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**Structural and Magnetic Characterization of the Chromium(III) Dimers
Di- μ -hydroxo-bis[(4-hydroxo-2,6-dicarboxylatopyridine)aquachromium(III)]
Tetrahydrate, [Cr(chel)(OH₂)OH]₂·4H₂O, and
Di- μ -hydroxo-bis[(4-chloro-2,6-dicarboxylatopyridine)aquachromium(III)] Dihydrate,
[Cr(Cl-dipic)(OH₂)OH]₂·2H₂O**

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The structural and magnetic properties of the dimeric chromium(III) complexes di- μ -hydroxo-bis[(4-hydroxo-2,6-dicarboxylatopyridine)aquachromium(III)] tetrahydrate, (CrC₇H₆NO₇)₂·4H₂O, [Cr(chel)(OH₂)OH]₂·4H₂O, and di- μ -hydroxo-bis[(4-chloro-2,6-dicarboxylatopyridine)aquachromium(III)] dihydrate, (CrC₇H₅ClNO₆)₂·2H₂O, [Cr(Cl-dipic)(OH₂)OH]₂·2H₂O, have been investigated. The chel complex crystallizes in space group $P\bar{1}$ of the triclinic system with one dimeric formula unit in a cell of dimensions $a = 6.978$ (10) Å, $b = 7.941$ (12) Å, $c = 11.008$ (13) Å, $\alpha = 85.17$ (9)°, $\beta = 68.41$ (7)°, and $\gamma = 66.35$ (7)°. The structure has been refined by full-matrix least-squares techniques to a final value of the conventional R factor (on F) of 0.080 based on 1511 observations. The Cl-dipic complex crystallizes in the space group $C\bar{1}$ of the triclinic system with two dimeric formula units in a cell of dimensions $a = 6.785$ (5) Å, $b = 12.361$ (9) Å, $c = 12.615$ (11) Å, $\alpha = 99.25$ (4)°, $\beta = 103.87$ (3)°, and $\gamma = 88.04$ (4)°. The structure has been refined to a final R factor of 0.042 based on 1303 observations. Both complexes consist of discrete dimeric units. The coordination around the chromium centers is roughly octahedral, the ligating atoms being the nitrogen and two oxygen atoms of the tridentate chel or Cl-dipic ligand, a water molecule, and two bridging hydroxo groups. The Cr–Cr separations and Cr–O–Cr angles are 2.981 (5) Å and 99.5 (2)° and 2.997 (3) Å and 100.7 (2)° in the chel and Cl-dipic complexes, respectively. The magnetic susceptibilities of powdered samples of the two complexes have been fitted to the Van Vleck model. The data for the chel complex give an excellent fit to this model with a singlet–triplet splitting of 4.27 (3) cm⁻¹. The data for the Cl-dipic complex do not fit as well, apparently because of the presence of a large quantity of impurity in the bulk sample, but the data indicate a singlet–triplet splitting of 10.24 (6) cm⁻¹.

Introduction

Experimental and theoretical investigations of the correlation between the structural and magnetic properties of dimeric transition-metal complexes of the type [M(L)_nOH]₂ have been very successful in the simplest case where M is Cu(II).²⁻⁹ Hodgson and co-workers have shown that the magnetic exchange parameter, J , varies linearly with the Cu–O–Cu bridging angle, ϕ , for all the characterized members of this series^{2,9} and have provided a qualitative molecular orbital discussion which explains this behavior.² The semiquantitative molecular orbital calculations of Hoffmann¹⁰ have set this principle on a firm theoretical basis. This simple correlation, however, does not hold for complexes in which the geometry at copper deviates markedly from planarity as demonstrated by Sinn, Bertrand, and their co-workers.⁴⁻⁸ Hodgson has recently noted that J is a function of both ϕ and τ (a measure of the nonplanarity at copper),¹¹ in the simple dihydroxo-bridged dimers, however, the geometry at copper has been observed to be approximately planar.^{2,11-13}

In the more complicated case in which M is Cr(III), Hoffmann's theoretical work¹⁰ and our own recent experimental results¹⁴⁻¹⁷ have demonstrated that a more complex dependence of J on ϕ exists. Since the precise nature of this correlation is still not understood, investigations of the structural and magnetic properties of complexes of the type [Cr(L)_nOH]₂ are continuing; the results of studies of di- μ -hydroxo-bis[(4-hydroxo-2,6-dicarboxylatopyridine)aquachromium(III)] tetrahydrate, [Cr(chel)(OH₂)OH]₂·4H₂O (where chel is the chelidamate, or 4-hydroxo-2,6-dicarboxylatopyridine, dianion), and di- μ -hydroxo-bis[(4-chloro-2,6-dicarboxylatopyridine)aquachromium(III)] dihydrate, [Cr(Cl-dipic)(OH₂)OH]₂·2H₂O (where Cl-dipic is the 4-chlorodipicolinate, or 4-chloro-2,6-dicarboxylatopyridine, dianion), are reported here.

Experimental Section

(a) Di- μ -hydroxo-bis[(4-hydroxo-2,6-dicarboxylatopyridine)aquachromium(III)] Tetrahydrate, [Cr(chel)(OH₂)OH]₂·4H₂O. The

complex was generously donated to us by Professor H. J. Schugar of Rutgers University. Dark blue crystals of the complex were assigned to the triclinic space groups $P1$ or $P\bar{1}$ on the basis of Weissenberg and precession photographs. The latter choice was substantiated by the subsequent structure refinement. The cell constants, obtained by the least-squares procedure of Busing and Levy,¹⁸ are $a = 6.978$ (10) Å, $b = 7.941$ (12) Å, $c = 11.008$ (13) Å, $\alpha = 85.17$ (9)°, $\beta = 68.41$ (7)°, and $\gamma = 66.35$ (7)°. The observed density of 1.96 (2) g cm⁻³ (floatation in CCl₄ and CHBr₃) is consistent with the density of 1.95 g cm⁻³ calculated for one dimeric unit in the cell. Hence, in the centrosymmetric space group $P\bar{1}$ the dimers are constrained to lie on an inversion center.

