Inorganica Chimica Acta, 22 (1977) 175–183

Magnetic and Structural Characterization of the Chromium(III) Dimer Sodium Di-μ-hydroxobis[bis(oxalato)chromate(III)] Hexahydrate, $Na_4[Cr(C_2O_4)_2OH]_2{\cdot}6H_2O$

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Received August 18, 1976

The crystal and molecular structure of the sodium di-μ-hydroxobis[bis(oxalato)chromate(III)] hexahydrate, $Na_4[Cr(C_2O_4)_2OH]_2{\cdot}6H_2O$ [or $Na_4[Cr(ox)_2OH]_2{\cdot}6H_2O$], has been determined from three-dimensional X-ray diffraction data collected by counter methods. The material crystallizes in the monoclinic space group $P2_1/c$ with four dimeric formula units in a cell of dimensions a = 19.530(12), b = 9.860(7), c = 12.657(10) Å and β = 106.93(4)°: least-squares refinement of the structure has led to a final R-factor (on F) of 0.061 using 3278 independent intensities. The structure consists of two crystallographically independent dimeric $[Cr(ox)_2OH]_2^{4-}$ anions which interact with sodium cations and water molecules in the cell. The geometry around each independent chromium(III) center is roughly octahedral. The bridging unit is strictly planar, there being an inversion center in the middle of each dimer. The Cr–O–Cr bridging angles are 99.6(2) and 99.7(2)°, and the Cr–Cr separations are 2.999(3) and 3.001(2) Å. There is extensive hydrogen bonding between the oxalate ligands and the water molecules. The magnetic susceptibility of a single crystal of the complex has been examined in the temperature range 2–70 K, and has been interpreted by means of application of the magnetization expression for coupled pairs of S = 3/2 ions with a small value of |J|. The dimer exhibits a very small exchange interaction, the best fit to the magnetization expression yielding $J = -0.31$ cm^{-1} and $\gamma = 0.28$; the latter value gives an inter-dimer lattice interaction parameter, J′, of 0.034 cm^{-1}, for four nearest neighbors.

Introduction

Recent experimental investigations of the structural and magnetic properties of hydroxo-bridged copper(II) complexes having the general formula $[Cu(L)OH]_2^{2+}$, where L is a bidentate ligand, have revealed that there exists a nearly linear correlation between the Cu–O–Cu bridging angle, φ and the singlet–triplet splitting, 2J [1–12]. This correlation can be understood in terms of the Goodenough–Kanamori rules [13], or alternatively from a molecular orbital treatment [14]. Similar considerations, when applied to the analogous Cr(III) complexes of the type $[Cr(L)_2OH]_2^{n+}$, do not provide a clearcut indication as to what effect structural changes will have on the magnetic properties of the complex. The origin of this complexity is that the single exchange parameter derived from magnetic studies, J, is actually the sum of several distinct "elementary contributions" [15] each of which will vary independently in response to structural changes in the complex; this is insignificant for copper(II) dimers since one contribution dominates the others for complexes of this type [14]. If one contribution is much larger than the others, for the cases of both chromium(III) and copper(II), qualitative molecular orbital theory has been used to show that there should exist a correlation between J and φ [16]. In order to investigate experimentally the influence of structural features on the magnetic properties of chromium(III) dimers of this type we have studied a variety of these complexes. The results for the glycinato dimer, $[Cr(gly)_2OH]_2$, and the chloride and iodide salts of the phenanthroline dimer, $[Cr(phen)_2OH]_2Cl_4{\cdot}6H_2O$ and $[Cr(phen)_2OH]_2I_4{\cdot}4H_2O$, have already been reported [17–20]. We now wish to report the results of our structural and magnetic investigations of the sodium salt of the oxalate dimer, $Na_4[Cr(ox)_2OH]_2{\cdot}6H_2O$.

Experimental

A powdered sample of the complex $Na_4[Cr(ox)_2(OH)]_2{\cdot}6H_2O$ was obtained by the reaction of aqueous ammonia with the monomeric complex *cis*-$NH_4[Cr(ox)_2(OH_2)_2]$ and subsequent metathesis with sodium bromide [21]. Suitable single crystals were obtained by slow evaporation of an aqueous solution of the powdered material.

After examination by precession and Weissenberg photography the crystals were assigned to the monoclinic system; systematic absences were observed for reflections 0k0 with k odd and for h0l with l odd, which uniquely determines the space group as $P2_1/c$-(C_{2h}^5). The cell constants obtained by least-squares methods [22] are $a = 19.530(12)$, $b = 9.860(7)$, $c = 12.657(10)$Å and $\beta = 106.93(4)^\circ$; the wavelength used for these measurements was 0.7093Å(MoKα_1). The density of 1.966 gcm^{-3} calculated for four dimeric units in the cell agrees well with the observed value of 1.97(2) gcm^{-3} obtained by flotation in bromoform/carbon tetrachloride solution. Thus, with four formula units per cell, no crystallographic symmetry need be imposed upon the dimers.

