Structural and Magnetic Properties of Di-μ-hydroxo-bis[bis(ethylenediamine)chromium(III)] Dithionate

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The crystal and molecular structure of the title complex $[\{Cr(en)_2(OH)\}_2][S_2O_6]_2$ has been determined from three dimensional single-crystal *X*-ray counter data. The complex crystallizes in the orthorhombic space group *Pbca* with four molecules in a cell of dimensions a = 13.58(1), b = 18.42(2), and c = 10.02(1) Å. The observed and calculated densities are 1.85(2) and 1.851 g cm^{-3}, respectively. The structure has been refined by full-matrix least-squares techniques to a value of R (on F) 0.049. The complex consists of dimeric $[\{Cr(en)_2(OH)\}_2]^{4+}$ units which are hydrogen bonded to the dithionate anions. The dimeric cation isolated is the *meso* form, there being a crystallographic inversion centre in the middle of the dimer. The geometry around each chromium(III) centre is approximately octahedral, the Cr–Cr separation and bridging Cr–O–Cr angle being 3.032(3) Å and 100.0(2)°, respectively. The dithionate anion has the staggered conformation [S–S 2.127(3) Å, S–O 1.435(6)—1.460(5) Å]. The hydrogen bonding is extensive, with all the possible donor and acceptor atoms participating. The magnetic susceptibility of a powdered sample of the complex shows a maximum near 7.3 K, indicative of antiferromagnetic coupling between the metal centres. The best fit of the susceptibility data to the Van Vleck equation (modified by the inclusion of biquadratic exchange) yields values for g, J, j, and ΔE (the singlet–triplet splitting) of1.947 (7), −1.08(2) cm^{-1}, 0.234(7) cm^{-1} and −3.68 cm^{-1}, respectively.

MUCH recent experimental and theoretical attention has been focused on the structural and magnetic properties of dimeric transition-metal complexes of the type $[\{ML_n(OH)\}_2]$, in which two transition-metal centres are bridged by two hydroxo-groups.[1-12] For the simplest case, in which $M = Cu^{II}$, several groups of workers have noted important correlations between the structural and magnetic properties of this class of dimers. Thus, for example, we have shown that the magnetic-exchange parameter, J, varies linearly with the Cu–O–Cu bridging angle, ϕ, for all of the characterized members of this series [1,12] and have provided a qualitative molecular-orbital (m.o.) discussion which explains this behaviour.[1] More recently, Hoffmann and his co-workers [2] set this principle on a firm theoretical basis as the result of semiquantitative m.o. calculations. Sinn and Bertrand and their co-workers,[13-17] however, demonstrated that this simple correlation does not hold for complexes in which the geometry at copper deviates markedly from planarity, and showed that J is often more sensitive to this distortion than to changes in ϕ. Hodgson [18] recently noted that J is a function of both ϕ and τ (a measure of the non-planarity at copper); in the simple dihydroxo-bridged dimers, however, the geometry at copper has been observed to be approximately planar.[1,18,19,†]

The success of this simple model initially led us to propose that a similar linear relation between J and ϕ would obtain for the more complicated case in which $M = Cr^{III}$.[7] Hoffmann's theoretical work [2] and our own recent experimental results,[9,10] however, have demonstrated that a more complex dependence of J on ϕ exists for chromium(III) dimers. Since the precise nature of this correlation is still not understood, we are continuing our investigations of the structural and magnetic properties of complexes of the type $[\{CrL_2(OH)\}_2]^{n+}$ (L = bidentate ligand); here we report the results of our study of di-μ-hydroxo-bis[bis(ethylenediamine)chromium(III)] dithionate, $[\{Cr(en)_2(OH)\}_2][S_2O_6]_2$.

EXPERIMENTAL

Red prismatic crystals of the title complex were prepared by the method of Springborg and Schaffer.[20] On the basis of precession and Weissenberg photographs, the crystals were assigned to the orthorhombic system; 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 were obtained by least-squares

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† An important exception to this statement is the $[\{Cu(bipy)(OH)\}_2]^{2+}$ cation in $[\{Cu(bipy)(OH)\}_2][SO_4]\cdot5H_2O$ (bipy = 2,2′-bipyridyl).[19]

[1] D. J. Hodgson, *Progr. Inorg. Chem.*, 1975, **19**, 173 and refs. therein.

