

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, MORAVIAN COLLEGE, BETHLEHEM, PENNSYLVANIA 18018, AND VILLANOVA UNIVERSITY, VILLANOVA, PENNSYLVANIA 19085

## Transition Metal–Bromine Reactions in Dimethylformamide

BY ROBERT R. WINDOLPH<sup>1</sup> AND AMOS J. LEFFLER\*

Received April 21, 1971

The reaction between some first-row transition metals and bromine in dimethylformamide was examined. The products with vanadium and chromium were the trivalent metal hexakis(dimethylformamide) tris(tribromide) while with nickel and cobalt the corresponding divalent salts were formed. In the case of titanium the product was  $\text{TiBr}(\text{DMF})_6(\text{Br}_3)_3$ . The vanadium complex was found to oxidize slowly to  $\text{VO}(\text{DMF})_6^{2+}$  ion while the cobalt complex disproportionated in nitromethane to octahedral and tetrahedral complex ions. Magnetic susceptibility, conductivity, and spectral data are presented for the complexes and the stability of the tribromide ion is discussed.

In recent years there have been a number of investigations carried out on transition metal oxidations in nonaqueous media. The oxidizing agents have included the halogens<sup>2–4</sup> and nitrosyl fluoroborate.<sup>5,6</sup> Only diethyl ether and acetonitrile have been employed as solvents. The present work has studied the use of dimethylformamide as the medium for the reaction of first-row transition elements with bromine.

### Results

In all cases studied, the reaction occurs spontaneously and exothermally on addition of the bromine to the powdered metal slurried in the solvent. With the exception of titanium, the product of the reaction is the hexacoordinated metal dimethylformamide ion,  $[\text{M}(\text{DMF})_6]^{n+}$ . The oxidation states of the metals were determined by magnetic susceptibility studies and are shown in Table I. In the case of titanium, the cation is believed to be  $[\text{TiBr}(\text{DMF})_6]^{3+}$  on the basis of its diamagnetic character and conductivity studies described below. In all cases the tribromide anion was formed and its instability made it difficult to remove the last traces of excess solvent. Because of this the products are formulated with excess solvent based on analytical data reported in Table I.

Conductivity studies of the products in dimethylformamide were carried out and representative conductance values are reported in Table I. Although the Onsager limiting relation is not valid for such highly charged species, comparison can be made for similar ions of the same charge and this was done using the corresponding perchlorate salts of the chromium, nickel, and cobalt complexes as shown in Table II. The results show clearly that the oxidation states of the metals and the charges on the ions are correctly formulated and that the difference between the conductivity of the tribromide and perchlorate species is small enough not to affect the results. The limiting conductivity values are not of sufficient precision to assign absolute ionic conductance values. The limiting value for the titanium compound is within the range predicted for a triply charged species.

Infrared spectral data for the complexes are shown in Table III. The carbonyl frequency is shifted to a lower wavelength as would be expected for coordination of the organic molecule to the metal through the oxygen atom. The shifts are in agreement with earlier work.<sup>7–9</sup> A comparison of the values for the tribromide and perchlorate complexes supports the formulation of the ions as given.

The visible–ultraviolet spectral data for the compounds are shown in Table IV. Again the agreement with the perchlorate complex is good where available. Assignment of the spectral frequencies to particular transitions was made on the basis of comparison with known species and relative spectral intensities. In the tribromide salts a number of additional lines were found that are due to transitions in the anion. These have been discussed earlier.<sup>4</sup> In the case of the titanium complex no transitions were observed below  $20,000\text{ cm}^{-1}$  in agreement with the  $d^0$  formulation and a  $4+$  oxidation state of the complex.

### Discussion

Dimethylformamide appears to be unique in its ability to stabilize the formation of the tribromide ion. The chromium complex is stable above  $100^\circ$  while the others decompose at somewhat lower temperatures. In an earlier study<sup>4</sup> of acetonitrile complexes it was proposed that two mechanisms are responsible for the stabilization of the tribromide species: (1) coordination to a positively charged metal that can accept electrons from the tribromide by back-donation and (2) by lattice energy factors. In the case of dimethylformamide only the second mechanism appears to be operative. A partial X-ray study<sup>10</sup> of the chromium salt clearly shows the tribromide ions as seen in Figure 1. An attempt<sup>11</sup> was made to measure the quadrupolar resonance of the bromide atoms but unfortunately no resonance was observed.

