

each of the complexes over the concentration range of  $10^{-2}$ – $10^{-4}$  *M* and were compared to corresponding values obtained for a series of standard 1:1, 1:2, and 1:3 electrolytes. The curves for each of the standards showed distinct shapes and were located in definite regions over the concentration range studied. Assignment of the nature of each tribromide complex was made by comparison of these conductance curves with those of known perchlorate complexes. Unless otherwise noted the conductance studies were carried out in DMF.

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## The Crystal and Molecular Structure of Tris(ethylenediamine)cobalt(III) Hexachlorocadmiate(II) Dichloride Dihydrate, $[\text{Co}(\text{N}_2\text{C}_2\text{H}_8)_3]_2[\text{CdCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

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The crystal and molecular structure of tris(ethylenediamine)cobalt(III) hexachlorocadmiate(II) dichloride dihydrate,  $[\text{Co}(\text{en})_3]_2[\text{CdCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in the space group  $C_{2h}^5-P2_1/c$  of the monoclinic system with two molecules in a cell of dimensions  $a = 13.303$  (10),  $b = 9.434$  (8),  $c = 14.160$  (15) Å, and  $\beta = 110.22$  (3)°. The observed and calculated densities are 1.80 (2) and 1.815 g cm<sup>-3</sup>, respectively. Least-squares refinement of the structure has yielded a final value for the conventional *R* factor (on *F*) of 0.049 for 1941 independent reflections having  $F^2 > \sigma(F^2)$ . The  $\text{CdCl}_6^{4-}$  anion is a distorted octahedron, the Cd–Cl bond distances being 2.588 (3), 2.617 (2), and 2.765 (2) Å, and the bond angles at Cd ranging from 84.67 (8) to 95.33 (8)°. The  $\text{Co}(\text{en})_3^{3+}$  cation is found to have the low-energy conformation of  $\Lambda(\delta\delta\delta)$  ( $\equiv \Delta(\lambda\lambda\lambda)$ ). Intermolecular interactions between hydrogen atoms of the ethylenediamine ligands and the chlorine atoms in the cadmate anion are also observed.

### Introduction

In an attempt to synthesize a diamagnetic host lattice for the magnetically important tris(ethylenediamine)cobalt(III) di- $\mu$ -chloro-bis(trichlorocuprate(II)) dichloride hydrate,  $[\text{Co}(\text{en})_3]_2[\text{Cu}_2\text{Cl}_8]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , system,<sup>1</sup> cadmium dichloride,  $\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$ , was allowed to react with tris(ethylenediamine)cobalt(III) chloride in aqueous acid solution. The product of this reaction has the empirical formula  $[\text{Co}(\text{en})_3]_2\text{CdCl}_8 \cdot 2\text{H}_2\text{O}$ . Recent work<sup>2</sup> has shown that when  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  or  $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$  are allowed to react with  $\text{CdCl}_2$  under similar conditions, the reaction products are  $\text{Co}(\text{NH}_3)_6\text{CdCl}_5$  or  $\text{Cr}(\text{NH}_3)_6\text{CdCl}_5$ , with trigonal-bipyramidal geometry at the cadmium. A complete three-dimensional structural investigation of the complex  $[\text{Co}(\text{en})_3]_2\text{CdCl}_8 \cdot 2\text{H}_2\text{O}$  was undertaken in part to determine the nature of the anionic species present and in part in order to investigate further the conformations of tris(ethylenediamine)cobalt(III) systems.

### Experimental Section

The golden-yellow compound was prepared by treating 1.77 g of  $\text{Co}(\text{en})_3\text{Cl}_3$  (0.005 mol) with 2.28 g of  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$  (0.01 mol) in 80 ml of 3 *M* HCl. The reaction mixture was concentrated to 50 ml on a steam bath and allowed to stand at room temperature. After 2 hr the large crop of golden-yellow crystals was filtered and air-dried. The material was recrystallized from 3 *M* HCl, yielding well-formed hexagonal plates.

*Anal.*<sup>3</sup> Calcd for  $\text{C}_{12}\text{N}_{12}\text{H}_{52}\text{Co}_2\text{CdCl}_8\text{O}_2$ : C, 15.83; N, 18.46; H, 5.76; Co, 12.95; Cd, 12.35; Cl, 31.15; mol wt 910.52. Found: C, 15.74; N, 18.40; H, 5.75; Co, 12.70; Cd, 12.49; Cl, 31.06.

