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Low-Temperature Structural and Magnetic Characterization of the Chromium(III) Dimers Bis(μ-hydroxo)bis[tetraamminechromium(III)] Dithionate Tetrahydrate and Bis(μ-hydroxo)bis[tetraamminechromium(III)] Chloride Tetrahydrate, $[Cr(NH_3)_4OH]_2(S_2O_6)_2{\cdot}4H_2O$ and $[Cr(NH_3)_4OH]_2Cl_4{\cdot}4H_2O$

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The crystal and molecular structures of the dimeric chromium(III) complexes bis(μ-hydroxo)bis[tetraamminechromium(III)] dithionate tetrahydrate, $[Cr(NH_3)_4OH]_2(S_2O_6)_2{\cdot}4H_2O$, and bis($\mu$-hydroxo)bis[tetraamminechromium(III)] chloride tetrahydrate, $[Cr(NH_3)_4OH]_2Cl_4{\cdot}4H_2O$, have been determined from three-dimensional X-ray data collected at 90 K. The dithionate salt crystallizes in space group *Pbca* of the orthorhombic system with four formula units in a cell of dimensions $a = 13.621$ (9) Å, $b = 12.839$ (7) Å, and $c = 13.954$ (9) Å. The structure has been refined to a final value of the conventional R factor (on F) of 0.033 based on 4324 independent observations. The chloride salt crystallizes in the monoclinic space group $P2_1/n$ with two formula units in a cell of dimensions $a = 10.678$ (2) Å, $b = 10.005$ (2) Å, $c = 9.351$ (2) Å, and $\beta = 98.60$ (17)°. This structure has been refined to a final R factor of 0.036 based on 8197 independent observations. In both salts the cation consists of dihydroxo-bridged chromium(III) dimers, the Cr–Cr′ separations being 3.045 (1) (dithionate) and 3.023 (1) Å (chloride). The bridging units are constrained to be planar by symmetry. The geometry around each chromium center is roughly octahedral, the coordination sphere being occupied by the two cis-hydroxo bridges and four terminal ammine ligands. The bridging Cr–O(1)–Cr′ angles ϕ are 101.54 (5) and 99.92 (3)° in the dithionate and chloride salts, respectively. In each case, the hydrogen atom on the bridge is markedly out of the bridge plane, the dihedral angle θ between the O–H vector and the Cr–O–Cr′–O′ plane being 24° in the dithionate and 41° in the chloride. The magnetic susceptibilities of the complexes indicate antiferromagnetic coupling. The susceptibility data were fitted to the Van Vleck expression corrected for biquadratic exchange and led to triplet energies of 5.77 (1) cm^{-1} for the dithionate and 4.11 (2) cm^{-1} for the chloride.

Introduction

Considerable recent experimental and theoretical attention has been focused on the relationship between the magnetic properties of chromium(III) dimers and their structures.[2-15] While it has been noted for the bis(μ-hydroxo) dimers $[CrL_4(OH)]_2^{n+}$ that the magnitude of the exchange coupling parameter for the ground states, J, depends on the Cr–O–Cr bridging angle (ϕ),[3,4,6,11,13] the Cr–O bridging bond length (r),[3,13] and the dihedral angle between the bridge plane and the O–H vector of the bridging hydroxo group (θ),[3,4,5,12,16] it has not yet been possible to quantify this complex set of relationships.

In order to more fully investigate the relative significance of changes in ϕ, r, and θ on J, we are continuing our systematic structural and magnetic studies on dimers of this general type. In order to obtain reliable positional parameters for the hydrogen atom on the bridge, which are of paramount importance in the determination of the dihedral angle θ, we have used the smallest available terminal ligand L and have obtained the crystallographic data at low temperatures. We here report the syntheses, magnetic properties, and structures of the dithionate and chloride salts of the dimeric cation bis(μ-hydroxo)bis[tetraamminechromium(III)], $[(NH_3)_4Cr(OH)]_2^{4+}$.

Experimental Section

Bis(μ-hydroxo)bis[tetraamminechromium(III)] Dithionate Tetrahydrate. (a) Preparation of the Crystallographic Sample. $[(NH_3)_4Cr(OH)]_2Br_4{\cdot}4H_2O$ was prepared by the method of Springborg and Schäffer.[17] The $S_2O_6^{2-}$ salt was obtained from the Br^- salt by anion substitution. The Br^- salt was dissolved in 0.01 M HBr, and the solution was placed in a test tube and covered with gel.[18] When the gel was almost firm, a saturated solution of $Na_2S_2O_6$ was poured onto it. After the mixture stood 2 days in the dark, crystals of $[(NH_3)_4Cr(OH)]_2(S_2O_6)_2{\cdot}4H_2O$ were obtained, which were suitable for single-crystal X-ray analysis. It should be noted that all solutions of this cation are light sensitive.

(b) Crystallography. Red crystals of the complex were assigned to the orthorhombic system on the basis of precession and Weissenberg photographs; the observed systematic absences of $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd are consistent only with the space group *Pbca* (No. 61). The cell constants at 90 K obtained by least-squares methods with the wavelength assumed as $\lambda(\text{Mo } K\bar{\alpha}) = 0.71069$ Å are $a = 13.621$ (9), $b = 12.839$ (7), and $c = 13.954$ (9) Å. The observed room-temperature density of 1.80 (2) g cm^{-3} (flotation in a mixture of bromoform and chloroform) is consistent with the density of 1.815 g cm^{-3} calculated for four dimeric units in a cell. Thus, in space group *Pbca*, the cation is constrained to lie on an inversion center.