Intensity data were collected from a severely twinned, prismatic crystal bound by faces of the forms [001], [140], and [10 $\bar{1}$]. A crystal of dimensions 0.08 × 0.45 × 0.17 mm was mounted parallel to (001), and in this orientation intensity data were collected on a Picker FACS-1 four-circle automatic diffractometer equipped with a graphite monochromator and using Mo K α (0.7093 Å) radiation. The data were collected in the manner described elsewhere¹⁹ by the θ – 2θ scan technique at a rate of 1° min⁻¹. Peaks were scanned from 1.0° in 2θ below the calculated K α_1 peak position to 1.0° in 2θ above the calculated K α_2 peak position. Stationary-counter, stationary-crystal background counts of 20 s were taken at each end of the scans.

A unique data set having 2° ≤ 2θ ≤ 55° was gathered; a total of 2487 intensities was recorded. The intensities of three standards, measured after every 100 reflections, showed no significant decline as a function of total exposure time.

Data processing was carried out as described by Corfield et al.²⁰ After correction for background, the intensities were assigned standard deviations according to the formula²⁰ in eq 1, and the value of p was

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

selected as 0.04. No absorption correction was applied; the linear absorption coefficient of this compound for Mo K α radiation is 11.2 cm⁻¹. Neglect of absorption effects for the sample chosen was calculated to have a maximum effect of 3% on F . Of the 2487 data collected, only 1511 were greater than 3 times their estimated standard deviations; only these data were used in the subsequent structure analysis and refinement.²¹

(b) Di- μ -hydroxo-bis[(4-chloro-2,6-dicarboxylatopyridine)aquachromium(III)] Dihydrate, [Cr(Cl-dipic)(OH₂)OH]₂·2H₂O. On the

basis of Weissenberg and precession photographs, dark green crystals of this complex (also provided by Professor Schugar) were assigned to the triclinic system; the observed systematic absences of $(h+k)$ odd for hkl are consistent with the space groups $C\bar{1}$ or $C1$, which are nonstandard settings of the primitive space groups $P\bar{1}$ or $P1$. The centrosymmetric choice was substantiated by the subsequent structure refinement. The cell constants, obtained as described above, are $a = 6.785$ (5) Å, $b = 12.361$ (9) Å, $c = 12.615$ (11) Å, $\alpha = 99.25$ (4)°, $\beta = 103.87$ (3)°, and $\gamma = 88.04$ (4)°. The observed density of 1.996 (2) g cm⁻³ (floatation in CCl₄ and CHBr₃) is in excellent agreement with the value 1.996 g cm⁻³ calculated for two dimeric formula units per cell. Hence, in space group $C\bar{1}$, the dimers are constrained to lie on an inversion center.

The data were collected from a prismatic crystal of dimensions 0.06 × 0.22 × 0.14 mm, bound by faces [001], [144], and [110] and mounted parallel to (001). The intensity data were collected as described above. The takeoff angle was 3.3°, the scan rate was 0.5°/min, and the scan range was from 0.75° (2θ) below the calculated $K\alpha_1$ peak position to 0.75° (2θ) above the calculated $K\alpha_2$ peak position. Backgrounds were counted for 20 s. The value of p selected was 0.04.

A unique data set having $2^\circ \leq 2\theta \leq 52^\circ$ was gathered. Of the 2004 data collected, only 1303 were greater than 3 times their estimated standard deviation, and only these data were used to refine the structure. The absorption coefficient for this compound was 13.9 cm⁻¹, and for the crystal chosen, the transmission coefficients evaluated by numerical integration ranged from 0.77 to 0.94.

Solution and Refinement of Structures

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 all nonhydrogen atoms were from ref 22 and those for H from Stewart, Davidson, and Simpson.²³ The effects of the anomalous dispersion of Cr and Cl were included in the calculation of F_c , the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer and Liberman.²⁴

(a) [Cr(chel)(OH)₂OH]₂·4H₂O. The position of the one independent chromium atom was deduced from a three-dimensional Patterson function, and the remaining nonhydrogen atoms were located after subsequent least-squares iterations and difference Fourier summations. Isotropic least-squares refinement of these atoms gave values of the conventional agreement factors $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o^2)]^{1/2}$ of 0.142 and 0.176, respectively. Anisotropic refinement reduced these values to 0.116 and 0.149, respectively. All hydrogen atoms except those on water oxygen atom O(8) were located in a subsequent difference Fourier map; attempts to locate these two hydrogen atoms were unsuccessful. The located hydrogen atoms were included at their observed positions but their coordinates were not refined. The final least-squares calculations involved anisotropic refinement of the nonhydrogen atoms with 1511 observations and 163 variables. The final values of R_1 and R_2 were 0.080 and 0.097, respectively.

In the final cycle of least squares, no atomic parameter exhibited a shift greater than 0.4σ , which is taken as evidence of convergence. Examination of the values of $|F_o|$ and $|F_c|$ suggested that no correction for secondary extinction was necessary, and none was applied. A final difference Fourier map contained residual density around Cr but exhibited no chemically meaningful peaks. The value of R_2 showed no unusual dependence on $\sin \theta$ or on $|F_c|$, which suggests that our weighting scheme is appropriate.

The atomic positional parameters, along with their standard deviations as estimated from the inverse matrix, are listed in Table I. The thermal parameters and a listing of observed and calculated structure amplitudes are available as supplementary material.

(b) [Cr(Cl-dipic)(OH)₂OH]₂·2H₂O. Examination of a three-dimensional Patterson map gave the position of the one independent chromium atom; subsequent least-squares iterations and Fourier summations revealed the positions of the remaining nonhydrogen atoms. The values of R_1 and R_2 were 0.138 and 0.191 following isotropic least-squares refinement; anisotropic refinement reduced these values to 0.052 and 0.066, respectively. The hydrogen atoms were located in subsequent difference Fourier maps. The final least-squares cycles involved anisotropic refinement of the nonhydrogen atoms and isotropic refinement of the hydrogen atoms, with 1303 observations and 182 variables. The final values of R_1 and R_2 were 0.042 and 0.047, respectively. A final difference Fourier map was featureless, with no peak higher than 0.026 e Å⁻³.

