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Preparation, Properties, and Crystal and Molecular Structure of Ethylenediammonium Tetrachlorocobaltate(II) Chloride, $(NH_3CH_2CH_2NH_3)_2(CoCl_4)Cl_2$

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The compound ethylenediammonium tetrachlorocobaltate(II) chloride, $(NH_3CH_2CH_2NH_3)_2(CoCl_4)Cl_2$, has been prepared and its structure determined crystallographically. This substance crystallizes in the centrosymmetric orthorhombic space group *Pnam* [$D_{2h}{}^{16}$; No. 62] with $a = 12.884\ (9)$, $b = 6.151\ (5)$, $c = 19.291\ (7)$ Å; $Z = 4$. X-ray diffraction data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-I diffractometer, and the structure was solved by means of Patterson and Fourier syntheses. All atoms, including hydrogens, have been located; convergence of the least-squares refinement process occurred with $R_F = 4.4\%$ and $R_{wF} = 3.7\%$ for 1477 independent reflections. The crystal is formed from distorted tetrahedral $CoCl_4{}^{2-}$ ions: the largest difference in Co–Cl bond lengths is 0.041 Å and the largest difference in the Cl–Co–Cl angles is 23.0°; it also contains diprotonated ethylenediamine ions and chloride ions. An extensive hydrogen-bonding network connects these species and probably accounts for the $CoCl_4{}^{2-}$ ion distortions. Visible and infrared spectra are consistent with the structural data.

Introduction

Several years ago while attempting to prepare the well-known green *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride following a published procedure,[2] we obtained varying mixtures of the desired compound with an unexpected blue product. The blue product, which had been reported by earlier workers,[3,4] was found to have the composition $CoCl_2 \cdot 2en \cdot 4HCl$ (en = ethylenediamine). In agreement with earlier work, we found that the controlling factor in the synthesis of these two compounds is the concentration of hydrochloric acid. A curious additional feature of our study was the discovery that two different crystalline forms of the blue compound could be isolated, only one of which had been reported previously, and this suggested the possibility of isomerism or some other structural difference.

A limited investigation of the electronic spectrum had led Schultz[5] to the speculation that the blue compound was a salt of the formula $(enH_2)_2(CoCl_6)$. This would be consistent with the empirical formula, but the blue color strongly suggests the presence of the tetrahedral $CoCl_4{}^{2-}$ chromophore. Since no other examples of a hexachlorocobaltate(II) ion are known, we undertook a more complete characterization of the compound, including determination of the x-ray crystal structure, in order to establish unambiguously the structure of the negative ion present. We also investigated possible structural differences in the two crystal modifications of the compound.

Experimental Section

Preparation and Properties. (a) Plate Crystals. Cobalt(II) chloride hexahydrate (10 g, 44 mmol) was dissolved in 30 mL of concentrated hydrochloric acid (350 mmol). To this mixture a solution of ethylenediamine (2.7 g, 45 mmol) in 10 mL of water was added dropwise with stirring, producing a highly exothermic reaction. The mixture was heated briefly to produce a clear solution and then allowed to cool slowly to 0 °C. Blue thin tabular crystals were deposited in high yield. These were washed with ethanol and ether and dried at 100 °C. Anal. Calcd for $(C_2H_{10}N_2)_2CoCl_6$: C, 12.1; H, 5.1; N, 14.1; Cl, 53.7. Found: C, 11.9; H, 5.1; N, 14.0; Cl, 53.5 ± 0.1. (Cl was determined gravimetrically as AgCl; C, H, and N analyses were performed by Midwest Microlab.)

(b) Needle Crystals. The same quantities of reagents were used as above, but the cobalt chloride was first dissolved in water along with the ethylenediamine, followed by slow addition of the concentrated HCl. After brief heating and slow cooling of the mixture to 0 °C, blue long prismatic crystals were deposited in high yield. These were

Table I. Positional and Thermal Parameters for $(enH_2)_2(CoCl_4)Cl_2$

Atom	x	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.20535 (5)[a]	0.1154 (1)	0.25	2.30 (3)	3.00 (4)	2.30 (3)	0.01 (3)	0.0	0.0
Cl(1)	0.17697 (9)	−0.2548 (2)	0.25	3.35 (6)	2.80 (6)	3.02 (6)	−0.38 (5)	0.0	0.0
Cl(2)	0.38026 (9)	0.1752 (2)	0.25	2.23 (6)	4.19 (8)	4.77 (7)	−0.27 (5)	0.0	0.0
Cl(3)	0.14429 (7)	0.2217 (2)	0.14522 (4)	3.97 (5)	3.88 (5)	2.73 (4)	0.44 (4)	−0.58 (4)	0.35 (4)
Cl(4)	0.40005 (6)	0.2079 (1)	0.01081 (4)	2.32 (4)	2.41 (4)	3.60 (4)	0.18 (3)	0.05 (3)	−0.08 (4)
N(1)	0.3441 (2)	0.7038 (5)	0.0243 (2)	2.5 (2)	2.4 (2)	3.3 (2)	−0.3 (1)	−0.4 (1)	−0.1 (1)
N(2)	0.4963 (3)	0.8593 (6)	0.1387 (2)	3.1 (2)	5.4 (2)	3.0 (2)	−0.5 (2)	−0.5 (1)	−0.3 (2)
C(1)	0.3273 (3)	0.7081 (7)	0.1002 (2)	2.4 (2)	3.8 (2)	3.3 (2)	−0.5 (2)	0.5 (1)	−0.1 (2)
C(2)	0.4249 (3)	0.6723 (6)	0.1404 (2)	4.0 (2)	3.3 (2)	3.0 (2)	−0.4 (2)	−0.2 (2)	0.3 (2)

