermination shows that this was indeed the mer isomer.

Acknowledgments. We are grateful to the South African Council for Scientific and Industrial Research for a grant to cover running expenses and for the use of their computational facilities and to the Chemistry Department of California Institute of Technology for a grant to cover the cost of the final refinement. M. L. wishes to thank the faculty of the Chemistry Department of San Fernando Valley State College and especially Dr. R. E. Marsh of the California Institute of Technology for their generosity and hospitality during his stay in Los Angeles, Calif., in 1970. The diagrams were prepared by Miss Lillian Casler.

---

[15] R. F. Trimble, *J. Chem. Educ.*, **31**, 176 (1954).

[16] A. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1961.

[17] R. B. Hagel and L. F. Druding, *Inorg. Chem.*, **9**, 1496 (1970).

[18] S. M. Jorgensen, *Z. Anorg. Allg. Chem.*, **17**, 475 (1898).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA 27514

The Crystal and Molecular Structure of Tris(ethylenediamine)cobalt(III) Di-μ-chloro-bis(trichlorocuprate(II)) Dichloride Dihydrate, $[Co(N_2C_2H_8)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$

BY DEREK J. HODGSON,* POLLEY K. HALE, AND WILLIAM E. HATFIELD

Received August 19, 1970

The crystal and molecular structure of tris(ethylenediamine)cobalt(III) di-μ-chloro-bis(trichlorocuprate(II)) dichloride dihydrate, $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in space group D_{2h}^{15}-*Pbca* of the orthorhombic system with four molecules in a cell of dimensions a = 13.560 (9), b = 14.569 (9), and c = 17.885 (12) Å. The observed and calculated densities are 1.86 and 1.862 g cm^{-3}, respectively. Least-squares refinement of the structure has yielded a final value of the conventional R factor (on F) of 0.065 for 1275 independent reflections having $F^2 > 3\sigma(F^2)$. The $Cu_2Cl_8^{4-}$ anion consists of two distorted trigonal bipyramids sharing a common edge, the bridging Cu–Cl distances being 2.325 (5) and 2.703 (5) Å while the Cu–Cu separation is 3.722 (5) Å. The $Co(en)_3^{3+}$ cation is found to have the relatively high energy configuration $\Delta(\lambda\delta\delta)$ ($\equiv\Lambda(\delta\lambda\lambda)$) as a result of intermolecular interactions within the crystal.

Introduction

A complex of formulation $Co(en)_3CuCl_5(H_2O)$ (where en = ethylenediamine, $NH_2CH_2CH_2NH_2$) was first reported by Kurnakow[1] in 1898, and it has long been assumed that the anionic moiety consisted of either the trigonal-bipyramidal $CuCl_5^{3-}$ ion, as found[2] in [Cr-

---

[1] N. S. Kurnakow, *Z. Anorg. Chem.*, **17**, 225 (1898).

[2] (a) K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968); (b) M. Mori, Y. Saito, and T. Watanabe, *Bull. Chem. Soc. Jap.*, **34**, 295 (1961).

$(NH_3)_6][CuCl_5]$, or the pseudooctahedral $CuCl_5(OH_2)^{3-}$ ion. The near-infrared spectrum of the complex, however, cannot be interpreted on the basis of either of these geometries since the absorption falls at 10,400 cm^{-1}, intermediate between the values of 8200 and 12,200 cm^{-1} found for copper in trigonal-bipyramidal and octahedral environments,[3] respectively. This absorption is, of course, at much higher energy than would be expected[3] for a tetrahedral copper complex, and hence the possibility that the anionic species present might be tetrahedral $CuCl_4^{2-}$ and uncoordinated Cl^- also appears to be precluded by the spectral data.

A further structural possibility, which has not been previously considered, is the square-pyramidal $CuCl_5^{3-}$ ion, analogous to $InCl_5^{2-}$ in tetraethylammonium pentachloroindate(III)[4] and to $MnCl_5^{2-}$[5] in 2,2′-bipyridinium pentachloromanganate(III). Such a structure has not been considered because of the known[2] trigonal-bipyramidal geometry in $[Cr(NH_3)_6][CuCl_5]$. The energy difference between these two idealized five-coordinate geometries is quite small, however, as has been amply demonstrated by Raymond, Corfield, and Ibers[6] in the case of $[Cr(en)_3][Ni(CN)_5]\cdot 1.5H_2O$, in which both geometries are found to occur in the same crystal. The two forms occur in order to take advantage of hydrogen bonding with the water molecules in the cell, which implies that the energy of conversion from trigonal-bipyramidal to square-pyramidal geometry cannot be greater than a few kilocalories per mole.

In view of the apparent difference between the observed spectrum and that predicted for any of the proposed structures and partly in the hope of demonstrating the existence of square-pyramidal $CuCl_5^{3-}$, a complete three-dimensional structural determination of the complex was undertaken.