The behavior of titanium differs from the remainder of the elements studied by incorporating a bromide ion into the complex. It is similar to aquo complexes where charge reduction occurs by polarization of the water molecule or in the case of strong acids where the anion is incorporated in the complex ion. Bromide

\* To whom correspondence should be addressed at Villanova University.

(1) Abstracted in part from the thesis presented to Villanova University for the Ph.D. degree.

(2) (a) B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, 2400, 2408 (1964); (b) *ibid.*, 537 (1965).

(3) D. G. Brown, D. G. Holah, and C. E. F. Rickard, *Chem. Commun.*, 651 (1968).

(4) R. R. Windolph and A. J. Leffler, *J. Chem. Soc. A*, 2593 (1969).

(5) B. J. Hathaway, D. G. Holah, and A. E. Underhill, *ibid.*, 2444 (1962).

(6) B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, 8, 971 (1969).

(7) L. J. Bellamy and R. F. Branch, *J. Chem. Soc.*, 4491 (1951).

(8) R. C. Aggarwal and P. P. Singh, *Z. Anorg. Allg. Chem.*, 332, 103 (1964).

(9) R. C. Aggarwal and P. P. Singh, *J. Inorg. Nucl. Chem.*, 28, 1665 (1966).

(10) T. H. Doyne and J. Gordon, Villanova University, personal communication.

(11) G. Peterson, Bell Laboratories, personal communication.

TABLE I  
ANALYTICAL DATA FOR METAL-*N,N*-DIMETHYLFORMAMIDE-TRIBROMIDE COMPLEXES

Complex	% metal		% bromide		% bromine		% DMF <sup>a</sup>		$\mu$ , BM	$\Delta M^b$
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
[TiBr(DMF) <sub>6</sub> ](Br <sub>3</sub> ) <sub>3</sub> ·1.8DMF orange-brown	3.56	3.56	23.78	23.63	35.67	35.87	36.98	36.94	0.00	319
[V(DMF) <sub>6</sub> (Br <sub>3</sub> ) <sub>3</sub> ]·0.3DMF medium brown	4.14	4.18	19.78	19.48	38.96	38.12	37.42	37.92	2.61	300
[Cr(CMF) <sub>6</sub> ](Br <sub>3</sub> ) <sub>3</sub> ·1.0DMF red-brown	4.05	4.03	18.69	18.89	37.37	37.54	39.89	39.54	3.74	237
[Co(DMF) <sub>6</sub> ](Br <sub>3</sub> ) <sub>2</sub> ·0.3DMF·0.35Br <sub>2</sub>	5.59	5.59	15.15	15.06	35.60	35.58	43.66	43.77	5.23	195
[Ni(DMF) <sub>6</sub> ](Br <sub>3</sub> ) <sub>2</sub> ·0.2DMF rust brown	5.92	6.02	16.12	16.42	32.24	31.12	45.72	46.37	3.32	177

<sup>a</sup> Determined by difference. <sup>b</sup> Determined in DMF; units are ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> at a concentration of 1.0 × 10<sup>-3</sup> M.

TABLE II  
ANALYTICAL DATA FOR METAL-*N,N*-DIMETHYLFORMAMIDE-PERCHLORATE COMPLEXES

Complex	% metal		$\mu$ , BM	$\Delta M^a$
	Found	Calcd		
[Cr(DMF) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub> (steel blue)	6.60	6.88	3.90	221
[Co(DMF) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (pink)	8.46	8.37	5.67	177
[Ni(DMF) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> (blue-green)	8.43	8.27	3.12	182

<sup>a</sup> Determined in DMF; units are ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> at a concentration of 1.0 × 10<sup>-3</sup> M.