Atom	x	y	z	Atom	x	y	z
H(11)	0.293 (3)	0.841 (6)	0.109 (2)	H(21)	0.460 (3)	0.553 (6)	0.123 (2)
H(12)	0.283 (3)	0.609 (6)	0.108 (2)	H(22)	0.406 (3)	0.647 (6)	0.186 (2)
H(13)	0.367 (3)	0.581 (6)	0.012 (2)	H(23)	0.468 (3)	0.964 (6)	0.150 (2)
H(14)	0.377 (3)	0.820 (6)	0.011 (2)	H(24)	0.547 (3)	0.834 (6)	0.163 (2)
H(15)	0.283 (3)	0.712 (6)	0.004 (2)	H(25)	0.518 (3)	0.879 (6)	0.096 (2)

[a] Numbers in parentheses here and throughout the paper are estimated standard deviations in the least significant digits. [b] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The values of U have been multiplied by 100.

washed and dried as above. Anal. Found: C, 12.5; H, 5.5; N, 14.2; Cl, 53.5 ± 0.1.

Both forms were found to be thermally stable at 120 °C, with no weight loss and no change in the infrared spectrum when kept at this temperature for 8 days. Both forms had identical visible spectra in the solid state (Figure 4) and identical infrared spectra.

Infrared spectra were run on a Perkin-Elmer Model 457 spectrophotometer, using the KBr pellet technique, and calibrated against polystyrene. Electronic spectra in the visible region were obtained with a Beckman ACTA III spectrophotometer, using the technique of diffuse transmission through Nujol mulls on filter paper.

Crystallographic Data Collection. A blue needle crystal of $(en)_2H_4CoCl_6$ was mounted in a glass capillary for the preliminary x-ray examination, since the crystals appeared to be slightly hygroscopic. Weissenberg photographs using Cu Kα radiation showed *mmm* Laue symmetry indicating that the crystals belong to the orthorhombic system. The observed extinctions, $0kl$ for $k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$, are consistent with either space group $Pna2_1$ or *Pnam*. The choice of space group *Pnam* [D_{2h}^{16}; No. 62] is based on the successful refinement in this space group.

The prismatic b crystal selected for data collection had a and c thicknesses of 0.1 mm and a length of 0.3 mm. The crystal was mounted on a goniometer head without angular adjustments to reduce the possibility of crystal motion during the experiment. The crystallographic b axis was roughly aligned with the diffractometer ϕ axis, in order to reduce the variation in absorption during data collection. All measurements were made using a Picker FACS-I computer-controlled four-circle x-ray diffractometer equipped with a scintillation counter, pulse height analyzer, and graphite monochromator. Cell constants were obtained from a least-squares refinement of the setting angles of 12 reflections with 2θ values from 13 to 45°, which had been centered on the Mo Kα peak, λ 0.71069 Å. The refinement was carried out on a SDS-SIGMA 2 computer using the logic of the FACS-I system.[6] The unit cell parameters are $a = 12.884$ (9) Å, $b = 6.151$ (5) Å, $c = 19.291$ (7) Å, and $V = 1529$ Å^3. The density calculated for four formula units in the unit cell with a formula weight of 395.88 is 1.719, which agrees with the experimental density of 1.71 (2) g cm^{-3} measured by suspension in a mixture of carbon tetrachloride and 1,1,2,2-tetrabromoethane. Hence the cobalt atom is constrained to lie on either a mirror plane or a center of symmetry in space group *Pnam*.

Intensity data were collected using molybdenum radiation reflected from the (002) face of a graphite crystal. The intensities were measured by the θ–2θ scan technique at a takeoff angle of 2.20°. A symmetric scan in 2θ was used, the scan ranging from 1.0° below the Mo Kα peak center to 1.0° above. The background was measured for 20 s at each end of the scan. Data were measured out to $2\theta = 50°$ at a scan rate of 1° min^{-1}. Three standard reflections, which were examined periodically, showed no significant changes in intensity during data collection. Reflection intensities, I, were computed as $N - B(t_s/t_b)$ and the standard deviation was $\sigma(I) = [N + B(t_s/t_b)^2 + (0.5I)^2]^{1/2}$, where N and B are the total counts accumulated during the scan period (t_s) and the total background counting time (t_b), respectively. Intensities measured in three octants of reciprocal space were averaged to yield 1818 unique reflections, of which 1479 had a positive intensity in all three octants and were used in subsequent refinement. The standard deviation of the averaged intensities were obtained by averaging the standard errors of the individual measurements. A comparison of the average difference from the mean for each set of averaged intensities with the standard deviation suggested that the standard deviations were overestimated by about 5%. The data were corrected for Lorentz and polarization effects, but no absorption ($\mu = 22$ cm^{-1}) or extinction corrections were applied.

