Inorg. Chem. **1980**, *19*, 3116–3121

be present in the centrosymmetrically related dimer.

As is evident from Tables IV and V, there is excellent agreement between corresponding structural parameters of the two azo oxime ligands. The mean C=N and N=O distances of 1.306 (6) and 1.346 (6) Å, respectively, agree well with typical values found in metal complexes of dimethylglyoxime and other *vic*-dioximes.[23] The mean N=N distance of 1.284 (6) Å is within the range of values found for metal-bonded azo groups.[24] The ligand as a whole is very nearly planar, with only a small deviation (ca. 0.06 Å) of the methyl carbon atom and small (1.4°) twisting of the phenyl ring from the plane of the chelate ring.

The coordination about the copper atoms is distorted tetrahedral, as expected for a Cu(I) complex. The Cu–N(azo) and Cu–N(oxime) distances differ only slightly. The mean Cu–N(azo) distance of 1.996 (4) Å agrees well with the value of 1.993 (16) Å found in a copper (I) chloride–azomethane complex.[25] A shorter Cu(I)–N(azo) distance of 1.90 (2) Å has been reported in a cuprous chloride complex of a bicyclic azo ligand.[26]

The observed physical properties of the title compound and its homologues[1] are consistent with their formulation as copper(I) complexes. All members of this series are diamagnetic, as determined by magnetic susceptibility measurements and NMR spectra. The dimeric nature of a representative member of this series in benzene indicates that the hydrogen bonds remain intact in this solvent. The nature of the reduction process whereby the Cu(I) complex is obtained from the starting Cu(II) complex is unclear. This point is being investigated, as are other physical and chemical properties of this complex.[27]

Registry No. ((Phenylazo)acetaldoximato-*N,N'*)((phenylazo)acetaldoxime-*N,N'*)copper(I), 74366-53-3.

Supplementary Material Available: A table of observed and calculated structure amplitudes (19 pages). Ordering information is given on any current masthead page.

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Structural and Magnetic Characterization of the Chromium(III) Dimer *cis*-[Hydroxotetraamminechromium(III)-μ-hydroxo-pentaamminechromium(III)] Dithionate Trihydrate, $[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)](S_2O_6)_2\cdot 3H_2O$

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The crystal and molecular structure of the title complex *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH](S_2O_6)_2\cdot 3H_2O$ has been determined by three-dimensional, single-crystal counter X-ray diffraction methods. The complex crystallizes in the space group *Cc* of the monoclinic system with four formula units in a cell of dimensions a = 7.395 (2) Å, b = 19.417 (10) Å, c = 16.892 (5) Å, and β = 96.86 (2)°. The structure has been refined by least-squares methods to a final value of the conventional R factor (on F) of 0.044 on the basis of 1457 independent intensities. The structure consists of *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH]^{4+}$ cations which interact through extensive hydrogen-bonding networks with the dithionate anions and the solvent molecules. The geometry around each chromium(III) center in the dimeric cation is roughly octahedral, the nine Cr–N distances falling in the range 2.055 (11)–2.111 (10) Å with an average value of 2.09 (2) Å. The terminal Cr–O bond length is 1.915 (9) Å. The Cr–O bridging distances and associated Cr–O–Cr bridging angle are 1.962 (8) Å, 1.989 (8) Å, and 142.8 (5)°. The magnetic susceptibility of the complex in the range 4–290 K indicates antiferromagnetic interaction. The data were fitted to a model assuming independent triplet, quintet, and septet energies. The results were almost consistent with the Van Vleck equation with a triplet energy of 20.56 (2) cm^{-1}. No statistical evidence was found for the necessity of a biquadratic exchange term. A similar triplet energy was found in the corresponding chloride dihydrate.

Introduction

The well-known rhodo and erythro chromium(III) dimers, first reported by Jørgensen[3] in 1882, have been the subjects of intense magnetic[4-13] and spectroscopic[14-17] interest. The weakly paramagnetic basic rhodo complex has been shown by crystallographic methods to contain a linear Cr–O–Cr linkage,[10,18,19] while the acid rhodo complex contains a bent Cr–OH–Cr unit.[12,17,18]

The magnetic properties of dimeric transition-metal complexes have been shown to be dependent upon their structures. In the simplest cases of the copper(II) complexes of formulation $[Cu(L)OH]_2^{n+}$ where L is a bidentate ligand, the magnetic-exchange parameter J has been found[20] to be de-

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termined by the bridging Cu–O–Cu angle, φ; for the complexes currently available, J varies linearly with φ.[21] In attempting to extend this correlation to the analogous chromium(III) dimers, $[Cr(L)_2OH]_2^{n+}$, we have shown that while J is again dependent on φ, the relationship is not a simple linear one.[22-24] We now wish to turn our attention to the singly bridged acid rhodo and erythro complexes and seek a structural–magnetic correlation for these materials also. We here report the structural and magnetic properties of one such complex, *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH](S_2O_6)_2{\cdot}3H_2O$, and the magnetic properties of the corresponding chloride dihydrate.

Experimental Section

Synthesis of the Complex. The measurements of the magnetic susceptibility of this complex were in the early stages hampered by the difficulty of obtaining sufficiently pure samples; we, therefore, give the details of the syntheses. The initial material, acid rhodo chloride, was prepared by a modification of Linhard and Weigel's procedure[25] as follows.