TABLE III  
INFRARED SPECTRA<sup>a</sup> OF  
*N,N*-DIMETHYLFORMAMIDE COMPLEXES

	Tribromide complexes				Perchlorate complexes			
	$\nu_{C=O}$	$\Delta\nu_{C=O}$	$\delta_{OCN}$	$\Delta\delta_{OCN}$	$\nu_{C=O}$	$\Delta\nu_{C=O}$	$\delta_{OCN}$	$\Delta\delta_{OCN}$
DMF	1679		660		1679		660	
Cr	1645	-34	720	60	1645	-34	720	60
Co	1635	-44	687	27	1625	-55	687	27
Ni	1650	-29	690	30	1640	-39	690	30
V	1645	-34	710	50				
Ti	1645	-34	800	40				

<sup>a</sup> All values are in cm<sup>-1</sup>.

rather than tribromide is incorporated because the high charge on the titanium ion together with the relatively high d-orbital energies prevent any back-donation of electrons to the metal. The metal ion polarizes

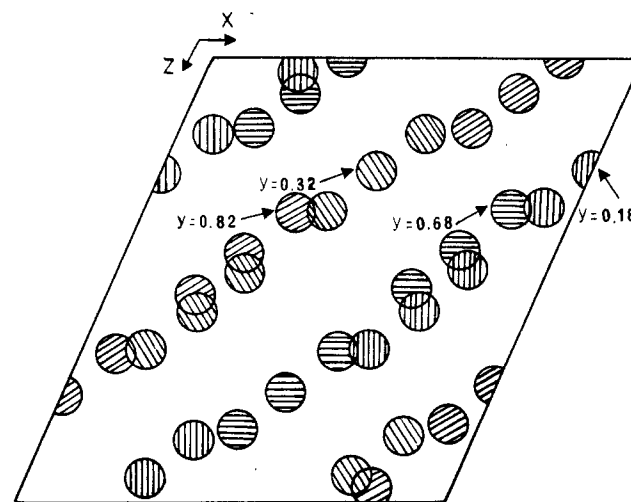


Figure 1.—Br atoms in Cr(DMF)<sub>6</sub>(Br<sub>3</sub>)<sub>3</sub>.

the tribromide ion thus destabilizing it compared with a bromide ion and bromine molecule.

Using the electronic spectral data, values of 10*Dq* were calculated for the various ions. These are shown in Table V. The values for the dimethylformamide complexes are very similar to those of water but smaller

TABLE IV  
ELECTRONIC SPECTRA<sup>a</sup> OF *N,N*-DIMETHYLFORMAMIDE COMPLEXES

Metal	Tribromide complexes		Perchlorate complexes		Assignment
	Soln max	Solid max	Soln max	Solid max	
Cr	14,430 (8.2)		14,450 (8)		<sup>4</sup> A <sub>2g</sub> (F) → <sup>2</sup> E <sub>g</sub>
	15,150 (16)		15,290		<sup>4</sup> A <sub>2g</sub> (F) → <sup>2</sup> T <sub>1g</sub>
	16,950 (54)	17,300	16,950 (54)	17,240	<sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F)
		20,200			Lattice tribromide
Co		23,640	23,700 (46)	23,700	<sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (F)
	27,470				Soln tribromide
	6,798 (0.64) sh <sup>b</sup>		6,730 (0.70) sh		
	7,250 (1.47) sh		7,250 (1.58)		
	7,750 (2.76)		7,760 (2.81)		<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F)
	8,250 (2.02) sh		8,270 (2.02) sh		
	19,000 vw, sh		18,980 (18.8)		<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F)
19,000 tribromide abs		19,880 (15.4) w, sh			
Ni	8,260 (6.11)		20,600 (12.2)		<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)
	8,389 (6.58)		8,500		<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>2g</sub> (F)
	13,755 (5.07)				
	14,925 (5.54)		13,600		<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F)
	14,925 (5.54)		14,900		
V	19,000 tribromide abs				
	15,720 (29.1)	16,130			<sup>3</sup> T <sub>1g</sub> (F) → <sup>3</sup> T <sub>2g</sub> (F)
		20,790			Lattice tribromide
		23,420			Lattice tribromide
Ti	12,800-27,800 (>2000)				Soln tribromide
		20,790			Lattice tribromide
		23,420			Lattice tribromide
	23,800-27,800 (>2000)			Soln tribromide	

<sup>a</sup> All values are in cm<sup>-1</sup>. <sup>b</sup> Shoulder.

