

- (7) For an assessment see M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, N.Y., 1967.
- (8) See for example: (a) H. Yamazaki, K. Aoki, Y. Yamamoto, and Y. Wakatsuki, *J. Am. Chem. Soc.*, **97**, 3547 (1975); (b) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *ibid.*, **95**, 597 (1973); (c) J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, **7**, 1298 (1968); (d) R. Burt, M. Cooke, and M. Green, *J. Chem. Soc. A*, 2981 (1970); (e) J. Browning, M. Green, A. Laguna, L. E. Smart, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 723 (1975).
- (9) (a) L. S. Meriwether, E. C. Colthup, G. M. Kennerly, and R. N. Reusch, *J. Org. Chem.*, **26**, 5155 (1961); (b) L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *ibid.*, **27**, 3930 (1962); (c) R. J. Kern, *Chem. Commun.*, 706 (1968).
- (10) A. J. Carty, M. Mathew, T. J. O'Connor, and G. J. Palenik, *J. Organomet. Chem.*, **38**, C15 (1972).
- (11) A. J. Carty, M. Mathew, H. N. Paik, and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 25 (1974).
- (12) H. A. Patel, R. G. Fischer, A. J. Carty, D. V. Naik, and G. J. Palenik, *J. Organomet. Chem.*, **60**, C49 (1973).
- (13) N. J. Taylor, H. N. Paik, P. C. Chieh, and A. J. Carty, *J. Organomet. Chem.*, **87**, C31 (1975).
- (14) (a) P. W. R. Corfield and H. M. N. Shearer, *Acta Crystallogr.*, **20**, 502 (1966); (b) P. W. R. Corfield and H. M. N. Shearer, *ibid.*, **21**, 957 (1966).
- (15) (a) O. M. Abu Salah and M. I. Bruce, *J. Chem. Soc., Dalton Trans.*, 2302, (1974); (b) M. I. Bruce, R. Clark, J. Howard, and P. Woodward, *J. Organomet. Chem.*, **42**, C107 (1972).
- (16) (a) O. M. Abu Salah and M. I. Bruce, *J. Chem. Soc., Dalton Trans.*, 2311 (1975); (b) O. M. Abu Salah, M. I. Bruce, R. E. Davis, and N. V. Raghavan, *J. Organomet. Chem.*, **64**, C48 (1974).
- (17) (a) O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and B. G. DeBoer, *J. Chem. Soc., Chem. Commun.*, 688 (1974); (b) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **14**, 2630 (1975).
- (18) (a) O. M. Abu Salah, M. I. Bruce, M. R. Churchill, and S. A. Bezman, *J. Chem. Soc., Chem. Commun.*, 858 (1972); (b) M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, **13**, 1418 (1974).
- (19) (a) Y. S. Wong, H. N. Paik, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 309 (1975); (b) A. J. Carty, N. J. Taylor, H. N. Paik, W. Smith, and J. G. Yule, *ibid.*, 41 (1976).
- (20) (a) M. H. Chisholm and D. A. Couch, *J. Chem. Soc., Chem. Commun.*, 42 (1974); (b) R. A. Bell and M. H. Chisholm, *ibid.*, 818 (1974); (c) R. A. Bell, M. H. Chisholm, D. A. Couch, and L. A. Rankel, *Inorg. Chem.*, **16**, 677 (1977).
- (21) A. J. Carty, N. K. Hota, H. A. Patel, T. J. O'Connor, and T. W. Ng, *Can. J. Chem.*, **49**, 2706 (1971).
- (22) D. Mootz, H. Alfenberg, and D. Lücke, *Z. Kristallogr., Kristalloggeom., Kristallphys., Kristallchem.*, **130**, 239 (1969).
- (23) M. Fild, O. Stelzer, and R. Schmutzler, *Inorg. Synth.*, **14**, 4 (1973).
- (24) A. J. Carty, H. N. Paik, and G. J. Palenik, *Inorg. Chem.*, **16**, 300 (1977).
- (25) A. J. Carty, T. Hinsperger, L. Mihichuk, and H. D. Sharma, *Inorg. Chem.*, **9**, 2563 (1970).
- (26) (a) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202-211; (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (27) J. G. Smith and D. T. Thompson, *J. Chem. Soc. A*, 1694 (1967).
- (28) F. W. Grevels, D. Schulz, E. K. Von Gustorf, and D. St. P. Bunbury, *J. Organomet. Chem.*, **91**, 341 (1975).
- (29) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).
- (30) See for example: P. C. Ellgen and J. N. Gerlach, *Inorg. Chem.*, **12**, 2526 (1973); P. C. Ellgen and J. N. Gerlach, *ibid.*, **13**, 1944 (1974); J. N. Gerlach, S. L. McMullin, and P. C. Ellgen, *ibid.*, **15**, 1232 (1976); J. N. Gerlach, R. M. Wing, and P. C. Ellgen, *ibid.*, **15**, 2959 (1976).
- (31) D. M. Adams, "Metal-Ligand and Related Vibrations", Arnold, London, 1967, p 212.
- (32) D. A. Allison, J. Clardy, and J. G. Verkade, *Inorg. Chem.*, **11**, 2804 (1972).
- (33) B. T. Kilbourn, U. A. Raeburn, and D. T. Thompson, *J. Chem. Soc. A*, 1906 (1969).
- (34) O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Pettersen, and W. G. Town, Ed., "Molecular Structures and Dimensions", Vol. A1, N. V. A. Oosthoek, Utrecht, 1972, p S2.
- (35) G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc. A*, 1750 (1967).
- (36) S. D. Ittel and J. A. Ibers, *Adv. Organomet. Chem.*, **14**, 33 (1976); S. Otsuka and A. Nakamura, *ibid.*, **14**, 245 (1976).
- (37) P. J. Fraser and R. S. Dickson, *Adv. Organomet. Chem.*, **12**, 323 (1974).
- (38) J. M. Coleman and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 542 (1967).
- (39) A. J. Carty, G. Ferguson, H. N. Paik, and R. Restivo, *J. Organomet. Chem.*, **74**, C14 (1974).
- (40) N. N. Greenwood and T. C. Gibb, "Mössbauer Spectroscopy", Chapman and Hall, London, 1971, pp 221-233.
- (41) T. C. Gibb, R. Greatrex, N. N. Greenwood, and D. T. Thompson, *J. Chem. Soc. A*, 1663 (1967).
- (42) R. L. Collins and R. Pettit, *J. Chem. Phys.*, **34**, 3933 (1963).
- (43) R. H. Herber, R. B. King, and M. N. Ackermann, *J. Am. Chem. Soc.*, **96**, 5437 (1974).
- (44) J. A. de Beer, R. J. Haines, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 3271 (1971).
- (45) A. J. Carty, S. E. Jacobson, R. T. Simpson, and N. J. Taylor, *J. Am. Chem. Soc.*, **97**, 7254 (1975).
- (46) K. Yasufuku and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, **45**, 2664 (1972).
- (47) A. J. Deeming, S. Hasso, and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1614 (1975).
- (48) For example, whereas simple disubstituted alkynes form only transient copper(I) π complexes, the derivative $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_2\text{Ph}(\text{CuCl})_2]$ is quite stable in air and solution.
- (49) J. B. Keister and J. R. Shapley, *J. Organomet. Chem.*, **85**, C29 (1975).
- (50) G. Jackson, B. F. G. Johnson, J. W. Kelland, J. Lewis, and K. T. Schorpp, *J. Organomet. Chem.*, **87**, C27 (1975).
- (51) M. R. Churchill, B. G. DeBoer, J. R. Shapley, and J. B. Keister, *J. Am. Chem. Soc.*, **98**, 2357 (1976).