Solution and Refinement of Structure. Scattering factors for the cobalt(II) ion, the chloride ion, and neutral carbon and nitrogen were obtained from the compilation by Ibers.[7] The scattering factors of the cobalt and chloride ions were modified both for the real and imaginary components of anomalous dispersion.[8] Scattering factors for hydrogen are those of Stewart, Davidson, and Simpson.[9] The function minimized during least-squares refinement processes was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Discrepancy indices used below are $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The Earlham College IBM 1130 computer was used for all computing, except the final cycles of full-matrix anisotropic least-squares refinement which were done on the Indiana University CDC 6600 computer.[10]

The tetrahedral $CoCl_4^{2-}$ ion was located about the mirror plane at $z = {}^1/_4$ from the analysis of a sharpened,[11] three-dimensional Patterson map. A Fourier synthesis phased by these atoms showed the position of the other chloride ion in the asymmetric unit. Isotropic full-matrix least-squares refinement of the cobalt and chlorine atoms gave $R_F = 36\%$. A second difference Fourier located the two carbon and two nitrogen atoms of the ethylenediammonium ion. Further isotropic least-squares refinement on nonhydrogen atoms followed by a third difference Fourier unambiguously located the ten hydrogen atoms at reasonable positions on the ethylenediammonium ion. Each of these hydrogen atoms were assigned an isotropic thermal parameter, B, equal to 3.0 Å^2; which was not varied in further refinements.

Anisotropic thermal parameters on all nonhydrogen atoms and the positional parameters on all atoms were then refined by block-diagonal least squares, which led to convergence at $R_F = 4.6\%$. At this point the two most intense reflections (008 and 020), which appeared to be affected by extinction, were given a zero weight. Three cycles of full-matrix least squares, in which the correction for anomalous dispersion was included for the first time, led to final convergence, with maximum shift in any parameter divided by the error in that parameter on the final cycle less than 0.2, at $R_F = 4.4\%$ and $R_{wF} = 3.7\%$. The "goodness of fit" defined by $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ was 0.787, where the number of reflections, NO, was 1477 and the total number of parameters refined, NV, was 103; the ratio NO/NV = 14.3/1. The correctness of the determined structure was confirmed by a final difference Fourier synthesis, on which the maximum was a peak of 0.5 e Å^{-3} (close to the position of Co) and −0.5 e Å^{-3} (close to the position of Cl(2)). The final positional and thermal parameters for all atoms are collected in Table I. The standard deviations were calculated from the inverse matrix of the

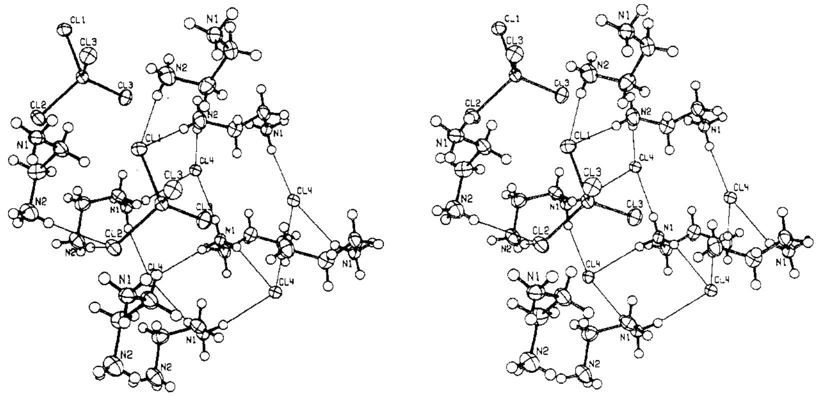

Figure 1. Stereoscopic drawing of $(enH_2)_2(CoCl_4)Cl_2$ viewed nearly perpendicular to the mirror plane at $z = {}^1/_4$, showing the $CoCl_4^{2-}$ ion and its environment. Hydrogen bonds are shown with slim "bonds".