[2] P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1975, **97**, 4884.

[3] J. A. Thich, C. C. Ou, D. Powers, B. Vasiliou, D. Mastropaolo, J. A. Potenza, and H. J. Schugar, *J. Amer. Chem. Soc.*, 1976, **98**, 1425.

[4] J. Springborg and H. Toftlund, *J.C.S. Chem. Comm.*, 1975, 422.

[5] K. T. McGregor, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 421.

[6] R. P. Scaringe, P. Singh, R. P. Eckberg, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1975, **14**, 1127.

[7] D. J. Hodgson in 'Extended Interactions Between Metal Ions,' Symposium Series, American Chemical Society, no. 5, ch. 9 and refs. therein.

[8] K. Kaas, *Acta Cryst.*, 1976, **B32**, 2021.

[9] R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chim. Acta*, 1977, **22**, 175.

[10] R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, unpublished work.

[11] S. F. Pavkovic, personal communication.

[12] V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107.

[13] R. M. Countryman, W. T. Robinson, and E. Sinn, *Inorg. Chem.*, 1974, **13**, 2013.

[14] E. Sinn, *J.C.S. Chem. Comm.*, 1975, 665.

[15] E. Sinn, *Inorg. Chem.*, 1976, **15**, 358, 366.

[16] R. J. Butcher and E. Sinn, *Inorg. Chem.*, 1976, **15**, 1604.

[17] J. A. Bertrand and P. G. Eller, *Progr. Inorg. Chem.*, 1976, **21**, 29 and refs. therein.

[18] D. J. Hodgson, *Inorg. Chem.*, 1976, **15**, 3174.

[19] B. F. Hoskins and F. D. Whillans, *J.C.S. Dalton*, 1975, 1267.

[20] J. Springborg and E. Schaffer, *Inorg. Synth.*, in the press.

methods from the 2θ, χ, and ϕ values of 12 accurately centred reflections using Mo-$K_{\alpha1}$ radiation (0.709 3 Å).

Crystal Data.—$C_8H_{34}Cr_2N_8O_{14}S_4$, $M = 698.7$, Orthorhombic, $a = 13.58(1)$, $b = 18.42(2)$, $c = 10.02(1)$ Å, $U = 2\,506.6$ Å^3, $D_m = 1.85(2)$ (flotation in CCl_4–$CHBr_3$), $Z = 4$, $D_c = 1.851$ g cm^{-3}, μ(Mo-K_α) = 12.3 cm^{-1}.

Data Collection.—Intensity data were collected from a prismatic crystal bound by faces of the forms {100} and {120} and by $(10\bar{1})$ and (101). A crystal of dimensions $0.12 \times 0.08 \times 0.30$ mm was mounted roughly normal to $(10\bar{1})$ and in this orientation intensity data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator and using Mo-K_α radiation. Intensity data were collected as described elsewhere.[21] A unique data set having $2 \leqslant 2\theta \leqslant 50°$ was gathered; a total of 2 257 intensities was recorded. The intensities of three standard reflections, measured after every 75 reflections, showed no noticeable decline as a function of total exposure time.

Data processing was carried out as described by Corfield *et al.*[22] After correction for background, the intensities were assigned standard deviations according to [22] $\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{\frac{1}{2}}$ and the value of p was selected as 0.05. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption factors. The absorption coefficient for this complex for Mo-K_α radiation is 12.3 cm^{-1}, and for the crystal chosen the transmission coefficients evaluated by numerical integration ranged from 0.81 to 0.93. Of the 2 257 data collected, 1 389 were greater than three times their estimated standard deviations; only these data were used in the subsequent structure analysis and refinement.[23]

Solution and Refinement of the Structure.—All the least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o)^2$. In all the calculations of F_c, the atomic-scattering factors for non-hydrogen atoms were from International Tables,[24] and those for H from Stewart *et al.*[25] The effects of the anomalous dispersion of Cr and Br were included in the calculation of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer and Liberman.[26]

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 $R = \Sigma||F_o - F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$ of 0.101 and 0.137, respectively. Anisotropic refinement reduced these values to 0.082 and 0.112, respectively. The hydrogen atoms were located in a subsequent difference-Fourier map. The final least-squares cycles involved anisotropic refinement of the non-hydrogen atoms and isotropic refinement of the hydrogen atoms, with 1 389 observations and 231 variables. The final values of R and R' were 0.049 and 0.062, respectively.