$[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5{\cdot}H_2O$. A 1.00-kg sample of chromium(III) chloride hexahydrate (3.75 mol) was dissolved in 1650 mL of 1.7 M hydrochloric acid. The solution was covered with a layer of pentane and reduced by addition of 150 g of zinc (unspecified technical quality in the shape of residuals from dry battery production). Reduction was continued until the color of the solution was deep sky blue (about 1 h), and then the solution was cooled to 2 °C. Meanwhile, a mixture of 2.00 kg of ammonium chloride and 6.5 L of 12 M aqueous ammonia was cooled to −15 °C by pouring liquid ammonia directly into the mixture with stirring. The Cr(II) solution was quickly added through a very coarse filter to remove the excess zinc. The solution was reoxidized by a vigorous stream of oxygen for 1 h. The red precipitate was washed with 4 M hydrochloric acid and ethanol. The yield of crude product was 545 g or 60% on the basis of chromium. The product was recrystallized as the monohydrate according to the literature method.[25]

***cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)](S_2O_6)_2{\cdot}3H_2O$** was prepared in the usual way[3] but recrystallized twice as follows. The crude product was dissolved in water by addition of 12 M hydrochloric acid (the cis-aqua complex is much more soluble) until approximately 75% of the product was dissolved. The mixture was filtered, and the cis-hydroxo complex was reprecipitated by addition of aqueous 12 M ammonia. The addition was stopped after precipitation of approximately 10% of the theoretical yield. With this low-yield procedure, the samples contained very small amounts of monomeric material, typically <0.03 mol %, as suggested by the magnetic data. Elemental analyses for Cr, N, H, Cl, and S were within 0.3% of the theoretical values.

***cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]Cl_4{\cdot}2H_2O$** was prepared by dissolving the cis-aqua erythro chloride[25] in 1 M aqueous ammonia followed by precipitation with ethanol.

Magnetic Susceptibility. The magnetic susceptibility of powdered samples was measured by the Faraday method at a field strength of 12 000 Oe in the temperature range 4–290 K. Preliminary descriptions of the instrument are found elsewhere.[10,26,27]

Crystallographic Data. Reddish purple needle-shaped crystals of the complex were assigned to the monoclinic system on the basis of Weissenberg and precession photography. The observed systematic absences of hkl for $h + k$ odd and $h0l$ for l odd suggest that the space group is either $C2/c$ (C_{2h}^6, No. 15) or Cc (C_s^4, No. 9). The cell constants, obtained by least-squares methods, with the wavelength assumed as $\lambda(\text{Mo K}\alpha_1) = 0.7093$ Å, are $a = 7.395$ (2) Å, $b = 19.417$ (10) Å, $c = 16.892$ (5) Å, and $\beta = 96.86$ (2)°. The density of 1.836 g cm^{-3}, calculated for 4 molecules/cell, is in acceptable agreement with the value of 1.78 (3) g cm^{-3} observed by flotation in carbon tetrachloride/iodoethane mixtures. Thus, in the centrosymmetric space group $C2/c$, the cations would be constrained to lie on an inversion center or a twofold axis, either of which choices would require some form of disorder; in the space group Cc, however, no crystallographic symmetry is imposed on the complex.

Diffraction data were collected from a needle-shaped crystal of dimensions 0.054 × 0.006 × 0.011 cm in the [100], $[02\bar{1}]$, and $[00\bar{1}]$ directions, respectively. The data were collected with the use of a Picker four-circle automatic diffractometer equipped with a molybdenum tube and a graphite monochromator. The crystal was mounted on a glass fiber roughly parallel to the crystallographic a axis, and intensity data were collected by the $\theta/2\theta$ scan method at a takeoff angle of 1.6°. To allow for the presence of both Kα_1 and Kα_2 radiations, we scanned the peaks from 0.75° in 2θ below the calculated Kα_1 peak position to 0.75° in 2θ above the calculated Kα_2 peak position. Stationary-counter, stationary-crystal background counts of 20-s duration were collected at each end of the scans. A unique data set having $3° \lesssim 2\theta \lesssim 50°$ was gathered, a total of 2334 intensities (including standards) being recorded. The intensities of three standard reflections were measured after every 50 reflections. As the result of a machine failure, the data were collected in two distinct sections; the intensities of the standards in the second section were approximately 5% lower than those obtained earlier, so two separate scale factors were used and refined in the subsequent least-squares procedure.

Data processing was carried out by using the method described by Ibers and co-workers.[28] After correction for background, the intensities were assigned standard deviations according to the formula[28]

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(\text{BH} + \text{BL}) + (pI)^2]^{1/2} \tag{1}$$

and the value of p was selected as 0.04. The data were corrected for absorption and for Lorentz–polarization effects by using the expression[29]

$$\frac{1}{Lp} = \frac{2 \sin 2\theta}{\cos^2 2\theta_m + \cos^2 2\theta} \tag{2}$$

where the monochromator angle, $2\theta_m$, was 11.74°. The attenuation coefficient for this complex with Mo Kα radiation is 12.94 cm^{-1}, and for the sample chosen, the transmission coefficients ranged from 0.84 to 0.95 with an average value of 0.91. Of the 2194 independent reflections collected, only 1457 had intensities greater than 3 times their estimated standard deviations; only these reflections were used in the subsequent structure analysis and refinement.[30]