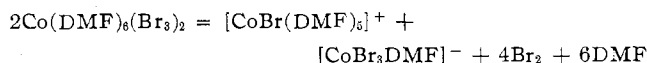
TABLE V  
VALUES OF  $10Dq$  FOR  $[M(\text{DMF})_6]^{n+}$  IONS

M	$10Dq, \text{cm}^{-1}$	M	$10Dq, \text{cm}^{-1}$
Cr	17,120	Co	8890
V	17,300	Ni	8500

than the value of  $18,700 \text{ cm}^{-1}$  estimated earlier<sup>4</sup> for the tribromide ion, coordinated to chromium(III).

With the exception of the vanadium complex all were found to be air stable. The former, on standing, was slowly oxidized to the  $[\text{VO}(\text{DMF})_5]^{2+}$  ion which was identified by comparison of the observed spectrum with that reported in the literature.<sup>12</sup> The tribromide complexes are all hydrolyzed by moisture. The rates vary considerably with the chromium complex being stable for several days in the laboratory atmosphere while the others are much less stable.

The cobalt complex was found to disproportionate in solvents such as chloroform, nitromethane, and ethanol to give blue-green solutions indicative of tetrahedral coordination. Conductance measurements plotted as a function of  $C^{1/2}$  in nitromethane gave a curve that fell midway between that of  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$ , a 1:1 electrolyte, and  $\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2$ , a 1:2 electrolyte that showed no disproportionation in nitromethane. A plot of conductance as a function of  $(C/2)^{1/2}$  gave values much above those for the corresponding nickel complex and out of the region expected for normal 1:2 complexes in nitromethane. The most reasonable explanation for this behavior is the coordination disproportionation



The choice of the ionic species is based on the spectral and conductance data. In Table VI are shown the

TABLE VI  
ELECTRONIC SPECTRUM OF  
 $\text{Co}(\text{DMF})_6(\text{Br}_3)_2$  IN NITROMETHANE

Obsd spectrum, $\text{cm}^{-1}$	Spectrum of $\text{CoBr}_4^{2-}$ , $\text{cm}^{-1}$
6,730 (26.9)	4,500
7,200 (27.9)	5,600
7,580 (30.2)	
14,540 (505) sh	
14,860 (561)	13,900
15,020 (548) sh	14,400 sh
16,000 (462)	14,900
16,670 (234) sh	15,500 sh

observed values together with those reported<sup>13</sup> in the literature for  $\text{CoBr}_4^{2-}$  and the agreement is poor. The possibility of  $[\text{Co}(\text{DMF})_4]^{2+}$  formed by decomposition of the hexacoordinate complex has been suggested but this would require a 1:2 electrolyte and the conductance measurements rule against this. Finally similar disproportionations have been reported in other cases.<sup>14-16</sup>

### Experimental Section

**Materials.**—The metal powders used in the work were obtained from commercial sources. In each case the stated purity was at least 99%. The bromine was from Dow Chemical Co. and was stated to be 99.9% pure. The hexahydrates of nickel(II),

cobalt(II), and chromium(III) perchlorates were supplied by Alfa Inorganics.

*N,N*-Dimethylformamide (0.1% water maximum) was obtained from Matheson Coleman and Bell. This was used as received for all preparative reactions but was further purified by drying over molecular sieves for the conductivity studies. The 2,2-dimethoxypropane was also supplied by Matheson Coleman and Bell and was used as received. All other solvents were commercially available materials of either Certified or Spectral Grade purity. The nitromethane used in several of the conductivity studies was further purified by drying over molecular sieves.