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A Ferromagnetically Coupled Chromium(III) Dimer: Synthesis, Structure, and Magnetic Properties of Sodium Di- μ -hydroxo-bis[bis(malonato)chromate(III)] Pentahydrate

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The dimeric chromium(III) complex sodium di- μ -hydroxo-bis[bis(malonato)chromate(III)] pentahydrate, $\text{Na}_4[\text{Cr}(\text{C}_2\text{H}_3\text{O}_4)_2\text{OH}]_2 \cdot 5\text{H}_2\text{O}$ or $\text{Na}_4[\text{Cr}(\text{mal})_2\text{OH}]_2 \cdot 5\text{H}_2\text{O}$, has been synthesized and its magnetic and structural properties have been examined. The complex crystallizes in the triclinic space group $P\bar{1}$ with one dimeric formula unit in a cell of dimensions $a = 8.937$ (6), $b = 10.279$ (7), $c = 8.310$ (6) Å; $\alpha = 75.20$ (3), $\beta = 76.01$ (3), $\gamma = 112.07$ (3)°. The structure has been refined by a full-matrix least-squares method to a conventional R factor (on F) of 0.039 using 2902 independent single-crystal counter data. The structure is comprised of dimeric $[\text{Cr}(\text{mal})_2\text{OH}]_2^{4-}$ anions which interact with sodium cations and water molecules in the cell. The geometry around each chromium(III) center is six-coordinate, approximately octahedral. The bridging Cr_2O_2 unit is strictly planar, as required by the crystallographic symmetry. The $\text{Cr}-\text{O}-\text{Cr}'$ bridging angle is 99.34 (7)° and the $\text{Cr}-\text{Cr}'$ separation is 3.031 (2) Å. The malonato ligands are bidentate, each coordinating through two oxygen atoms; the uncoordinated oxygen atoms are involved in extensive hydrogen bonding in the crystal. The magnetic susceptibility of the complex has been examined in the range 2-50 K, and the data have been analyzed by application of the magnetization expression for coupled pairs of $S = 3/2$ ions. The exchange interaction is small, but J is clearly positive (i.e., the coupling is ferromagnetic), the best fit to the data giving $g = 1.988$ (3), $J = +1.08$ (2) cm^{-1} , and $\gamma = -0.106$. This complex, therefore, represents the first documented example of a ferromagnetically coupled chromium(III) dimer.

Introduction

Recent experimental studies of the structural and magnetic properties of a variety of dihydroxo-bridged complexes of copper(II) have demonstrated that the singlet-triplet splitting,

$2J$, is dependent upon the $\text{Cu}-\text{O}-\text{Cu}$ bridging angle, ϕ .¹⁻¹² The functional form of this correlation is nearly linear, at least over the range of ϕ 's observed to date. The theoretical basis for this correlation can be understood in terms of the Good-

enough-Kanamori rules¹³ and has been discussed in some detail from a molecular orbital viewpoint by Hoffmann.¹⁴ Theoretical treatments of this type when applied to dihydroxo-bridged complexes of Cr(III) clearly indicate that a correlation between J and ϕ should also exist for these systems. The functional form of this dependence is not, however, easily extracted from arguments that are entirely qualitative. This situation arises from the fact that J is actually the sum of several "elementary contributions"¹⁵ which are different in magnitude and sign. Moreover, it can be shown through molecular orbital theory¹⁴ that each will respond independently to structural distortions of the complex. When one contribution dominates the others, qualitative molecular orbital considerations¹⁶ indicate that a correlation similar to that for the copper(II) complexes will obtain for the chromium(III) systems as well.

The structural and magnetic properties of several of these complexes have been investigated in order to experimentally determine the influence of structural changes on the magnetic properties of these systems. Completely characterized members of this series now include $[\text{Cr}(\text{gly})_2\text{OH}]_2$,^{17,18} $[\text{Cr}(\text{phen})_2\text{OH}]_2\text{Cl}_4 \cdot 6\text{H}_2\text{O}$,¹⁹ $[\text{Cr}(\text{phen})\text{OH}]_2\text{I}_4 \cdot 4\text{H}_2\text{O}$,²⁰ and $\text{Na}_4[\text{Cr}(\text{ox})_2\text{OH}]_2 \cdot 6\text{H}_2\text{O}$.²¹ In this present work we report the first example of a ferromagnetically coupled chromium(III) dimer, $\text{Na}_4[\text{Cr}(\text{mal})_2\text{OH}]_2 \cdot 5\text{H}_2\text{O}$.

Experimental Section

A powdered sample of the complex $\text{Na}_4[\text{Cr}(\text{mal})_2\text{OH}]_2 \cdot 5\text{H}_2\text{O}$ was obtained by the reaction of sodium hydroxide with the monomeric complex $\text{cis-Na}_4[\text{Cr}(\text{mal})_2(\text{OH})_2]_2$ and subsequent metathesis with sodium bromide. The preparation of the monomer was essentially that of Hamm and Perkins,²² except that NaOH was substituted for KOH. The preparation of the dimer is essentially similar to Werner's method²³ for the oxalate analogue except that the sodium salt of the monomer was used instead of the ammonium salt. Suitable blue-violet single crystals were obtained by slow evaporation of an aqueous solution of the powdered material. These crystals were found to decompose to a light blue powder upon removal from the mother liquor; this prevented a chemical analysis of the complex of interest from being obtained.