In the final cycle of least squares, no atomic parameter exhibited a shift greater than 0.4σ, which is taken as evidence of convergence. Examination of the values of $|F_o|$ and $|F_c|$ suggested that no correction for secondary extinction was necessary, and none was applied. A final difference Fourier was featureless, with no peak higher than 0.73 eÅ^{-3}. The value of R' showed no unusual dependence on sinθ or on $|F_c|$, which suggests that our weighting scheme is appropriate.

The atomic positional parameters, together with their standard deviations as estimated from the inverse matrix, are listed in Table 1. Observed and calculated structure amplitudes and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22065 (11 pp., 1 microfiche).*

TABLE 1

Positional parameters ($\times 10^4$) for $[\{Cr(en)_2(OH)\}_2][S_2O_6]_2$

Atom	x	y	z
Cr	469(1)	715(0)	396(1)
S(1)	743(1)	4 124(1)	440(2)
S(2)	1 715(1)	3 317(1)	1 194(2)
O(1)	650(3)	−84(3)	−901(6)
O(2)	2 499(4)	3 727(3)	1 837(6)
O(3)	1 123(4)	2 914(3)	2 158(6)
O(4)	2 016(3)	2 897(3)	45(6)
O(5)	401(4)	4 478(3)	1 643(6)
O(6)	−1(4)	3 741(3)	−295(6)
O(7)	1 370(5)	4 565(3)	−382(7)
N(1)	1 695(4)	1 295(4)	−244(9)
N(2)	1 488(5)	280(3)	1 723(9)
N(3)	81(5)	1 511(3)	1 772(6)
N(4)	−385(5)	1 353(3)	−869(7)
C(1)	2 595(6)	1 051(5)	465(13)
C(2)	2 327(6)	794(6)	1 837(13)
C(3)	−751(5)	1 944(4)	1 202(9)
C(4)	−545(6)	2 071(3)	−252(8)
N(1)H(1) *	165(9)	119(7)	−101(13)
N(1)H(2)	167(6)	176(5)	−41(9)
N(2)H(1)	139(7)	20(6)	246(12)
N(2)H(2)	165(5)	−16(5)	151(9)
N(3)H(1)	−9(7)	145(5)	251(11)
N(3)H(2)	58(6)	182(4)	209(9)
N(4)H(1)	−4(5)	139(4)	−169(8)
N(4)H(2)	−88(5)	120(4)	−114(7)
C(1)H(1)	309(5)	140(4)	32(7)
C(1)H(2)	273(7)	60(6)	−11(10)
C(2)H(1)	290(6)	54(5)	215(9)
C(2)H(2)	228(8)	120(6)	201(12)
C(3)H(1)	−88(5)	238(4)	176(8)
C(3)H(2)	−127(5)	170(3)	146(7)
C(4)H(1)	−100(4)	230(3)	−69(6)
C(4)H(2)	4(5)	238(3)	−31(7)
H(1)	60(5)	6(4)	−152(7)

* Hydrogen-atom parameters are $\times 10^3$.

DISCUSSION

Description of the Structure.—The structure consists of dimeric $[\{Cr(en)_2(OH)\}_2]^{4+}$ cations which are hydrogen bonded to $[S_2O_6]^{2-}$ anions. A view of the cation is shown in Figure 1. The geometry around the chromium(III) centres is approximately octahedral, the ligating atoms being the nitrogen atoms from two ethylenediamine ligands and the oxygen atoms from two bridging hydroxo-groups. The four independent Cr–N bond

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[21] E. D. Estes, W. E. Estes, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1975, **14**, 106.

[22] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[23] For a description of the programs used, see ref. 6.