Collection and Reduction of the X-Ray Data

Amber, well-formed crystals were prepared by the method of Kurnakow.[1] On the basis of optical goniometry and precession photography the crystals were assigned to the orthorhombic system. The observed systematic absences are $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd, which strongly suggests that the space group is D_{2h}^{15}-$Pbca$, a unique space group. The lattice constants, obtained by the least-squares procedure described below, are $a = 13.560$ (9), $b = 14.569$ (9), and $c = 17.885$ (12) Å. The observations were made at 22° with the wavelength assumed as λ(Mo $K\alpha_1$) 0.7093 Å. A density of 1.872 g cm^{-3} calculated for eight monomeric formula units in the cell agrees well with the value of 1.86 (2) g cm^{-3} obtained by flotation in diiodomethane–bromoethane solution. Hence, no crystallographic symmetry need be imposed on monomeric species in the cell. Since the anion proved to be dimeric, however, there are four molecules in the cell, and the dimer is constrained to have a center of inversion.

Diffraction data were collected from a hexagonal prismatic crystal in which the hexagonal faces were (100) and ($\bar{1}$00) and the six rectangular faces were (01$\bar{1}$), (0$\bar{1}$1), (001), (00$\bar{1}$), (011), and (0$\bar{1}\bar{1}$). The separation of the hexagonal faces was 0.024 cm and the distance between opposite pairs of rectangular faces was 0.013 cm. The crystal was mounted on a glass fiber normal to the (100) planes, and in this orientation intensity data were collected at room temperature on a Picker four-circle automatic diffractometer using Mo $K\alpha$ radiation. The mosaicity of the crystal was examined by means of the narrow-source, open-counter, ω-scan technique; the width at half-height for a typical strong reflection was found to be approximately 0.06°, which is acceptably low.[7] Twelve reflections from the crystal were accurately centered through a narrow vertical slit at a takeoff angle of 0.8°. These observations formed the basis for the least-squares refinement of cell parameters and orientation, which was effected using the logic documented by Busing and Levy[8] for the PDP-8/L computer.

Intensity data were collected at a takeoff angle of 1.5°; at this angle the peak intensity of a typical strong reflection was approximately 90% as a function of takeoff angle. The receiving aperture size, selected to minimize extraneous background, was 4.0 mm high by 4.0 mm wide and was positioned 30 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 1°/min. Allowance was made for the presence of both $K\alpha_1$ and $K\alpha_2$ radiation, the scan range for a reflection at $2\theta = 0°$ being 1.5° while the scan range for a reflection at $2\theta = 40°$ was 1.75°. Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan. The Mo $K\alpha$ beam was filtered through 1.5-mil Nb foil after diffraction from the crystal. Attenuators were inserted automatically when the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan; the attenuators were Cu foils, their thickness being chosen to give attenuator factors of approximately 2.3. These attenuator factors were determined by the method which we have previously described.[9] The pulse height analyzer was set for approximately a 90% window centered on the Mo $K\alpha$ peak.

A unique data set having $2\theta < 45°$ was gathered; a total of 2078 independent intensities were recorded. The intensities of three standard reflections, measured after every 100 reflections, remained essentially constant throughout the run, showing only the deviations from the mean predicted from counting statistics. There were very few reflections above background at values of $2\theta > 45°$.

Data processing was carried out as described by Corfield, *et al.*[10] After correction for background the intensities were assigned standard deviations according to the formula

$$\sigma(I) = (C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2)^{1/2}$$

and the value of p was selected as 0.04 since the mosaicity of the crystal was quite small. This term in the expression is used to prevent extremely high weight being given to very strong reflections.[11] The values of I and $\sigma(I)$ were corrected for Lorentz–polarization and for absorption factors. The absorption coefficient for

---

[3] W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, **3**, 841 (1964).

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

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

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

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

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

[9] D. J. Hodgson and J. A. Ibers, *ibid.*, *Sect. B*, **25**, 469 (1969).

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

[11] W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

this compound for Mo Kα radiation is 29.75 cm^{-1}, and for the sample chosen the transmission coefficients evaluated by numerical integration were found to range from 0.675 to 0.763.[12] Of the 2078 independent reflections, 1285 were greater than 3 times their estimated standard deviations.

Solution and Refinement

The positions of the two metal atoms were determined from a three-dimensional Patterson function, although it was not possible at this stage to distinguish the cobalt atom from the copper atom. It was also apparent from the Patterson function that there were some remarkably short (approximately 3.7 Å) metal–metal vectors. Two cycles of least-squares refinement of these positions with both metals assigned as cobalt were run. All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o)^2$. In all calculations of F_c the atomic scattering factors for Cu and Co were taken from Cromer and Waber,[13] that for H was from Stewart, Davidson, and Simpson,[14] and those for Cl, C, and N were from the tabulation of Ibers.[15] The effects of anomalous dispersion[16] were included in calculations of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer.[17] Only the 1285 independent intensities which were greater than 3 times their estimated standard deviations were used in the refinement of the structure.

Initially, the two metal atoms were assigned isotropic thermal parameters. After two cycles of least-squares refinement, the usual agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2$ were 0.596 and 0.654, respectively. A difference Fourier synthesis revealed the positions of four of the five chlorine atoms, and a further cycle of least-squares refinement yielded values of R_1 and R_2 of 0.376 and 0.394, respectively.