Table I. Positional Parameters for [Cr(chel)(OH)₂OH]₂·4H₂O^a

atom	x	y	z
Cr	0.1976 (2)	-0.1374 (1)	-0.1026 (1)
O1	0.1303 (8)	0.0466 (6)	0.0306 (5)
O2	0.2347 (9)	-0.3709 (7)	-0.0072 (5)
O3	0.1962 (9)	0.0172 (6)	-0.2546 (5)
O4	0.5313 (9)	-0.2093 (7)	-0.1613 (5)
O5	0.2813 (10)	-0.6639 (7)	-0.0217 (5)
O6	0.2211 (11)	0.0234 (7)	-0.4603 (5)
O7	0.2330 (10)	-0.6414 (7)	-0.4956 (5)
O8	0.2490 (11)	-0.3739 (8)	0.2511 (6)
O9	0.2981 (11)	-0.0263 (8)	0.2807 (6)
N	0.2255 (10)	-0.3098 (7)	-0.2318 (5)
C1	0.2360 (12)	-0.4792 (9)	-0.1980 (6)
C2	0.2372 (12)	-0.5964 (9)	-0.2848 (7)
C3	0.2280 (12)	-0.5346 (9)	-0.4059 (7)
C4	0.2172 (13)	-0.3584 (10)	-0.4374 (7)
C5	0.2177 (12)	-0.2491 (9)	-0.3474 (7)
C6	0.2497 (12)	-0.5098 (9)	-0.0653 (6)
C7	0.2122 (13)	-0.0554 (9)	-0.3579 (7)
O1H	0.083	0.115	-0.013
O7H	0.320	-0.743	-0.500
C2H	0.259	-0.715	-0.279
C4H	0.168	-0.288	-0.518
O4H1	0.601	-0.269	-0.119
O4H2	0.530	-0.098	-0.146
O9H1	0.292	-0.115	0.257
O9H2	0.287	-0.018	0.358

^a The positions of the hydrogen atoms were not varied in the least-squares process.

Table II. Positional Parameters (×10⁴) for [Cr(Cl-dipic)(OH)₂OH]₂·2H₂O

atom	x	y	z
Cr	412 (1)	-279 (1)	-1127 (1)
Cl	-384 (2)	1870 (1)	-5467 (1)
O1	688 (8)	-904 (4)	220 (4)
O2	3138 (5)	452 (3)	-823 (3)
O3	-2373 (5)	-755 (3)	-1991 (3)
O4	1464 (8)	-1645 (3)	-1894 (3)
O5	5057 (6)	1501 (3)	-1453 (3)
O6	-4779 (6)	-600 (4)	-3505 (3)
O7	-4701 (10)	-2079 (5)	-1215 (6)
N	126 (6)	447 (3)	-2435 (3)
C1	1719 (8)	997 (4)	-2534 (4)
C2	1611 (9)	1464 (4)	-3470 (4)
C3	-188 (9)	1345 (4)	-4276 (4)
C4	-1850 (8)	781 (4)	-4153 (4)
C5	-1608 (8)	323 (4)	-3212 (4)
C6	3468 (8)	1000 (4)	-1548 (4)
C7	-3100 (8)	-398 (4)	-2907 (4)
O1H ^a	140 (9)	-107 (5)	45 (5)
C2H	295 (14)	155 (7)	-351 (7)
C4H	-314 (11)	68 (6)	-470 (6)
O4H1	91 (13)	-205 (6)	-176 (6)
O4H2	249 (11)	-170 (5)	-172 (5)
O7H1	-475 (18)	-189 (9)	-88 (8)
O7H2	-395 (16)	-156 (9)	-141 (8)

^a Hydrogen parameters are ×10³.

The atomic positional parameters and their standard deviations as estimated from the inverse matrix are listed in Table II. The thermal parameters and a listing of observed and calculated structure amplitudes are available as supplementary material.

Description of the Structures

The structures consist of dimeric [(L)Cr(OH)₂(OH)]₂ units; the chel and Cl-dipic dimeric units are shown in Figures 1 and 2, respectively. The geometry around the chromium(III) centers is roughly octahedral; the ligating atoms are two carboxyl oxygen atoms and the nitrogen atom from the chelidamate or 4-chlorodipicolinate ligand, an oxygen atom from a coordinating water molecule, and the oxygen atoms from the two bridging hydroxo groups. The Cr-N bond lengths in the two structures are essentially equal; in the chel

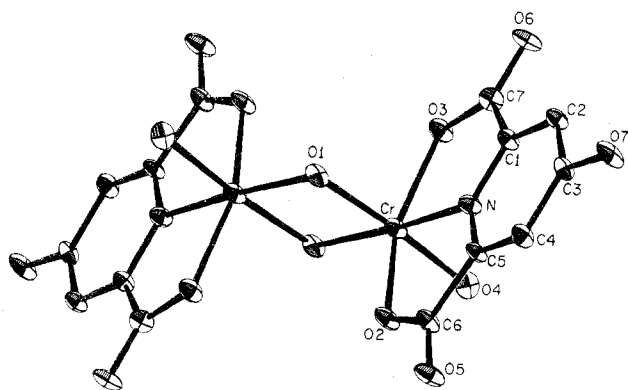


Figure 1. View of the dimeric unit in $[\text{Cr}(\text{chel})(\text{OH}_2)\text{OH}]_2 \cdot 4\text{H}_2\text{O}$. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