Intensity data were collected from a diamond shaped plate bounded by faces $(10\bar{1})$, $(0\bar{1}1)$, (011), $(0\bar{1}\bar{1})$, (100), $(\bar{1}00)$, the distances between opposite faces being 0.048, 0.040, and 0.0075 cm., respectively. The blue–violet crystals were found to decompose very quickly when removed from the mother liquor. Hence, the crystal used for data collection was mounted in a capillary roughly colinear with [011] with a drop of the mother liquor. The capillary was sealed with grease which also served to keep the crystal from moving. The crystal mosaicity was examined in the usual way [23] and was found to be acceptable. The data were collected in a manner described previously [11–23] with a Picker four-circle diffractometer using a molybdenum tube and a graphite monochromator. The take off angle was 1.3°, the scan rate was 1.0 °/min, the scan range was from 0.90° below the calculated Kα_1 peak position to 0.90° above the calculated Kα_2 peak position; backgrounds were counted for 20 sec. at each end of the scan. A unique data set of 5236 reflections having 2θ(Mo) $\leqslant 52^\circ$ was collected; 3278 of these were found to have intensities greater than three times their estimated standard deviations.

The intensities of three standard reflections, measured after every one hundred reflections, showed a continued decline so that, by the end of the run, the intensity of the average standard was only 61% of its original value. A linear correction was applied to the data for diminishing intensity with cumulative exposure. No absorption correction was applied, partly because the grease and mother liquor made measurement of the crystal very approximate, but mainly because absorption effects for this small specimen were judged to be minor; the linear absorption coefficient, μ, for this complex with Mo radiation is 10.9 cm^{-1}. The data were processed in the usual manner [11, 23].

Solution and Refinement of the Structure

The positions of the two chromium atoms were obtained by the heavy atom technique [24]. Two cycles of least-squares refinement of these positions using variable isotropic thermal parameters yielded values of the usual residuals $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$ and $R_2 = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$ of 0.51 and 0.57, respectively. In all least-squares refinements in this analysis, the function minimized was $\Sigma w(| F_o | - | F_c |)^2$, with the weights w being assigned as $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c the atomic scattering factors for Cr and Na were from Cromer and Waber [25], those for O, N, and C were from Ibers [26], and those for H were from Stewart, Davidson and Simpson [27]. The effects of the anomalous dispersion of chromium and sodium were included in the calculation of F_c [28]; the values of $\Delta f'$ and $\Delta f''$ were taken from Cromer [29].

Two sets of least-squares refinements and difference Fourier syntheses indicated the positions of all remaining non-hydrogen atoms. Three cycles of least-squares refinement on these 38 atoms with variable isotropic thermal parameters yielded $R_1 = 0.095$ and $R_2 = 0.102$. An additional two cycles of least-squares refinement with anisotropic thermal parameters gave values of 0.065 and 0.082 for R_1 and R_2. The subsequent difference map showed electron density in the range 0.5 to 0.9 eÅ^{-3} within 1.0 Å of all water and bridging oxygen atoms; some of these peaks could be interpreted on the basis of reasonable geometry as hydrogen atoms, but we were unable to locate the hydrogen atoms of two water molecules. The hydrogen atoms on the bridging hydroxo groups were given isotropic thermal parameters of 3.8 Å^2 and those on the water molecules 6.5 Å^2. A least-squares refinement which included these contributions gave $R_1 = 0.061$, $R_2 = 0.077$.

In the final cycle of least-squares refinement, no atomic parameter experienced a shift of more than 7% of its estimated standard deviation, which is taken as evidence of convergence. An examination of the values of $| F_o |$ and $| F_c |$ suggested to us that no correction for secondary extinction was necessary, and none was applied. The value of R_2 showed no unexpected trends as a function of $\sin\theta$ or $| F_o |$. The positional and thermal parameters derived from this final least-squares calculation, along with their standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A compilation of observed and calculated structure amplitudes is available [30].

Description of Structure

The structure consists of $[Cr(ox)_2OH]_2^{4-}$ ions which are hydrogen bonded to water molecules and also interact with sodium cations. All of the dimeric anions in this structure lie on inversion centers although they are not constrained to do so; hence, with four dimers in a cell there are two crystallographically independent half-dimers. The geometry of the anions is depicted in Figures 1 and 2. The geometry around the chromium atoms is roughly

TABLE I. Positional Parameters for $Na_4[Cr(ox)_2(OH)]_2 \cdot 6H_2O$.