Table II. Interatomic Distances (Å) for $(enH_2)_2(CoCl_4)Cl_2$

(a) Distances within the $CoCl_4^{2-}$ anion

Co-Cl(1)	2.306 (2)	Cl(1)···Cl(3)	3.585 (2)
Co-Cl(2)	2.283 (2)	Cl(2)···Cl(3)	3.662 (2)
Co-Cl(3)	2.265 (1)	Cl(3)···Cl(3^i)[a]	4.043 (1)
Cl(1)···Cl(2)	3.722 (3)		

(b) Distances within the enH_2^{2+} cation

N(1)-C(1)	1.480 (4)	N(2)-H(24)	0.82 (4)
N(2)-C(2)	1.473 (5)	N(2)-H(25)	0.87 (4)
C(1)-C(2)	1.495 (5)	C(1)-H(11)	0.94 (4)
N(1)-H(13)	0.84 (4)	C(1)-H(12)	0.85 (4)
N(1)-H(14)	0.87 (4)	C(2)-H(21)	0.95 (3)
N(1)-H(15)	0.88 (3)	C(2)-H(22)	0.93 (3)
N(2)-H(23)	0.77 (3)		

[a] The superscript i refers to the atom modified by the following symmetry operation: $x, y, {}^1/_2 - z$.

Table III. Interatomic Angles (deg) for $(enH_2)_2(CoCl_4)Cl_2$

(a) Angles Involving the Cobalt atom

Cl(1)-Co-Cl(2)	108.39 (5)	Cl(2)-Co-Cl(3)	107.23 (4)
Cl(1)-Co-Cl(3)	103.29 (4)	Cl(3)-Co-Cl(3^i)[a]	126.32 (5)

(b) Angles within the enH_2^{2+} Cation

N(1)-C(1)-C(2)	112.9 (3)	H(11)-C(1)-H(12)	106 (3)
N(2)-C(2)-C(1)	113.5 (3)	H(21)-C(2)-N(2)	108 (2)
H(13)-N(1)-C(1)	110 (3)	H(22)-C(2)-N(2)	109 (2)
H(14)-N(1)-C(1)	110 (3)	H(21)-C(2)-C(1)	110 (2)
H(15)-N(1)-C(1)	108 (3)	H(22)-C(2)-C(1)	107 (2)
H(13)-N(1)-H(14)	119 (4)	H(21)-C(2)-H(22)	109 (3)
H(13)-N(1)-H(15)	103 (4)	H(23)-N(2)-C(2)	111 (3)
H(14)-N(1)-H(15)	105 (4)	H(24)-N(2)-C(2)	109 (3)
H(11)-C(1)-N(1)	105 (2)	H(25)-N(2)-C(2)	109 (2)
H(12)-C(1)-N(1)	105 (3)	H(23)-N(2)-H(24)	111 (4)
H(11)-C(1)-C(2)	115 (2)	H(23)-N(2)-H(25)	108 (4)
H(12)-C(1)-C(2)	112 (3)	H(24)-N(2)-H(25)	108 (4)

[a] See footnote to Table II.

final least-squares cycle. Bond lengths and angles are listed in Tables II and III, respectively.

Discussion

The crystallographic results, as shown in Figure 3, indicated that the compound is in fact a double salt, $enH_2Cl_2 \cdot enH_2(CoCl_4)$. Further, the coordination geometry of the cobalt is clearly tetrahedral rather than octahedral as suggested by the formula. The highly distorted tetrahedral coordination of the tetrachlorocobaltate(II) anion is shown in Figure 1. The ion contains two Co–Cl bonds of 2.265 (1) Å and two longer Co–Cl bonds of 2.283 (2) and 2.306 (2) Å, for a maximum difference of 0.041 Å. Two of the four unique bond angles show considerable deviation from the tetrahedral value with the Cl(1)–Co–Cl(3) angle compressed to 103.3° and the Cl(3)–Co–Cl(3^i) angle widened to 126.3°, which yields a difference of 23.0°.

Table IV. Range of Bond Distances and of Bond Angles and the Shape-Determining Dihedral Angles in Several $CoCl_4^{2-}$ Ions

Compd	Co–Cl, Å	Cl–Co–Cl, deg	δ′ angles, deg
$Cs_2(CoCl_4)$[a]	2.23	107.3–116.1	105.8, 108.5
$Cs_3(CoCl_4)Cl$[b]	2.252	106.0–111.2	107.8, 107.8
$[N(CH_3)_4]_2(CoCl_4)$[c]	2.229–2.266	108.3–112.8	106.8, 107.4
$(HistH_2)(CoCl_4)$[d]	2.233–2.295	105.7–115.3	105.3, 105.6
$(enH_2)_2(CoCl_4)Cl_2$	2.265–2.306	103.3–126.3	98.9, 103.6

[a] See ref 11. [b] See ref 12. [c] See ref 13. [d] See ref 14.

Table V. Hydrogen-Bonding Distances (Å) and Angles (deg) for $(enH_2)_2(CoCl_4)Cl_2$

Atoms	Cl···N	Cl···H	Cl···H–N
Cl(1)···H(24^{iv})–N(2^{iv})[a]	3.231 (4)	2.41 (4)	171 (4)
Cl(2)···H(23^{ii})–N(2^{ii})	3.259 (4)	2.59 (4)	147 (4)
Cl(4)···H(13)–N(1)	3.145 (4)	2.33 (4)	161 (4)
Cl(4)···H(14^{ii})–N(1^{ii})	3.194 (4)	2.40 (4)	152 (3)
Cl(4)···H(15^{v})–N(1^{v})	3.217 (4)	2.38 (4)	159 (3)
Cl(4)···H(25^{iii})–N(2^{iii})	3.205 (4)	2.38 (4)	157 (3)

[a] The superscript refers to the atom modified by the following symmetry operation: (ii) $x, y - 1, z$; (iii) $1 - x, 1 - y, -z$; (iv) $x - {}^1/_2, {}^1/_2 - y, z$; (v) ${}^1/_2 - x, y - {}^1/_2, -z$.