Diffraction data were obtained from a roughly octagonally shaped crystal of dimensions 0.412 mm × 0.377 mm × 0.380 mm × 0.431 mm in the (111), $(1\bar{1}1)$, $(11\bar{1})$, and $(1\bar{1}\bar{1})$ directions, respectively,

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(1) (a) Chemistry Department I, H. C. Ørsted Institute. (b) The University of North Carolina. (c) Chemistry Department IV, H. C. Ørsted Institute.

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(18) The gel used was an aqueous gelatin preparation; the gelatin used was a standard preparation available in any Danish grocery store as "husblas".

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mounted roughly parallel to the crystallographic *a* axis. The data were collected with a Picker FACS-1 automatic diffractometer, equipped with a modified Enraf-Nonius low-temperature device, a molybdenum tube, and a graphite monochromator. Intensity data were collected at 90 ± 2 K by the $\theta/2\theta$ scan technique at a rate of 2° min^{-1}. Peaks were scanned from 1.0° + (0.231 tan θ)° in 2θ below the calculated peak position to 1.7° + (0.462 tan θ)° above the calculated peak position. Stationary-counter, stationary-crystal background counts of 10 s were taken at each end of the scans.

A unique data set having $2.4° \leq 2\theta(\mathrm{Mo}) \leq 70°$ was gathered; in addition, symmetry-related reflections having $2.4° \leq 2\theta \leq 45°$ were measured. The intensities of four standards measured after every 100 reflections showed no significant decline as a function of exposure time. Data processing was carried out with a data reduction program of local origin. After correction for background, Lorentz, polarization, and absorption effects (μ(Mo Kα) = 12.42 cm^{-1}), the symmetry-related reflections were averaged. The agreement factor between symmetry-related reflections was 0.0269. The intensities were assigned standard deviations according to the formula[19]

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

where

$$Lp = (2 \sin 2\theta)/(\cos^2 2\theta_m + \cos^2 2\theta)$$

and the monochromator angle, θ_m, was 6.083°. Of the 5331 independent reflections collected, only the 4324 with intensities greater than 2 times their estimated standard deviations were used in the subsequent structure analysis and refinement.

Bis(μ-hydroxo)bis[tetraamminechromium(III)] Chloride Tetrahydrate. (a) Preparation of the Crystallographic Sample. The bromide salt[17] was converted to the perchlorate by precipitation with saturated $NaClO_4$ solution. The perchlorate salt was then redissolved in water and converted to the chloride by the addition of solid ammonium chloride; the resulting solution was cooled to 0 °C and allowed to stand at that temperature (in the dark). Suitable crystals of $[(NH_3)_4Cr(OH)]_2Cl_4 \cdot 4H_2O$ were obtained after a few hours.

(b) Crystallography. Red crystals of the chloride salt were assigned to the monoclinic system on the basis of preliminary Weissenberg and precession photographs; the observed systematic absences of 0*k*0 for *k* odd and *h*0*l* for (*h* + *l*) odd are consistent only with the space group $P2_1/n$, which is a nonstandard setting of the space group $P2_1/c$ (No. 14).[20] The cell constants, obtained as above at 90 K, are *a* = 10.678 (2) Å, *b* = 10.005 (2) Å, *c* = 9.351 (2) Å, and β = 98.60 (17)°. The observed room-temperature density of 1.60 (2) g cm^{-3} (flotation in chloroform/1,2-dibromomethane mixture) is in acceptable agreement with that of 1.641 g cm^{-3} calculated for two dimeric units in the cell at low temperature. Thus, in space group $P2_1/n$, the cation is constrained to lie on an inversion center.

Diffraction data were collected as described for the dithionate salt above, except that the data set was extended to the range $2.4° \leq 2\theta(\mathrm{Mo}) \leq 92.5°$, a total of 8680 data being recorded. The data were processed as above, the absorption coefficient being 16.05 cm^{-1}. Of the 8680 data, 8197 had intensities more than twice their estimated standard deviations, and only these data were used in the subsequent analysis and refinement.

Solution and Refinement of the Structures

All the least-squares refinements in these analyses were carried out on *F*, the function minimized being $\sum w(|F_o| - |F_c|)^2$. In calculations of F_c, the atomic scattering factors for non-hydrogen atoms were taken from ref 21a while those for hydrogen were from Stewart, Davidson, and Simpson.[22] The effects of the anomalous dispersion of chromium, chlorine, and sulfur were included in the calculation of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from ref 21b.

Table I. Positional Parameters in $[Cr(NH_3)_4OH]_2(S_2O_6)_2 \cdot 4H_2O$

atom	*x*	*y*	*z*
Cr	0.07921 (1)	0.06621 (2)	0.04703 (2)
O1	0.05475 (7)	−0.07735 (7)	0.00364 (7)
N1	0.22184 (9)	0.03016 (11)	0.08812 (10)
N2	0.08630 (10)	0.22087 (10)	0.09122 (10)
N3	0.03351 (9)	0.03104 (10)	0.18571 (9)
N4	0.13660 (10)	0.11780 (11)	−0.08275 (10)
S1	0.27434 (2)	0.16692 (3)	0.31835 (2)
S2	0.34391 (2)	0.27307 (2)	0.22182 (2)
O2	0.31816 (7)	0.06682 (7)	0.29356 (8)
O3	0.17093 (7)	0.17554 (8)	0.29427 (8)
O4	0.29978 (8)	0.20422 (8)	0.41374 (7)
O5	0.30470 (8)	0.24529 (8)	0.12834 (7)
O6	0.44962 (7)	0.25441 (9)	0.23053 (8)
O7	0.31401 (8)	0.37600 (8)	0.25458 (8)
OW1	0.00182 (9)	0.13702 (10)	0.44736 (9)
OW2	0.37220 (9)	0.46870 (10)	0.43273 (9)
H1	0.093 (1)	−0.112 (2)	−0.013 (2)
H11	0.256 (2)	0.006 (2)	0.039 (1)
H12	0.254 (2)	0.083 (2)	0.103 (2)
H13	0.223 (1)	−0.015 (2)	0.129 (2)
H21	0.054 (1)	0.230 (2)	0.141 (2)
H22	0.144 (2)	0.239 (2)	0.100 (2)
H23	0.060 (1)	0.265 (2)	0.045 (2)
H31	0.069 (2)	0.068 (2)	0.228 (2)
H32	−0.030 (2)	0.050 (2)	0.198 (1)
H33	0.043 (2)	−0.034 (2)	0.201 (2)
H41	0.098 (2)	0.151 (2)	−0.110 (2)
H42	0.190 (2)	0.158 (2)	−0.075 (2)
H43	0.151 (1)	0.070 (2)	−0.111 (1)
H51	0.050 (3)	0.094 (3)	0.431 (2)
H52	−0.014 (2)	0.164 (2)	0.406 (2)
H61	0.360 (1)	0.442 (2)	0.383 (2)
H62	0.397 (3)	0.433 (3)	0.465 (3)