Atom	x/a	y/b	z/c
Cr(1)	0.04998(5)	−0.04515(10)	−0.06330(8)
Cr(2)	0.45490(5)	0.07226(10)	0.06008(8)
Na(1)	0.3332(2)	−0.0949(3)	0.2219(2)
Na(2)	0.1636(1)	0.1672(3)	−0.1761(3)
Na(3)	0.4115(2)	−0.2669(3)	−0.0031(2)
Na(4)	0.0554(2)	0.3184(3)	0.0254(2)
O(1)	0.0176(2)	−0.1033(4)	0.0614(3)
O(2)	0.4874(2)	0.0932(5)	−0.0718(4)
AC(1)	0.1857(4)	−0.1468(7)	0.0329(6)
AC(2)	0.1874(3)	0.0037(7)	0.0684(5)
AO(1)	0.1257(2)	−0.1855(5)	−0.0326(4)
AO(2)	0.1294(2)	0.0685(5)	0.0224(4)
AO(3)	0.2410(3)	−0.2150(5)	0.0655(5)
AO(4)	0.2403(2)	0.0537(5)	0.1331(4)
BC(1)	0.0252(3)	−0.0408(7)	−0.2910(6)
BC(2)	−0.0328(3)	−0.1372(6)	−0.2666(5)
BO(1)	0.0688(2)	0.0100(5)	−0.2030(4)
BO(2)	−0.0226(2)	−0.1614(5)	−0.1650(4)
BO(3)	0.0243(3)	−0.0175(6)	−0.3849(4)
BO(4)	−0.0792(2)	−0.1818(5)	−0.3440(4)
CC(1)	0.3244(3)	0.1965(7)	−0.0339(5)
CC(2)	0.3134(3)	0.0443(6)	−0.0605(5)
CO(1)	0.3867(2)	0.2271(4)	0.0255(4)
CO(2)	0.3673(2)	−0.0297(4)	−0.0171(4)
CO(3)	0.2732(3)	0.2757(5)	−0.0657(5)
CO(4)	0.2549(2)	0.0038(5)	−0.1207(4)
DC(1)	0.4889(3)	0.1001(7)	0.2871(5)
DC(2)	0.5473(3)	0.1811(6)	0.2488(5)
DO(1)	0.4393(2)	0.0478(5)	0.2083(4)
DO(2)	0.5357(2)	0.1855(5)	0.1456(4)
DO(3)	0.4951(3)	0.0925(5)	0.3843(4)
DO(4)	0.5963(2)	0.2348(5)	0.3175(4)
WO(1)	0.1767(3)	0.3232(6)	0.1466(5)
WO(2)	0.3723(3)	−0.4805(6)	−0.0909(5)
WO(3)	0.3869(4)	0.3818(7)	0.2239(5)
WO(4)	0.2636(4)	−0.4930(7)	0.0777(8)
WO(5)	0.1141(4)	−0.3561(9)	−0.2240(6)
WO(6)	0.2626(4)	−0.2655(7)	−0.1802(8)
BH(1)	0.0385	−0.1358	0.1197
BH(2)	0.4488	0.0919	−0.0827
1H(1)	0.1889	0.2594	0.1108
1H(2)	0.2081	0.3892	0.1440
2H(1)	0.3372	0.4663	−0.1015
2H(2)	0.4150	0.4687	−0.0921
5H(1)	0.1375	−0.1939	0.2449
5H(2)	0.1498	−0.3971	−0.1650
6H(1)	0.2675	−0.2129	−0.2476
6H(2)	0.2607	−0.1979	−0.1375

octahedral, with two *cis* hydroxo groups and two *cis* oxalato ligands occupying the coordination sites. The bond lengths and angles in the inner coordination sphere are given in Table III. The actual symmetry of the anions is $C_i(\bar{1})$, but it approximates $C_{2h}(2/m)$; in this respect they are similar to the related dimer $[Cr(gly)_2OH]_2$ but different from $[Cr(phen)OH]_2^{4+}$, which approximates $D_2(222)$ symmetry [17–19, 20].

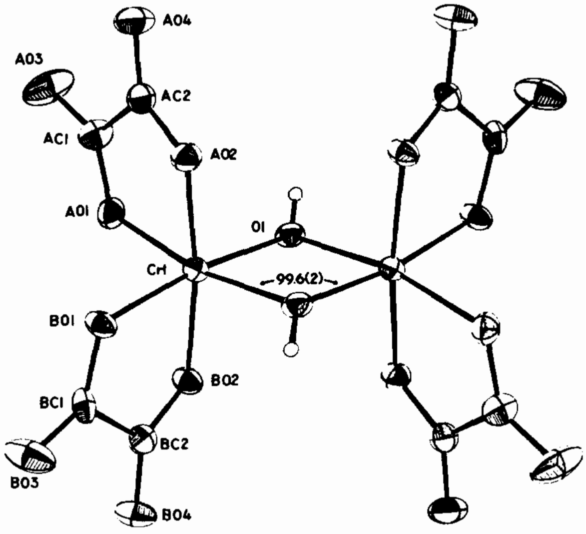


Figure 1. View of the $[Cr(ox)_2OH]_2^{4-}$ anion whose center is at the origin (0, 0, 0). The hydrogen atoms are shown as spheres of arbitrary size.