On the basis of Weissenberg and precession photographs the crystals were assigned to the monoclinic system. The observed systematic absences are  $h0l$  for  $l$  odd and  $0k0$  for  $k$  odd, which strongly suggests that the space group is  $C_{2h}^5-P2_1/c$ , a unique space group. The lattice constants, obtained by the least-squares procedure described previously,<sup>4</sup> are  $a = 13.303$  (10),  $b = 9.434$  (8),  $c = 14.160$  (15) Å, and  $\beta = 110.22$  (3)°. A density of 1.815 g cm<sup>-3</sup> calculated for two formula units in the cell agrees well with the value of 1.80 (2) g cm<sup>-3</sup> obtained by flotation in ethyl iodide-carbon tetrachloride solution. Hence, the Cd atoms are constrained to lie on a crystallographic inversion center.

Diffraction data were collected at 22° with the wavelength assumed as  $\lambda(\text{Mo K}\alpha_1)$  0.7093 Å using a Picker four-circle automatic diffractometer. A hexagonal-plate crystal in which the hexagonal faces were (100) and ( $\bar{1}00$ ) and the six rectangular faces were (010), (0 $\bar{1}0$ ), (01 $\bar{1}$ ), (0 $\bar{1}1$ ), (011), and (0 $\bar{1}1$ ) was chosen. The separation of the hexagonal faces was 0.032 mm, the distance between the (011) and (0 $\bar{1}1$ ) faces was 0.340 mm, and the distance between the (0 $\bar{1}0$ ) and (010) faces was 0.635 mm. The crystal was mounted on a glass fiber normal to the (0 $\bar{1}1$ ) planes, and in this orientation intensity data were collected. The mosaicity of the crystal was examined by means of the narrow-source, open-counter  $\omega$ -scan technique.<sup>5</sup> The width at half-height for a typical strong reflection was found to be approximately 0.12°; this value is as large as we would normally consider acceptable, but since the general shape of the  $\omega$  scans was symmetric and unsplit, we are confident that this is a single crystal. Twelve reflections, accurately centered through a nar-

(1) J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *Chem. Phys. Lett.*, **7**, 374 (1970); D. J. Hodgson, P. K. Hale, J. A. Barnes, and W. E. Hatfield, *Chem. Commun.*, 786 (1970).

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

(3) Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(4) D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, **10**, 1061 (1971).

(5) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

row vertical slit at a takeoff angle of  $1.0^\circ$ , formed the basis for the least-squares refinement of cell parameters and orientation. This refinement was effected using the logic documented by Busing and Levy<sup>6</sup> in the PDP-8/L computer.

Intensity data were collected at a takeoff angle of  $1.3^\circ$ ; at this angle the peak intensity for a typical strong reflection was about 85% of the maximum value as a function of takeoff angle. The counter aperture was 4.0 mm high by 4.0 mm wide and was positioned 32 cm from the crystal. The data were collected by the  $\theta$ - $2\theta$  scan technique at a scan rate of  $1^\circ/\text{min}$ . Allowance was made for the presence of both  $K\alpha_1$  and  $K\alpha_2$  radiations, the scan range for each reflection being from  $1.0^\circ$  below the calculated  $K\alpha_1$  peak position to  $1.0^\circ$  above the calculated  $K\alpha_2$  peak position.

Stationary-counter, stationary-crystal background counts of 10 sec were taken at each end of the scan. The diffracted beam was filtered through a 3.0-mil Nb foil. Cu foil attenuators giving attenuator factors of approximately 2.3 were inserted automatically when the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan; these attenuator factors were determined by the method previously described.<sup>7</sup> The pulse height analyzer was set for approximately a 90% window, centered on the Mo  $K\alpha$  peak.

A unique data set having  $2\theta < 45^\circ$  was gathered; a total of 2482 independent intensities were recorded. The intensities of three standard reflections were measured after every 100 reflections and showed only the deviations from the mean predicted from counting statistics. There were very few data above background at values of  $2\theta > 45^\circ$ .