$[(NH_3)_4Cr(OH)]_2(S_2O_6)_2 \cdot 4H_2O$. The position of the one independent chromium atom was deduced from a three-dimensional Patterson function, and the remaining non-hydrogen 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 0.053 and 0.061, respectively. Anisotropic refinement of the chromium atom parameters and the two sulfur atom parameters reduced these values to 0.048 and 0.058, respectively. At this stage, all hydrogen atoms were located, and their isotropic refinement lowered R_1 and R_2 to 0.039 and 0.042, respectively. In the final cycles of least squares, the weights were changed from unit weights to weights of the form

$$w = [4.0\sigma^2(F) + 0.005F + 0.0005F^2 - 2(\sin \theta)/\lambda]^{-1}$$

The final cycle of refinement involved anisotropic refinement of all non-hydrogen atoms and isotropic refinement of the hydrogen atoms with 4324 observations and 213 variables. In the final cycle of least squares, no atomic parameter exhibited a shift greater than 0.18σ, indicating convergence. The final values of R_1 and R_2 were 0.033 and 0.035, respectively.

Examination of the values of $|F_o|$ and $|F_c|$ suggested that no correction for secondary extinction was necessary, and none was applied. The final value of R_2 showed no unusual dependence on sin θ or on $|F_c|$, which suggests that the weighting scheme is appropriate. The final difference Fourier map was featureless with no peak higher than 0.70 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 listed in Table I. The thermal parameters and a table of observed and calculated structure amplitudes are available as supplementary material.

$[(NH_3)_4Cr(OH)]_2Cl_4 \cdot 4H_2O$. The structure was solved in a manner entirely similar to that described above for the dithionate salt. The final cycle of refinement involved anisotropic refinement of all non-hydrogen atoms and isotropic refinement of all hydrogen atoms, with 8197 observations and 159 variables. No parameter experienced a shift larger than 0.19σ, which suggests to us that the refinement had converged. The final values of R_1 and R_2 were 0.036 and 0.044, respectively. A final difference Fourier map was again featureless. The positional parameters derived from the final cycle, along with their standard deviations as estimated from the inverse matrix, are listed in Table II. Tabulations of the thermal parameters and observed

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(21) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England; Vol. IV: (a) Table 2.2A; (b) Table 2.1C.

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Table II. Positional Parameters in $[Cr(NH_3)_4OH]_2Cl_4 \cdot 4H_2O$

atom	*x*	*y*	*z*
Cr	−0.11935 (1)	0.07056 (1)	0.02722 (1)
O1	0.06690 (5)	0.09250 (6)	0.06567 (6)
N1	−0.14602 (7)	0.24684 (7)	0.13547 (8)
N2	−0.31399 (7)	0.03567 (8)	−0.02074 (8)
N3	−0.13509 (7)	0.18159 (8)	−0.16321 (8)
N4	−0.12528 (7)	−0.03502 (7)	0.21815 (7)
Cl1	0.13404 (2)	0.10083 (2)	0.40565 (2)
Cl2	0.62014 (2)	0.12403 (2)	0.31645 (3)
OW1	0.09195 (8)	0.41151 (9)	0.16195 (9)
OW2	−0.11775 (9)	0.24718 (10)	0.48619 (12)
H1	0.098 (2)	0.111 (2)	0.146 (2)
H11	−0.076 (2)	0.295 (2)	0.148 (2)
H12	−0.204 (2)	0.300 (2)	0.082 (2)
H13	−0.173 (2)	0.242 (2)	0.222 (3)
H21	−0.361 (2)	0.067 (2)	0.048 (3)
H22	−0.343 (2)	0.068 (2)	−0.111 (2)
H23	−0.331 (2)	−0.050 (2)	−0.016 (2)
H31	−0.156 (2)	0.133 (2)	−0.233 (2)
H32	−0.209 (2)	0.228 (2)	−0.172 (2)
H33	−0.065 (2)	0.228 (2)	−0.170 (2)
H41	−0.061 (2)	−0.019 (2)	0.274 (2)
H42	−0.188 (2)	−0.016 (2)	0.255 (2)
H43	−0.128 (2)	−0.123 (2)	0.205 (2)
H51	0.039 (2)	0.482 (2)	0.156 (3)
H52	0.101 (2)	0.403 (2)	0.074 (3)
H61	−0.045 (2)	0.215 (2)	0.479 (2)
H62	−0.178 (2)	0.189 (2)	0.474 (3)