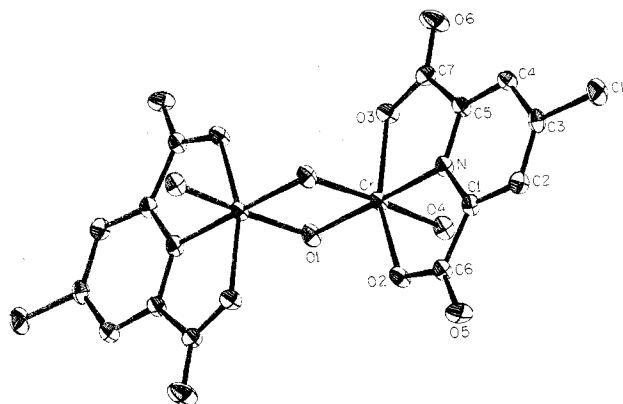


Figure 2. View of the dimeric unit in $[\text{Cr}(\text{Cl-dipic})(\text{OH}_2)\text{OH}]_2 \cdot 2\text{H}_2\text{O}$. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

complex this distance is 1.961 (6) Å while in the Cl-dipic structure it is 1.969 (4) Å. These distances are considerably shorter than the 2.070 (6) and 2.057 (5) Å distances reported for the Fe-N coordination distance in the analogous Fe(III) dimers of dipic and chel²⁵ and the 2.088 (2) Å distance reported for the V-N distance in ammonium oxoperoxo-(pyridine-2,6-dicarboxylato)vanadate(V) hydrate²⁶ but are comparable to the Cr-N distance of 1.978 (4) Å found in the parent Cr(III) dimer $[\text{Cr}(\text{dipic})(\text{OH}_2)\text{OH}]_2 \cdot 2\text{H}_2\text{O}$.²⁷ The bridging Cr-O distances of 1.951 (5) and 1.955 (6) Å in the chel complex and 1.944 (5) and 1.950 (5) Å in the Cl-dipic complex are symmetric and similar to other such bonds in a variety of di- μ -hydroxo- (1.91–1.976 Å)^{14–16,27–32} and di- μ -alkoxo- (1.951–1.962 Å)^{33,34} chromium(III) dimers. The Cr-O distances (where O is a carboxyl oxygen atom) are asymmetric both in the chel complex, where the Cr-O2 distance is 2.024 (6) Å and the Cr-O3 distance is 1.991 (6) Å, and in the Cl-dipic complex, where the distances are 2.011 (4) and 1.997 (4) Å, respectively. Although this asymmetry is expected from previous structures,^{25,26} the Cr-dipic complex is a notable exception in which the distances are crystallographically constrained to be equal.²⁷ These Cr-O bond lengths are similar to the 2.018 (3) Å distance found in the Cr-dipic complex but considerably shorter than the 2.078 (4) and 2.053 (5) Å lengths reported for the Fe-dipic complex and other similar distances reported elsewhere.^{25,26} The Cr-O distance when the oxygen is from the coordinated water molecule is 2.013 (7) Å in the chel complex and 2.005 (5) Å in the Cl-dipic complex; these distances are slightly shorter than the 2.021 (5) and 2.044 (4) Å distances, reported in the Fe-dipic and Fe-chel complexes, respectively, while slightly longer than the 1.990(4) Å distance reported in the Cr-dipic complex. The bond lengths in these complexes are presented in Table III. The Cr-Cr separations

Table III

(A) Interatomic Distances (Å) in $[\text{Cr}(\text{chel})(\text{H}_2\text{O})\text{OH}]_2 \cdot 4\text{H}_2\text{O}$

Cr-Cr'	2.981 (5)	C1-C2	1.385 (9)
Cr-O1	1.951 (5)	C2-C3	1.396 (10)
Cr-O1'	1.955 (6)	C3-C4	1.391 (10)
Cr-O2	2.024 (6)	C4-C5	1.373 (9)
Cr-O3	1.991 (6)	C5-N	1.335 (9)
Cr-O4	2.013 (7)	C3-O7	1.338 (7)
Cr-N	1.961 (6)	O1-O1H ^a	0.75
O3-C7	1.266 (8)	O7-O7H	0.78
C7-O6	1.236 (9)	C2-C2H	0.89
C6-C1	1.492 (9)	C4-C4H	1.10
O2-C6	1.271 (8)	O4-O4H1	0.79
C6-O5	1.240 (8)	O4-O4H2	0.90
C7-C5	1.518 (9)	O9-O9H1	0.80
N-C1	1.346 (8)	O9-O9H2	0.83

(B) Interatomic Distances (Å) in $[\text{Cr}(\text{Cl-dipic})(\text{H}_2\text{O})\text{OH}]_2 \cdot 2\text{H}_2\text{O}$

Cr-Cr'	2.997 (3)	N-C1	1.337 (6)
Cr-O1	1.944 (5)	C1-C2	1.381 (7)
Cr-O1'	1.950 (5)	C2-C3	1.384 (8)
Cr-O2	2.011 (4)	C3-C4	1.399 (7)
Cr-O3	1.997 (4)	C4-C5	1.368 (7)
Cr-O4	2.005 (5)	C5-N	1.334 (6)
Cr-N	1.969 (4)	C3-C1	1.705 (5)
O3-C7	1.285 (6)	O1-O1H	0.55 (6)
C7-O6	1.215 (6)	O4-O4H1	0.070 (7)
C6-C1	1.499 (7)	O4-O4H2	0.68 (7)
O2-C6	1.286 (5)	O7-O7H1	0.44 (9)
C6-O5	1.232 (6)	O7-O7H2	0.88 (10)
C7-C5	1.525 (6)	C2-C2H	0.93 (9)
		C4-C4H	0.97 (5)

^a No esd is given for bonds involving hydrogen atoms whose positions were not refined.

in the chel and Cl-dipic dimers are 2.981 (5) and 2.997 (3) Å, respectively, well within the range of 2.974–3.059 Å observed in other chromium(III) dimers of this general type.^{14–16,27–34}

The bond angles around chromium are normal with the exception of the O2-Cr-O3 angle which is 156.5 (2)° in the chel complex and 156.7 (1)° in the Cl-chel complex; this deviation from octahedral symmetry, also observed in the Fe-chel and Cr-dipic structures,^{25,27} is due to the limited bite of the tridentate ligand. The Cr-O1-Cr' angles subtended at the bridging oxygen atoms in chel and Cl-dipic are 99.5 (2)° and 100.7 (2)°, respectively, intermediate between the values from 98.2 (2) to 102.6 (6)° observed in other dimers of this type.^{14–17,27–32} The bond angles in the complexes are listed in Table IV.