Examination of a three-dimensional Patterson function demonstrated that the structure was noncentrosymmetric and revealed the locations of the two independent chromium atoms in space group Cc; two cycles of isotropic least-squares refinement were carried out on these positions. All least-squares refinements in this analysis were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$, where the weighting factor w was taken as $4F_o^2/\sigma^2(F_o^2)$. In calculations of F_c, the atomic scattering factors for nonhydrogen atoms were taken from ref 31a while those for hydrogen were from Stewart et al.[32] The anomalous dispersion of copper and sulfur was included in the calculation of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from ref 31b. The remaining nonhydrogen atoms were located in subsequent difference Fourier maps. All atoms in the chromium coordination sphere (except the bridging atom) were initially assigned as nitrogen; the terminal oxygen atom O(2) was then readily distinguished on the basis of its shorter separation from the metal and its smaller apparent thermal motion brought about by assigning oxygen as nitrogen. Isotropic least-squares refinement of these positions yielded 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 0.069 and 0.078, respectively. Anisotropic refinement of these same atoms gave $R_1 = 0.051$ and $R_2 = 0.058$. At this stage of the refinement, the model was checked to see if the correct enantiomer had been selected. A least-squares calculation was run in which the atomic coordinates (x, y, z) for all atoms were replaced by ($-x$, $-y$, $-z$). This brought about

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Table I. Positional Paramters in *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH](S_2O_6)_2 \cdot 3H_2O$

atom	*x*	*y*	*z*
Cr(1)	0.0[a]	−0.0775 (1)	0.0[a]
Cr(2)	−0.2105 (4)	−0.2115 (1)	−0.1415 (2)
S(1)	−0.6045 (6)	−0.0566 (2)	0.2640 (2)
S(2)	−0.3267 (6)	−0.0560 (2)	0.2415 (2)
S(3)	−0.1520 (6)	−0.1621 (2)	−0.5192 (2)
S(4)	−0.0798 (7)	−0.2152 (2)	−0.4114 (2)
N(1)	0.0330 (17)	−0.0007 (5)	0.0890 (6)
N(2)	−0.2695 (15)	−0.0465 (6)	−0.0269 (6)
N(3)	−0.0803 (18)	−0.1477 (6)	0.0838 (6)
N(4)	0.2757 (15)	−0.1046 (6)	0.0297 (6)
N(5)	0.0856 (15)	−0.0081 (5)	−0.0801 (6)
N(6)	−0.0042 (16)	−0.2508 (5)	−0.2038 (6)
N(7)	−0.2691 (14)	−0.1403 (6)	−0.2309 (6)
N(8)	−0.1450 (16)	−0.2875 (5)	−0.0566 (6)
N(9)	−0.3962 (15)	−0.2797 (6)	−0.2026 (7)
O(1)	−0.0297 (12)	−0.1476 (4)	−0.0843 (5)
O(2)	−0.4019 (13)	−0.1753 (4)	−0.0868 (5)
O(3)	−0.6693 (15)	0.0120 (5)	0.2421 (6)
O(4)	−0.6924 (14)	−0.1076 (5)	0.2106 (6)
O(5)	−0.6000 (16)	−0.0751 (6)	0.3463 (5)
O(6)	−0.2604 (15)	−0.1253 (5)	0.2493 (7)
O(7)	−0.3322 (15)	−0.0300 (5)	0.1610 (6)
O(8)	−0.2434 (13)	−0.0090 (5)	0.3007 (6)
O(9)	0.0506 (16)	−0.2643 (5)	−0.4309 (6)
O(10)	−0.2476 (19)	−0.2449 (6)	−0.3924 (7)
O(11)	−0.0028 (20)	−0.1631 (6)	−0.3561 (6)
O(12)	−0.2746 (15)	−0.1100 (5)	−0.5006 (7)
O(13)	0.0204 (16)	−0.1350 (5)	−0.5393 (6)
O(14)	−0.2260 (16)	−0.2157 (5)	−0.5710 (7)
OW(1)	−0.2209 (14)	−0.3682 (6)	0.3342 (6)
OW(2)	−0.1074 (19)	−0.3153 (8)	0.1593 (8)
OW(3)	−0.0844 (18)	−0.4473 (6)	0.0566 (7)
HO1[b]	0.117	−0.157	−0.071
HO2	−0.386	−0.128	−0.085
H1N1	0.036	0.043	0.068
H1N2	0.141	−0.008	0.121
H1N3	−0.057	−0.003	0.120
H1N2	−0.348	−0.058	0.016
H2N2	−0.319	−0.066	−0.072
H2N3	−0.274	0.000	−0.033
H1N3	−0.003	−0.175	0.078
H2N3	−0.208	−0.156	0.054
H3N3	−0.042	−0.141	0.143
H1N4	0.392	−0.083	0.002
H2N4	0.282	−0.151	0.020
N3N4	0.302	−0.097	0.082
H1N5	0.021	−0.003	−0.112
H2N5	0.189	−0.022	−0.097
H3N5	0.105	0.034	−0.056
H1N6	−0.042	−0.266	−0.250
H2N6	0.051	−0.287	−0.177
H3N6	0.079	−0.218	−0.210
H1N7	−0.405	−0.137	−0.254
H2N7	−0.206	−0.151	−0.272
H3N7	−0.233	−0.098	−0.213
H1N8	−0.254	−0.309	−0.031
H2N8	−0.066	−0.270	−0.017
H3N8	−0.088	−0.323	−0.080
H1N9	−0.364	−0.326	−0.216
H2N9	−0.439	−0.259	−0.250
H3N9	−0.491	−0.284	−0.173
H1W1	−0.635	−0.112	−0.132
H2W1	−0.792	−0.156	−0.143

[a] The *x* and *z* coordinates of one atom must be fixed in space group *Cc*. [b] Hydrogen atom coordinates were not refined.

a slight reduction in R_1 and R_2, with values of 0.050 and 0.057, respectively; this improvement in R_2 suggested to us that this reversed model is correct.