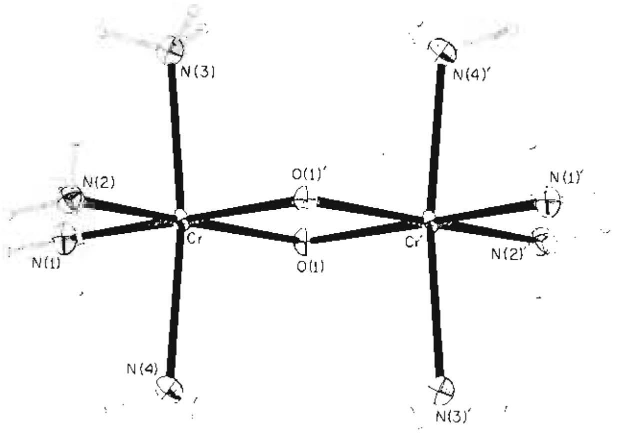

Figure 1. View of the $[Cr(NH_3)_4OH]_2^{4+}$ cation in $[Cr(NH_3)_4OH]_2(S_2O_6)_2 \cdot 4H_2O$. Thermal ellipsoids in this figure and in subsequent figures are drawn at the 50% probability level, but hydrogen atoms are shown as spheres of arbitrary size.

and calculated structure amplitudes are available as supplementary material.

Description of the Structures

It should be noted at the outset that both of these salts, and presumably most other salts of this cation, crystallize in several forms. For example, the chloride salt studied here is a monoclinic form and is not isomorphous with the cobalt(III) analogue, which crystallizes in a triclinic space group and whose structure has been determined by Prout[23] and by Vannerberg.[24] We have, however, crystallized a triclinic form of the chromium chloride complex, which is isomorphous with the known cobalt complex, and Güdel has evidently made this triclinic chromium complex without forming the monoclinic isomer.[25] Moreover, by seeding with the monoclinic chromium crystals, we have now crystallized an isomorphous monoclinic form of the cobalt(III) complex, whose structure has not yet been examined in detail. Similarly, we have now obtained crystals of *five* different modifications of the dithionate salt, all of which have different X-ray powder patterns. Necessarily, therefore, the descriptions that follow refer only to the crystal modifications that were studied by single-crystal diffractometry, and great care should be taken in applying the finer structural details to bulk properties.

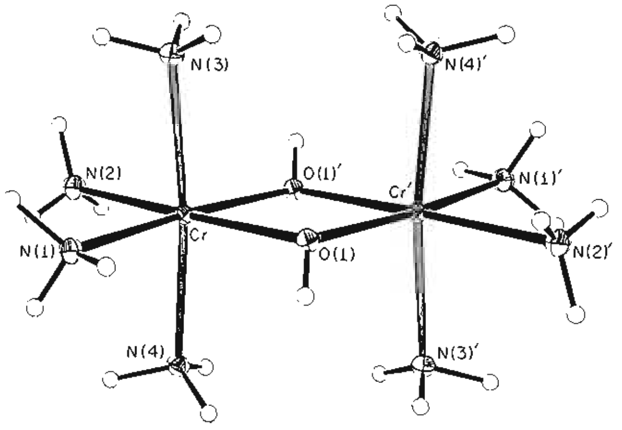

Figure 2. View of the $[Cr(NH_3)_4OH]_2^{4+}$ cation in $[Cr(NH_3)_4OH]_2Cl_4 \cdot 4H_2O$.

Table III. Bond Distances (A) in the Dimeric Cations

atoms	dithionate	chloride	atoms	dithionate	chloride
Cr–Cr	3.045 (1)	3.023 (1)	N1–H13	0.81 (2)	0.90 (2)
Cr–O1	1.968 (1)	1.980 (1)	N2–H21	0.83 (2)	0.93 (2)
Cr–O1′	1.962 (2)	1.969 (1)	N2–H22	0.83 (2)	0.92 (2)
Cr–N1	2.078 (2)	2.074 (1)	N2–H23	0.93 (2)	0.88 (2)
Cr–N2	2.081 (2)	2.089 (2)	N3–H31	0.89 (3)	0.82 (2)
Cr–N3	2.082 (2)	2.084 (1)	N3–H32	0.91 (2)	0.90 (2)
Cr–N4	2.081 (2)	2.083 (1)	N3–H33	0.87 (2)	0.89 (2)
O1–H1	0.73 (2)	0.80 (2)	N4–H41	0.78 (2)	0.81 (2)
N1–H11	0.89 (2)	0.88 (2)	N4–H42	0.90 (3)	0.82 (2)
N1–H12	0.84 (2)	0.91 (2)	N4–H43	0.76 (2)	0.88 (2)

Table IV. Bond Angles (deg) in the Dimeric Cations

atoms	dithionate	chloride
Cr–O1–Cr′	101.54 (5)	99.92 (3)
O1–Cr–O1′	78.46 (4)	80.08 (3)
O1–Cr–N1	91.98 (5)	91.40 (3)
O1–Cr–N2	172.86 (9)	176.2 (3)
O1–Cr–N3	91.84 (5)	92.67 (3)
O1–Cr–N4	95.39 (6)	93.39 (3)
O1′–Cr–N1	170.1 (1)	171.44 (6)
O1′–Cr–N2	94.61 (5)	96.10 (3)
O1′–Cr–N3	94.17 (6)	93.25 (3)
O1′–Cr–N4	90.72 (5)	90.29 (3)
N1–Cr–N2	95.01 (5)	92.42 (3)
N1–Cr–N3	88.55 (6)	87.95 (3)
N1–Cr–N4	87.70 (6)	89.37 (4)
N2–Cr–N3	86.87 (6)	87.43 (3)
N2–Cr–N4	86.37 (6)	86.70 (3)
N3–Cr–N4	171.96 (7)	173.44 (7)
Cr–O1–H1	123 (2)	118 (2)
Cr′–O1–H1	127 (2)	120 (2)