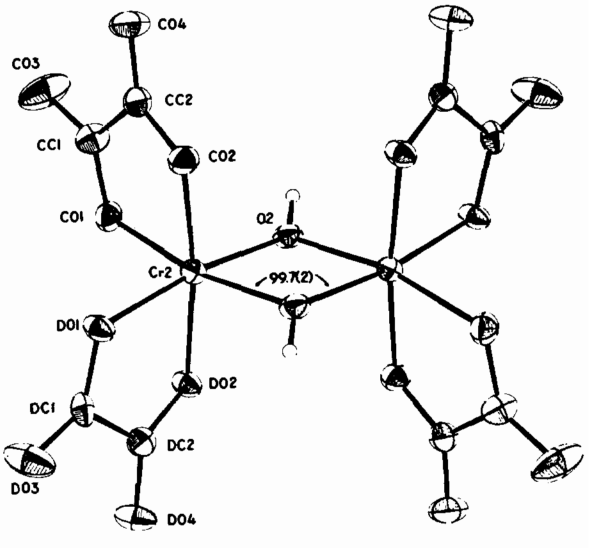


Figure 2. View of the $[Cr(ox)_2OH]_2^{4-}$ anion whose center is at (1/2, 0, 0).

The eight independent Cr–oxalato oxygen distances range from 1.965(5) to 2.001(5) Å with an average distance of 1.982(11) Å. This compares with the average Cr–O separation of 1.965(14) Å found in the double salt $[Cr(en)_2(ox)][Cr(en)(ox)_2]$ [31], the two Cr–O independent distances of 1.970(4) and 1.977(4) in $[Cr(gly)_2OH]_2$ [18], the value 1.964(10) Å in the malonato complex $Na_4[Cr(mal)_2OH]_2 \cdot 5H_2O$ [32] and 1.965(2) Å in $[Cr(gly)_3] \cdot H_2O$ [33].

The Cr–O distances in the bridging unit are in the range 1.950(4) to 1.976(5) Å with an average value of 1.963(11) Å. These values appear to be significantly longer than those found in $[Cr(phen)_2OH]_2I_4 \cdot$-

TABLE II. Thermal Parameters for $Na_4[Cr(ox)_2(OH)]_2 \cdot 6H_2O$.

Atom	β_{11}[a] (or BÅ^2)	β_{22}	β_{23}	β_{12}	β_{13}	β_{23}
Cr(1)	96(2)	388(10)	205(7)	−7(4)	36(3)	−17(7)
Cr(2)	92(3)	351(10)	223(7)	−10(4)	27(3)	−27(7)
Na(1)	177(8)	736(32)	469(21)	98(13)	22(11)	20(21)
Na(2)	123(7)	616(31)	613(23)	43(12)	16(11)	8(22)
Na(3)	309(10)	517(29)	337(19)	21(14)	96(12)	40(19)
Na(4)	254(9)	738(32)	322(19)	−51(14)	64(11)	−43(21)
O(1)	11(1)	47(5)	19(3)	3(2)	2(2)	9(3)
O(2)	8(1)	43(5)	27(3)	1(2)	2(2)	5(3)
AC(1)	13(2)	52(7)	40(5)	0(3)	4(3)	2(5)
AC(2)	12(2)	53(7)	27(4)	−1(3)	7(2)	3(5)
AO(1)	12(1)	46(5)	38(3)	1(2)	8(2)	−8(3)
AO(2)	11(1)	44(5)	31(3)	0(2)	4(2)	−5(3)
AO(3)	15(1)	57(6)	93(6)	10(2)	−7(2)	4(5)
AO(4)	14(1)	70(6)	38(4)	1(2)	−4(2)	−6(4)
BC(1)	15(2)	46(7)	31(5)	−2(3)	13(2)	−3(5)
BC(2)	13(2)	34(6)	32(5)	0(3)	5(2)	−7(4)
BO(1)	13(1)	52(5)	22(3)	−10(2)	5(2)	−3(3)
BO(2)	13(1)	45(5)	21(3)	−5(2)	5(2)	1(3)
BO(3)	31(2)	90(7)	29(4)	−22(3)	2(2)	8(4)
BO(4)	18(2)	64(6)	30(3)	−10(2)	−2(2)	−6(4)
CC(1)	12(2)	49(7)	30(4)	3(3)	8(2)	−8(5)
CC(2)	10(2)	51(7)	20(4)	2(3)	5(2)	−5(4)
CO(1)	13(1)	40(5)	32(3)	0(2)	7(2)	−10(3)
CO(2)	8(1)	38(5)	34(3)	0(2)	5(2)	2(3)
CO(3)	16(1)	39(5)	72(5)	7(2)	−6(2)	−6(4)
CO(4)	12(1)	52(5)	44(4)	0(2)	−2(2)	−5(4)
DC(1)	13(2)	42(7)	21(4)	−1(3)	6(2)	1(4)
DC(2)	11(2)	32(6)	23(4)	1(3)	5(2)	−9(4)
DO(1)	14(1)	51(5)	20(3)	−6(2)	4(2)	−7(3)
DO(2)	10(1)	50(5)	23(3)	−9(2)	−1(2)	−7(3)
DO(3)	22(2)	71(6)	25(3)	−15(3)	2(2)	−2(4)
DO(4)	16(1)	56(5)	24(3)	−9(2)	6(2)	−10(3)
WO(1)	26(2)	60(6)	67(5)	0(3)	3(2)	−26(4)
WO(2)	25(2)	63(6)	54(4)	1(3)	1(2)	0(4)
WO(3)	38(3)	141(10)	66(5)	23(4)	−15(3)	−50(6)
WO(4)	39(3)	95(8)	163(10)	−1(4)	21(4)	3(7)
WO(5)	38(3)	194(12)	99(7)	−27(5)	15(4)	−65(8)
WO(6)	55(3)	96(9)	165(10)	5(5)	56(5)	−52(8)
BH(1)	3.8					
BH(2)	3.8					
1H(1)	6.5					
1H(2)	6.5					
2H(1)	6.5					
2H(2)	6.5					
5H(1)	6.5					
5H(2)	6.5					
6H(1)	6.5					
6H(2)	6.5					