Data processing was carried out as described by Corfield, *et al.*<sup>8</sup> 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 0.05. This term in the expression is used to prevent extremely high weight being given to very large reflections.<sup>9</sup> The values of  $I$  and  $\sigma(I)$  were corrected for Lorentz and polarization effects and for absorption factors. The absorption coefficient for this compound for Mo  $K\alpha$  radiation is  $23.04 \text{ cm}^{-1}$ , and for the sample chosen the transmission coefficients evaluated by numerical integration were found to range from 0.49 to 0.92. Of the 2482 independent reflections, 1946 were greater than their estimated standard deviations.

### Solution and Refinement

All least-squares refinements in this analysis were carried out on  $F$ , the function minimized being  $\sum w(|F_o| - |F_c|)^2$ ; 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 Cd and Co were taken from Cromer and Waber,<sup>10</sup> that for H was taken from Stewart, Davidson, and Simpson,<sup>11</sup> and those for Cl, C, and N were taken from the tabulation of Ibers.<sup>12</sup> The effects of anomalous dispersion<sup>13</sup> were included in calculations of  $F_c$ , the values of  $\Delta f'$  and  $\Delta f''$  being taken from the tabulations of Cromer.<sup>14</sup> The 1689 independent intensities which were greater than three times their estimated standard deviations were used for the initial refinement of the structure, and the 1946 independent intensities which were greater than their estimated standard deviations were used for the final refinement.

The Cd atom is constrained to lie at the origin in space group  $P2_1/c$ ; the position of the Co atom was determined from a three-dimensional Patterson function. Two cycles of least-squares refinement on the Cd and Co positions using isotropic thermal parameters were run. The usual agreement factors,  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_2$  (or weighed  $R$  factor) =

$(\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2)^{1/2}$ , were 0.623 and 0.662, respectively.<sup>16</sup>

The remaining nonhydrogen atoms were located in subsequent difference Fourier maps, and least-squares refinement of these atoms with isotropic thermal parameters yielded values of 0.118 and 0.132 for  $R_1$  and  $R_2$ . Two further cycles in which the atoms were assigned variable anisotropic thermal parameters were run, the resulting values of  $R_1$  and  $R_2$  being 0.074 and 0.106.

The positions of the ethylenediamine hydrogen atoms were 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.<sup>16</sup> The hydrogen atoms were assigned fixed isotropic thermal parameters of  $3.5 \text{ \AA}^2$ , and their positions were not refined. Two cycles of least-squares yielded values for  $R_1$  and  $R_2$  of 0.049 and 0.062.

A difference Fourier synthesis completed at this stage showed no peak higher than  $1.5 \text{ e \AA}^{-3}$ , but there were three peaks between 1.0 and  $1.5 \text{ e \AA}^{-3}$  in the vicinity of the oxygen atom; these peaks could not be interpreted as hydrogen atoms in view of the known geometry of water. All other peaks greater than  $0.7 \text{ e \AA}^{-3}$  were close to the two metal atoms and can probably be ascribed to the inadequacy of our description of the thermal motion of these atoms. The peak height of a typical carbon atom in this analysis was about  $3.5 \text{ e \AA}^{-3}$ .

After two cycles of least-squares refinement, using all intensities greater than their estimated standard deviations, no atomic parameter experienced a shift as great as its estimated standard deviation, which indicated the refinement had converged. 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 this last least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. The calculated positional parameters of the

TABLE I

POSITIONAL PARAMETERS FOR  $[\text{Co}(\text{N}_2\text{C}_2\text{H}_8)_3]_2[\text{CdCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ 

Atom	X	Y	Z
Cd	0.00	0.00	0.00
Co	0.2612 (1) <sup>a</sup>	0.4691 (1)	0.1965 (1)
Cl1	0.1380 (1)	0.0160 (2)	0.1807 (1)
Cl2	-0.0714 (2)	0.2485 (2)	0.0296 (1)
Cl3	0.1544 (1)	0.3606 (2)	0.4454 (1)
Cl4	-0.4503 (2)	0.2960 (2)	0.1524 (1)
N1	0.3359 (5)	0.4747 (6)	0.3440 (4)
N2	0.3133 (4)	0.2727 (5)	0.2040 (4)
N3	0.1263 (4)	0.4045 (6)	0.2092 (4)
N4	0.2070 (4)	0.6627 (5)	0.2021 (4)
N5	0.3881 (4)	0.5479 (6)	0.1722 (4)
N6	0.1975 (4)	0.4576 (5)	0.0491 (4)
C1	0.4079 (5)	0.3503 (8)	0.3746 (5)
C2	0.3502 (6)	0.2263 (7)	0.3111 (5)
C3	0.0508 (6)	0.5274 (8)	0.1895 (6)
C4	0.1138 (6)	0.6548 (8)	0.2383 (6)
C5	0.3569 (6)	0.5932 (8)	0.0655 (5)
C6	0.2819 (6)	0.4809 (7)	0.0042 (5)
O1	0.3515 (6)	-0.0407 (8)	0.1185 (7)