Both structures consist of dimeric $[Cr(NH_3)_4OH]_2^{4+}$ cations that are hydrogen bonded to anions (dithionate or chloride) and water molecules. A view of the cation in the dithionate salt is given in Figure 1, and a view of the cation in the chloride salt is shown in Figure 2. The bond lengths and angles in the cation are compared for the two structures in Tables III and IV, respectively. In each case, the geometry around the chromium(III) centers is roughly octahedral, the ligating atoms being four ammonia nitrogen atoms and two oxygen atoms from the hydroxo bridges. In the dithionate salt, none of the Cr–N bond lengths are significantly different, ranging from 2.078 (2) to 2.082 (2) Å as compared to those of 2.080

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Table V. Probable A–H···B Hydrogen Bonds in $[Cr(NH_3)_4OH]_2(S_2O_6)_2 \cdot 4H_2O$

A	H	B	A···B, Å	A–H···B, deg	H···B, Å
O1	H1	O4[a]	2.856 (2)	170 (2)	2.14 (2)
N1	H11	OW2[b]	2.983 (2)	148 (2)	2.19 (2)
N1	H12	O5	3.036 (2)	165 (2)	2.22 (2)
N1	H13	O7[c]	3.090 (2)	164 (2)	2.30 (2)
N2	H21	O6[d]	3.137 (2)	174 (2)	2.31 (2)
N2	H22	O5	3.036 (3)	166 (2)	2.22 (2)
N2	H23	OW1[b]	2.947 (2)	178 (2)	2.02 (2)
N3	H31	O3	3.040 (2)	164 (2)	2.17 (2)
N3	H32	O2[d]	2.983 (3)	167 (2)	2.09 (2)
N3	H33	O7[c]	3.033 (2)	131 (2)	2.38 (2)
N4	H42	O4[b]	3.188 (2)	162 (2)	2.32 (3)
N4	H43	O2[a]	2.996 (2)	174 (2)	2.24 (2)
OW1	H51	OW2[c]	2.767 (2)	157 (3)	1.927 (4)
OW1	H52	O6[d]	2.990 (2)	175 (3)	2.27 (2)
OW2	H61	O7	2.868 (2)	175 (2)	2.08 (2)
OW2	H62	OW1[e]	2.786 (2)	162 (4)	2.07 (4)

[a] Symmetry operation: $^1/_2 - x, -y, z - {}^1/_2$. [b] Symmetry operation: $x, {}^1/_2 - y, z - {}^1/_2$. [c] Symmetry operation: $^1/_2 - x, y - {}^1/_2, z$. [d] Symmetry operation: $x - {}^1/_2, y, {}^1/_2 - z$. [e] Symmetry operation: $^1/_2 + x, {}^1/_2 - y, 1 - z$.

(6)–2.081 (7) Å obtained in $[Cr(en)_2(OH)]_2(S_2O_6)_2$,[6] 2.081 (9)–2.091 (9) Å in $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5 \cdot 3H_2O$,[8] and 2.05–2.15 Å reported for a variety of other complexes containing Cr(III)–N bonds.[4,7,9–12,14,15,26] In the chloride salt the range is slightly larger, 2.074 (1)–2.089 (2) Å, and may be associated with differences in the degree of hydrogen bonding involving the ligating ammines.

In the dithionate the bridging unit is slightly asymmetric, with Cr–O(1) and Cr–O(1)′ bond lengths of 1.968 (1) and 1.962 (2) Å, respectively; in the chloride this asymmetry is heightened, with Cr–O(1) and Cr–O(1)′ separations of 1.980 (1) and 1.969 (1) Å, respectively. All of these distances are within the range of 1.91–1.980 Å previously reported for bis(μ-hydroxo) chromium(III) dimers. Simiarly, the Cr–Cr′ separations of 3.045 (1) (dithionate) and 3.023 (1) Å (chloride) are typical of chromium dimers of this type.

The Cr–O(1)–Cr′ bridging angles (ϕ) are 101.54 (5)° for the dithionate and 99.92 (3)° for the chloride; these values are significantly different from each other but are within the range of 97.6 (1)–103.4 (1)° observed for dimers of this kind. In the dithionate salt, the hydrogen atom on the bridging hydroxyl group is 0.30 (2) Å out of the plane of the bridge, which corresponds to a dihedral angle θ of 24°. In the chloride salt the hydrogen atom is 0.53 (2) Å out of this plane, corresponding to a dihedral angle θ of 41°. Thus, the chloride has a larger θ but a smaller ϕ than the dithionate, but both salts show substantial values of θ; in some analogous complexes, θ is reported[2] to be less than 6°.

The hydrogen bonding in the dithionate crystal is extensive, all possible donor atoms and all but one possible acceptor atom participating. The probable hydrogen bonds are listed in Table V. The bridging oxygen atom, O(1), is the only possible hydrogen-bond acceptor that does not participate. Only one of the hydrogen atoms, H(41) on nitrogen atom N(4), does not form a hydrogen bond. The two solvent water molecules are hydrogen bonded to each other and to dithionate oxygen atoms (Table V). The bridging hydroxo hydrogen atom apparently forms a hydrogen bond to a dithionate oxygen atom, with O(1)···O(4) and H(1)···O(4) separations of 2.856 (2) and 2.14 (2) Å and an associated O(1)–H(1)···O(4) angle of 170 (2)°. This interaction may be responsible for the rleatively large θ angle observed in this structure (vide supra). In the chloride crystals there is also extensive hydrogen bonding, as is summarized in Table VI. All of the potential donor atoms except ammine hydrogen atom H(31) [on nitrogen atom N(3)] participate in hydrogen bonding in the crystals, the acceptor atoms being the anions and the water molecules. The bridging hydroxo group forms a hydrogen bond to chloride ion Cl(1), with O(1)···Cl(1) and H(1)···Cl(1) distances of 3.154 (2) and 2.40 (2) Å, respectively, and an associated O(1)–H(1)···Cl(1) angle of 158 (2)°. Views of the packing in the unit cells are shown in Figures 3.