[a] Anisotropic Thermal Parameters are ×10^5 for chromium and sodium, ×10^4 for all other atoms. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

$4H_2O$ [20] and $[Cr(phen)_2OH]_2Cl_4 \cdot 6H_2O$ [19] which are 1.920(3) and 1.927(11) Å, respectively, but similar to those for $[Cr(gly)_2OH]_2$ [18] and $Na_4[Cr(mal)_2OH]_2 \cdot 5H_2O$ [32] which average 1.967 and 1.988 Å, respectively. Owing to the inversion symmetry, the Cr–O–Cr–O bridging unit is strictly planar; the two independent Cr–O–Cr angles are essentially identical at 99.6(2) and 99.7(2). This value is smaller than that in the two salts of $[Cr(phen)_2OH]_2^{4+}$ and larger than that in $[Cr(gly)_2OH]_2$. The "in-plane" oxalate oxygen atoms range from 0.25 to 0.31 Å out of the bridge plane.

TABLE III. Interatomic Distances (Å) and Angles (deg.) in the $[Cr(ox)_2OH]_2^{4-}$ Ion.

Cr(1)–O(1)	1.950(4)
Cr(1)–O(1)'	1.976(5)
Cr(1)–AO(1)	1.980(5)
Cr(1)–AO(2)	1.964(5)
Cr(1)–BO(1)	1.984(5)
Cr(1)–BO(2)	1.979(5)
Cr(2)–O(2)	1.961(5)
Cr(2)–O(2)'	1.965(5)
Cr(2)–CO(1)	1.989(5)
Cr(2)–CO(2)	1.980(4)
Cr(2)–DO(1)	2.001(5)
Cr(2)–DO(2)	1.978(4)
Cr(1)–Cr(1')	2.999(3)
Cr(2)–Cr(2')	3.001(2)
O(2)–Cr(2)–O(2)'	80.3(2)
O(2)–Cr(2)–CO(1)	95.4(2)
O(2)–Cr(2)–CO(2)	94.6(2)
O(2)–Cr(2)–DO(1)	170.3(2)
O(2)–Cr(2)–DO(2)	90.1(2)
O(2)'–Cr(2)–CO(1)	170.8(2)
O(2)'–Cr(2)–CO(2)	90.6(2)
O(2)'–Cr(2)–DO(1)	94.0(2)
O(2)'–Cr(2)–DO(2)	94.5(2)
CO(1)–Cr(2)–CO(2)	81.6(2)
CO(1)–Cr(2)–DO(1)	91.4(2)
CO(1)–Cr(2)–DO(2)	93.6(2)
CO(2)–Cr(2)–DO(1)	93.2(2)
CO(2)–Cr(2)–DO(2)	173.6(2)
DO(1)–Cr(2)–DO(2)	82.5(2)
Cr(2)–O(2)–Cr(2)	99.7(2)
O(1)–Cr(1)–O(1)'	80.4(2)
O(1)–Cr(1)–AO(1)	92.0(2)
O(1)–Cr(1)–AO(2)	96.4(2)
O(1)–Cr(1)–BO(1)	171.9(2)
O(1)–Cr(1)–BO(2)	90.9(2)
O(1)'–Cr(1)–AO(1)	168.3(2)
O(1)'–Cr(1)–AO(2)	89.6(2)
O(1)'–Cr(1)–BO(1)	96.0(2)
O(1)'–Cr(1)–BO(2)	94.7(2)
AO(1)–Cr(1)–AO(2)	82.3(2)
AO(1)–Cr(1)–BO(1)	92.6(2)
AO(1)–Cr(1)–BO(2)	94.3(2)
AO(2)–Cr(1)–BO(1)	90.8(2)
AO(2)–Cr(1)–BO(2)	172.0(2)
BO(1)–Cr(1)–BO(2)	82.1(2)
Cr(1)–O(1)–Cr(1)'	99.6(2)

The sodium ions interact with oxalate oxygen atoms and water molecules; most of the Na–O contacts are in the range 2.3–2.6 Å, and these are collected in Table IV. Na(2) has an additional contact with oxalate oxygen atom AO(1) at 2.946(6) Å, and Na(4) also has a contact with AO(1) at 2.863(6) Å; separations in this range have been considered significant by other authors [34].