A difference Fourier map run at this stage revealed the positions of all remaining nonhydrogen atoms. The metal atom in the vicinity of the carbon and nitrogen atoms was assigned as cobalt while the atom near the chlorine atoms was taken as copper. Least-squares refinement of the parameters derived from this Fourier map yielded a value of 0.107 for both R_1 and R_2. Two further cycles of least-squares refinement with anisotropic thermal parameters assigned to all atoms yielded values of $R_1 = 0.065$ and $R_2 = 0.071$. The ethylenediamine hydrogen atoms were included in the calculation, their positions being calculated assuming tetrahedral geometry at the carbon and nitrogen atoms and carbon–hydrogen and nitrogen–hydrogen bond distances of 1.00 and 0.95 Å, respectively. These distances, which are shorter than the known average values for such bonds, were chosen to allow for the contraction of bonds involving hydrogen atoms normally calculated in X-ray experiments.[9,14,18,19] The hydrogen atoms were assigned isotropic thermal parameters of 3.5 Å^2.

At this stage the ten reflections for which 2θ was less than 7.0° were removed from the refinement, since for all of these reflections $|F_o|$ was much greater than $|F_c|$. This effect, which has previously been observed by Manojlovic-Muir, Muir, and Ibers,[20] is presumably due to inadequate filtering. For the very close-in reflections, the Mo Kβ radiation will also enter the counter if the filter is insufficiently thick, thereby causing an increase in the values of $|F_o|$ for this class of reflections. In the present experiment, where only 0.0015-in. niobium foil was used, it must be assumed that the filter was inadequate to reduce the contribution of the Mo Kβ peak to an insignificant level. A final cycle of least-squares calculation, carried out with the remaining 1275 reflections, yielded values of $R_1 = 0.065$ and $R_2 = 0.069$. This significant improvement in R_2 supports the validity of the decision to reject the ten close-in reflections.

A difference Fourier synthesis run at this point gave no clear evidence as to the locations of the hydrogen atoms of the water molecule. The map showed no peak greater than 1.6 $e^-/Å^3$, the peak height for an average carbon atom being about 4 $e^-/Å^3$. The largest peaks in the vicinity of the oxygen atom were only 0.4 $e^-/Å^3$; all of the 13 peaks above 0.8 $e^-/Å^3$ in the map are in the neighborhood of the cation and can probably be ascribed to anisotropy of thermal motion of the ethylenediamine hydrogen atoms.

In the last cycle of least-squares refinement, no atomic parameter experienced a shift as great as its estimated standard deviation, which is taken as evidence that the refinement had converged. The value of R_2 showed no dependence on sin θ or on $|F_o|$, which indicates that our choice of $p = 0.04$ is essentially correct. Examination of the final values of $|F_o|$ and $|F_c|$ suggests to us that no correction for secondary extinction is necessary.

The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. The mean-square amplitudes of vibration, U_{ij}, calculated from the thermal parameters are listed in Table III. The calculated positional parameters of the ethylenediamine hydrogen atoms are present in Table IV. The final values of $|F_o|$ and $|F_c|$ (in electrons) are given in Table V; only the 1275 reflections which were used in the final cycle are listed in Table V, in order of increasing values of sin θ.

Description of the Structure[21]

The structure consists of dimeric $Cu_2Cl_8^{4-}$ ions which are moderately well separated from discrete Cl^- ions and tris(ethylenediamine)cobalt(III) cations. The geometry of the $Cu_2Cl_8^{4-}$ anion is shown in Figure 1, and the coordination around the copper atoms is shown in Figure 2. The dimeric anion is best described as con-

---

[12] In addition to various local programs, the programs for the IBM 360/75 used in this analysis were local modifications of Hamilton's GONO9 absorption correction program, Busing, Levy, and Martin's ORFLS least-squares and ORFFE function and error programs, Zalkin's FORDAP Fourier program, Ibers' PICKOUT processing program, and Doeden's RSCAN program.

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

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

[15] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, Table 3.3.1A.

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

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

[18] R. G. Delaplane and J. A. Ibers, *J. Chem. Phys.*, **45**, 3451 (1966).

[19] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 64.

[20] L. Manojlovic-Muir, K. W. Muir, and J. A. Ibers, *Inorg. Chem.*, **9**, 447 (1970).

[21] A preliminary account of this structure has already been published: D. J. Hodgson, P. K. Hale, J. A. Barnes, and W. E. Hatfield, *Chem. Commun.*, 786 (1970).

TABLE I

POSITIONAL PARAMETERS FOR $[Co(N_2C_2H_8)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$

Atom	*x*	*y*	*z*
Cu	−0.0295 (1)[a]	−0.0096 (1)	0.1013 (1)
Co	0.3407 (1)	0.1713 (1)	0.1127 (1)
Cl1	0.1334 (3)	−0.0304 (2)	0.1368 (3)
Cl2	0.0197 (3)	0.1112 (2)	0.0249 (2)
Cl3	−0.1744 (3)	0.0613 (3)	0.1292 (3)
Cl4	−0.0782 (3)	−0.1380 (3)	0.1620 (3)
Cl5	0.0987 (3)	0.3765 (2)	0.0724 (2)
O	0.4624 (9)	0.2424 (8)	0.3325 (7)
N1	0.3067 (9)	0.0875 (7)	0.0304 (7)
N2	0.3124 (9)	0.2670 (8)	0.0381 (7)
N3	0.2037 (9)	0.1755 (7)	0.1457 (7)
N4	0.3626 (9)	0.2597 (7)	0.1934 (7)
N5	0.3749 (9)	0.0677 (7)	0.1812 (7)
N6	0.4824 (9)	0.1692 (7)	0.0879 (7)
C1	0.3130 (12)	0.1344 (10)	−0.0419 (9)
C2	0.2643 (12)	0.2293 (10)	−0.0278 (10)
C3	0.1999 (11)	0.2094 (10)	0.2248 (9)
C4	0.2691 (12)	0.2891 (10)	0.2273 (9)
C5	0.4842 (13)	0.0640 (10)	0.1907 (9)
C6	0.5322 (12)	0.0888 (10)	0.1167 (9)