The geometry of the chelidamate ligand is normal. The atoms exhibiting the largest deviations from planarity are the terminal carboxyl oxygen atoms O5 and O6, which are both 0.07 Å out of the plane of the ligand, while the chelidamate hydroxyl oxygen, O7, is only 0.027 Å out of the plane of the ligand. The Cl-dipic ligand is similar, but the deviations for O5 and O6 are less than 0.02 Å out of the plane while the chlorine atom is 0.06 Å out of the plane.

While it is difficult to assess the significance of any hydrogen-bonding interactions in a structure in which we were unable to locate the hydrogen atoms with certainty, it is apparent that the lattice water hydrogen atoms associated with O9 are involved in hydrogen bonds. One such interaction involves the terminal carboxyl atom O6, with an O9...O6 distance of 2.732 (8) Å and associated O9-H...O6 angle of 172°, while the second is to the other lattice water molecule with an O9...O8 separation of 2.972 (9) Å and O9-H...O8 angle of 164°.

The bridging hydroxyl hydrogen atom in Cl-dipic forms hydrogen bonds to O5'', with an O1...O5'' distance of 3.061 (7) Å and an O1-HO1-O5'' angle of 169 (8)°. The coordinated water hydrogen atoms in this case participate in intermolecular hydrogen bonds. One lattice water hydrogen

Table IV

(A) Bond Angles (deg) in $[\text{Cr}(\text{chel})(\text{H}_2\text{O})\text{OH}]_2 \cdot 4\text{H}_2\text{O}$

O1-Cr-O1'	80.5 (2)	O2-C6-O5	125.0 (7)
O1-Cr-O2	103.7 (2)	O5-C6-C1	120.0 (6)
O1-Cr-O3	99.8 (2)	O3-C7-C5	115.0 (6)
O1-Cr-O4	92.7 (2)	O3-C7-O6	123.5 (6)
O1-Cr-N	172.9 (2)	O6-C7-C5	121.5 (6)
O1'-Cr-O2	92.7 (2)	Cr-N-C1	119.2 (5)
O1'-Cr-O3	92.4 (2)	Cr-N-C5	118.1 (4)
O1'-Cr-O4	173.2 (2)	C1-N-C5	122.5 (6)
O1'-Cr-N	92.5 (2)	N-C1-C2	119.6 (6)
O2-Cr-N	77.6 (2)	C1-C2-C3	118.6 (6)
O3-Cr-N	79.2 (2)	C2-C3-C4	120.2 (6)
O4-Cr-N	94.2 (2)	C3-C4-C5	118.5 (6)
O2-Cr-O3	156.5 (2)	C4-C5-N	120.6 (6)
O2-Cr-O4	88.9 (2)	C2-C3-O7	121.9 (6)
O3-Cr-O4	88.7 (2)	C4-C3-O7	117.9 (6)
Cr-O1-Cr'	99.5 (2)	C7-C5-C4	129.1 (6)
Cr-O2-C6	117.6 (5)	C7-C5-N	110.2 (5)
Cr-O3-C7	117.2 (4)	C6-C1-N	110.3 (6)
O2-C6-C1	114.9 (6)	C6-C1-C2	130.0 (6)

(B) Bond Angles (deg) in $[\text{Cr}(\text{Cl-dipic})(\text{H}_2\text{O})\text{OH}]_2 \cdot 2\text{H}_2\text{O}$

O1-Cr-O1'	79.3 (2)	O2-C6-O5	124.1 (5)
O1-Cr-O2	100.5 (2)	O5-C6-C1	121.9 (4)
O1-Cr-O3	102.8 (2)	O3-C7-C5	113.0 (4)
O1-Cr-O4	92.1 (2)	O3-C7-O6	125.8 (4)
O1-Cr-N	176.3 (4)	O6-C7-C5	121.2 (5)
O1'-Cr-O2	93.6 (2)	Cr-N-C1	118.4 (3)
O1'-Cr-O3	91.3 (2)	Cr-N-C5	118.8 (3)
O1'-Cr-O4	170.9 (2)	C1-N-C5	122.7 (4)
O1'-Cr-N	97.2 (2)	N-C1-C2	120.0 (5)
O2-Cr-N	78.3 (1)	C1-C2-C3	117.6 (4)
O3-Cr-N	78.5 (1)	C2-C3-C4	121.6 (4)
O4-Cr-N	91.4 (2)	C3-C4-C5	117.2 (5)
O2-Cr-O3	156.7 (1)	C4-C5-N	120.8 (4)
O2-Cr-O4	90.8 (2)	C2-C3-C1	119.7 (4)
O3-Cr-O4	87.8 (2)	C4-C3-C1	118.7 (4)
Cr-O1-Cr'	100.7 (2)	C7-C5-C4	128.1 (5)
Cr-O2-C6	117.7 (3)	C7-C5-N	111.1 (4)
Cr-O3-C7	118.6 (3)	C6-C1-N	111.5 (4)
O2-C6-C1	113.9 (4)	C6-C1-C2	128.4 (4)

atom forms an intramolecular hydrogen bond while the other hydrogen atom forms an intermolecular hydrogen bond. A list of the probable hydrogen bonds in this structure is given in Table V.

Magnetic Properties

The magnetic susceptibilities of powdered samples of the complexes were measured at Copenhagen in the temperature range 4.95–291.2 K using the Faraday method.¹⁵ The results were in agreement with similar measurements performed at Chapel Hill in the range 4.03–69.5 K using a Foner-type PAR vibrating-sample magnetometer.¹⁴ In both cases $\text{Hg}[\text{Co}(\text{NCS})_4]$ was used as a calibrant.³⁵ The Faraday measurements were used in the fitting procedures discussed below because of larger data sets from these. Elemental analyses for Cr, C, H, N, and Cl were within 0.1% of the theoretical values.