TABLE IV. Sodium–Oxygen Interactions (Å).

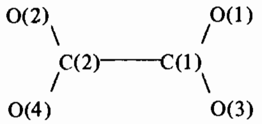
Na(1)–DO(4)	2.316(5)
Na(1)–AO(4)	2.348(6)
Na(1)–WO(2)	2.387(7)
Na(1)–WO(6)	2.514(7)
Na(1)–AO(3)	2.547(7)
Na(1)–DO(1)	2.553(5)
Na(2)–BO(4)	2.290(6)
Na(2)–WO(1)	2.334(7)
Na(2)–CO(4)	2.354(6)
Na(2)–BO(1)	2.362(5)
Na(2)–CO(3)	2.437(6)
Na(3)–DO(4)	2.398(6)
Na(3)–WO(2)	2.401(6)
Na(3)–DO(3)	2.432(6)
Na(3)–DO(2)	2.458(5)
Na(3)–CO(2)	2.481(5)
Na(3)–O(2)	2.578(5)
Na(4)–WO(1)	2.419(7)
Na(4)–BO(3)	2.431(6)
Na(4)–BO(4)	2.472(6)
Na(4)–BO(2)	2.566(5)
Na(4)–BO(3)'	2.568(6)
Na(4)–O1	2.613(6)

The bond lengths and angles for the four oxalate groups are given in Table V, and are very similar to those found in $[Cr(en)_2(ox)][Cr(en)(ox)_2]$ [31]. The oxalate groups deviate somewhat from planarity, the average distance of an atom from the best least-squares plane being 0.03, 0.04, 0.03 and 0.005 Å for the A, B. C and D groups, respectively. The chromium atoms are not in these planes, but range from 0.13 to 0.20 Å out of them. The average C(1)–C(2) bond length is 1.56(2) Å, which compares with 1.53(1) Å for $[Cr(en)_2(ox)]$ $[Cr(en)(ox)_2]$ and is in good agreement with the separation observed in other oxalate structures [35]. As one would expect, the oxalate groups are not symmetric, the C–O separations involving coordinated oxygen atoms being longer than those not involved in coordination to the chromium atoms. Inspection of Table V reveals that the C–C–O angles in the chelate ring (AC(1)–AC(2)–AO(2), AC(2)–AC(1)–AO(1) *etc.*) are compressed relative to those outside the chelate ring. This kind of asymmetry is observed even in non-chelating oxalate groups [35], but the effect is more pronounced here. It is noteworthy that all of the oxalate oxygen atoms are involved in coordination to chromium, in interactions with sodium ions or in hydrogen bonding (*vide infra*).

Hydrogen Bonding

Each located hydrogen atom appears to be hydrogen bonded to a water or oxalate oxygen atom. The H-----O contacts which probably represent hydrogen bonds are given in Table VI. Since the hydrogen atom positions were not refined, little significance should

TABLE V. Intramolecular Distances (Å) and Angles (deg) in the Oxalate Ligands.



	ox A	ox B	ox C	ox D	Average
C(1)–C(2)	1.547(10)	1.578(9)	1.539(9)	1.580(9)	1.561(21)
C(1)–O(1)	1.281(9)	1.290(8)	1.266(8)	1.278(8)	1.279(10)
C(2)–O(2)	1.283(8)	1.265(8)	1.267(7)	1.260(8)	1.269(10)
C(1)–O(3)	1.237(9)	1.205(8)	1.240(8)	1.203(8)	1.221(20)
C(2)–O(4)	1.220(8)	1.207(8)	1.241(8)	1.212(8)	1.220(15)
O(1)–C(1)–C(2)	114.3(6)	113.3(5)	114.3(5)	114.5(5)	114.1(5)
O(2)–C(2)–C(1)	113.9(6)	113.8(6)	114.9(5)	114.1(5)	114.2(5)
O(3)–C(1)–C(2)	118.8(6)	120.2(6)	119.6(6)	118.6(6)	119.3(7)
O(4)–C(2)–C(1)	121.1(6)	118.2(6)	119.6(6)	119.4(6)	119.6(12)
O(1)–C(1)–O(3)	126.8(7)	126.4(6)	126.0(6)	129.9(6)	126.5(4)
O(2)–C(2)–O(4)	124.5(7)	128.0(6)	125.5(6)	126.5(6)	126.1(15)

TABLE VI. Probable A–H-----B Hydrogen Bonds in $Na_4[Cr(OX)_2OH]_2 \cdot 6H_2O$.