After examination by precession and Weissenberg photography the crystals were assigned to the triclinic system; no systematic absences were observed and the space group was assigned as either $P\bar{1}$ or $P1$. Successful refinement in the centrosymmetric space group $P\bar{1}(C)$ suggests that this is the correct assignment. The cell constants, obtained by least-squares methods²⁴ using 19 reflections, are $a = 8.937(6)$, $b = 10.279(7)$, $c = 8.310(6)$ Å; $\alpha = 75.20(3)$, $\beta = 76.01(3)$, $\gamma = 112.07(3)^\circ$; these observations were made at 16°C with the wavelength assumed as $\lambda(\text{Mo K}\alpha_1)$ 0.7093 Å. The density of 1.91 g cm^{-3} calculated for one dimeric unit in a cell is in acceptable agreement with the value of $1.92(2)\text{ g cm}^{-3}$ observed by flotation in carbon tetrachloride-bromoform solution. Thus, with one formula unit per cell, the center of the dimer is constrained to lie on the inversion center.

Intensity data were collected from a diamond-shaped plate, mounted parallel to the a axis and bounded by faces (100), ($\bar{1}00$), (010), ($0\bar{1}0$), (001), and ($00\bar{1}$); the distances between opposite faces were 0.39, 0.38, and 0.14 mm, respectively. In order to avoid decomposition during data collection, it was necessary to coat the crystal with grease upon removal from the mother liquor. The crystal mosaicity was examined in the usual manner²⁵ and was found to be acceptable. The data were collected in a manner described previously¹¹ with an automatic Picker four-circle diffractometer using a molybdenum tube and a graphite monochromator. The takeoff angle was 2.0° , the scan rate was $1.0^\circ/\text{min}$, and the scan range was from 0.85° below the calculated $\text{K}\alpha_1$ peak position to 0.85° above the calculated $\text{K}\alpha_2$ peak position; backgrounds were counted for 20 s at each end of the scan. A unique data set of 3695 reflections having $2\theta \leq 58^\circ$ was collected; 2902 of these were found to have intensities greater than 3 times their estimated standard deviations. The intensities of three standard reflections, measured after every 100 reflections, showed no decline during the run. No absorption correction was applied, partly because the grease made measurement of the crystal approximate but mainly because

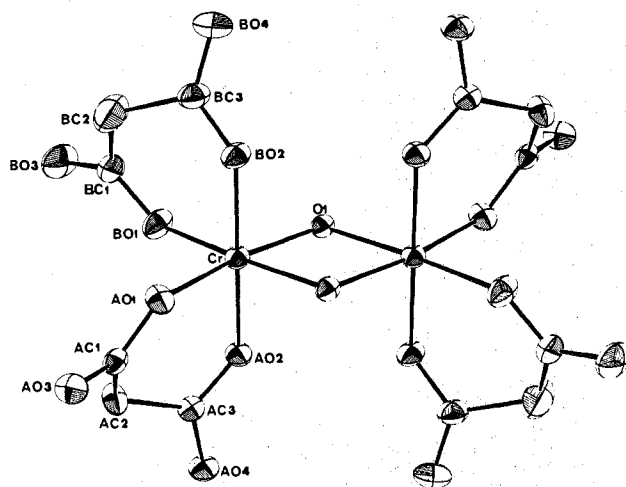


Figure 1. View of the $[\text{Cr}(\text{mal})_2\text{OH}]_2^{4-}$ anion. Hydrogen atoms were omitted for clarity.

absorption effects for this small specimen were judged to be minor; the linear absorption coefficient, μ , for this complex with Mo radiation is 10.8 cm^{-1} . The data were processed in the usual manner.^{11,25}

Solution and Refinement of the Structure

The position of the chromium atom was obtained by the heavy-atom technique.²⁶ Two cycles of least-squares refinement with this position and an isotropic thermal parameter yielded values for the usual residuals $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 0.64 and 0.65, respectively. In all least-squares refinements in this analysis, the function minimized was $\sum w(|F_o| - |F_c|)^2$, with the weights, w , being assigned as $4F_o^2 / \sigma^2(F_o)$. In all calculations of F_o , the atomic scattering factors for Cr and Na were from Cromer and Waber,²⁷ those for O, N, and C were from Ibers,²⁸ and those for H were from Stewart, Davidson, and Simpson.²⁹ The effects of the anomalous dispersion of chromium and sodium were included in the calculation of F_o ,³⁰ the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.³¹

From the subsequent series of several sets of difference Fourier syntheses and least-squares refinements, the positions of all remaining nonhydrogen atoms were determined. After several cycles of isotropic refinement, the values of R_1 and R_2 were 0.099 and 0.151, respectively. At this point the temperature factor of water oxygen atom WO(3) was nearly twice as large as the next largest temperature factor in the refinement, that of water oxygen atom WO(2). The occupancy parameter of atom WO(3) was, therefore, assigned as 0.5, and an additional cycle of least squares, varying only the positional and thermal parameters of atom WO(3), yielded values of R_1 and R_2 of 0.094 and 0.142, respectively. This improved agreement with experiment and the resulting thermal parameter for WO(3), which was now approximately equal to that of WO(2), was taken as evidence that our change in the model was sensible, and that, therefore, the complex is correctly formulated as the pentahydrate. After two cycles of anisotropic refinement, the positions of the malonate ring and water hydrogen atoms, except for those of the half water molecule, WO(3), were located. The malonate ring hydrogen atom positions were found to be very close to their calculated positions. Attempts to refine these positions with isotropic thermal parameters resulted in unreasonable shifts in position in several cases; hence, it was decided to fix all hydrogen atom parameters at their initial values for the remainder of the refinement.