[24] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[25] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[26] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

lengths are essentially equal [2.080(6)—2.081(7) Å]. These bond lengths are entirely consistent with the values [2.075(2) and 2.081(5) Å] reported for the [Cr(en)$_3$]$^{3+}$ cation,[27,28] those [2.072(2) to 2.092(2) Å] in the chloride perchlorate salt of the present cation,[8] and the average value [2.096(3) Å] in the structurally similar tris(propane-1,3-diamine)chromium(III) cation,[29] as well as values (2.052—2.152 Å) reported for a variety of other complexes containing Cr^{III}–N bonds.[6,30-33] The bridging Cr–O distances [1.978(5) and 1.980(5) Å] are also symmetric but are longer than the majority of such bonds observed in a variety of di-μ-hydroxo- (1.91—1.976 Å)[6,8-10,31,32,34] and di-μ-alkoxo-chromium(III) dimers (1.951—1.962 Å).[35-37] The bond lengths in the complex are presented in Table 2. The Cr–Cr separation in the dimer is 3.032(3) Å; this value is within the range (2.974—3.059 Å) observed in other chromium(III) dimers of this general type.[6,8-10,31,32,34-36]

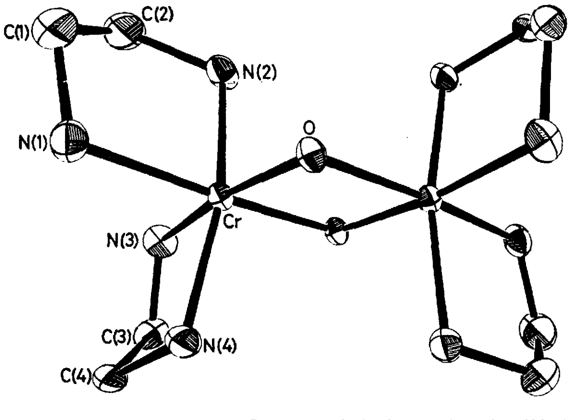

FIGURE 1 View of the [{Cr(en)$_2$(OH)}$_2$]$^{4+}$ cation in [{Cr(en)$_2$(OH)}$_2$][S$_2$O$_6$]$_2$. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity

TABLE 2

Interatomic distances (Å) in [{Cr(en)$_2$(OH)}$_2$][S$_2$O$_6$]$_2$

Atoms	Distance	Atoms	Distance
Cr–Cr′	3.032(3)	S(1)–S(2)	2.127(3)
Cr–O(1)	1.980(5)	S(1)–O(5)	1.447(6)
Cr–O(1′)	1.978(5)	S(1)–O(6)	1.435(6)
Cr–N(1)	2.080(6)	S(1)–O(7)	1.437(6)
Cr–N(2)	2.081(7)	S(2)–O(2)	1.456(5)
Cr–N(3)	2.080(6)	S(2)–O(3)	1.460(5)
Cr–N(4)	2.081(6)	S(2)–O(4)	1.446(6)
N(1)–C(1)	1.483(11)	N(2)–N(2)H(1)	0.76(12)
C(1)–C(2)	1.498(16)	N(2)–N(2)H(2)	0.87(9)
C(2)–N(2)	1.487(11)	N(3)–N(3)H(1)	0.78(10)
N(3)–C(3)	1.496(10)	N(3)–N(3)H(2)	0.94(8)
C(3)–C(4)	1.501(11)	N(4)–N(4)H(1)	0.95(8)
C(4)–N(4)	1.475(9)	N(4)–N(4)H(2)	0.78(7)
N(1)–N(1)H(1)	0.79(13)	C(3)–C(3)H(1)	0.99(7)
N(1)–N(1)H(2)	0.87(9)	C(3)–C(3)H(2)	0.88(6)
C(1)–C(1)H(1)	0.94(7)	C(4)–C(4)H(1)	0.87(6)
C(1)–C(1)H(2)	1.02(10)	C(4)–C(4)H(2)	0.98(7)
C(2)–C(2)H(1)	0.96(9)	O(1)–H(1)	0.68(7)
C(2)–C(2)H(2)	0.76(11)		

The bond angles at chromium are normal [*cis*, 80.0(2)—96.9(3); *trans*, 167.8(3)—174.5(3)°]. The Cr–O–Cr bridging angle, ϕ, is 100.0(2)°; this considerably smaller than the value [103.42(8)°] found[8] in the chloride perchlorate salt of this ion, but is intermediate between the values [98.2(2)—102.6(6)°] observed in other dimers of this type.[6,9,10,31,32,34-37] Thus, to the extent that the magnetic behaviour of complexes of this type is dominated by ϕ, we anticipate that J for this complex is between those of [{Cr(phen)$_2$(OH)}$_2$]$^{4+}$ (phen = 1,10-phenanthroline (ϕ 102.1)[6] and [{Cr(C$_2$O$_4$)$_2$(OH)}$_2$]$^{4-}$ (ϕ 99.7°)[9] (see below). The bond angles in the complex are listed in Table 3.