The hydrogen atoms were located in subsequent difference Fourier maps, except those associated with two of three water molecules (OW2 and OW3). The hydrogen atoms were included (but not refined) in subsequent least-squares calculations as isotropic atoms with $B = 4.0$ Å^2; this value of B is approximately equal to 1.5 plus the average value of the isotropic B's of the N and O atoms. The isotropic thermal parameters of the hydrogen atoms associated with the water molecule OW1 were set to 5.5 Å^2. Since it was apparent that the **U** tensors for two of the water oxygen atoms (OW2 and OW3) were large, a refinement was undertaken in which these two positions were assigned occupancy factors of 0.5, i.e., the formulation of the complex was changed to a dihydrate; it should be noted that this formulation is more consistent with our density measurement than is that of a trihydrate. This refinement was unsuccessful, leading to values of 0.101 and 0.103 for R_1 and R_2, respectively. Hence, in the final cycle of least squares, these occupancy factors were returned to unity. The final cycle of least squares, which involved 1457 observations, 288 variables, and 63 atoms, converged to values of 0.044 and 0.049 for R_1 and R_2, respectively. No parameter underwent a shift of more than 0.12σ, indicating that the process had converged. There was no evidence for the need of a correction for secondary extinction, and none was applied. A final difference Fourier map was featureless, with no peak in excess of 0.50 e Å^{-3}.

The positional parameters derived from the final least-squares cycle, along with their standard deviations as estimated from the inverse matrix, are presented in Table I. The thermal parameters and a table of observed and calculated structure amplitudes are available.[33]

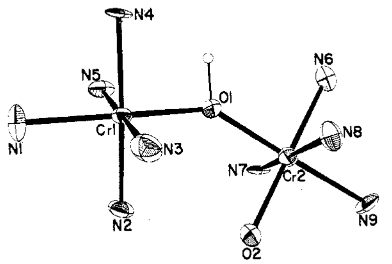

Figure 1. View of the binuclear $[(NH_3)_5Cr(OH)Cr(NH_3)_4OH]^{4+}$ cation. Thermal ellipsoids are drawn at the 40% probability level. The bridging hydroxyl hydrogen atom is shown as a sphere of arbitrary size, and other hydrogen atoms are omitted for clarity.

Table II. Interatomic Distances (Å) in *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH](S_2O_6)_2 \cdot 3H_2O$

atoms	dist	atoms	dist
Cr(1)–Cr(2)	3.744 (3)	S(1)–S(2)	2.133 (5)
Cr(1)–O(1)	1.962 (8)	S(1)–O(3)	1.450 (10)
Cr(1)–N(1)	2.111 (10)	S(1)–O(4)	1.441 (10)
Cr(1)–N(2)	2.079 (11)	S(1)–O(5)	1.432 (9)
Cr(1)–N(3)	2.102 (11)	S(2)–O(6)	1.433 (10)
Cr(1)–N(4)	2.107 (11)	S(2)–O(7)	1.447 (10)
Cr(1)–N(5)	2.062 (10)	S(2)–O(8)	1.437 (10)
Cr(2)–O(1)	1.989 (8)	S(3)–S(4)	2.105 (5)
Cr(2)–O(2)	1.915 (9)	S(3)–O(12)	1.418 (11)
Cr(2)–N(6)	2.097 (11)	S(3)–O(13)	1.456 (11)
Cr(2)–N(7)	2.055 (11)	S(3)–O(14)	1.427 (10)
Cr(2)–N(8)	2.075 (10)	S(4)–O(9)	1.423 (11)
Cr(2)–N(9)	2.090 (10)	S(4)–O(10)	1.439 (12)
O(1)–H(1)[a]	1.10	S(4)–O(11)	1.446 (11)

[a] Hydrogen atom coordinates were not varied.

Discussion

Description of the Structure. The structure consists of *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH]^{4+}$ cations, dithionate anions, and water molecules which are hydrogen bonded to each other. A view of the binuclear cation is given in Figure 1. The bond lengths and angles in the complex are given in Tables II and III, respectively. The geometry around the two independent chromium(III) centers is roughly octahedral. For atom Cr(1) the ligating atoms are the oxygen atom O(1) of the bridging hydroxyl group and five ammine nitrogen atoms, while for Cr(2) one of the ammonia ligands has been substituted by the terminal hydroxyl oxygen atom O(2). The nine independent Cr–N bond lengths fall in the range 2.055 (11)–2.111 (10) Å, with an average value of 2.09 (2) Å. The longest Cr–N bond is the Cr(1)–N(1) bond, N(1) being the

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(33) Supplementary material.