In the final cycle of least squares, no parameter experienced a shift of more 9.0% of its estimated standard deviation, and the final values for R_1 and R_2 were 0.039 and 0.055, respectively. The final cycle of least squares involved, therefore, full-matrix refinement of 190 variables using 2902 independent intensities. The positional and thermal parameters are given in Tables I and II; a table of observed and calculated structure amplitudes is available.³²

Description of the Structure

The geometry and labeling scheme for the $[\text{Cr}(\text{mal})_2\text{OH}]_2^{4-}$ anion is depicted in Figure 1, and the inner coordination sphere is shown in Figure 2. The anions interact with sodium cations

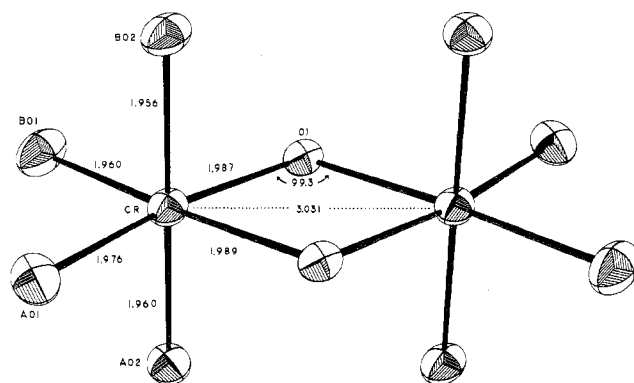
Table I. Positional Parameters ($\times 10^4$) for $\text{Na}_4[\text{Cr}(\text{mal})_2(\text{OH})]_2 \cdot 5\text{H}_2\text{O}$

Atom	x	y	z
Cr ^a	10047 (4)	13602 (3)	3911 (4)
Na(1)	4758 (1)	1745 (1)	4401 (1)
Na(2)	-2931 (1)	925 (1)	131 (1)
O(1)	-153 (2)	876 (1)	-1294 (2)
AO(1)	1951 (2)	1517 (2)	2290 (2)
AO(2)	-1199 (2)	1122 (2)	1935 (2)
AO(3)	2002 (2)	1726 (2)	4860 (2)
AO(4)	-3021 (2)	1064 (2)	4296 (2)
AO(1)	1400 (2)	1803 (2)	3670 (3)
AC(2)	-12 (3)	2302 (3)	3807 (3)
AC(3)	-1516 (2)	1427 (2)	3333 (2)
BO(1)	1809 (2)	3555 (2)	-659 (2)
BO(2)	3200 (2)	1615 (2)	-1178 (2)
BO(3)	3685 (3)	5983 (2)	-1937 (3)
BO(4)	5558 (2)	2851 (2)	-3640 (2)
BC(1)	3340 (3)	4643 (2)	-1559 (3)
BC(2)	4876 (4)	4290 (3)	-1981 (5)
BC(3)	4507 (3)	2840 (2)	-2363 (3)
WO(1)	4124 (2)	109 (2)	1885 (2)
WO(2)	-1591 (5)	3602 (3)	-867 (4)
WO(3)	1028 (7)	4792 (7)	-4206 (9)
O1H ^b	53	130	-235
AH(1)	61	338	282
AH(2)	-49	226	507
BH(1)	517	417	-76
BH(2)	587	513	-299
W1H(1)	344	52	209
W1H(2)	387	-37	285
W2H(1)	-233	353	-107
W2H(2)	-204	391	17

^a Positional parameters for chromium atom are $\times 10^5$. ^b Positional parameters for hydrogen atoms are $\times 10^3$.

and water molecules through the malonato and bridging hydroxo oxygen atoms.

Each chromium atom is six-coordinate, approximately octahedral, the ligating atoms being two cis hydroxo groups

**Figure 2.** View of the inner coordination sphere of the $[\text{Cr}(\text{mal})_2(\text{OH})]_2^{4-}$ anion.

and two cis malonato groups. The bond lengths and angles for the anion are given in Table III. The crystallographic symmetry at the anion is $C_i(\bar{1})$, but it approximates $C_{2h}(2/m)$; in this respect it is similar to all of the previously reported hydroxo-bridged chromium(III) dimers^{17,21,33} with the exception of the two salts of the $[\text{Cr}(\text{phen})_2(\text{OH})]_2^{4+}$ cation.^{19,20} The four independent chromium-malonato oxygen distances range from 1.956 (2) to 1.976 (2) Å with an average of 1.963 (9) Å. This compares with the average chromium-carboxyl oxygen distances found in $[\text{Cr}(\text{en})_2(\text{ox})][\text{Cr}(\text{en})(\text{ox})_2]$,³⁴ $[\text{Cr}(\text{gly})_2(\text{OH})]_2$,^{17,18} and $[\text{Cr}(\text{gly})_3] \cdot \text{H}_2\text{O}$ ³⁵ which are 1.965 (14), 1.974 (5), and 1.965 (2) Å, respectively. The two Cr-O distances in the bridging unit are 1.987 (2) and 1.989 (2) Å. These are somewhat longer than those observed for $[\text{Cr}(\text{phen})_2(\text{OH})]_2^{4+}$ and $[\text{Cr}(\text{en})_2(\text{OH})]_2^{4+}$ but not significantly different from those for $[\text{Cr}(\text{ox})_2(\text{OH})]_2^{4-}$ and $[\text{Cr}(\text{gly})_2(\text{OH})]_2$.^{17-21,33} Owing to the inversion symmetry, the Cr-O-Cr angle being 99.34 (7)°. This value is smaller than that in the two phen salts, larger than that for the gly complex, and not

Table II. Thermal Parameters (U_{ij} in Å²) for $\text{Na}_4[\text{Cr}(\text{mal})_2(\text{OH})]_2 \cdot 5\text{H}_2\text{O}^a$