Table IV lists for comparison the range of bond distances and angles found for several compounds containing the tetrachlorocobaltate(II) ion.[12-15] The dihedral angles listed in Table IV can be used to describe more precisely the distortion of a particular four-coordinate structure between the ideal extremes, the regular tetrahedron and the square plane.[16] In the case of a distorted tetrahedron, a shape-determining dihedral angle (δ′) was defined by Muetterties and Guggenberger as the angle formed by the normals of the pair of triangular faces, which become a square face in the square-planar limit. The two δ′ angles are each equal to 109.5° for a regular tetrahedron and 0.0° for a square plane. While all of the structures shown in Table IV are nearly tetrahedral in shape, none have precisely T_d symmetry and a marked distortion is apparent in the ethylenediammonium structure.

The cation consists of a diprotonated ethylenediamine species as shown in Figure 2. Aside from the shortening of the bond distances involving hydrogen, all distances and angles are normal. The N–C–C–N dihedral angle is 72.5°.

The crystal packing is dominated by an extended hydrogen-bonding network. A stereographic view of the unit cell looking down the *b* axis is shown in Figure 3. Both types of anions are located in layers perpendicular to the *c* axis, with the $CoCl_4^{2-}$ ions located on mirror planes at $z = {}^1/_4, {}^3/_4$ and Cl^- ions very close to the $z = 0, {}^1/_2$ planes. These anion layers are connected by ethylenediammonium ions. All available amine protons are involved in hydrogen bonds to chlorine

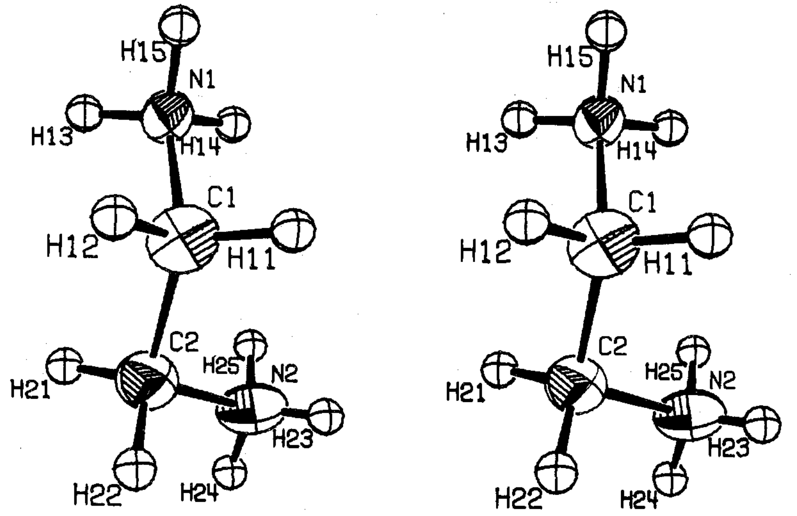

Figure 2. Stereoscopic illustration of the ethylenediammonium ion. The carbon and nitrogen atoms are represented by 50% probability ellipsoids. The spheres corresponding to the hydrogen atoms are on an arbitrary scale.

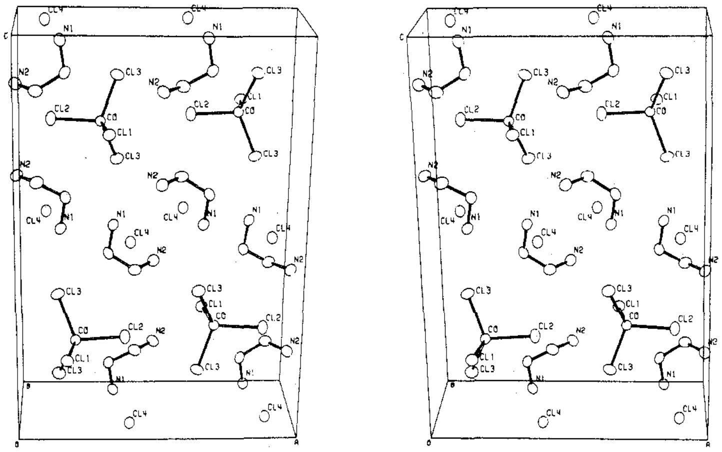

Figure 3. Contents of the unit cell of $(enH_2)_2(CoCl_4)Cl_2$ looking down the *b* axis. The hydrogen atoms have been omitted for clarity.