Table III. Selected Bond Angles (Deg) in *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH](S_2O_6)_2{\cdot}3H_2O$

atoms	angle	atoms	angle
Cr(1)-O(1)-Cr(2)	142.8 (5)	S(2)-S(1)-O(3)	104.2 (5)
O(1)-Cr(1)-N(1)	178.9 (7)	S(2)-S(1)-O(4)	105.4 (5)
O(1)-Cr(1)-N(2)	91.2 (4)	S(2)-S(1)-O(5)	105.3 (5)
O(1)-Cr(1)-N(3)	91.3 (4)	O(3)-S(1)-O(4)	111.2 (6)
O(1)-Cr(1)-N(4)	91.2 (4)	O(3)-S(1)-O(5)	116.5 (6)
O(1)-Cr(1)-N(5)	89.6 (4)	O(4)-S(1)-O(5)	113.1 (7)
N(1)-Cr(1)-N(2)	88.7 (4)	S(1)-S(2)-O(6)	107.7 (5)
N(1)-Cr(1)-N(3)	89.8 (4)	S(1)-S(2)-O(7)	104.5 (5)
N(1)-Cr(1)-N(4)	88.9 (4)	S(1)-S(2)-O(8)	102.8 (4)
N(1)-Cr(1)-N(5)	89.3 (4)	O(6)-S(2)-O(7)	112.6 (7)
N(2)-Cr(1)-N(3)	89.7 (5)	O(6)-S(2)-O(8)	114.8 (7)
N(2)-Cr(1)-N(4)	177.4 (5)	O(7)-S(2)-O(8)	113.2 (6)
N(2)-Cr(1)-N(5)	91.6 (4)	S(4)-S(3)-O(12)	105.1 (5)
N(3)-Cr(1)-N(4)	91.2 (5)	S(4)-S(3)-O(13)	103.9 (5)
N(3)-Cr(1)-N(5)	178.3 (6)	S(4)-S(3)-O(14)	102.2 (5)
N(4)-Cr(1)-N(5)	87.4 (4)	O(12)-S(3)-O(13)	113.3 (7)
O(1)-Cr(2)-O(2)	91.6 (4)	O(12)-S(3)-O(14)	116.6 (7)
O(1)-Cr(2)-N(6)	89.1 (4)	O(13)-S(3)-O(14)	113.7 (7)
O(1)-Cr(2)-N(7)	90.4 (4)	S(3)-S(4)-O(9)	103.6 (5)
O(1)-Cr(2)-N(8)	91.1 (4)	S(3)-S(4)-O(10)	104.7 (6)
O(1)-Cr(2)-N(9)	178.8 (7)	S(3)-S(4)-O(11)	104.8 (5)
O(2)-Cr(2)-N(6)	178.8 (4)	O(9)-S(4)-O(10)	114.2 (7)
O(2)-Cr(2)-N(7)	90.3 (4)	O(9)-S(4)-O(11)	113.1 (8)
O(2)-Cr(2)-N(8)	93.0 (4)	O(10)-S(4)-O(11)	114.9 (7)
O(2)-Cr(2)-N(9)	89.5 (4)		
N(6)-Cr(2)-N(7)	88.7 (4)		
N(6)-Cr(2)-N(8)	88.0 (4)		
N(6)-Cr(2)-N(9)	89.8 (4)		
N(7)-Cr(2)-N(8)	176.3 (4)		
N(7)-Cr(2)-N(9)	89.7 (4)		
N(8)-Cr(2)-N(9)	88.7 (4)		

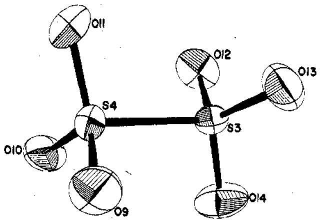

Figure 2. View of one $[S_2O_6]^{2-}$ anion in the structure. The other anion is entirely similar. Thermal ellipsoids are drawn at the 40% probability level.

Table IV. Probable A–H···B Hydrogen Bonds in the Structure

A	B	H	A···B, Å	B···H, Å	A–H···B, deg
O(1)	OW1	HO1	2.82	2.16	116
N(1)	O(13)	H1N1	3.41	2.54	158
N(1)	O(3)	H1N2	3.20	2.37	150
N(1)	O(7)	H1N3	3.14	2.28	160
N(2)	O(7)	H1N2	3.28	2.50	134
N(2)	O(12)	H3N2	3.07	2.20	159
N(3)	O(10)	H1N3	3.21	2.45	162
N(3)	O(9)	H2N3	3.20	2.40	134
N(3)	O(6)	H3N3	3.27	2.58	125
N(4)	O(10)	H2N4	3.22	2.53	133
N(4)	O(4)	H3N4	3.04	2.17	162
N(5)	O(8)	H1N5	2.99	2.31	166
N(5)	OW1	H2N5	3.23	2.55	133
N(5)	O(13)	H3N5	2.92	2.09	150
N(6)	O(14)	H2N6	2.93	2.28	128
N(6)	OW1	H3N6	3.13	2.30	154
N(7)	OW2	H1N7	3.05	2.17	142
N(7)	O(11)	H2N7	3.09	2.20	166
N(7)	O(8)	H3N7	2.95	2.10	157
N(8)	O(13)	H1N8	2.94	1.98	152
N(8)	O(5)	H3N8	3.17	2.34	151
N(9)	O(4)	H1N9	3.12	2.27	145
N(9)	OW2	H2N9	3.23	2.36	160
N(9)	O(14)	H3N9	3.49	2.59	170

atom trans to the bridging hydroxyl group O(1). Similarly, around Cr(2), the bonds to N(6) and N(9) (trans to O(2) and O(1), respectively) of lengths 2.097 (11) and 2.090 (10) Å, respectively, are slightly longer than the remaining Cr(2)–N bonds. A similar trend occurs[12,17] in both reports of the structure of the related symmetric $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$, but in no case (including the present one) is any individual bond length significantly different from the average of the others. The Cr–N distances observed here are comparable to those of 2.081 (9)–2.091 (9) Å in $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$,[17] 2.080 (6) and 2.081 (7) Å in $[Cr(en)_2OH]_2^{4+}$,[34] 2.096 (3) Å in the tris(propane-1,3-diamine)chromium(III) cation,[35] and 2.05–2.15 Å reported for a variety of other complexes containing Cr(III)–N bonds.[12,36]