A	H	B	A•••B(Å)	H•••B(Å)	A–H•••B(deg.)
WO(1)	1H(1)	AO(2)	2.96	2.32	133
WO(1)	1H(1)	AO(4)	2.98	2.27	142
WO(1)	1H(2)	WO(4)	2.79	1.94	157
WO(2)	2H(1)	CO(3)	3.16	2.37	156
WO(2)	2H(2)	DO(3)	2.74	1.78	166
WO(5)	5H(1)	WO(6)	2.93	2.38	123
WO(6)	6H(1)	AO(3)	3.13	2.38	129
WO(6)	6H(2)	CO(4)	2.78	2.01	141
O(2)	BH(2)	CO(2)	2.89	2.33	135
O(2)	BH(2)	CO(1)	2.92	2.47	122
O(2)	BH(2)	WO(3)	2.77	2.41	112
O(1)	BH(1)	AO(2)	2.93	2.56	124
O(1)	BH(1)	WO(5)	2.85	2.41	132

be attached to the exact values in Table VI; in most cases, however, they seem accurate enough to indicate the presence of hydrogen bonds with reasonable certainty. Hamilton and Ibers have suggested [36] that the criterion for hydrogen bonding is that both the O–H and H-----O separations are less than the van der Waals radius sums of oxygen and hydrogen. Pauling [37] has given these van der Waals' radii as 1.4 and 1.2 Å for oxygen and hydrogen, respectively. Examination of Table VI shows that H-----O and O-----O separations are also in the correct range. For the bridging hydrogen atoms, Table VI lists more than one H-----O contact which meets the Hamilton–Ibers criterion. Since the H–O-----H angles are very similar for the various alternatives, it is difficult to say which of these represent true hydrogen bonds. On the other hand, it seems likely that the two entries for 1H(1) represent a bifurcated hydrogen bond, the WO(1)–1H(1)–AO(2) and WO(1)–1H(1)–AO(4) angles being 133° and 142°, respectively. Our inability to locate the hydrogen atoms on WO(3) and WO(4) precludes any serious discussion of hydrogen bonding for these water molecules, but examination of oxygen–oxygen contacts involving the above suggest that O(2), CO(1) and WO(4) could form hydrogen bonds with WO(3), while AO(3) and CO(3) are possibilities for WO(4).

Magnetic Properties

The magnetic susceptibility (corrected for diamagnetism using Pascal's constants) of a large single crystal of $Na_4[Cr(ox)_2(OH)]_2 \cdot 6H_2O$ was measured in

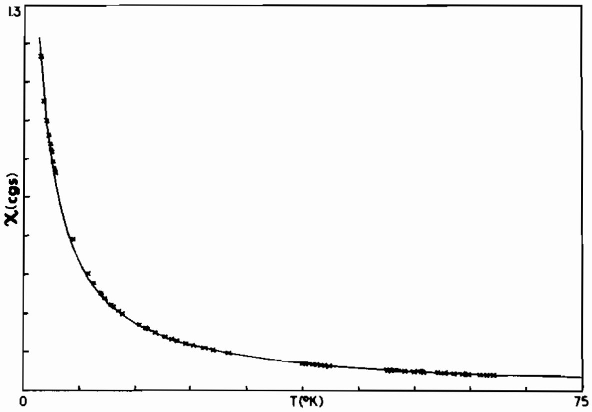


Figure 3. The temperature dependence of the magnetic susceptibility of a single crystal of $Na_4[Cr(ox)_2OH]_2 \cdot 6H_2O$, measured at a field strength of 10 kG. The experimental data are shown as crosses, and the solid line represents the best fit to magnetization expression for coupled S = 3/2 ions with g = 1.931(6), J = −0.31(2), and γ = 0.28(4).

the range 2°–70°K using a Foner-type PAR vibrating sample magnetometer [38] at a magnetic field strength of 10 KG. Temperatures were measured by a calibrated gallium arsenide diode; mercury tetrathiocyanatocobaltate(II) was used as the susceptibility standard [39]. The crystal was mounted in grease parallel to the crystallographic *b*-axis. The sample was rotated several times during the run, but no anisotropy in the magnetization was observed. The expression for the magnetization of two exchange-coupled S = 3/2 ions was derived in the usual manner [40], and this can be expressed as follows:

$$\begin{aligned} M^c = {} & Ng\beta\{2e^{2J/kT}\sinh(G/kT) + e^{6J/kT}[2\sinh(G/kT) + 4\sinh(2G/kT)] + e^{12J/kT}[2\sinh(G/kT) + 4\sinh(2G/kT) + 6\sinh(3G/kT)]\} \times \\ & \times \{1 + e^{2J/kT}[1 + 2\cosh(G/kT)] \\ & + e^{6J/kT}[1 + 2\cosh(G/kT) + 2\cosh(2G/kT)] \\ & + e^{12J/kT}[1 + 2\cosh(G/kT) + 2\cosh(2G/kT) + \\ & + 2\cosh(3G/kT)]\}^{-1}, \end{aligned} \tag{1}$$