Atom	U_{11}^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	149 (2)	180 (2)	213 (2)	86 (1)	-51 (1)	-73 (1)
Na(1)	250 (4)	274 (4)	449 (5)	141 (3)	-113 (4)	-92 (4)
Na(2)	293 (4)	376 (5)	417 (5)	208 (4)	-173 (4)	-193 (4)
O(1)	174 (6)	181 (6)	186 (6)	79 (5)	-51 (5)	-48 (5)
AO(1)	206 (7)	332 (7)	313 (7)	168 (6)	-126 (6)	-176 (6)
AO(2)	162 (6)	290 (7)	250 (6)	118 (5)	-79 (5)	-124 (5)
AO(3)	246 (7)	391 (8)	285 (7)	175 (6)	-134 (6)	-136 (6)
AO(4)	187 (7)	320 (7)	284 (7)	150 (6)	-59 (5)	-118 (6)
AC(1)	155 (8)	193 (8)	256 (8)	80 (6)	-72 (6)	-81 (6)
AC(2)	238 (9)	336 (10)	351 (10)	178 (8)	-150 (8)	-216 (8)
AC(3)	183 (8)	206 (8)	225 (8)	125 (7)	-79 (6)	-75 (6)
BO(1)	241 (7)	191 (7)	412 (8)	100 (6)	-42 (6)	-77 (6)
BO(2)	172 (6)	213 (6)	308 (7)	97 (5)	-21 (5)	-80 (5)
BO(3)	440 (10)	186 (7)	504 (10)	111 (7)	-33 (8)	-57 (7)
BO(4)	338 (9)	536 (11)	367 (9)	145 (8)	40 (7)	-208 (8)
BC(1)	298 (10)	203 (8)	285 (9)	75 (8)	-43 (8)	-81 (7)
BC(2)	306 (13)	347 (13)	732 (19)	74 (10)	-51 (12)	-241 (13)
BC(3)	208 (9)	288 (10)	292 (9)	117 (8)	-22 (7)	-88 (8)
WO(1)	341 (8)	512 (10)	283 (7)	282 (8)	-113 (6)	-109 (7)
WO(2)	1114 (24)	561 (15)	846 (18)	550 (16)	-166 (17)	-172 (13)
WO(3)	392 (25)	668 (33)	1140 (48)	69 (23)	-119 (28)	-325 (33)
O1H	51 (U)					
AH(1)	51 (U)					
AH(2)	51 (U)					
BH(1)	51 (U)					
BH(2)	51 (U)					
W1H(1)	51 (U)					
W1H(2)	51 (U)					
W2H(1)	51 (U)					
W2H(2)	51 (U)					

^a Anisotropic thermal parameters are $\times 10^4$; isotropic thermal parameters are $\times 10^3$. ^b The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table III. Interatomic Distances (Å) and Angles (deg) in $[\text{Cr}(\text{mal})(\text{OH})_2]_2^{4-}$

Distances			
Cr-O(1)	1.987 (2)	Cr-BO(1)	1.960 (2)
Cr-O(1')	1.989 (2)	Cr-BO(2)	1.956 (2)
Cr-AO(1)	1.976 (2)	Cr-Cr'	3.031 (2)
Cr-AO(2)	1.960 (2)		
Angles			
O(1)-Cr-O(1')	80.66 (7)	O(1')-Cr-BO(2)	88.42 (7)
O(1)-Cr-AO(1)	171.52 (6)	AO(1)-Cr-AO(2)	90.28 (8)
O(1)-Cr-AO(2)	87.50 (8)	AO(1)-Cr-BO(1)	92.91 (8)
O(1)-Cr-BO(1)	95.22 (8)	AO(1)-Cr-BO(2)	90.36 (8)
O(1)-Cr-BO(2)	91.95 (8)	AO(2)-Cr-BO(1)	88.79 (8)
O(1')-Cr-AO(1)	91.25 (7)	AO(2)-Cr-BO(2)	179.20 (65)
O(1')-Cr-AO(2)	92.06 (8)	BO(1)-Cr-BO(2)	90.68 (8)
O(1')-Cr-BO(1)	175.75 (12)	Cr-O(1)-Cr'	99.34 (7)

Table IV. Sodium-Oxygen Interactions <3.0 Å

Na(1)-BO(3)'	2.307 (3)	Na(2)-WO(2)	2.360 (4)
Na(1)-BO(4)	2.313 (3)	Na(2)-WO(1)	2.370 (3)
Na(1)-AO(4)	2.330 (2)	Na(2)-AO(2)	2.392 (2)
Na(1)-AO(3)	2.391 (2)	Na(2)-BO(2)'	2.429 (2)
Na(1)-AO(4)'	2.478 (3)	Na(2)-WO(1)'	2.449 (2)
		Na(2)-O(1)	2.505 (2)

significantly different from that found in $\text{Na}_4[\text{Cr}(\text{ox})_2(\text{OH})]_2 \cdot 6\text{H}_2\text{O}$. The "in-plane" malonato oxygen atoms, AO(1) and BO(1), are 0.088 and 0.036 Å out of the bridge plane, respectively.

The sodium ions interact with malonato oxygen atoms, the hydroxo group, and water molecules. All sodium-oxygen contacts that are less than 3.0 Å are in the range from 2.307 (2) to 2.505 (2) Å; these distances are listed in Table IV. The average Na(1)-O distance is 2.36 (7) Å while the average Na(2)-O separation is 2.42 (5) Å; these values are within the range normally observed.^{21,36}

The bond lengths and angles for the two independent malonato groups are given in Table V. The C-C bond lengths range from 1.516 (3) to 1.534 (4) Å with an average of 1.526 (9) Å, which is well within the range normally observed in malonato complexes.³⁷⁻⁴¹ The C-O separations involving coordinated oxygen atoms are lengthened significantly as compared to those involving uncoordinated oxygen atoms, the average coordinated C-O separation being 1.276 (7) Å while the value for uncoordinated C-O separation is 1.233 (6) Å. This effect is common in coordinated carboxylate structures, but this is probably the best example for a malonate complex since most of such structures have been polymeric utilizing the nonchelating oxygen atoms to continue the sequence.³⁷⁻⁴¹ The AO(1), AO(2), AC(1), AC(2) unit is very nearly planar, the average deviation of an atom from the best least-squares plane being 0.002 Å, while for the BO(1), BO(2), BC(1), BC(2) unit, this value is 0.081 Å. Both malonato groups are in the boat conformation, Cr and AC(3) being displaced to the same side of the A plane, 0.32 and 0.49 Å, respectively, while Cr and BC(3) are displaced 0.16 and 0.51 Å from the B plane, respectively. The boat conformation appears to be the most common in malonate structures,³⁷⁻⁴¹ but the chair conformation has been observed.³⁹

Hydrogen Bonding

The hydrogen atoms located on the water molecules and the hydroxohydrogen atom form hydrogen bonds with water and malonato oxygen atoms. Hamilton and Ibers have suggested⁴² that the criterion for hydrogen bonding is that both the O-H and H---O separations are less than the van der Waals radius sum of oxygen and hydrogen. The van der Waals radii as taken from Pauling⁴³ are 1.40 and 1.20 Å for oxygen and hydrogen, respectively. The pertinent O-H and H---O contacts, as well as O-H---O angles, are collected in Table VI; since the hydrogen atoms were not refined, no standard deviations for separations and angles involving these atoms