The terminal Cr(2)–O(2) bond length of 1.915 (9) Å can be compared with those of 1.900 (4) and 1.901 (4) Å recently reported[37] for the terminal Cr–OH distances in the related dimeric species $[(en)_2OHCr{-}OH{-}Cr(en)_2OH]^{3+}$. These distances are, of course, considerably shorter than the Cr–OH_2 distances of 2.005 (5) and 2.013 (7) Å reported recently for binuclear chromium(III) complexes with terminally coordinated water molecules.[23]

The bridging unit is not significantly asymmetric, the Cr(1)–O(1) and Cr(2)–O(1) bond lengths of 1.962 (8) and 1.989 (8) Å comparing well with the value of 1.974 (3) Å reported for the symmetric acid rhodo ion[17] and with the values of 1.986–1.990 Å observed in the related ethylenediamine complexes.[37,38] The Cr(1)–O(1)–Cr(2) bridging angle of 142.8 (5)° in this complex is significantly smaller, however, than the values of 154, 158.4 (7), and 166 (1)° reported for the corresponding angle in the symmetric acid rhodo ion, $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$,[12,17,18] but is larger than the value of 135.4 (2)° found[37] in $[(en)_2OHCr{-}OH{-}Cr(en)_2OH]^{3+}$. This difference between the bridging geometry in the present complex and that in the acid rhodo ion is reflected in the magnetic properties of the two ions (vide infra). As anticipated for a hydroxo-bridged system, the bridging Cr–O distances are longer and the Cr–O–Cr angle is smaller than the corresponding values of 1.821 (3) Å and 180° in the basic rhodo ion, $[(NH_3)_5Cr(O)Cr(NH_3)_5]^{4+}$, which contains a linear oxo bridge.[19] Since the hydrogen atom parameters in the present structure were not refined, little reliance can be placed on these coordinates. It is interesting to note, however, that the hydrogen atom on the bridging hydroxyl group appears to be out of the plane of the Cr(1)–O(1)–Cr(2) bridging moiety, the observed distance from the plane being 0.48 Å.

The two independent dithionate anions are substantially similar, and a view of one of them is given in Figure 2. The S–S bond lengths of 2.105 (5) and 2.133 (5) Å are similar to the values of 2.097 (4)–2.146 (5) Å reported recently for this ion.[34,38-40] The S–O bond lengths of 1.432 (9)–1.450 (10) Å, with an average value of 1.440 (7) Å, are likewise within the reported range.[34,38-40] The geometry at each sulfur atom is distorted tetrahedral, with S–S–O angles in the range 102.2 (5)–107.7 (5)° with an average of 104.5° and O–S–O angles ranging from 111.2 (6) to 116.6 (7)° with an average of 113.9°. The conformation of both independent anions is staggered, the ions approximating D_{3d} ($\bar{3}m$) symmetry. For

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Table V. Results of the Digital-Fitting Procedure for Susceptibilites[a]

	dithionate trihydrate			chloride dihydrate	
	model 1	model 2	model 3	model 1	model 2
J, cm^{-1}	20.56 (2)	20.62 (6)		21.08 (2)	20.40 (3)
j, cm^{-1}		0.008 (8)			−0.19 (2)
$E(1)$, cm^{-1}	20.56 (2)[c]	20.57 (8)[c]	20.96 (4)	21.08 (2)[c]	21.6 (1)[c]
$E(2)$, cm^{-1}	61.68 (6)[c]	61.7 (2)[c]	61.91 (7)	63.24 (6)[c]	63.8 (3)[c]
$E(3)$, cm^{-1}	123.4 (1)[c]	123.6 (4)[c]	126.8 (3)	126.5 (1)[c]	124.1 (3)[c]
g[b]	1.960 (1)	1.960 (2)	1.979 (2)	2.015 (1)	2.028 (1)
f[d]	395	394	393	824	923
var/f	1.40	1.40	1.11	2.43	2.09

[a] Other parameters included were a temperature-independent susceptibility term besides the standard diamagnetic corrections (results (40–100) × 10^{-6} cgsu) and monomeric impurities (0–0.3 mol %). [b] The g factors obtained depend on the elemental analyses, g^2 being proportional to the formula weight assumed. The sample of the chloride salt is obviously slightly dehydrated. [c] Calcualted values for comparison with other models. [d] f = degrees of freedom.

example, in idealized D_{3d} geometry, atom O(14) would lie in the plane defined by atoms S(3), S(4), and O(11) while atoms O(9), O(10), O(12), and O(13) would be equidistant from the plane; in the observed structure (as can be seen in Figure 2), atom O(14) lies only 0.005 Å from the plane, with O(9) and O(13) 1.21 and 1.24 Å, respectively, above and O(10) and O(12) 1.19 and 1.16 Å, respectively, below the plane.

There is an extensive network of hydrogen bonding in the crystals, and a list of probable hydrogen bonds is given in Table IV. The bridging hydroxyl group probably forms a hydrogen bond to the water molecule OW1, with an O···O separation of 2.82 Å, although the calculated O–H···O angle of 116° suggests that this interaction may be weak. There is apparently no hydrogen bonding between the terminal hydroxyl group and the bridge. All of the dithionate oxygen atoms appear to participate in hydrogen bonding with the ammine ligands. It is noteworthy that the longest S–O bond observed is that to atom O(13) [S(3)–O(13) = 1.456 (11) Å] and that this atom appears to be involved in hydrogen bonding to the greatest extent.