<sup>a</sup> The numbers in parentheses here and elsewhere in this paper refer to the estimated standard deviations in the least significant figure.

ethylenediamine hydrogen atoms are given in Table III. A table of observed and calculated structure factors is available.<sup>17</sup>

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

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

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

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

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

(11) R. S. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(12) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, Table 3.3.1A.

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

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

(15) 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 FORAP Fourier program, Ibers' PICKOUT processing program, and Doeden's RSCAN program.

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

(17) A table of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

TABLE II  
THERMAL PARAMETERS FOR  $[\text{Co}(\text{C}_2\text{N}_2\text{H}_8)_3]_2[\text{CdCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ 

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cd	0.00518 (6)	0.00464 (9)	0.00456 (5)	0.00012 (5)	0.00147 (4)	-0.00033 (4)
Co	0.00426 (7)	0.00455 (11)	0.00351 (6)	-0.00018 (6)	0.00118 (5)	0.00005 (5)
Cl1	0.00515 (12)	0.00820 (23)	0.00503 (12)	-0.00063 (12)	0.00134 (9)	0.00018 (11)
Cl2	0.00808 (15)	0.00612 (21)	0.00454 (11)	0.00216 (14)	0.00115 (9)	0.00004 (10)
Cl3	0.00733 (15)	0.00790 (23)	0.00540 (12)	0.00181 (14)	0.00299 (10)	0.00128 (11)
Cl4	0.00696 (15)	0.01013 (26)	0.00668 (14)	0.00268 (15)	0.00241 (11)	0.00222 (14)
N1	0.00593 (44)	0.00915 (77)	0.00395 (36)	-0.00112 (44)	0.00133 (31)	0.00009 (38)
N2	0.00471 (39)	0.00646 (70)	0.00515 (37)	0.00073 (40)	0.00133 (30)	0.00002 (40)
N3	0.00491 (40)	0.00697 (69)	0.00494 (38)	-0.00063 (43)	0.00104 (30)	0.00060 (38)
N4	0.00640 (45)	0.00510 (66)	0.00428 (35)	0.00017 (42)	0.00095 (31)	0.00015 (36)
N5	0.00500 (40)	0.00853 (73)	0.00430 (36)	-0.00054 (43)	0.00173 (30)	-0.00020 (38)
N6	0.00545 (41)	0.00607 (65)	0.00396 (35)	0.00035 (41)	0.00106 (30)	-0.00008 (35)
C1	0.00471 (51)	0.00992 (104)	0.00515 (49)	0.00013 (57)	0.00027 (39)	0.00248 (54)
C2	0.00642 (61)	0.00714 (94)	0.00519 (50)	0.00095 (56)	0.00087 (42)	0.00148 (50)
C3	0.00427 (49)	0.00988 (102)	0.00670 (55)	0.00128 (55)	0.00276 (41)	0.00093 (54)
C4	0.00709 (61)	0.00789 (94)	0.00602 (52)	0.00185 (59)	0.00338 (45)	0.00085 (53)
C5	0.00621 (57)	0.00745 (89)	0.00477 (47)	0.00025 (54)	0.00262 (40)	0.00038 (48)
C6	0.00771 (60)	0.00691 (90)	0.00405 (44)	0.00011 (56)	0.00279 (42)	-0.00031 (46)
O1	0.00923 (58)	0.02013 (123)	0.01515 (75)	0.00464 (66)	0.00517 (52)	0.00069 (72)