[a] The numbers in parentheses here and elsewhere in this paper refer to the estimated standard deviation in the least significant figure.

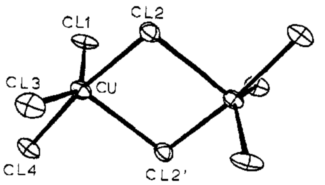

Figure 1.—View of the dimeric anion $Cu_2Cl_8^{4-}$. Cl2 is axial to the labeled copper atom and equatorial to the unlabeled copper atom. The thermal ellipsoids in all figures in this paper are drawn at the 40% probability level.

sisting of two distorted trigonal bipyramids which share a common edge. Hence, the bridging atom Cl2 is axial to one copper atom and equatorial to the other. The Cu–Cl2–Cu′–Cl2′ moiety is strictly planar, there being a crystallographic inversion center in the middle of the dimer.

This anion represents the first known example of edge sharing of two trigonal bipyramids. The distortions from trigonal-bipyramidal geometry, while severe, are insufficient to justify consideration of tetragonal-pyramidal geometry as an appropriate description of the co-

TABLE II

THERMAL PARAMETERS FOR $[Co(C_2N_2H_8)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00265 (13)	0.00190 (9)	0.00229 (8)	0.00008 (9)	0.00013 (10)	0.00040 (7)
Co	0.00199 (14)	0.00140 (8)	0.00166 (8)	−0.00010 (9)	−0.00003 (9)	−0.00009 (8)
Cl1	0.0022 (3)	0.0017 (2)	0.0045 (2)	−0.0002 (2)	−0.0007 (2)	0.0006 (2)
Cl2	0.0038 (3)	0.0023 (2)	0.0021 (2)	−0.0004 (2)	0.0004 (2)	0.0003 (1)
Cl3	0.0030 (3)	0.0027 (2)	0.0038 (2)	0.0008 (2)	0.0002 (2)	0.0001 (2)
Cl4	0.0027 (3)	0.0024 (2)	0.0033 (2)	0.0002 (2)	0.0006 (2)	0.0008 (2)
Cl5	0.0033 (3)	0.0022 (2)	0.0023 (2)	0.0000 (2)	−0.0002 (2)	−0.0002 (1)
O	0.0051 (9)	0.0045 (7)	0.0021 (6)	0.0004 (7)	−0.0011 (6)	−0.0002 (5)
N1	0.0038 (9)	0.0029 (6)	0.0007 (5)	0.0002 (6)	0.0003 (5)	−0.0004 (4)
N2	0.0033 (9)	0.0026 (7)	0.0017 (5)	0.0004 (6)	−0.0010 (6)	0.0002 (5)
N3	0.0030 (9)	0.0023 (6)	0.0018 (5)	−0.0009 (6)	0.0004 (6)	0.0002 (5)
N4	0.0034 (9)	0.0010 (6)	0.0024 (6)	0.0000 (6)	−0.0013 (6)	−0.0004 (5)
N5	0.0029 (10)	0.0020 (6)	0.0023 (5)	0.0006 (6)	−0.0012 (6)	−0.0004 (5)
N6	0.0035 (9)	0.0022 (6)	0.0016 (5)	−0.0009 (6)	0.0004 (6)	0.0000 (4)
C1	0.0036 (12)	0.0033 (9)	0.0012 (6)	0.0003 (8)	0.0002 (7)	−0.0003 (6)
C2	0.0028 (12)	0.0026 (8)	0.0021 (7)	−0.0001 (8)	−0.0012 (8)	0.0000 (6)
C3	0.0015 (11)	0.0029 (8)	0.0017 (7)	0.0002 (7)	0.0008 (7)	0.0001 (6)
C4	0.0027 (12)	0.0028 (8)	0.0020 (8)	0.0001 (8)	−0.0002 (8)	−0.0005 (6)
C5	0.0047 (14)	0.0025 (8)	0.0016 (7)	0.0007 (8)	−0.0019 (8)	0.0001 (6)
C6	0.0029 (11)	0.0035 (8)	0.0011 (6)	0.0008 (8)	0.0004 (8)	−0.0002 (6)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE III

MEAN-SQUARE AMPLITUDES OF VIBRATION (Å²)