atoms. Hydrogen-bonding distances and angles are listed in Table V. As shown in Figure 1, Cl(1) and Cl(2) on the tetrachlorocobaltate ion are each hydrogen bonded to two mirror-related ethylenediammonium ions at the N(2) end. The third hydrogen atom, H(25), on the N(2) is involved in a hydrogen bond to Cl(4), the noncoordinated chloride ion; as are all three of the hydrogen atoms on the N(1) end of enH_2^{2+}. This arrangement gives the crystal a continuous three-dimensional hydrogen-bonded network, essentially the same as that found for $(enH_2)_2(CuBr_4)Br_2$ by Anderson and Willett.[17]

The mirror-related Cl(3) atoms of the $CoCl_4^{2-}$ unit are the only chlorine atoms not involved in hydrogen bonding, as was reported for the corresponding bromine atoms in the $CuBr_4^{2-}$ ion. However, Cl(3) is surrounded by nine hydrogen atoms at contact distances ranging from 2.94 to 3.16 Å. These hydrogens are associated with five different enH_2^{2+}; six of these hydrogen atoms are on two amine groups having their C–N bond axes pointing toward Cl(3), while the other three hydrogens are each located on different enH_2^{2+}. This tight packing of the Cl(3) atoms and the hydrogen bonding of Cl(1) and Cl(2) provide a reasonable explanation of the distortions of the $CoCl_4^{2-}$ tetrahedron observed in this structure. In particular, a reduction of the 126° Cl(3)–Co–Cl(3^i) angle to 109° would reduce the three Cl(3)···H contacts on N(2) by approximately 0.2 Å, while increasing the distance to hydrogens on N(1) by a similar amount. Finally, it should be noted that the presence or absence of hydrogen bonding is related to bond length; i.e., the Co–Cl bond length for the Cl(3) atom, which is not hydrogen bonded, is shorter than the Co–Cl bond lengths for the Cl atoms, which are hydrogen bonded.

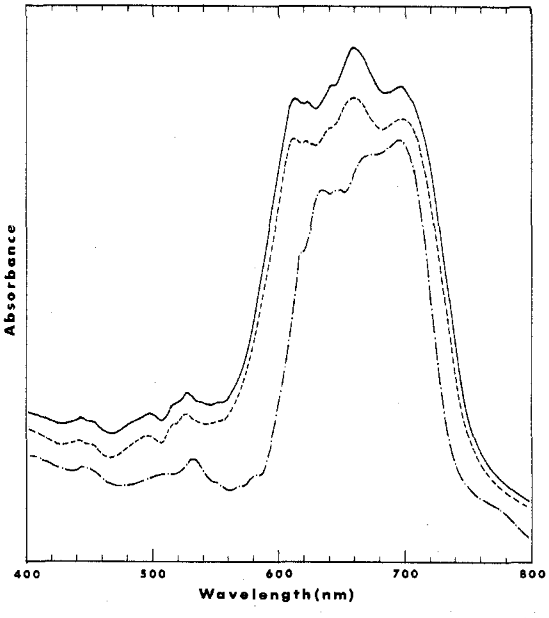

Figure 4. Solid-state electronic absorbtion spectra of $(enH_2)_2(CoCl_4)Cl_2$ needles (—), $(enH_2)_2(CoCl_4)Cl_2$ plates (- - - -), and $Cs_2(CoCl_4)$ (- • • •). Absorbance is in arbitrary units.

The electronic spectrum of the title compound, along with that of $Cs_2(CoCl_4)$, is shown in Figure 4. Both spectra show

Table VI. Major Infrared Absorption Bands in the Region 4000–250 cm^{-1}

$Cs_2(CoCl_4)$	$(enH_2)Cl_2$	$(enH_2)_2$-$(CoCl_4)Cl_2$	Assignment[a]
	3180 s		N–H str
	2950 vs, b	3000 vs, b	C–H str
	1591 m	1606 m	NH_3^+ def, asym
	1564 m	1582 m	NH_3^+ def, sym
		1492 s	
	1510 s	1477 s	CH_2 def
		1446 s	CH_2 wag
	1353 m	1340 m	
	1321 m	1323 m	
		1175 m	
	1036 s	1039 s	C–N str
	1010 s	1028 s	
		968 s	
		896 m	
	810 m	809 m	NH_3^+ rock
		470 s	
305 s		317 s	Co–Cl str