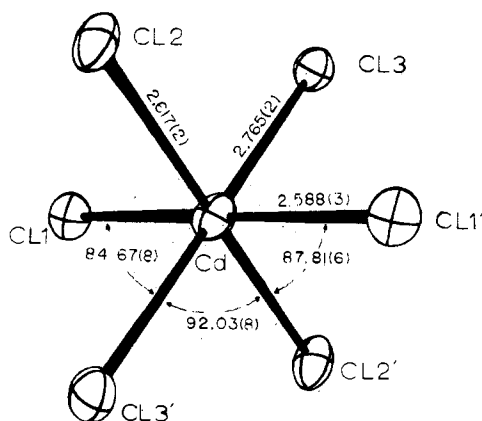
TABLE III  
CALCULATED POSITIONAL PARAMETERS OF  
ETHYLENEDIAMINE HYDROGEN ATOMS

Atom <sup>a</sup>	X	Y	Z	Atom <sup>a</sup>	X	Y	Z
H11	0.2838	0.4729	0.3767	H13	0.4250	0.3307	0.4487
H12	0.3754	0.5612	0.3616	H14	0.4771	0.3701	0.3631
H21	0.2571	0.2122	0.1634	H23	0.2871	0.1986	0.3311
H22	0.3714	0.2677	0.1785	H24	0.3997	0.1426	0.3225
H31	0.1383	0.3687	0.2748	H33	-0.0070	0.5053	0.2179
H32	0.0957	0.3305	0.1613	H34	0.0166	0.5401	0.1146
H41	0.1837	0.7051	0.1361	H43	0.1404	0.6463	0.3133
H42	0.2617	0.7212	0.2460	H44	0.0687	0.7430	0.2184
H51	0.4428	0.4776	0.1865	H53	0.4226	0.6026	0.0458
H52	0.4150	0.6271	0.2160	H54	0.3199	0.6878	0.0560
H61	0.1653	0.3651	0.0309	H63	0.3225	0.3883	0.0758
H62	0.1430	0.5268	0.0253	H64	0.2487	0.5097	-0.0684

<sup>a</sup> 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; H31 is bonded to N3.

### Description of the Structure

The structure consists of  $\text{CdCl}_6^{4-}$  ions well separated from discrete  $\text{Cl}^-$  ions, tris(ethylenediamine)cobalt(III) cations, and water molecules. The geometry of the  $\text{CdCl}_6^{4-}$  anion is shown in Figure 1, and it is apparent

Figure 1.—The  $\text{CdCl}_6^{4-}$  ion in  $[\text{Co}(\text{en})_3][\text{CdCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ .

that the coordination around the cadmium is considerably distorted from octahedral symmetry. The Cd-Cl1 and Cd-Cl2 bond lengths of 2.588 (3) and 2.617 (2)

Å fall in the range reported<sup>18</sup> for cadmium-chlorine bond distances, but the Cd-Cl3 bond length of 2.762 (2) Å is considerably longer than any Cd-Cl bond which could be found in the literature. The most severe angular distortion from the expected octahedral geometry is the Cl3-Cd-Cl1 angle of 84.67 (8)°. The only reasonable cause of the observed distortions of the anion is hydrogen bonding involving the hydrogen atoms of the ethylenediamine rings and the chlorine atoms of the anion.

Hydrogen bonding between amine nitrogen atoms and chlorine atoms has been postulated for N-H...Cl separations in the range 3.11–3.41 Å.<sup>19–25</sup> On this basis, Cl1 is involved in one hydrogen bond with a Cl-N separation of 3.293 Å, Cl2 is involved in three with Cl-N distances of 3.231, 3.263, and 3.306 Å, and Cl3 is involved in three with Cl-N separations of 3.260, 3.307, and 3.374 Å. Cl3 may also be involved in hydrogen bonding with the water molecule, the O...Cl separation of 3.360 Å being in the range of 2.86–3.40 Å reported in the literature.<sup>20,22,24–27</sup> The possible hydrogen bonds are presented in Table IV. The numbers of probable interactions for the three chlorine atoms are in the

TABLE IV  
POSSIBLE A-H...B HYDROGEN BONDS

A	B	A...B, Å	Angle at H, deg	A	B	A...B, Å	Angle at H, deg
N2	Cl1	3.293	140.3	N3	Cl3	3.260	161.4
N6	Cl2	3.231	154.4	N6	Cl3	3.307	151.4
N4	Cl2	3.263	159.2	N1	Cl3	3.374	155.7
N3	Cl2	3.306	144.1	O1 <sup>a</sup>	Cl3	3.450	...