Atom	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.024713	0.020446	0.037090	0.000765	0.001538	0.005251
Co	0.018531	0.015013	0.026934	−0.000956	−0.000326	−0.001239
Cl1	0.020496	0.017983	0.073026	−0.002093	−0.008932	0.007532
Cl2	0.035831	0.024850	0.033433	−0.003780	0.004317	0.004141
Cl3	0.027704	0.028593	0.060857	0.007523	0.002472	0.001532
Cl4	0.024766	0.026117	0.053775	0.001569	0.007835	0.010933
Cl5	0.030645	0.023750	0.037232	−0.000257	−0.002276	−0.003012
O	0.047557	0.048872	0.033882	0.004420	−0.013073	−0.003177
N1	0.035004	0.030847	0.010709	0.002253	0.004041	−0.005010
N2	0.030804	0.028271	0.028036	0.004394	−0.011748	0.002384
N3	0.028211	0.024323	0.029867	−0.008784	0.004391	0.003107
N4	0.031244	0.010850	0.039588	0.000494	−0.016357	−0.004996
N5	0.027227	0.020996	0.037216	0.006162	−0.014993	−0.005397
N6	0.032228	0.023424	0.025708	−0.008645	0.004349	−0.000183
C1	0.033254	0.035908	0.019654	0.002680	0.003033	−0.003319
C2	0.026080	0.027618	0.034662	−0.001133	−0.014620	0.000303
C3	0.013787	0.029901	0.027009	0.002049	0.010318	0.001422
C4	0.024779	0.029728	0.032959	0.000953	−0.001869	−0.006869
C5	0.043574	0.026934	0.026545	0.007233	−0.023491	0.000986
C6	0.026791	0.037238	0.018456	0.007878	0.005044	−0.002624

[a] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23} \cdot klb^*c^*)]$.

TABLE IV

CALCULATED POSITIONAL PARAMETERS OF ETHYLENEDIAMINE HYDROGEN ATOMS

Atom[a]	x	y	z
H11	0.3503	0.0377	0.0310
H12	0.2428	0.0657	0.0374
H21	0.2718	0.3111	0.0595
H22	0.3718	0.2945	0.0238
H31	0.1682	0.2152	0.1147
H32	0.1762	0.1169	0.1423
H41	0.4023	0.2325	0.2301
H42	0.3956	0.3108	0.1743
H51	0.3447	0.0764	0.2273
H52	0.3529	0.0125	0.1605
H61	0.4890	0.1698	0.0359
H62	0.5120	0.2213	0.1076
H13	0.2767	0.0992	−0.0812
H14	0.3837	0.1416	−0.0574
H23	0.1922	0.2212	−0.0183
H24	0.2746	0.2699	−0.0718
H33	0.2219	0.1596	0.2597
H34	0.1314	0.2285	0.2380
H43	0.2803	0.3082	0.2806
H44	0.2411	0.3420	0.1988
H53	0.5039	0.0006	0.2064
H54	0.5041	0.1087	0.2305
H63	0.5248	0.0366	0.0809
H64	0.6033	0.1024	0.1247

[a] The digits define to which atom the H atom is bonded. If the right digit is 1 or 2, the H atom is bonded to the N atom given by the left digit; if the right digit is 3 or 4, the H atom is bonded to the corresponding C atom. Thus H34 is an atom bonded to C3, and H31 is bonded to N3.

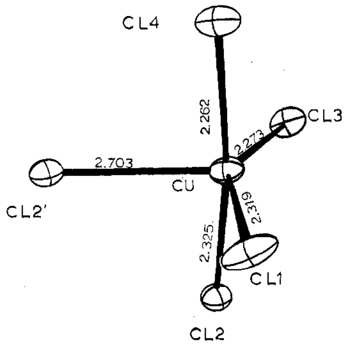

Figure 2.—View of the inner coordination sphere about Cu in $Cu_2Cl_8^{4-}$. Cl1, Cl3, and Cl2′ are the equatorial ligands while Cl2 and Cl4 are axial.

ordination at the copper atom; hence, this ion is markedly different from the recently reported[22] $Ni_2Cl_8^{4-}$ ion, in which the Ni atoms clearly have tetragonal-pyramidal geometry. For trigonal-bipyramidal geometry at the copper, the atoms Cl1, Cl2′, and Cl3 are the equatorial ligands while Cl2 and Cl4 are axial. The Cu atom and these three equatorial atoms are very nearly coplanar, the deviations from the least-squares plane through them being less than 0.02 Å; the angle between this "trigonal" plane and the axial plane defined by Cu, Cl2, and Cl4 is 89.1°, very close to the value of 90° predicted for perfect trigonal-bipyramidal geometry. The principal distortion from trigonal-bipyramidal geometry is caused by the opening of the Cl1–Cu–Cl3 bond angle to 145.3 (2)°, along with the associated closing of the Cl1–Cu–Cl2′ angle to 96.3 (2)°. If the geometry around copper is viewed as a distorted tetragonal pyramid, the axial ligand is Cl2′ (a bridging atom) and the basal ligands are Cl1, Cl2, Cl3, and Cl4. Hence, even in this view the geometry is quite different from that of $Ni_2Cl_8^{4-}$, where the bridging atoms Cl2 and Cl2′ are both in the basal plane, and a terminal chlorine ligand is axial.[22] It is noteworthy that in $Ni_2Cl_8^{4-}$ the four Cl(axial)–Ni–Cl(basal) angles lie in the range 99–106°, as is usually the case for tetragonal-pyramidal transition metal complexes; *i.e.*, the metal lies above the basal plane. In $Cu_2Cl_8^{4-}$, however, two of the Cl(axial)–Cu–Cl(equatorial) angles would be less than 90° and two greater than 90°. This is taken as further evidence that the geometry at Cu is much more readily described as being a distorted trigonal bipyramid. The bond lengths and angles found in the dimeric anion are listed in Table VI, and the angles are compared with those predicted for each of the two idealized five-coordinate geometries.