[a] Assignments based on those given by Colthup et al.[21] and Bellamy.[22]

a strong absorption band at ca. 1.5 μm^{-1} with considerable fine structure, which is characteristic for tetrahedral cobalt(II) complexes. The band has been assigned to the ${}^4A_2 \rightarrow {}^4T_1(P)$ transition.[18] The fine structure is commonly attributed to spin–orbit coupling, although no completely satisfactory theoretical interpretation has yet been given. The most extensive discussion of this problem has been given by Ferguson.[19] It is observed (Figure 4) that the center of gravity of the major band for the ethylenediammonium salt (1.515 μm^{-1}) is slightly blue-shifted from that of the cesium salt (1.481 μm^{-1}) and that the detailed shapes of the two bands are quite different. The lowest energy component remains nearly unchanged, whereas all other components of the band appear to be shifted to higher energies and have increased in their relative intensities. It was these differences, plus other differences in the electronic spectra, which led Schultz[5] to postulate the presence of a $CoCl_6^{4-}$ ion. It is probably not possible to make any detailed interpretation of the differences in spectra for the cesium and ethylenediammonium salts, but the differences are undoubtedly related to the degree of distortion from tetrahedral symmetry for the $CoCl_4^{2-}$ ion. Ferguson has done perhaps the most careful measurements of the electronic spectra of $CoCl_4^{2-}$ salts, using doped crystals of the isomorphous zinc salts. His spectrum of $Cs_2(CoCl_4)$ agrees very well with ours (Figure 4). It is noteworthy that his spectrum of the quinolinium salt $(QH)_2(CoCl_4)$ at room temperature has a shape very similar to that of the ethylenediammonium salt reported here and has a band center at ca. 1.50 μm^{-1}. Although no structural data are available for the quinolinium salt, it is reasonable to postulate the presence of hydrogen bonding and a resulting distortion from T_d symmetry for the $CoCl_4^{2-}$ ion similar to that of the ethylenediammonium salt. On the other hand, the tetramethylammonium salt, which is relatively undistorted (Table IV), was found by Ferguson to have a spectrum quite similar to that of the cesium salt.

The major infrared bands for the title compound are given in Table VI, along with data for $(enH_2)Cl_2$ and for $Cs_2(CoCl_4)$. The strong band at ca. 300 cm^{-1} is assigned to the $CoCl_4^{2-}$ stretching vibration[20] and is the only important infrared feature for $Cs_2(CoCl_4)$ in the region studied. The rest of the spectrum of $(enH_2)_2(CoCl_4)Cl_2$ is roughly similar to that of $(enH_2)Cl_2$, although there are greater differences than might be expected. The assignments and interpretation of shifts are based on those given by Colthup et al.[21] and Bellamy.[22] Bands due to CH_2 groups appear at ca. 3000, 1500, and 1300 cm^{-1} as expected, but the CH_2 deformation mode which exhibits a single strong band in $(enH_2)Cl_2$ appears to be split into three bands in the cobalt compound. The N–H stretching vibration at 3180 cm^{-1} is greatly attenuated (or shifted to a lower frequency and buried in the C–H band) for the cobalt compound, which indicates significant hydrogen bonding.[21] The NH_3^+ deformation modes at 1591 and 1564 cm^{-1} are shifted upward by ca. 15 cm^{-1}, again indicating hydrogen bonding. Other bands are assigned as shown. Finally, however, there remain four unassigned bands in the cobalt compound at 1175, 968, 896, and 470 cm^{-1} which are absent in $(enH_2)Cl_2$.

The title compound was obtained in two different crystal modifications, having the same empirical formula and identical electronic and vibrational spectra. Only the needle form was subjected to a complete crystallographic study, but preliminary results on the plate form indicate that it is crystallographically identical. It is not apparent to us why the order of combining reagents should lead to the different crystal morphologies.

The title compound was initially observed accidentally while attempting a routine preparation of *trans*-$[Co(en)_2Cl_2]Cl$. We understand that other workers have encountered similar difficulties with an unwanted blue impurity in the synthesis of this compound. In light of the study reported here, it is apparent that the controlling factor is the concentration of hydrochloric acid which is often added to buffer the amine during the oxidation step. If too much HCl is present, the ethylenediamine is protonated in preference to coordinating with cobalt(II). Only when coordinated with ethylenediamine will the cobalt undergo oxidation to the stable $Co(en)_2Cl_2^+$ ion. The synthesis is probably best performed without any addition of HCl prior to the oxidation step. Thus the procedure given by Bailar and Rollinson[23] should cause no difficulty.

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Registry No. $(enH_2)_2(CoCl_4)Cl_2$, 62521-17-9; $Cs_2(CoCl_4)$, 15007-14-4.

Supplementary Material Available: Listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Structural and Magnetic Properties of Di-μ-chloro-bis[bis(η^5-cyclopentadienyl)titanium(III)] and Di-μ-chloro- and Di-μ-bromo-bis[bis(η^5-methylcyclopentadienyl)titanium(III)]