<sup>a</sup> Hydrogens for the water molecule were not located.

(18) H. Paulus and S. Gottlicher, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **130**, 267 (1969); L. Cavalca, P. Domiano, A. Musatti, and P. Sgarabotto, *Chem. Commun.*, 1136 (1968); L. Pauling and J. L. Hoard, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **74**, 546 (1930); M. Nardelli, L. Cavalca, and A. Braibanti, *Gazz. Chim. Ital.*, **87**, 138 (1957).

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

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

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

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

(23) W. P. Binne and J. M. Robertson, *ibid.*, **2**, 180 (1949).

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

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

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

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

right order to account for the differences in the Cd-Cl bond lengths; *i.e.*, the Cd-Cl3 bond is elongated as a result of its greater degree of hydrogen bonding. It is noteworthy that the angles at the calculated hydrogen positions are more nearly linear for the hydrogen bonds involving Cl3 and, hence, that the Cl...H separations are shorter for Cl3 than for Cl1 or Cl2. These interactions also account for the angular distortions in the anion noted previously.

Distortions of chlorocadmate anions due to apparent hydrogen bonding have also been seen in the structure of  $(\text{N}_2\text{H}_5)_3\text{CdCl}_5$  reported by Braibanti and Tiripicchio.<sup>28</sup> The anion consists of a zigzag polymeric chain with bridging chlorine atoms *cis* to each other. The  $\text{N}_2\text{H}_5^+$  units sit in the holes of the alternating chain giving rise to several N-H...Cl interactions. The Cd-Cl bonds for the terminal chlorine atoms in this system range from 2.549 to 2.642 Å; the angles in the inner coordination sphere range from 82.64 to 90.27°. There are sixteen N-H...Cl contacts in the system with distances between 2.96 and 3.30 Å, and the degree of distortion of the Cd-Cl bonds seems to be roughly proportional to the number of hydrogen bonds formed by the chlorine, as is also the case in the present system.

There has been much recent discussion of the conformations of  $\text{Co}(\text{en})_3^{3+}$  and related molecules, and the structure of the cation found in this complex is shown in Figure 2. In the figure we show a  $\Lambda$  configuration,<sup>29</sup>

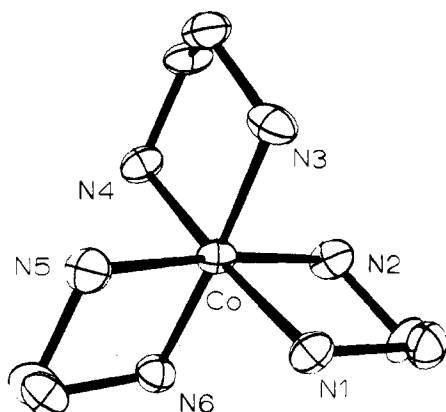


Figure 2.—The  $\text{Co}(\text{N}_2\text{C}_2\text{H}_8)_3^{3+}$  ion. The configuration shown is  $\Lambda(\delta\delta\delta)$ , but in this centrosymmetric space group there are an equal number of  $\Delta(\lambda\lambda\lambda)$  forms.

but in this centrosymmetric space group there are an equal number of  $\Lambda$  and  $\Delta$  forms. Corey and Bailar<sup>30</sup> have demonstrated that, for a  $\Lambda$  configuration at the metal, the lowest energy conformation is the  $\Lambda(\delta\delta\delta)$  form, although recent calculations by Gollogly and Hawkins<sup>31</sup> have shown that the  $\Lambda(\delta\delta\lambda)$  form is of very little higher energy than the  $\Lambda(\delta\delta\delta)$  conformer. Ibers, Raymond, and coworkers,<sup>32</sup> however, have recently demonstrated the existence of all possible combinations of  $\delta$  and  $\lambda$  rings and have suggested that deviations from the lowest energy forms arise as the result of intermolecular hydrogen bonds involving the ethylenedi-