There is clearly no copper–copper bond in the dimer, the Cu–Cu distance of 3.722 (5) Å being much greater than the values of 2.63–2.99 Å found for Cu–Cu bonds in other dimers.[23] This relatively short nonbonded Cu–Cu separation brings about exchange coupling in the dimer,[21] perhaps through the orbitals of the bridging ligands, and preliminary magnetic studies at low temperatures demonstrate[24] that the complex exhibits antiferromagnetic behavior. The bridged Cu–Cl bonds are of unequal lengths, but the values of 2.325 (4) and 2.703 (5) Å fall within the range of 2.303–3.185 Å found[25] in other metal–chloride bridged systems. The Cl2–Cl2′ separation of 3.403 (8) Å is quite large and falls well outside the range of 3.05–3.35 Å reported for 17 other four-membered ring systems involving chlorine bridges.[22] Moreover, there are four intramolecular Cl–Cl separations in $Cu_2Cl_8^{4-}$ in the range 3.236 (6)–3.306 (6) Å which are significantly shorter than this intra-ring distance, and there are intramolecular Cl–Cl separations[26] of 3.315 Å in $CuCl_5^{3-}$. Ross and Stucky[22] have noted that chlorine-bridged four-membered ring geometries are probably determined by Cl–Cl intra-ring nonbonded forces and suggested that 3.14 ± 0.02 Å is the optimum separation. The much larger distance found in $Cu_2Cl_8^{4-}$ is a result of the relatively long Cu–Cl bond lengths as compared with Ni–Cl distances of 2.366 (2) and 2.449 (2) Å in $Ni_2Cl_8^{4-}$. For the average Cu–Cl bridged bond length of 2.514 Å in $Cu_2Cl_8^{4-}$ Ross and Stucky would predict a Cu–Cl–Cu′ angle of approximately 102°, well in excess of the observed value of 95.2 (1)°. Since the four-membered ring is constrained to be planar, the Cl2–Cu–Cl2′ angle is 84.8 (1)°. It is evident that in the present case the ring geometry is not determined by the Cl–Cl interaction.

The structure of the tris(ethylenediamine)cobalt(III) cation found in this molecule is of great interest and is shown in Figure 3. In the figure we show a Δ configuration, although in this centrosymmetric space group there are an equal number of Λ and Δ forms. Corey and Bailar[27] have calculated that for a Δ configuration at the metal atom, the lowest energy conformation of the ethylenediamine rings is the Δ(λλλ) conformation, although more recent calculations by Gollogly and

---

[22] F. K. Ross and G. D. Stucky, *J. Amer. Chem. Soc.*, **92**, 4538 (1970), and references therein.

[23] G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 5244 (1961); G. A. Barclay and B. F. Hoskins, *ibid.*, 1979 (1965).

[24] J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *Chem. Phys. Lett.*, **7**, 374 (1970).

[25] R. D. Willet and R. E. Rundle, *J. Chem. Phys.*, **40**, 838 (1964).

[26] Values calculated from the data given in ref 2a.