Table V. Interatomic Distances (Å) and Angles (deg) within the Malonato Ligands

	A malonate	B malonate
Distances		
C(1)-C(2)	1.521 (3)	1.532 (4)
C(2)-C(3)	1.516 (3)	1.534 (4)
C(1)-O(1)	1.285 (2)	1.269 (3)
C(1)-O(3)	1.234 (3)	1.226 (3)
C(3)-O(2)	1.274 (2)	1.275 (3)
C(3)-O(4)	1.240 (3)	1.230 (3)
O(1)-O(2)	2.790 (3)	2.785 (3)
C(1)-C(2)-C(3)	116.5 (2)	115.4 (2)
C(2)-C(1)-O(1)	118.5 (2)	119.3 (2)
C(2)-C(1)-O(3)	118.9 (2)	117.2 (2)
O(1)-C(1)-O(3)	122.6 (2)	123.0 (2)
C(2)-C(3)-O(2)	119.3 (2)	116.7 (2)
C(2)-C(3)-O(4)	118.8 (2)	120.3 (2)
O(2)-C(3)-O(4)	121.8 (2)	122.4 (2)

Table VI. Hydrogen Bonding in $\text{Na}_4[\text{Cr}(\text{mal})_2(\text{OH})]_2 \cdot 5\text{H}_2\text{O}$

Atoms A, H, B	A-H, Å	H---B, Å	A-H---B, deg
O(1), H(1), AO(3)	0.83	2.21	162
WO(1), W1H(1), AO(1)	0.87	1.97	174
WO(1), W1H(2), AO(4)	0.75	2.14	159
WO(2), W2H(2), BO(3)	1.04	1.87	157

are given. Examination of Table VI reveals that all of the located water hydrogen atoms appear to form good hydrogen bonds, with the exception of W2H(1), which has a contact with BO(3) at 2.76 Å. The mode of hydrogen bonding for water molecule 1 is rather interesting since it is simultaneously hydrogen bonded to both sides of the dimer, as opposed to linking dimers in adjacent cells.

Magnetic Properties

The magnetic susceptibility of a sample of $\text{Na}_4[\text{Cr}(\text{mal})_2(\text{OH})]_2 \cdot 5\text{H}_2\text{O}$ was measured in the range 2-50 K using a Foner-type PAR vibrating-sample magnetometer⁴⁴ at an applied field strength of 10 kG. Temperatures were measured by a calibrated gallium arsenide diode; mercury tetrathiocyanatocobalt(II) was used as the susceptibility⁴⁵ standard. Since we were unable to grow a large single crystal of the material and use of a powdered sample was not feasible owing to decomposition (vide supra), the sample used was made up of approximately 20 small, well-formed crystals, which were coated with grease. The sample was rotated several times during the run, but no anisotropy was observed. The data were corrected for the diamagnetism of the grease used for mounting the sample.

The expression for the magnetization (neglecting zero-field splitting and biquadratic exchange) of two exchange-coupled $S = 3/2$ ions has been given elsewhere²¹ and takes the form

$$M^{(e)} = N g \beta \{ 2e^{2J/kT} \sinh(G/kT) + e^{6J/kT} [2 \sinh(G/kT) + 4 \sinh(2G/kT)] + e^{12J/kT} [2 \sinh(G/kT) + 4 \sinh(2G/kT) + 6 \sinh(3G/kT)] \} \times \{ 1 + e^{2J/kT} [1 + 2 \cosh(G/kT)] + e^{6J/kT} [1 + 2 \cosh(G/kT) + 2 \cosh(2G/kT)] + e^{12J/kT} [1 + 2 \cosh(G/kT) + 2 \cosh(2G/kT) + 2 \cosh(3G/kT)] \}^{-1} \quad (1)$$

where $G = g\beta H$ and the exchange Hamiltonian is

$$\mathcal{H}_{\text{ex}} = -2J \vec{S}_1 \cdot \vec{S}_2 \quad (2)$$

Interactions between dimers were taken into account through

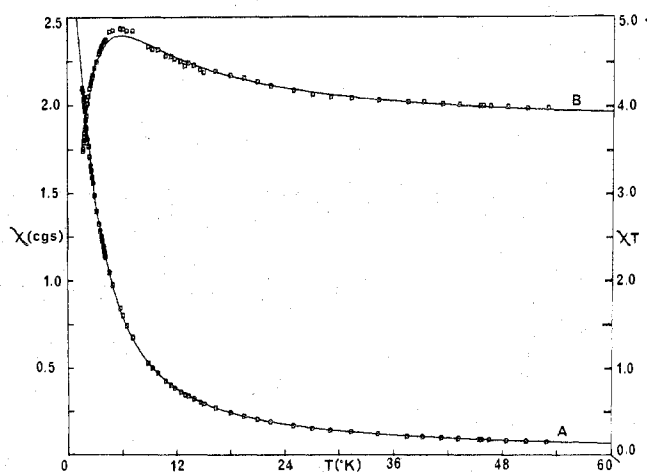


Figure 3. Temperature dependence of calculated magnetic susceptibility (curve A) and χT (curve B). Experimental points are shown as squares. The parameters used for the theoretical dependencies were $g = 1.988$ (3), $J = 1.08$ (2), and $\gamma = -0.106$ (2) cgsu.