Table VI. Possible A–H···B Hydrogen Bonds in $[Cr(NH_3)_4OH]_2Cl_4 \cdot 4H_2O$

A	H	B	A···B, Å	H···B, Å	A–H···B, deg
O1	H1	Cl1	3.154 (2)	2.40 (2)	158 (2)
N1	H11	OW1	3.007 (1)	2.13 (2)	176 (2)
N1	H12	Cl1[a]	3.309 (5)	2.42 (2)	167 (2)
N1	H13	Cl2[b]	3.446 (4)	2.77 (2)	134 (2)
N2	H21	Cl2[b]	3.447 (2)	2.62 (2)	150 (2)
N2	H22	OW1[a]	3.033 (3)	2.14 (2)	164 (2)
N2	H23	OW2[c]	3.006 (1)	2.12 (2)	175 (2)
N3	H32	Cl1[a]	3.421 (2)	2.58 (2)	155 (2)
N3	H33	Cl2[a]	3.377 (1)	2.49 (2)	175 (2)
N4	H41	Cl1	3.337 (4)	2.56 (2)	162 (2)
N4	H42	Cl2[b]	3.393 (2)	2.62 (2)	159 (2)
N4	H43	Cl2[d]	3.428 (1)	2.55 (2)	175 (2)
OW1	H51	Cl2[e]	3.135 (1)	2.25 (2)	164 (1)
OW1	H52	Cl2[a]	3.309 (1)	2.46 (3)	178 (2)
OW2	H61	Cl1	3.247 (2)	2.41 (2)	166 (2)
OW2	H62	Cl2[b]	3.247 (2)	2.52 (2)	144 (2)

[a] Symmetry operation: $-{}^1/_2 + x, {}^1/_2 - y, -{}^1/_2 + z$. [b] Symmetry operation: $-1 + x, y, z$. [c] Symmetry operation: $-{}^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$. [d] Symmetry operation: $^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$. [e] Symmetry operation: $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$.

Table VII. Bond Lengths (Å) and Angles (deg) in the Dithionate Anion in $[(NH_3)_4Cr(OH)]_2(S_2O_6)_2 \cdot 4H_2O$

S1–S2	2.1376 (9)	S2–O5	1.454 (1)
S1–O2	1.459 (1)	S2–O6	1.465 (1)
S1–O3	1.452 (1)	S2–O7	1.457 (1)
S1–O4	1.456 (1)		
O2–S1–S2	103.35 (6)	O5–S2–S1	104.25 (6)
O3–S1–S2	103.61 (6)	O6–S2–S1	106.21 (5)
O4–S1–S2	105.12 (6)	O7–S2–S1	104.88 (6)
O2–S1–O3	114.15 (7)	O5–S2–O6	113.29 (6)
O2–S1–O4	114.15 (6)	O5–S2–O7	113.67 (6)
O3–S1–O4	114.67 (7)	O6–S2–O7	113.40 (6)

The bond lengths and bond angles in the dithionate anion are listed in Table VII. The S–S bond length of 2.1376 (9) Å is consistent with the values of 2.097 (4)–2.146 (5) Å reported recently for this ion.[6,9,11,15,27] The S–O bonds are quite similar, ranging from 1.452 (1) to 1.465 (1) Å. The geometry around each sulfur atom is distorted tetrahedral, with S–S–O angles in the range 103.35 (6)–106.21 (5)° and O–S–O angles in the range 113.29 (6)–114.67 (7)°. The conformation is staggered: while the crystallographic symmetry is $C_1(1)$, the ion approximates the idealized $D_{3d}(\bar{3}m)$ symmetry, which would require, for example, that O(7) lie in the plane defined by atoms S(1), S(2), and O(2) while the pairs O(5), O(6) and O(3), O(4) were equidistant from the plane. In actual fact, O(7) lies 0.22 Å above the plane while O(5) and O(6) are respectively 1.32 Å below and 1.10 Å above the plane and O(3) and O(4) are respectively 1.33 Å below and 1.11 Å above. Thus, the distortion from idealized D_{3d} symmetry here is greater than that recently observed[11] in $[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)](S_2O_6)_2 \cdot 3H_2O$.

Magnetic Properties

The average magnetic susceptibilities and effective magnetic moments of polycrystalline samples of $[Cr(NH_3)_4OH]_2(S_2-$