[27] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

TABLE V

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES IN ELECTRONS

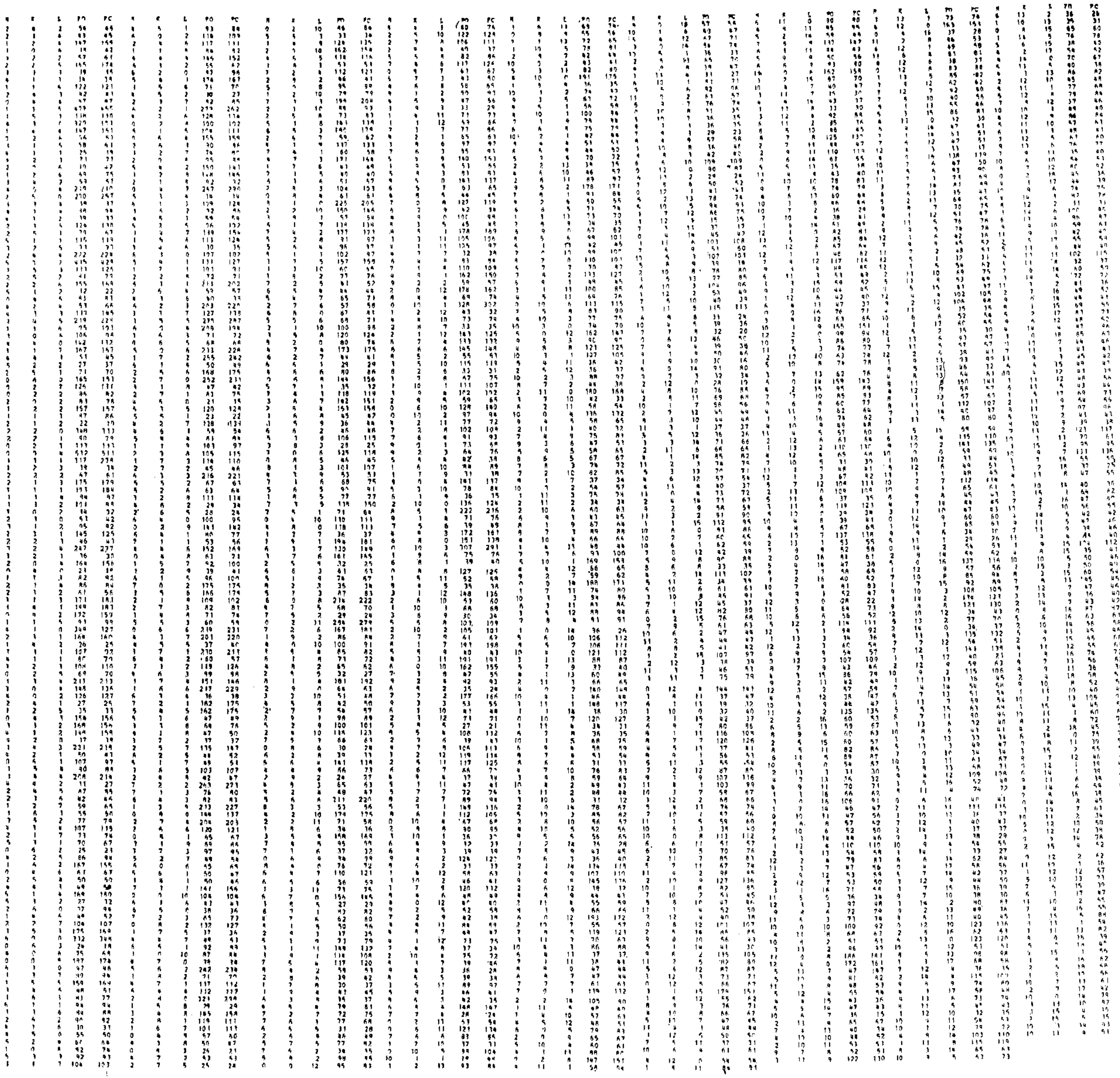

TABLE VI

INTRAMOLECULAR DISTANCES AND ANGLES IN $Cu_2Cl_8{}^{4-}$

Atoms	Distance, Å	Atoms	Angle, deg	TBP,[a] deg	SP,[b] deg
Cu-Cu′	3.722 (5)	Cl1-Cu-Cl2	89.2 (2)	90	90
Cu-Cl1	2.319 (5)	Cl1-Cu-Cl2′	96.3 (2)	120	90
Cu-Cl2	2.325 (4)	Cl1-Cu-Cl3	145.3 (2)	120	180
Cu-Cl3	2.273 (5)	Cl1-Cu-Cl4	92.2 (2)	90	90
Cu-Cl4	2.262 (4)	Cl2-Cu-Cl2′	84.8 (1)	90	90
Cu-Cl2′	2.703 (5)	Cl2-Cu-Cl3	91.9 (2)	90	90
Cl2-Cl2′	3.403 (8)	Cl2-Cu-Cl4	172.6 (2)	180	180
Cl1-Cl2	3.261 (6)	Cl2′-Cu-Cl3	118.3 (2)	120	90
Cl1-Cl2′	3.750 (7)	Cl2′-Cu-Cl4	87.8 (2)	90	90
Cl1-Cl3	4.383 (7)	Cl3-Cu-Cl4	91.1 (2)	90	90
Cl1-Cl4	3.301 (6)	Cu-Cl2-Cu′	95.2 (1)	...	...
Cl2-Cl3	3.306 (6)				
Cl2′-Cl3	4.278 (6)				
Cl2′-Cl4	3.458 (6)				
Cl3-Cl4	3.236 (6)				

[a] Angle predicted for trigonal-bipyramidal geometry at Cu, with Cl2 and Cl4 axial and Cl1, Cl2′, and Cl3 equatorial. [b] Angle predicted for square-pyramidal geometry at Cu, with Cl2′ axial and Cl1, Cl3, and Cl4 equatorial.

Hawkins[28] suggest that there is very little energy difference between the Δ(λλλ) and Δ(λλδ) forms. Ibers, Raymond, and their coworkers,[6,29] however, have demonstrated the existence of all possible combinations of δ and λ rings and have attributed the occurrence of the higher energy forms to the presence of intermolecular hydrogen bonds. This hypothesis received some confirmation by Enemark and his coworkers[30] in their recent study of $[Cr(en)_3][Cr(CN)_5NO]\cdot 2H_2O$, in which they find the Δ(λδδ) conformation. In the present case we also find that for a Δ configuration at the cobalt atom the conformation is the energetically unfavored Δ(δδλ) form. The deviations from the expected Δ(λλλ) structure can again be explained in terms of intermolecular interactions. The low-energy λ ring is involved in a strong hydrogen bond with the water molecule, the

---

(28) J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **9**, 576 (1970).

(29) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 842 (1968); K. N. Raymond and J. A. Ibers, *ibid.*, **7**, 2333 (1968).