the molecular field approximation. The magnetic field is expressed as⁴⁶

$$H = H_0 + \gamma M^{(c)} \quad (3)$$

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 parameter, J' , through the expression⁴⁷

$$ZJ' = \gamma N g^2 \beta^2 k / 2 \quad (4)$$

where Z is the number of nearest neighbors. The data were fitted using a nonlinear least-squares routine written in these laboratories. The function fitted was MT ; the function being minimized therefore was $\sum w_i [M_i^{(c)} T_i - M_i^{(0)} T_i]^2$, the weights being assigned as $w_i = 1/M_i^{(0)} T_i$. The best least-squares fit to the experimental data is shown in Figure 3, the solid lines being the calculated functions while the boxes are the experimental points. The function which displays a maximum at about 6 K is χT [i.e., MT/H_0] vs. T , the other being χ vs. T ; the shape of this curve clearly demonstrates that the ground state is not the singlet and that J is positive. For simple paramagnets χT vs. T would be a straight line with a zero slope. Systems with small positive J values which give rise to an array of states show a curvature away from this line tending toward larger values of χT as the temperature decreases. The maximum in the curve comes about from intermolecular exchange processes which are antiferromagnetic in nature as indicated by the values of γ . The parameters derived from the fitting process are $g = 1.988$ (3), $J = 1.08$ (2) cm^{-1} , and $\gamma = -0.106$ (2); examination of Figure 3 shows that with these values, eq 1 provides an acceptable fit to the experimental data. The uncertainties indicated here are the estimated standard deviations; the experimental accuracy of the measurements has been estimated to have an uncertainty of less than 2%.⁴⁸ The positive value for J implies ferromagnetic coupling for the pair. Triplet ground states for copper(II) systems analogous to the present complex have been observed previously, but to our knowledge this is the first example of such coupling for a Cr(III) system. The above value of γ and eq 4 yield $ZJ' = -0.055 \text{ cm}^{-1}$ for the interdimer exchange interaction.

Discussion

The structural and magnetic properties of $\text{Na}_4[\text{Cr}(\text{mal})_2\text{OH}]_2 \cdot 5\text{H}_2\text{O}$ are compared with those of the other well-characterized dihydroxo-bridged chromium(III) systems

Table VII. Structural and Magnetic Properties of Dihydroxo-Bridged Cr(III) Complexes

Complex	ϕ , deg	Cr-Cr,		Ref
		A	$2J$, cm^{-1}	
$[\text{Cr}(\text{phen})_2\text{OH}]_2\text{Cl}_4 \cdot 6\text{H}_2\text{O}$	102.7	3.008	-55	19
$[\text{Cr}(\text{phen})_2\text{OH}]_2\text{I}_4 \cdot 4\text{H}_2\text{O}$	102.1	2.986	-43.8	20
$[\text{Cr}(\text{dipic})(\text{H}_2\text{O})(\text{OH})]_2$	100.7	2.999	-8	50
$[\text{Cr}(\text{en})_2(\text{OH})]_2(\text{S}_2\text{O}_6)_2$	100.0	3.032	-2.16	49
$\text{Na}_4[\text{Cr}(\text{ox})_2\text{OH}]_2 \cdot 6\text{H}_2\text{O}$	99.6	3.000	-0.6	21
$\text{Na}_4[\text{Cr}(\text{mal})_2\text{OH}]_2 \cdot 5\text{H}_2\text{O}$	99.3	3.031	+2.16	This work
$[\text{Cr}(\text{gly})_2\text{OH}]_2$	98.2	2.974	-7.4	17, 18

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 dependence observed for the copper dimers. Even from the limited data in Table VII, it does appear that for $\phi \gtrsim 99^\circ$, J becomes monotonically more negative at least up to $\phi \approx 103^\circ$. Clearly, further systematic magnetic and structural studies are necessary before detailed analysis of the correlation between structural and magnetic properties can be attempted.

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Registry No. $\text{Na}_4[\text{Cr}(\text{mal})_2\text{OH}]_2 \cdot 5\text{H}_2\text{O}$, 62571-20-4.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970); B. F. Hoskins and F. D. Whillans, *J. Chem. Soc., Dalton Trans.*, 1267 (1975).
- (2) T. P. Mitchell, W. H. Bernard, and J. R. Wasson, *Acta Crystallogr., Sect. B*, **26**, 2096 (1970).
- (3) R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, **74**, 3497 (1970).
- (4) B. J. Cole and W. H. Brumage, *J. Chem. Phys.*, **53**, 4718 (1970).
- (5) J. A. Barnes, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **11**, 144 (1972).
- (6) D. Y. Jeter, D. L. Lewis, J. C. Hempel, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **11**, 1958 (1972).
- (7) D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **11**, 2216 (1972).
- (8) D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **13**, 147 (1974).
- (9) D. L. Lewis, K. T. McGregor, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **13**, 1013 (1974).
- (10) K. T. McGregor, N. T. Watkins, D. L. Lewis, R. F. Drake, D. J. Hodgson, and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, **9**, 423 (1973).
- (11) E. D. Estes, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **13**, 1654 (1974).
- (12) D. J. Hodgson, *Prog. Inorg. Chem.*, **19**, 173 (1974).
- (13) J. B. Goodenough, *Phys. Rev.*, **564** (1955); J. Kanomori, *J. Chem. Phys. Solids*, **10**, 87 (1959).
- (14) P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975).
- (15) J. C. M. Henning and H. van den Boom, *Phys. Rev. B*, **8**, 2255 (1973); G. G. P. van Gorkom, J. C. M. Henning, and R. P. van Staple, *ibid.*, **8**, 955 (1973).
- (16) D. J. Hodgson, *ACS Symp. Ser.*, No. 5, Chapter 9 (1975).
- (17) J. T. Veal, W. E. Hatfield, D. Y. Jeter, J. C. Hempel, and D. J. Hodgson, *Inorg. Chem.*, **12**, 342 (1973).
- (18) J. T. Veal, D. Y. Jeter, J. C. Hempel, R. P. Eckberg, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **12**, 2928 (1973) (footnote 44).
- (19) J. T. Veal, W. E. Hatfield, and D. J. Hodgson, *Acta Crystallogr., Sect. B*, **29**, 12 (1973).
- (20) R. P. Scaringe, P. Singh, R. P. Eckberg, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **14**, 1127 (1975).
- (21) R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chim. Acta*, in press.
- (22) R. E. Hamm and R. H. Perkins, *J. Am. Chem. Soc.*, **77**, 2083 (1955).
- (23) A. Werner, *Justus Liebigs Ann. Chem.*, **406**, 261 (1914).
- (24) The logic used was that of Hamilton's MODE 1 and Ibers' PICK 3 programs.
- (25) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
- (26) A. L. Patterson, *Phys. Rev.*, **46**, 372 (1934).
- (27) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
- (28) J. A. Ibers, "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, Table 3.3.1A.
- (29) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