The data were fitted to susceptibilities calculated from the isotropic Hamiltonians for two exchange coupled $S = 3/2$ chromium(III) ions (eq 2 and 3) and finally to a model as-

$$H_{\text{ex}} = J \cdot \bar{S}_1 \cdot \bar{S}_2 \quad (2)$$

$$H_{\text{ex}} = J \cdot \bar{S}_1 \cdot \bar{S}_2 + j(\bar{S}_1 \cdot \bar{S}_2)^2 \quad (3)$$

suming three independent energies for the triplet, quintet, and septet states relative to the singlet state. The susceptibilities were calculated from expression 4. Further parameters

$$\chi = -(N/H) \left(\sum_i (\partial E_i / \partial H) e^{-E_i/kT} / \sum_i e^{-E_i/kT} \right) \quad (4)$$

included in the fitting procedure were the average g factor,

Table V. Probable A-H...B Hydrogen Bonds in $[\text{Cr}(\text{Cl-dipic})(\text{H}_2\text{O})\text{OH}]_2 \cdot 2\text{H}_2\text{O}$

A	H	B	A...B, Å	B...H, Å	A-H...B, deg
O1	O1H	O5 ^a	3.061 (7)	2.52 (6)	169 (8)
O4	O4H1	O5 ^b	2.700 (5)	2.03 (8)	162 (9)
O4	O4H2	O7 ^c	2.590 (9)	1.91 (7)	174 (7)
O7	O7H1	O2 ^d	2.959 (8)	2.60 (9)	142 (15)
O7	O7H2	O3	2.710 (7)	1.84 (10)	171 (9)

^a Symmetry operation: $1-x, -y, -z$. ^b Symmetry operation: $x-1/2, y-1/2, z$. ^c Symmetry operation: $x+1, y, z$. ^d Symmetry operation: $-x, -y, -z$.

Table VI. Parameters Obtained from Magnetic Data Fitting

	$[\text{Cr}(\text{chel})(\text{H}_2\text{O})\text{OH}]_2 \cdot 4\text{H}_2\text{O}^a$ 4.95–291.2 K	$[\text{Cr}(\text{Cl-dipic})(\text{H}_2\text{O})\text{OH}]_2 \cdot 2\text{H}_2\text{O}^b$ 19.76–285.7 K
average g factor ^c	2.002 (2)	2.001 (1)
temp-independent term/cgsu	$69 (13) \times 10^{-6}$	$16 (7) \times 10^{-6}$
mol % monomer	$-2 (2) \times 10^{-2}$	50.7 (3)
J/cm^{-1}	4.27 (3)	10.24 (6)
degrees of freedom	326	326
variance	0.47	2.74

^a Diamagnetic correction -143×10^{-6} cgsu. ^b Diamagnetic correction -178×10^{-6} cgsu. ^c g^2 is proportional to the formula weight assumed. The data seem to indicate slight dehydration of the samples.

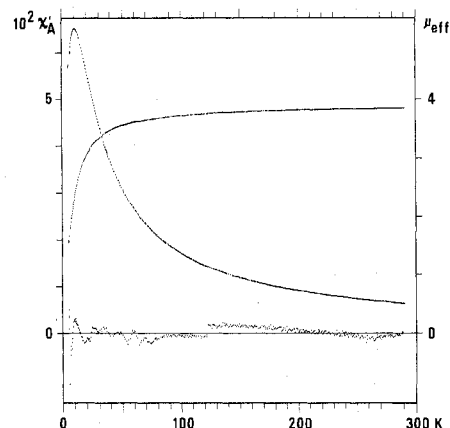


Figure 3. Magnetic properties of $[\text{Cr}(\text{chel})(\text{OH})(\text{OH})]_2 \cdot 4\text{H}_2\text{O}$. Experimental susceptibilities per chromium (shown in the curve which maximizes near $T = 10$ K) and effective magnetic moment. The dotted line in the lower part of the figure represents the difference between experimental and theoretical susceptibility values, recorded as $[(\chi_{\text{obsd}} - \chi_{\text{calcd}}) / \chi_{\text{obsd}}] \times 100$, as obtained from eq 2 using the parameters in Table VI.

a temperature-independent susceptibility contribution, and the molar percentage of chromium having susceptibility vs. temperature dependence according to the Curie law. The procedure was based on minimization of the function $\sum_i (\chi_i^{\text{obsd}} - \chi)^2 / [\sigma^2(\chi) + (\partial \chi / \partial T)^2 \sigma^2(T)]$, where χ_i^{obsd} is the susceptibility corrected for diamagnetism (see Table VI). Standard deviations of 0.05% for susceptibilities and 0.02 K + 0.05% of the deviation of the temperature from that of boiling nitrogen (used as the temperature reference) for the temperature were assumed.

For the hydroxo-substituted complex, the results of fitting the data to eq 2 are shown in Table VI. Application of two and three parameters did not significantly improve the data fitting; within the range of the standard deviations the ratios of the energies of the triplet, quintet, and septet states were 1:3:6 as implied by eq 2. The temperature dependence of the susceptibility and of the effective magnetic moment are shown in Figure 3. As is shown in Table VI, the data give an excellent fit to eq 2 with $J = 4.27 \pm 0.03 \text{ cm}^{-1}$.