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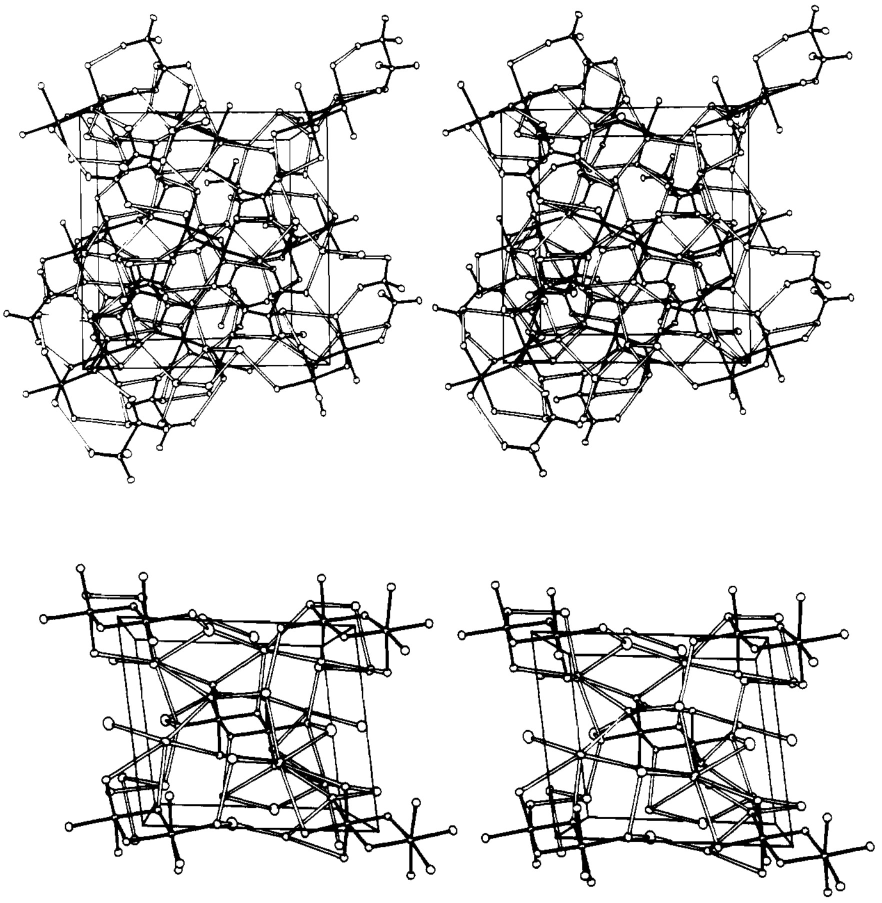

Figure 3. Stereoscopic views of the packing in the unit cells: (a, top) dithionate salt; (b, bottom) chloride salt.

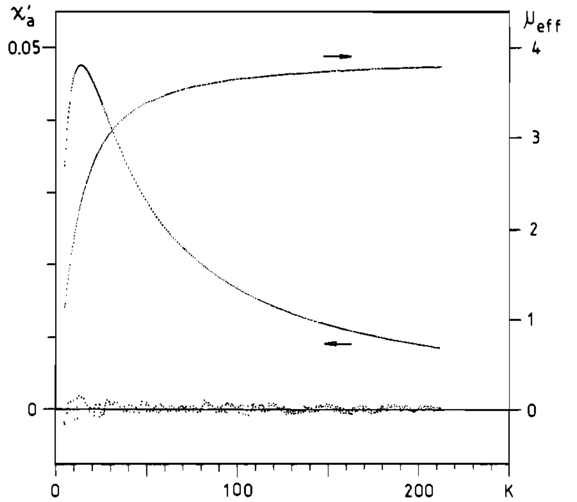

Figure 4. Magnetic susceptibility per chromium (left scale, cgs units) and effective magnetic moment (right scale, Bohr magnetons) of $[(NH_3)_4Cr(OH)]_2(S_2O_6)_2{\cdot}4H_2O$. The lower, almost random, distribution of dots around the abscissa indicates the corresponding values of $(\chi_{obsd} - \chi_{calcd}) \times 100$, where χ_{calcd} refers to the parameters of model 2 in Table VIII.

$O_6)_2{\cdot}4H_2O$ and $[Cr(NH_3)_4OH]_2Cl_4{\cdot}4H_2O$ are shown in Figures 4 and 5, respectively. We used the Faraday method at a field strength of 12000 Oe in the temperature range 1.8–290 K. Preliminary descriptions of the instrument are found elsewhere.[3] The only source of anisotropy in this d^3 situation is zero-field splitting, which can be estimated from ESR spectra to be approximately 0.5 cm^{-1} and certainly less than 1 cm^{-1} (vide infra). Consequently, the spatial averaging that would be necessary for a highly anisotropic system at very low temperatures[28,29] is not necessary here. The samples selected

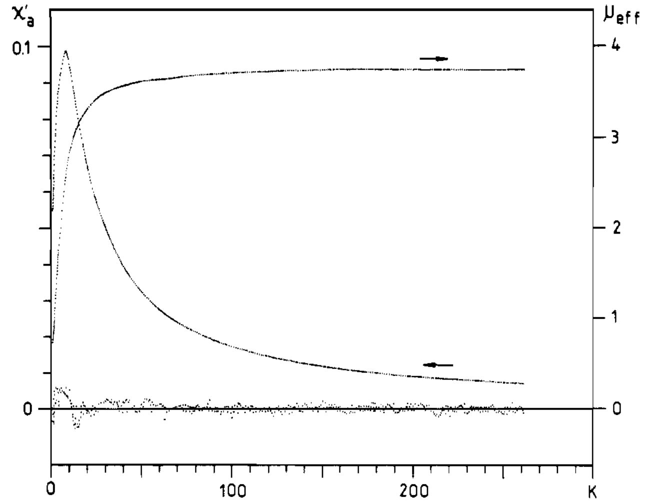

Figure 5. Magnetic susceptibility and effective magnetic moment of $[(NH_3)_4Cr(OH)]_2Cl_4{\cdot}4H_2O$, plotted as in Figure 4.

for the measurements were carefully controlled by optical and X-ray powder methods. The susceptibility data were fitted to the expression

$$\chi_A' = \frac{N}{H}\,\frac{\sum_i \left(\frac{\partial E_i}{\partial H}\right)\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}$$

where the quantitites E_i are the energies of the sixteen com-

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Table VIII. Parameters Derived from Magnetic Susceptibility Data

	dithionate		chloride	
parameter	model 1[a]	model 2	model 1	model 2
J, cm^{-1}	6.16 (1)	6.30 (1)	2.73 (1)	2.48 (2)
j, cm^{-1}		−0.082 (8)		0.25 (2)
$E(1)$, cm^{-1} [b]	6.16 (1)	5.77 (1)	2.73 (1)	4.11 (2)
$E(2)$, cm^{-1} [b]	18.48 (3)	17.79 (3)	8.19 (3)	10.82 (6)
$E(3)$, cm^{-1} [b]	36.96 (6)	37.06 (6)	16.38 (6)	17.1 (1)
g	1.978 (1)	1.986 (1)	1.975 (1)	1.960 (1)
var/f	3.3	2.5	2.6	1.0
% monomer	0.008 (2)	0.019 (1)	0	0.037 (3)