Magnetic Properties. The average magnetic susceptibility and effective moment of microcrystalline samples of *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)](S_2O_6)_2{\cdot}3H_2O$ as functions of temperature are shown in Figure 3. The susceptibility data were fitted to

$$\chi_A' = -\frac{N}{H}\,\frac{\sum_i(\partial E_i/\partial H)e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} \qquad (3)$$

where E_i refers to the energies of the 16 components of the ground states, by minimization of

$$\sum_i(\chi_i^{\mathrm{abs}} - \chi_A')^2/[\sigma^2(\chi) + (\partial\chi/\partial T)\sigma^2(T)] \qquad (4)$$

We assumed the Hamiltonian (later referred to as model 3)

$$\mathcal{H} = E(S') + g\beta M_{S'} \qquad (5)$$

where $S' = S_1 + S_2$. S' has the values 0, 1, 2, and 3. This Hamiltonian implies independent energies of the triplet, quintet, and septet levels, absence of zero-field splittings within these, and an isotropic Zeeman effect. This is a generalized version of the Van Vleck Hamiltonian (model 1) which in some cases has been expanded with a biquadratic exchange term (model 2) according to

$$\mathcal{H} = J{\cdot}S_1{\cdot}S_2 + j{\cdot}(S_1{\cdot}S_2)^2 \qquad (6)$$

Data fittings to these models were also performed. The discussion of the accuracies and standard deviations of the measurements is found elsewhere.[41] The results of the fitting of the data to the three different coupling models are shown in Table V. Also included are the results for the corresponding chloride salt. In this case the measurements were performed on an earlier version of our instruments.

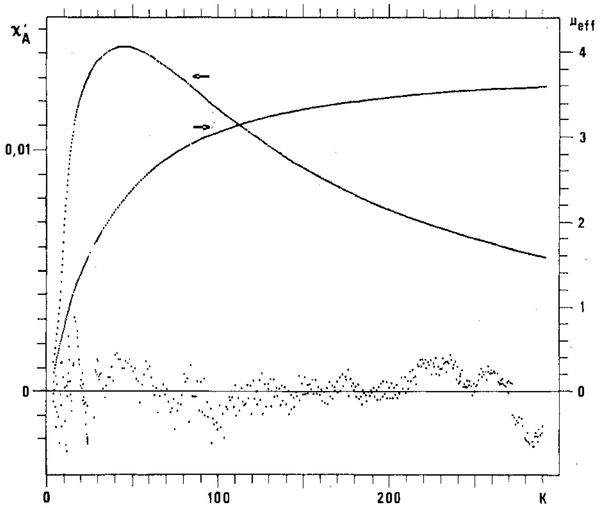

Figure 3. Magnetic susceptibility per chromium (left scale in cgsu) and effective magnetic moment (right scale in Bohr magnetons) of *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)](S_2O_6)_2{\cdot}3H_2O$. The dots represent 399 measurements. The lower, almost random distribution of dots around the abscissa indicates the corresponding values of $(X_{\mathrm{obsd}} - X_{\mathrm{calcd}}) \times 100$. X_{calcd} refers to the parameters of model 3 in Table V.

The susceptibility of the dithionate salt is well described by the simple Van Vleck equation, and the variance per degree of freedom ratio (var/f) is not reduced by including a biquadratic exchange term. The general Hamiltonian, eq 5, is, however, significantly better since $(\mathrm{var}_2/f_2)/(\mathrm{var}_3/f_3) = 1.25$ is close to the 97.5% fractile of the v^2 distribution, $v^2_{0.975}$ (294, 293).[42] For the chloride salt the value of the corresponding ratio was 1.16, close to the 95% fractile, $v^2_{0.95}$ (824, 823), which indicates significance for a biquadratic exchange term. For both salts, however, the simple Van Vleck equation with $J \approx$ 21 cm^{-1} is satisfactory.

These results differ slightly from those of earlier reports on this cation. On the basis of less complete data sets, the following triplet energies have been found: for the chloride monohydrate, 25 cm^{-1} [4] and 23 cm^{-1},[8] for the dithionate with 2.5 mol of water, 23 cm^{-1},[10] and for the bromide, 19 cm^{-1}.[5]

The magnetic interaction in the present cis-hydroxo erythro complex is much smaller than in the acid rhodo complex, $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$(aq), the only other chromium(III) dimer with a single μ-hydroxo bridge which has been well characterized both structurally and magnetical-

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ly.[12,13,15,16,43,44] In our view the very small Cr(1)–O(1)–Cr(2) bridging angle of 142.8 (5)° as compared with 154–166° reported for the rhodo salts is partially responsible for this difference. A discussion of such relations will be the subject of future publications from our laboratories.

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Registry No. $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$, 15007-47-3; *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)](S_2O_6)_2\cdot 3H_2O$, 74410-09-6; *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]Cl_4$, 74365-64-3.