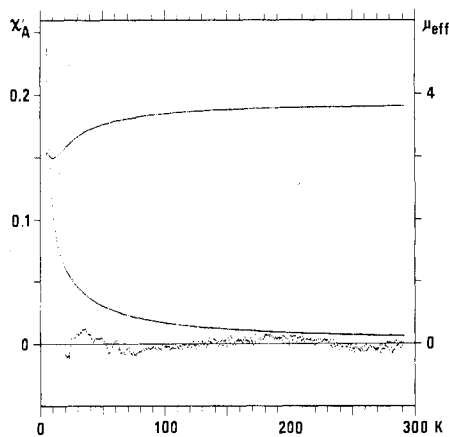


Figure 4. Magnetic properties of $[\text{Cr}(\text{Cl-dipic})(\text{H}_2\text{O})(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$. Experimental susceptibilities per chromium and effective magnetic moment (shown as the curve with the apparent minimum near $T = 10$ K). The dotted line in the lower part of the figure represents the difference between experimental and theoretical susceptibility values, recorded as $[(\chi_{\text{obsd}} - \chi_{\text{calcd}}) / \chi_{\text{obsd}}] \times 100$, as obtained from eq 2 using the parameters in Table VI.

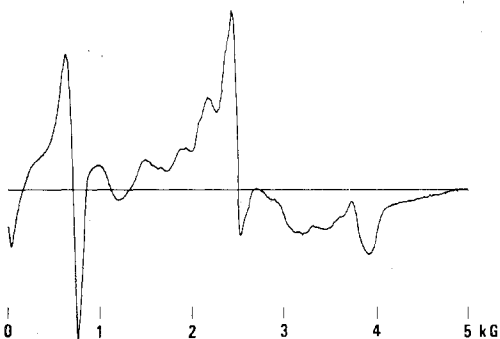


Figure 5. ESR spectrum of $[\text{Cr}(\text{Cl-dipic})(\text{OH}_2)(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$ in *N*-methylformamide; microwave frequency 9.182 GHz, temperature 123 K.

For the chloro-substituted complex the data-fitting procedure was still strongly oscillating after 50 cycles of refinement, and the experimental susceptibilities below 8 K were persistently several percent above the theoretical values. Omission of data below 19.7 K and application of eq 2 led to the results given in Table VI. Inclusion of more energy parameters did not improve the fitting significantly and showed correlation coefficients very close to ± 1 for the parameters involved. The temperature dependence of the susceptibility and the effective magnetic moment for the chloro complex are shown in Figure 4. It is apparent from the figure that the data for this complex do not fit eq 2 at low temperatures. The presence of 50 mol % monomeric impurities as suggested by the fitting procedure is inconsistent with the elemental analyses unless it is assumed that the dimers are partly cleaved followed by coordination of the two water molecules present in the lattice. X-ray powder patterns also indicate the presence of significant amounts of impurities in the bulk samples used for the magnetic measurements. However, the frozen-solution ESR spectrum of $[\text{Cr}(\text{Cl-dipic})(\text{H}_2\text{O})(\text{OH})]_2 \cdot 2\text{H}_2\text{O}$ in *N*-methylformamide (shown in Figure 5) indicates absence of significant amounts of monomers having large zero-field splittings such as expected in the cleavage product. Such species would give rise to one or two strong bands around 1700 G. We find it more reasonable to assume the presence of a virtually noninteracting or weakly ferromagnetic dimer such as the corresponding *cis* isomer.

The observed magnetic and structural properties of these two dimeric complexes are consistent with our general hypothesis that J is a function of ϕ . Thus, the value of 4.27 cm^{-1}

observed for J in the chel complex [$\phi = 99.5 (2)^\circ$] is similar to the value of 2.2 cm^{-1} in the dithionate salt of $[\text{Cr}(\text{en})_2\text{OH}]_2^{4+}$ [$\phi = 100.0 (2)^\circ$] and is much smaller than that of 35 cm^{-1} observed for the 2-(1-aminoethyl)pyridine complex [$\phi = 101.0 (2)^\circ$].³² While the J value of 10.24 cm^{-1} obtained for the Cl-dipic complex is relatively uncertain as a consequence of the large amounts of impurity present in the sample, it is again consistent that this value be higher than that for the chel complex and lower than that for the (aminoethyl)pyridine complex.

An alternative trend in the magnetic properties of dimers of this general type is also discernible.¹⁵ For those complexes in which the hydrogen (or α carbon) atom on the bridging oxygen atom lies in or near the Cr–O–Cr–O bridging plane, the value of J is relatively larger than for those in which this atom is substantially out of the plane. In the Cl-dipic complex the hydroxyl hydrogen atom OH1 lies 0.36 \AA out of the plane; for the chel complex, in which we were not able to refine the position of this hydrogen atom, this distance is approximately 0.7 \AA . These values can be compared with those of 0.57 and 0.67 \AA observed³⁶ in $[\text{Cr}(\text{en})_2\text{OH}](\text{S}_2\text{O}_6)_2$ ($J = 2.2 \text{ cm}^{-1}$) and $[\text{Cr}(\text{malonate})_2\text{OH}]_2^{4-}$ ($J = 2.2 \text{ cm}^{-1}$) and the more precisely determined^{33,34} carbon atom positions of 0.58 and 0.61 \AA in the methoxy-bridged dimers ($J = 8.5$ and 9.8 cm^{-1}) on the one hand and 0.06 and 0.04 \AA in the more strongly interacting chloride perchlorate ($J = 26.8 \text{ cm}^{-1}$) and bromide ($J = 28.6 \text{ cm}^{-1}$) salts of $[\text{Cr}(\text{en})_2\text{OH}]_2^{4+}$, respectively,³⁶ on the other hand.

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Registry No. $[\text{Cr}(\text{chel})(\text{OH}_2)\text{OH}]_2 \cdot 4\text{H}_2\text{O}$, 68630-25-1; $[\text{Cr}(\text{Cl-dipic})(\text{OH}_2)\text{OH}]_2 \cdot 2\text{H}_2\text{O}$, 68630-26-2.

Supplementary Material Available: Tables of anisotropic thermal ellipsoids (U_{ij} in \AA^2) and lists of observed and calculated structure amplitudes (in electrons $\times 10$) for both complexes (19 pages). Ordering information is given on any current masthead page.