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Single-crystal x-ray diffraction methods have been used to determine the molecular structures of $[(C_5H_5)_2TiCl]_2$ (I), $[(CH_3C_5H_4)_2TiCl]_2$ (II), and $[(CH_3C_5H_4)_2TiBr]_2$ (III). All three compounds crystallize as dibridged molecules whose magnetic properties show antiferromagnetic behavior due to interaction between the unpaired electrons on the titanium atoms. I crystallizes in the space group $P2_1/c$ with six dimers in a unit cell of dimensions $a = 13.422$ (8) Å, $b = 15.666$ (11) Å, $c = 13.083$ (12) Å, and $\beta = 94.21$ (4)°. Refinement has converged at a final weighted R factor of 0.047 based on 3615 independent reflections. II was found to be orthorhombic with space group *Pbca* and eight molecules per unit cell. Lattice parameters are $a = 16.357$ (9) Å, $b = 19.194$ (13) Å, and $c = 14.232$ (9) Å. The final weighted R factor obtained by least-squares refinement of 3935 reflections is 0.061. III crystallizes in the monoclinic space group $P2_1/c$ with two dimer molecules per unit cell and lattice parameters $a = 6.746$ (6) Å, $b = 10.591$ (10) Å, $c = 17.164$ (20) Å, and $\beta = 112.22$ (6)°. After least-squares refinement of 1459 reflections the weighted R factor is 0.036. Magnetic susceptibility measurements have been made on all three compounds in an attempt to correlate the magnitude of the antiferromagnetic coupling with trends in structural features. Computer fits of the experimental data yield J values of -111, -160, and -138 cm^{-1} for I, II, and III, respectively. The strength of the interaction increases as the metal–metal distance decreases in the case of the chloride-bridged compounds. An anomaly previously observed in the magnetic properties of I has been found to be due to introduction of impurities during sublimation rather than a phase transition in $[(C_5H_5)_2TiCl]_2$.

Introduction

A study of the magnetic properties of the titanium(III) dimers of the formula $[(C_5H_5)_2TiX]_2$, X = F, Cl, Br, I, to liquid nitrogen temperatures has been reported,[1] but trends found in the magnitude of the antiferromagnetic coupling observed between the two d^1 centers in this system could not be completely explained due to a lack of any structural data on these compounds. The order of interaction is F < Cl $\sim$ I < Br, the iodide seeming out of place. Additional anomalies were found in the magnetic properties of $[(C_5H_5)_2TiCl]_2$ and $[(C_5H_5)_2TiI]_2$ which show scatter in the data near the "turnover" temperature and this has been attributed to a phase transition.[2] The bromide and fluoride analogues do not exhibit this property.

While preparing bis(methylcyclopentadienyl)titanium halides in order to synthesize mixed-metal complexes containing titanium(III) in our laboratory,[3,4] it was noted that the magnetic properties were appreciably modified in some cases by introduction of the methyl group on the ring. Since these compounds present an opportunity to study the dependence of magnetic coupling on the geometry of the molecule when the halide is not changed, we felt that insight as to factors influencing coupling in the entire series could be gained by collecting both structural and magnetic susceptibility data. Properties of low-valent titanium dimers would provide a valuable contrast to the much more extensively studied Cu(II) d^9 complexes, due to differences in orbital occupation for the unpaired electron and the greater radial extension of titanium d orbitals. No previous work has involved interpretation of exchange coupling in Ti(III) systems for which detailed crystallographic information was available for all compounds. Of additional interest was the nature of the proposed phase transition and its effect on comparison of the magnetic properties between compounds. Accordingly, we wish to report x-ray structural results for $[(C_5H_5)_2TiCl]_2$, $[(CH_3C_5H_4)_2TiCl]_2$, and $[(CH_3C_5H_4)_2TiBr]_2$ as well as magnetic susceptibility measurements to liquid helium temperature for these three compounds.

Experimental Section

X-Ray Data. All x-ray intensity data were collected by a θ–2θ scan method using Mo Kα radiation on a Picker four-circle diffractometer equipped with a highly oriented graphite single-crystal monochromator. Stationary-background counts were measured for 10 s before and after each reflection and three standards were collected periodically to monitor crystal and diffractometer stability. A reflection was judged to be observed if the criterion $I_{obsd} > 3\sigma_c(I)$ was met where $\sigma_c = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$. Here T_c is the total counts, t_c/t_b is the ratio of time spent counting peak intensity to that counting backgrounds, and B_1 and B_2 are the background counts. Lorentz and polarization corrections and calculation of observed structure factor amplitudes from the data were carried out using the program VANDY1.[5] During early refinement, a data set comprised only of observed reflections was employed, but final refinement in all cases was completed using the entire data set and weights assigned on the basis of counting statistics. At convergence, no significant systematic variation of $w(F_o - F_c)^2$ with respect to $(\sin\theta)/\lambda$ or the magnitude of the structure factors was noted for any of the structures. Cromer and Waber's scattering factors[6] were used for C, Cl, Br, and Ti, Stewart's scattering factors used for H,[7] and Cromer and Liberman's anomalous dispersion corrections applied for Cl, Br, and Ti.[8] Additional programs used in solution, refinement, and interpretation of the data have been previously referenced.[4]

$[(C_5H_5)_2TiCl]_2$. Di-μ-chloro-bis[bis(η^5-cyclopentadienyl)titanium(III)] was prepared by reduction of $(C_5H_5)_2TiCl_2$ with activated aluminum[4,9] and sublimed in an evacuated sealed tube at 150 °C to form green crystal chunks of irregular shape. These were mounted in thin-wall glass capillaries using a helium atmosphere drybox. Precession photographs showed monoclinic symmetry and systematic