amine nitrogen atoms. The recent study of  $[\text{Cr}(\text{en})_3]\text{[Cr}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  by Enemark and his coworkers<sup>33</sup> and our recent investigation<sup>16</sup> of  $[\text{Co}(\text{en})_3]_2[\text{Cu}_2\text{Cl}_8]\text{Cl}_2\cdot 2\text{H}_2\text{O}$  tend to confirm this hypothesis. The present case, however, might be misconstrued as being in violation of the Ibers-Raymond rule, since we find considerable hydrogen bonding but the lowest energy conformation of the cation. It should be stressed, however, that Ibers and Raymond noted that distortions would not be expected to occur if the hydrogen bonding involves the axial ethylenediamine hydrogen atoms. In the present case, which does involve extensive hydrogen bonding to axial protons, distortion of any ring from the  $\delta$  conformer (for a  $\Lambda$  configuration) would appear to weaken the hydrogen bonding to the  $\text{CdCl}_6^{4-}$  anion. Similar results have recently been observed by Duesler and Raymond<sup>34</sup> for  $[\text{Co}(\text{en})_3]_2[\text{HPO}_4]_3\cdot 9\text{H}_2\text{O}$ , and we agree with these authors that the structure of  $[\text{Ni}(\text{en})_3]\text{[SO}_4]$ , reported by Mazhar-Ul-Haque, *et al.*,<sup>35</sup> to be in violation of the hypothesis, is also analogous to this system.

The bond distances and angles found in the cation are consistent with those found by other workers for similar systems<sup>16,32,33</sup> and are presented in Table V.

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

Atoms	Distance, Å	Atoms	Angle, deg	Atoms	Angle, deg
Co-N1	1.979 (6)	N1-Co-N2	86.0 (2)	Co-N1-C1	108.8 (2)
Co-N2	1.968 (5)	N3-Co-N4	85.7 (2)	Co-N2-C2	108.4 (2)
Co-N3	1.961 (6)	N5-Co-N6	85.2 (2)	Co-N3-C3	109.0 (2)
Co-N4	1.975 (5)	N1-Co-N3	93.1 (2)	Co-N4-C4	109.0 (2)
Co-N5	1.980 (6)	N1-Co-N4	89.5 (2)	Co-N5-C5	109.2 (2)
Co-N6	1.966 (6)	N1-Co-N5	91.5 (2)	Co-N6-C6	109.4 (2)
N1-C1	1.482 (9)	N1-Co-N6	175.5 (5)	N1-C1-C2	107.1 (5)
N2-C2	1.490 (9)	N2-Co-N3	91.1 (2)	N2-C2-C1	107.4 (5)
N3-C3	1.496 (9)	N2-Co-N4	174.3 (3)	N3-C3-C4	107.7 (6)
N4-C4	1.498 (9)	N2-Co-N5	93.3 (2)	N4-C4-C3	106.3 (6)
N5-C5	1.485 (9)	N2-Co-N6	91.1 (2)	N5-C5-C6	106.3 (6)
N6-C6	1.486 (9)	N3-Co-N5	173.9 (2)	N6-C6-C5	107.8 (5)
C1-C2	1.514 (10)	N3-Co-N6	90.4 (2)		
C3-C4	1.492 (11)	N4-Co-N5	90.3 (2)		
C5-C6	1.508 (10)	N4-Co-N6	93.7 (2)		

This study has demonstrated that the reaction of  $\text{Co}(\text{en})_3\text{Cl}_3$  with  $\text{CdCl}_2$  is not similar to either the reactions of  $\text{M}(\text{NH}_3)_6\text{Cl}_3$  ( $\text{M} = \text{Co}$  or  $\text{Cr}$ ) with  $\text{CdCl}_2$  or the reactions of  $\text{M}(\text{en})_3\text{Cl}_3$  with  $\text{CuCl}_2$  under similar reaction conditions. We have also discovered<sup>36</sup> that the reaction of  $\text{Cr}(\text{en})_3\text{Cl}_3$  with  $\text{CdCl}_2$  under these conditions gives rise to a product which is not analogous to those of any of the above-mentioned reactions, and we are currently investigating the structure of this reaction product.

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

(34) E. N. Duesler and K. N. Raymond, presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., 1971, paper INOR 117.

(35) Mazhar-Ul-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, **9**, 2421 (1970).

(36) J. T. Veal and D. J. Hodgson, presented at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., 1971, paper INOR 6.

(28) A. Braibanti and A. Tiripicchio, *Gazz. Chim. Ital.*, **96**, 1580 (1966).

(29) The recent IUPAC proposal for nomenclature is used here. See *Inorg. Chem.*, **9**, 1 (1970).

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

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

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