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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 18. Synthesis, Crystal Structure, and X-ray Diffuse Scattering Studies of the New Partially Oxidized Tetracyanoplatinate Complex $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{N}_3)_{0.25} \cdot 0.5\text{H}_2\text{O}^1$

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We report the first synthesis and X-ray structure study of a partially oxidized tetracyanoplatinate complex containing azide ion, $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{N}_3)_{0.25} \cdot 0.5\text{H}_2\text{O}$. This one-dimensional conducting salt crystallizes in the tetragonal space group $P4b2 [D_{2d}^7]$, No. 117] with cell dimensions $a = 13.089$ (2) Å, $c = 5.754$ (1) Å, and $V = 985.8$ Å³ and with a calculated density of 3.94 g/cm³ for four formula units per cell. A total of 4358 observed data were averaged to yield 1584 independent reflections of which 1362 had $F_o^2 > \sigma(F_o^2)$. The structure was solved by standard heavy-atom methods and was refined by full-matrix least-squares to a final $R(F_o^2) = 0.068$ and $R_w(F_o^2) = 0.088$. The crystal structure consists of perfectly linear chains of Pt atoms with Pt-Pt separations crystallographically constrained to a value of $c/2 = 2.877$ (1) Å and interchain Pt-Pt distances of 9.255 (2) Å. Using X-ray diffuse scattering techniques we have established the Pt oxidation state as 2.25 (2). The crystal structure is pseudo body centered and nearly isomorphous with the tetracyanoplatinate complexes $\text{M}_2[\text{Pt}(\text{CN})_4](\text{FHF})_x$ [$\text{M} = \text{Cs}$ ($x = 0.39, 0.23$) and $\text{M} = \text{Rb}$ ($x = 0.40$)].

Introduction

The one-dimensional (1-D) properties of both cation- and anion-deficient, partially oxidized tetracyanoplatinate (POTCP) salts are of considerable intrinsic and practical interest to chemists and physicists. The practical interests were spawned in large part by Little's proposal in 1964 that these systems could model 1-D high-temperature excitonic superconductors.² One of the major continuing difficulties regarding study of these systems has been the paucity of materials available. Within the past few years this handicap has been greatly relieved by work in this³ and other laboratories.¹¹ Since a detailed knowledge of the crystal structure is a necessary prerequisite to the understanding of the highly anisotropic properties of these systems, we have undertaken the crystal and molecular structure determinations of a number of these complexes.⁴⁻¹⁰ In separate studies the electrical conduction properties of several of these materials have been determined over a range of temperatures.¹¹ The combined results of these studies have given rise to new speculation regarding the important structural factors which affect the anisotropic properties of these complexes. In a continuing effort to synthesize previously unknown POTCP conductors, and to confirm and clarify many of our recent observations, we have prepared and structurally and chemically characterized the one-dimensional POTCP azide complex $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{N}_3)_{0.25} \cdot 0.5\text{H}_2\text{O}$. In many respects the structure of this salt is closely related to several previously characterized POTCP complexes, especially $\text{M}_2[\text{Pt}(\text{CN})_4](\text{FHF})_x$ [$\text{M} = \text{Cs}$ ($x = 0.39, 0.23$) and $\text{M} = \text{Rb}$ ($x = 0.40$)],^{6,7} and to $\text{Cs}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.30}$.¹⁰

Experimental Section

Crystal Preparation. The preparation of $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{N}_3)_{0.25} \cdot 0.5\text{H}_2\text{O}$, $\text{CsCP}(\text{N}_3)$ hereafter, was carried out by electrolyzing an aqueous solution containing a 1:4 molar ratio of $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$ and CsN_3 ,²³ respectively. A 9 mL aqueous solution containing 1.26 g (2.16 mmol) of $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$ was acidified to a pH of ~5.5 with 0.2 mL of 9 M sulfuric acid. To the resultant white suspension was added 1.5 g (8.57 mmol) of CsN_3 . After complete dissolution of the CsN_3 , the solution was filtered and the filtrate transferred to an electrolytic cell consisting of two opposing 25-mm platinum electrodes which were separated by 6 mm. After 72 h of electrolysis at 1.00 V dc, the reddish bronze colored crystals were isolated by filtration. The crystals were washed with two 3-mL portions of cold water and allowed to air-dry. The yield of 1.15 g (1.96 mmol) represents a 91% yield based on $\text{Cs}_2[\text{Pt}(\text{CN})_4] \cdot \text{H}_2\text{O}$. Anal. Calcd for $\text{Cs}_2[\text{Pt}(\text{CN})_4](\text{N}_3)_{0.25} \cdot 0.5\text{H}_2\text{O}$: Pt, 33.38; Cs, 45.48; C, 8.22; N, 11.39; O, 1.37; H, 0.17. Found²⁴ (Midwest Microlab Inc., Indianapolis, Ind.): Pt, 32.56; Cs, 44.54; C (12 determinations), 8.28 (1); N (18 determinations), 11.47 (2); O (4 determinations), 1.53 (1); H (10 determinations), 0.25 (41). The presence of Cs and Pt was also confirmed by emission spectrographic analyses at Argonne.¹⁹

Space Group Determination. A single crystal of $\text{CsCP}(\text{N}_3)$ was sealed in a glass capillary to prevent dehydration and was aligned, using oscillation photographs, along the crystallographic c axis. Weissenberg photographs of the levels with $l = 0 \rightarrow 4$ and precession photographs of the levels with $h = 0 \rightarrow 3$ were obtained using Ni-filtered $\text{Cu K}\alpha$ radiation. The crystal class is tetragonal and the unit cell constants and intensity distribution appear to be nearly identical with those for $\text{Cs}_2[\text{Pt}(\text{CN})_4]\text{Cl}_{0.30}$ ¹⁰ which belongs to the tetragonal space group $I4/mcm [D_{4h}^{18}]$, No. 140]. However, on long-exposure photographs of each level we observed a few (5-10) weak reflections which would be systematically absent in space group $I4/mcm$. The only systematic absence which could be positively identified was $0kl$