- (30) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).
 (31) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
 (32) Supplementary material.
 (33) K. Kaas, *Acta Crystallogr., Sect. B*, **32**, 2021 (1976).
 (34) J. W. Lethbridge, L. S. D. Glasser, and H. F. W. Taylor, *J. Chem. Soc. A*, 1862 (1970).
 (35) R. F. Bryan, P. T. Green, P. F. Stokely, and E. W. Wilson, Jr., *Inorg. Chem.*, **10**, 1465 (1971).
 (36) P. deMeester and D. J. Hodgson, submitted for publication (and references therein).
 (37) M. L. Post and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1922 (1974).
 (38) E. Hansson, *Acta Chem. Scand.*, **27**, 2841 (1973).
 (39) E. Hansson, *Acta Chem. Scand.*, **27**, 2827 (1973).
 (40) E. Hansson, *Acta Chem. Scand.*, **27**, 2441 (1973).
 (41) E. Hansson, *Acta Chem. Scand.*, **27**, 2813 (1973).
 (42) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968, p 16.
 (43) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960.
 (44) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).
 (45) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 3190 (1958) H. St. Råde, *J. Phys. Chem.*, **77**, 424 (1973).
 (46) B. E. Meyers, L. Beger, and S. A. Friedberg, *J. Appl. Phys.*, **40**, 1149 (1969).
 (47) J. S. Smart, "Effective Field Theories of Magnetism", W. B. Saunders, Philadelphia, Pa., 1966.
 (48) D. B. Losee and W. E. Hatfield, *Phys. Rev. B*, **10**, 212 (1974).
 (49) S. J. Cline, R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, submitted for publication.
 (50) H. Schugar, private communication.

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Structural and Magnetic Characterization of the Alkoxo-Bridged Chromium(III) Dimers Di- μ -methoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)] and Di- μ -ethoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)]

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The crystal structures of the complexes di- μ -methoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)], [Cr(3-Br-acac)₂OCH₃]₂, and di- μ -ethoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)], [Cr(3-Br-acac)₂OC₂H₅]₂, have been determined from three-dimensional counter x-ray data. The methoxy complex crystallizes in the monoclinic space group $P2_1/c$ with two dimeric formula units in a cell of dimensions $a = 7.769$ (7) Å, $b = 18.587$ (21) Å, $c = 11.353$ (10) Å, and $\beta = 112.99$ (4)°. Least-squares refinement of 1366 independent data has led to a final R factor (on F) of 0.034; this complex is isomorphous with the 3-chloro analogue. The ethoxy complex also crystallizes in the monoclinic space group $P2_1/c$ in a cell of dimensions $a = 8.428$ (3) Å, $b = 19.339$ (7) Å, $c = 11.376$ (4) Å, and $\beta = 109.10$ (1)°. Least-squares refinement of 1151 data has led to an R factor (on F) of 0.046. Both complexes consist of two chromium(III) ions which are symmetrically bridged by two alkoxide groups, the remaining coordination sites being occupied by the oxygen atoms of two bidentate 3-Br-acac ligands. The coordination around each chromium center is roughly octahedral; in the methoxy complex the average Cr-O(ligand) bond length is 1.958 (5) Å, the Cr-Cr separation is 3.038 (3) Å, and the Cr-O-Cr bridging angle is 101.5 (2)° while the corresponding values in the ethoxy complex are 1.952 (8) Å, 3.027 (3) Å, and 101.8 (3)°. The 3-Br-acac ligands are approximately planar. The magnetic susceptibilities of powdered samples of the complexes have been examined in the temperature range 4–100 K. The dimers exhibit antiferromagnetic exchange interactions with the best fit to the Van Vleck equation including biquadratic exchange yielding $2J = -7.10$ cm⁻¹ and $j = 0.22$ cm⁻¹ with $\langle g \rangle = 1.932$ for the methoxy complex and $2J = -17.88$ cm⁻¹, $j = 0$, and $\langle g \rangle = 1.945$. The data for the methoxy complex are similar to those for the corresponding 3-chloro complex and lead to a singlet-triplet splitting of -8.53 cm⁻¹, but those for the ethoxy complex show stronger magnetic coupling which can be attributed to the greater electron density at the bridging oxygen atom in this case.

Introduction

In many recent communications, considerable experimental evidence has been presented supporting the contention that the isotropic exchange parameter, J , is correlated to the Cr-O-Cr bridging angle, ϕ , in dihydroxo bridged complexes of Cr(III).²⁻¹¹ These studies, however, have focused on only one property of the bridging unit, its geometry. A second property is the electron density at the bridging atoms, and it has been pointed out^{2,12} that this should also influence J . More recently, Hoffmann¹³ and his co-workers have supported this view through results obtained using molecular orbital theory. Experimentally, there are several ways of altering the electron density at the bridging atoms, and for the dihydroxo-bridged species hydrogen bonding to the hydroxo hydrogen atoms is an obvious possibility. This approach, however, has the disadvantage that locating hydrogen atoms with sufficient accuracy to determine "hydrogen-bond strengths" is beyond the scope of conventional x-ray techniques. A more practical approach is to investigate the analogous alkoxo-bridged systems, which avoids the necessity of accurately determining hydrogen atom positions. The electron density at the bridging oxygen atom in these systems can be changed by using alk-

oxides of various chain length or by substitution at the α carbon.

The structure and magnetic properties of one such Cr(III) system, di- μ -methoxy-bis[bis(3-chloro-2,4-pentanedionato)chromium(III)], have been determined in these laboratories and reported.⁸ We here report the results of our structural and magnetic investigations of the 3-bromo-2,4-pentanedionato complex and of its ethoxy-bridged analogue.

Experimental Section

Di- μ -methoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)].
Synthesis. This complex was prepared by the method of Kasaga¹⁴ et al. Anal. Calcd for C₂₂H₃₀Br₄Cr₂O₁₀: C, 30.08; H, 3.42; Br, 36.42. Found: C, 30.21; H, 3.53; Br, 36.70. Single crystals for the crystallographic study (vide infra) were obtained by recrystallization from dichloromethane to which a few drops of ethanol had been added.

Magnetic Susceptibility. The magnetic susceptibility of a powdered sample of the dimer was measured from 4 to 78 K using a Foner-type PAR vibrating-sample magnetometer.¹⁵ All measurements were made at a field strength of 10 000 G. Temperatures were measured by a calibrated gallium arsenide diode, and mercury tetrathiocyanatocobaltate(II) was used as a susceptibility standard.¹⁶

Collection and Reduction of the X-Ray Data. On the basis of Weissenberg and precession photographs, the crystals were assigned