[a] See text for description of the models. [b] Calculated from the derived parameter(s) for comparative purposes.

ponents of the ground-state manifold. The fitting was accomplished by using three different models for the exchange Hamiltonian. In the first (model 1) we assumed the simple Van Vleck Hamiltonian

$$\mathcal{H} = J\vec{S}_1\cdot\vec{S}_2 + g\beta M_{S'}$$

where $\vec{S}' = \vec{S}_1 + \vec{S}_2$, the only exchange variable is J, and the triplet, quintet, and septet energies are J, $3J$, and $6J$, respectively. In the second model (model 2) we expanded the Hamiltonian to include a biquadratic exchange term of the type

$$\mathcal{H} = J\vec{S}_1\cdot\vec{S}_2 - j(\vec{S}_1\cdot\vec{S}_2)^2 + g\beta M_{S'}$$

where the variable exchange parameters are now J and j and the triplet, quintet, and septet energies are given by $(J + 6.5j)$, $(3J + 13.5j)$, and $(6J + 9.0j)$, respectively. Finally, in model 3, we used the generalized Hamiltonian

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

where the term $E(S')$ implies independent energies of the triplet, quintet, and septet states. This model merely assumes, as do earlier models, an isotropic Zeeman effect. In model 3, therefore, the variable magnetic parameters are $E(1)$, $E(2)$, and $E(3)$, the energies of the triplet, quintet, and septet states. In all three models, in addition to the magnetic parameters noted, we varied the isotropic g value, a temperature-independent susceptibility term, and a term which allows for the presence of a small quantity of monomeric impurity (assumed to obey the Curie law).

The results of the data fittings to these models are shown in Table VIII. It is apparent that the magnetic susceptibilities of these complexes are not perfectly described by the simple Van Vleck model (model 1) since the variances per degree of freedom (var/f) are relatively high, 3.3 and 2.6 for the dithionate and chloride salts, respectively. Inclusion of biquadratic exchange (model 2) leads to improvements in the fits (var/f = 2.5 and 1.0, respectively); application of model 3 was unsuccessful since it led to very high (>99%) correlations between the energies of the states for both salts. The improvements brought about by the inclusion of the additional variable in model 2 is significant beyond the 99.95% confidence level for both salts. It is noteworthy that the magnetic susceptibilities of the title compounds remain completely unchanged upon dilution to a 1% level into the isostructural diamagnetic cobalt(III) complexes. The exchange interactions observed must therefore be of intramolecular origin.

ESR spectra of powders and single crystals of such diluted complexes show significant zero-field splittings, especially for the triplet and septet states. According to preliminary estimates these splittings exceed 0.4 cm^{-1}. In view of this, it is not surprising that model 1 is imperfect for the present complexes having relatively low-lying triplet states. Attempts to expand model 1 by inclusion of a zero-field splitting term

$$D(S')[S'^2_z - \tfrac{1}{3}S'(S' + 1)] + E(S')[S'^2_x - S'^2_y]$$

with the relative magnitudes of $D(S')$ and $E(S')$ fixed to the values given by Owen and Harris[30] led to unsuccessful fittings, however.

The results obtained here confirm our contention that if, following the work of Hoffmann and co-workers,[31] we write the exchange coupling constant J as the sum of ferromagnetic and antiferromagnetic terms

$$J = J_{\mathrm{AF}} - J_{\mathrm{F}}$$

then the two contributions J_{F} and J_{AF} can be expressed as functions of the structural parameters ϕ, θ, and r discussed above, i.e.

$$J_{\mathrm{F}} = f(\phi,r) \qquad J_{\mathrm{AF}} = f'(\phi,\theta,r)$$

Using angular overlap considerations, we have developed a reasonable model for the form of these functions, such that

$$f(\phi,r) = c[\sin^2\phi/(1 - \cos\phi)^2]\exp(-ar)$$

$$f'(\phi,\theta,r) = b\{\cos^4\theta/[1 - \sin^2\theta/\tan^2(\phi/2)]^2\}\exp(-ar)$$

and hence that

$$J = \exp(-ar) \times \{b\cos^4\theta/[1 - \sin^2\theta/\tan^2(\phi/2)]^2 - c\sin^2\phi/(1 - \cos\phi)^2\}$$

The development of these expressions is the subject of a communication from our laboratories[32] and is not repeated here. We see that in the normal range of ϕ (i.e., 95–105°) the magnitude of J is very sensitive to both θ and r. In the present case, the $[\mathrm{Cr(NH_3)_4OH}]_2^{4+}$ cation evidently exhibits a triplet energy of approximately 5.8 cm^{-1} when $\phi = 101.54°$, $\theta = 24°$, and $r \approx 1.965$ Å and a triplet energy of approximately 4.1 cm^{-1} when $\phi = 99.92°$, $\theta = 41°$, and $r \approx 1.975$ Å. We shall examine other suitable complexes in the near future in order to further test this model.

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Registry No. $[\mathrm{Cr(NH_3)_4OH}]_2(\mathrm{S_2O_6})_2\cdot4\mathrm{H_2O}$, 84040-48-2; $[\mathrm{Cr(NH_3)_4OH}]_2\mathrm{Cl_4}\cdot4\mathrm{H_2O}$, 84028-63-7.

Supplementary Material Available: Tables of anisotropic thermal parameters and lists of observed and calculated structure amplitudes (electrons × 10) for both compounds (43 pages). Ordering information is given on any current masthead page.

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