where G = gβH and the exchange Hamiltonian is:

$$H_{ex} = -2JS_1 \cdot S_2 \tag{2}$$

Examination of the experimental data suggested that Eq. [1] would be more appropriate than the usual susceptibility expression (see, for example, ref. 20), because it seemed likely that the condition J >> gβH would *not* be satisfied in this case. In view of this, it would be inconsistent to approximate the trigonometric functions containing gβH/kT (this is essentially the usual practice) without also doing so for the exponentials containing J/kT. Moreover, all such approximations break down at low temperatures when gβH/kT and J/kT approach unity. Interactions between pairs were taken into account through the molecular field approximation. The magnetic field strength is expressed [41] as:

$$H = H_0 + \gamma M^c, \tag{3}$$

where H_0 is the applied field, and γ the parameter to be varied in the fitting process. This makes Eq. [1] a self-consistent equation which is solved iteratively. The molecular field parameter, γ, is related to the interdimer exchange paramter, J′, through the expression [40]:

$$J' = \gamma N g^2 \beta^2 k/2Z, \tag{4}$$

where Z is the number of nearest neighbors. The data were fitted using a non-linear least-squares fitting routine written in these laboratories. The function minimized was $\Sigma w_i[M_i^o - M_i^c]$, the weights being assigned as $w_i = 1/M_i^o$. The best least-squares fit to the experimental data is shown in Figure 3, the solid line representing the calculated dependence of the susceptibility (M^c/H_0): the crosses are the experimental points (M^o/H_0). The parameters derived from the fitting process are g = 1.931(6), J = −0.31(2) cm^{-1} and γ = 0.28(4). This value of γ and Eq. [4] yield J′ = 0.034(5) cm^{-1}, assuming four nearest neighbor pairs. This would seem a reasonable value, considering the numerous possible pathways *via* hydrogen bonding and sodium–oxygen interactions for interdimer exchange.

Clearly, the data depicted in Figure 3 could also be fitted using a model which considered only lattice exchange between chromium(III) ions which are not exchange-coupled in a pairwise manner. This, however, would ignore the obvious structural features of the complex and the large accumulation of magnetic data available for di-bridged complexes of chromium(III) [17–20, 42–45] which have been interpreted on the basis of pairwise exchange. Furthermore, in analogy with the hydroxo-bridged copper(II) systems [1–12] where the dependence of J on bridge angle (ϕ) is better understood, the existence of some ϕ such that J ~ 0 is an expected result.

It should be noted, that even though pairwise exchange is being taken into account, Eq. [1] may not be an adequate description of the magnetic properties of this complex. The reason for this is that chromium(III) complexes sometimes exhibit fine structure splittings on the order of 1 cm^{-1}; for small J values this would cause mixing of the various spin multiplets, thus changing the functional form of Eq. [1]. The fact that no measureable anisotropy was observed (*vide supra*) tends to weigh against this possibility, but does not rule it out completely. In view of this difficulty, the exact values extracted from the fitting process should be considered with some reservation. It is, however, certain that the exchange parameter is small, probably less than 0.5 cm^{-1}, and that some lattice exchange is present.

TABLE VII. Structural and Magnetic Properties of $[CrL_2(OH)]_2^{n+}$.

Complex	ϕ (deg)	Cr–Cr (Å)	2J (cm^{-1})	Reference
$[Cr(phen)_2OH]_2Cl_4$	102.7	3.008	–55	19
$[Cr(phen)_2OH]_2I_4$	102.1	2.986	–43.8	20
$[Cr(dipic)(OH_2)OH]_2$	100.7	2.999	–8	46
$Na_4[Cr(ox)_2OH]_2$	99.6	3.000	–0.6	This work
$[Cr(gly)_2OH]_2$	98.2	2.974	–7.4	17, 18

Discussion

The structural and magnetic properties of $Na_4[Cr(ox)_2OH]_2 \cdot 6H_2O$ are compared with those of the other well-characterized systems of the type $[Cr(L)_2OH]_2^{n+}$ in Table VII. As was anticipated (*vide supra*, Introduction), an examination of Table VII demonstrates that any correlation between ϕ and J is not the simple linear one observed for the copper dimers; indeed, while theoretical considerations dictate that a correlation exist, the functional form of the dependence of J on ϕ is not discernible from the available data. Clearly, further systematic magnetic and structural studies are necessary before we may deduce the nature of the correlation between structural and magnetic properties in these systems; such experiments are being conducted, both in our laboratories and elsewhere [46].

Acknowledgments

We are grateful to Professor Harvey Schugar for informing us of his results prior to their publication. This research was supported by the National Science Foundation through Grant No. MPS73-08703-A02 and by the Materials Research Center of the University of North Carolina through Grant No. GH-33632 from the National Science Foundation.

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