Supplementary Material Available: A table of anisotropic thermal parameters and a list of observed and calculated structure amplitudes (electrons × 10) (10 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Bis(δ-camphorquinone dioximato)nickel(II) and -palladium(II). Reactions and Structural Studies of Some M_3Ag_3 Cluster Complexes of Camphorquinone Dioxime

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Reactions of $AgNO_3$ with Ni(δ-HCQD)$_2$ or Pd(δ-HCQD)$_2$, where δ-HCQD$^-$ is δ-camphorquinone dioximato, yielded the hexanuclear metal cluster complexes [Ni(δ-HCQD)$_2$Ag]$_3\cdot$2.5CHCl$_3$, Ni–Ag, and [Pd(δ-HCQD)$_2$Ag]$_3\cdot$2CHCl$_3$, Pd–Ag, respectively. X-ray crystallographic studies performed on both complexes showed them to belong to space group $P2_12_12_1$. The unit cell dimensions of Ni–Ag are a = 15.990 (5) Å, b = 38.44 (1) Å, c = 13.437 (5) Å, V = 8260.97 Å^3, and Z = 4 while those of Pd–Ag are a = 16.110 (6), b = 38.92 (1), c = 13.393 (3) Å, V = 8395.55 Å^3, and Z = 4. Block-diagonal least-squares refinement of 3021 observed reflections for Ni–Ag and 6112 for Pd–Ag converged to R_F = 10.7 and 11.4 (R_w = 12.7 and 15.0) for the Ni–Ag and Pd–Ag structures, respectively. Their structures indicate that each hexanuclear molecule consists of three individual M(δ-HCQD)$_2^-$ units which act as multidentate ligands coordinating to a linear chain of three silver atoms. The coordination geometry around each M ion in the M(δ-HCQD)$_2^-$ units is square planar, and the δ-HCQD$^-$ ligands are coordinated to M via N and O atoms. The Ag in the center of the molecule is coordinated to six O atoms with average Ag–O distances of 2.49 (3) and 2.45 (2) Å for Ni–Ag and Pd–Ag, respectively. The two silver atoms at the ends of the chain are each coordinated to three nitrogen atoms from the M(δ-HCQD)$_2^-$ units with average Ag–N distances of 2.20 (4) and 2.27 (3) Å, respectively. The Ag–Ag distances, 3.059 (5) and 3.052 (5) Å in Ni–Ag and 3.173 (3) and 3.179 (3) Å in Pd–Ag, are somewhat longer than those (2.89 Å) in Ag metal and indicate that there are Ag–Ag interactions along the linear chains. The bis(pyridine) adduct of Ni(δ-HCQD)$_2$ was also prepared. A proposed structure for this complex is based on the similarity of its IR spectrum to those of the Ni–Ag and Pd–Ag clusters.

Introduction

Our earlier work,[1,2] as well as that of Nakamura et al.,[3] showed that α- and δ-camphorquinone dioximes (H_2CQD) form square-planar Ni(II) and Pd(II) complexes in which the ligands chelate via nitrogen and oxygen donor atoms. The structure[1] of Ni(δ-HCQD)$_2$ is shown in Figure 1.

In the present paper, we report the reactions of Ni(δ-HCQD)$_2$ and Pd(δ-HCQD)$_2$ with $AgNO_3$ to form hexanuclear clusters of the composition [M(δ-HCQD)$_2$Ag]$_3$, where M is Ni(II) or Pd(II). Results of crystallographic studies on both of these complexes are described. It has also been found that Ni(δ-HCQD)$_2$ reacts with pyridine to give an adduct whose proposed structure is related to that of the clusters.

Experimental Section

Spectral Data. Proton NMR spectra were obtained by using a Varian HA-100 spectrometer with Me_4Si as the internal reference and $CDCl_3$ as the solvent. The ^{13}C NMR spectra were recorded on a JEOL FX-90Q ^{13}C NMR/^1H spectrometer. Infrared spectra were obtained on KBr pellets with a Beckman IR-4250 (4000–200 cm^{-1}) spectrophotometer. Electronic spectra were recorded on a JASCO-ORD/UV-5 or Cary 14 spectrophotometer.

Starting Materials. The complexes Pd(δ-HCQD)$_2$, Ni(δ-HCQD)$_2$, and Ni(α-HCQD)$_2$ were prepared according to published procedures.[2] The Pd(PhCN)$_2$Cl$_2$ was prepared by the method of Doyle et al.[4]

Preparation of [Ni(δ-HCQD)$_2$Ag]$_3\cdot$2.5CHCl$_3$. To 3 mL of a $CHCl_3$ solution containing 0.05 g (0.11 mmol) of Ni(δ-HCQD)$_2$ was added approximately 5 mL of 0.05 M aqueous $AgNO_3$ solution. The two solution layers were mixed together by adding MeOH (15 mL) until a homogeneous solution was obtained. The resulting green solution was allowed to evaporate overnight at room temperature. After 24 h green needlelike crystals were obtained; yield 90%. IR (KBr): ν(C═N) 1615, 1560 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.20 (d), C4–H; 1.12 (s), 0.86 (s), 0.78 (s), Me. ^{13}C NMR ($CDCl_3$) (ppm): 153.76, 153.49, 147.42, 147.31, oxime C; 20.0, 17.35, 11.99, Me. UV-vis maxima ($CHCl_3$): 620 nm (53 cm^{-1} M^{-1}), 402 (1.2 × 10^3), 305 (1.5 × 10^4). Anal. Calcd for [Ni($C_{20}H_{29}N_4O_4$)Ag]$_3\cdot$2.5CHCl$_3$: C, 38.22; H, 4.60; N, 8.56; Cl, 13.54; Ag, 16.48. Found: C, 37.94; H, 4.70; N, 8.45; Cl, 13.60; Ag, 17.13.

Preparation of [Pd(δ-HCQD)$_2$Ag]$_3\cdot$2CHCl$_3$. Yellow crystals of [Pd(δ-HCQD)$_2$Ag]$_3\cdot$2CHCl$_3$ were prepared by using the same pro-

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