**Preparation of Complexes.**—The reactions between the various metals and bromine in DMF were carried out by slurring a sample of the metal powder in a moderate excess of DMF. The reaction was carried out in a 500-ml three-necked flask equipped with a nitrogen inlet, an addition funnel for bromine, a stirrer, a condenser, and a gas outlet. Under a slow nitrogen flow, the bromine was added dropwise at a rate sufficient to keep the temperature of the reaction mixture below about  $50^\circ$ . All subsequent purification procedures were carried out in a drybox or a nitrogen atmosphere to minimize hydrolysis of the products. The products were precipitated by addition of chloroform or carbon tetrachloride and dried by suction. The perchlorate complexes were prepared by the procedure of Drago, *et al.*<sup>17</sup>

**Analytical Procedures.**—The titanium content was determined by precipitation with *p*-hydroxyphenylarsonic acid<sup>18</sup> followed by ignition of the solid to titanium dioxide. Vanadium was analyzed by precipitation with 8-hydroxyquinoline<sup>18</sup> after bromate oxidation<sup>19</sup> of the complex. Chromium was precipitated as the hydroxide using a cyanate hydrolysis procedure<sup>18</sup> and then ignited to the oxide. The nickel content was determined by precipitation with dimethylglyoxime<sup>18</sup> while cobalt was isolated in the form of  $\text{Co}(\text{py})_4(\text{SCN})_2$ .<sup>18</sup>

The bromine content of the complexes was found by titration with standard sodium thiosulfate solution in the presence of aqueous potassium iodide and starch indicator.<sup>18</sup> Prior to the determination of the bromine content, the metal complex was decomposed using a two-phase carbon tetrachloride extraction procedure described previously.<sup>4</sup> The halide content was determined either by titration according to the Volhard procedure or by precipitation as the silver salt.<sup>18</sup>

Analyses for carbon, hydrogen, and nitrogen in the complexes using standard combustion techniques did not give reproducible results even though higher temperatures than normal were used for combustion. This is probably due to the formation of metal carbides and nitrides. Because of this difficulty, the DMF content had to be determined by difference.

**Physical Measurements. a. Spectral Studies.**—Infrared spectra were obtained using a Perkin-Elmer 337 Infracord spectrophotometer. Samples of the metal complexes were run either as potassium bromide disks or as paraffin oil mulls between sodium chloride plates.

Electronic spectra in solution were run with a Perkin-Elmer 202 spectrophotometer. Measurements in the near-infrared region were made with a Beckman DK-1 spectrophotometer. Solid spectra were obtained with a Cary 14 spectrophotometer equipped with a standard reflectance attachment and using a magnesium carbonate reference.

**b. Magnetic Susceptibility.**—The magnetic susceptibilities of the solid complexes were measured at about  $25^\circ$  using a Gouy balance. Calibrations were carried out using  $\text{Hg}(\text{Co}(\text{NCS})_4)$  prepared by the method of Figgis and Nyholm.<sup>20</sup> Diamagnetic corrections were made using tables of Pascal's constants and group correction values.<sup>21</sup>

**c. Conductance Studies.**—Conductance measurements were made using an A. H. Thomas "Serfass" bridge and an immersion type cell whose constant was approximately 0.1. The cell was frequently checked using aqueous solutions of potassium chloride of known concentration. Solvents were purified as described above. A reproducibility of about  $3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  was found between various runs. Conductance values were determined for

(17) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

(18) A. I. Vogel, "Quantitative Inorganic Analysis," Wiley, New York, N. Y., 1963.

(19) I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **2**, 140 (1930).

(20) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(21) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., pp 400-454.

(12) R. B. Jordan and N. S. Angerman, *J. Chem. Phys.*, **48**, 3983 (1968).

(13) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 286.

(14) W. Libus and D. Puchalska, *J. Phys. Chem.*, **71**, 3549 (1967).

(15) L. I. Katzin, *J. Chem. Phys.*, **36**, 3034 (1962).

(16) W. Libus, *Rocz. Chem.*, **35**, 411 (1961).

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.

**Acknowledgment.**—We wish to thank NASA for financial support to R. R. W. and Professor G. Zimmerman of Bryn Mawr College for permission to use the Cary 14 to obtain spectral data. In addition thanks are due to Dr. G. Peterson of Bell Laboratories for the attempt to find nuclear quadrupole resonance of the chromium tribromide complex.

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) Hexachlorocadmiate(II) Dichloride Dihydrate, $[\text{Co}(\text{N}_2\text{C}_2\text{H}_8)_3]_2[\text{CdCl}_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$

BY JACK T. VEAL AND DEREK J. HODGSON\*

Received May 17, 1971

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.