(30) J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *ibid.*, **9**, 2397 (1970).

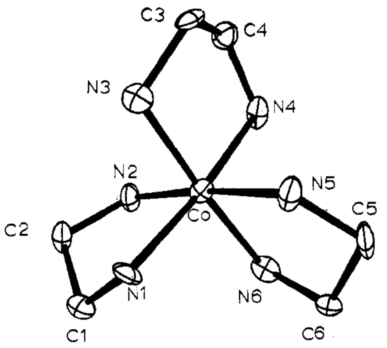

Figure 3.—View of the $Co(N_2C_2H_8)_3{}^{3+}$ ion. The configuration shown is Δ(δδλ), but in this centrosymmetric structure there are an equal number of Λ(λλδ) configurations. The λ ring is the central ring ($Co–N_4–C_4–C_3–N_3–Co$). The hydrogen atoms are not shown.

$N_4–H---O$ distance being 2.84 Å and the angle at the calculated position of H_{41} being 147°. This separation is shorter than any that could be found in the literature for similar compounds.[2,6,29,31] The distortions from the expected geometry of the two δ rings can be attributed to interactions between the rings and the chlorine and oxygen atoms. There are, for example, seven quite short N–H---Cl separations, ranging from 3.15 to 3.41 Å; these are in the range of 3.11–3.41 Å found in several related compounds.[32–37] Similarly, there are O---Cl distances of 3.18, 3.28, and 3.30 Å, in the range of 2.86–3.34 Å found in the literature.[32,34,36–39] While these interactions can be considered the causes of the conversions from λ to δ forms, this work provides further evidence for the conclusion that the difference in energy between the two forms cannot be much greater than 1 or 2 kcal/mol. A more complete analysis of the hydrogen bonding in this system is probably not justified in view of our failure to locate the hydrogen atoms of the water molecule and the fact that the other hydrogen atom locations are calculated rather than observed values.

The bond distances and angles found in the cation are consistent with those found by other workers for similar systems[6,27,29,32,33] and are presented along with their estimated standard deviations in Table VII.

TABLE VII

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES IN $Co(en)_3{}^{3+}$

Atoms	Distance, Å	Atoms	Angle, deg	Atoms	Angle, deg
Co–N1	1.968 (12)	Ni–Co–N2	83.5 (5)	Co–N1–C1	110.9 (9)
Co–N2	1.969 (12)	N3–Co–N4	83.3 (5)	Co–N2–C2	111.6 (8)
Co–N3	1.950 (13)	N5–Co–N6	84.3 (5)	Co–N3–C3	109.1 (9)
Co–N4	1.957 (12)	N1–Co–N3	91.3 (5)	Co–N4–C4	111.4 (9)
Co–N5	1.998 (12)	N1–Co–N4	174.8 (5)	Co–N5–C5	109.1 (9)
Co–N6	1.973 (13)	N1–Co–N5	92.6 (5)	Co–N6–C6	112.7 (10)
N1–C1	1.464 (19)	N1–Co–N6	92.8 (5)	N1–C1–C2	104.4 (13)
N2–C2	1.455 (18)	N2–Co–N3	89.8 (5)	N2–C2–N1	106.1 (12)
N3–C3	1.499 (20)	N2–Co–N4	93.6 (5)	N3–C3–C4	105.3 (13)
N4–C4	1.469 (20)	N2–Co–N5	174.9 (5)	N4–C4–C3	107.6 (12)
N5–C5	1.493 (20)	N2–Co–N6	92.7 (5)	N5–C5–C6	108.5 (13)
N6–C6	1.448 (18)	N3–Co–N5	93.4 (5)	N6–C6–C5	107.6 (13)
C1–C2	1.551 (21)	N3–Co–N6	175.3 (6)		
C3–C4	1.492 (20)	N4–Co–N5	90.6 (5)		
C5–C6	1.519 (22)	N4–Co–N6	91.6 (5)		

It is our belief that other, perhaps similar, polynuclear species will be obtained from aqueous solutions of transition metal halides, and we are continuing our magnetic and structural investigations in this area.

Acknowledgments.—We are grateful to Professors James A. Ibers and Robert J. Doedens and to Dr. Ward T. Robinson for programming assistance. We are also grateful to Professor John H. Enemark for giving us a preprint of his paper. This research was supported by the Materials Research Center of the University of North Carolina under Contract SD-100 with the Advanced Research Projects Agency and by a grant toward purchase of the diffractometer from the National Science Foundation under Grant GP-10300.

---

(31) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, p 287.

(32) K. Nakatsu, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **29**, 428 (1956).

(33) K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *ibid.*, **30**, 158 (1957).

(34) J. M. Broomhead, *Acta Crystallogr.*, **1**, 324 (1948).

(35) W. P. Binnie and J. M. Robertson, *ibid.*, **2**, 180 (1949).

(36) D. C. Phillips, *ibid.*, **7**, 159 (1954).

(37) J. Trommel and J. M. Bijvoet, *ibid.*, **7**, 703 (1954).

(38) Y. Sasada and I. Nitta, *Bull. Chem. Soc. Jap.*, **30**, 62 (1957).

(39) B. Jerslev, *Acta Crystallogr.*, **1**, 21 (1948).