TABLE 3

Bond angles (°) in [{Cr(en)$_2$(OH)}$_2$][S$_2$O$_6$]$_2$

Atoms	Angle	Atoms	Angle
O(1)–Cr–O(1′)	80.0(2)	C(1)–C(2)–N(2)	108.5(8)
O(1)–Cr–N(1)	94.6(3)		
O(1)–Cr–N(2)	92.9(3)	N(3)–C(3)–C(4)	108.2(6)
O(1)–Cr–N(3)	172.3(2)	C(3)–C(4)–N(4)	107.2(6)
O(1)–Cr–N(4)	95.2(3)		
O(1′)–Cr–N(1)	174.5(3)	S(2)–S(1)–O(5)	102.6(3)
O(1′)–Cr–N(2)	96.9(3)	S(2)–S(1)–O(6)	106.0(2)
O(1′)–Cr–N(3)	92.9(2)	S(2)–S(1)–O(7)	103.4(3)
O(1′)–Cr–N(4)	93.5(3)	O(5)–S(1)–O(6)	115.0(4)
N(1)–Cr–N(2)	82.1(3)	O(5)–S(1)–O(7)	114.4(4)
N(1)–Cr–N(3)	92.6(3)	O(6)–S(1)–O(7)	113.6(4)
N(1)–Cr–N(4)	88.2(3)	S(1)–S(2)–O(2)	104.3(2)
N(2)–Cr–N(3)	91.0(3)	S(1)–S(2)–O(3)	104.4(2)
N(2)–Cr–N(4)	167.8(3)	S(1)–S(2)–O(4)	105.5(3)
N(3)–Cr–N(4)	82.2(3)	O(2)–S(2)–O(3)	112.0(3)
Cr–O(1)–Cr′	100.0(2)	O(2)–S(2)–O(4)	115.1(3)
		O(3)–S(2)–O(4)	114.2(3)
N(1)–C(1)–C(2)			

The geometry of the ethylenediamine ligands is normal. The N–C and C–C bond length ranges [1.475(9)—1.496(10) and 1.498(16)—1.501(11) Å, respectively] are within the ranges reported for a variety of metal complexes of ethylenediamine,[27,28,38-42] as are the N ··· N bites [2.731(11) and 2.736(10) Å]. The conformations of the chelating ethylenediamine ligands are such that both ligands attached to any given metal

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[27] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1362.

[28] K. N. Raymond and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2338.

[29] F. Jurnak and K. N. Raymond, *Inorg. Chem.*, 1974, **13**, 2387.

[30] R. F. Bryan, P. T. Greene, P. F. Stokely, and E. W. Wilson, *Inorg. Chem.*, 1971, **10**, 1468.

[31] J. T. Veal, W. E. Hatfield, D. Y. Jeter, J. C. Hempel, and D. J. Hodgson, *Inorg. Chem.*, 1973, **12**, 342.

[32] J. T. Veal, W. E. Hatfield, and D. J. Hodgson, *Acta Cryst.*, 1973, **B29**, 12.

[33] J. T. Veal, D. Y. Jeter, J. C. Hempel, R. P. Eckberg, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1973, **12**, 2928.

[34] H. J. Schugar, personal communication.

[35] E. D. Estes, R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1976, **15**, 1179.

[36] E. D. Estes, R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, in the press.

[37] R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, unpublished work.

[38] D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, 1971, **10**, 1061.

[39] J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 597.

[40] J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *Inorg. Chem.*, 1970, **9**, 2397.

[41] M.-U.-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, 1970, **9**, 2421.

[42] E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, 1971, **10**, 1468.

have the same conformation;* thus, in Figure 1, the rings attached to the chromium atom on the left (labelled) are both λ, while those on the right are both δ. The presence of the inversion centre, of course, constrains each dimer to contain an equal number of λ and δ rings. Similarly, in each dimer, one chromium atom has the Δ configuration and one the Λ configuration. In Figure 1, therefore, the left-hand chromium centre is Δλλ and the right-hand chromium atom is Λδδ. This is the same conformation as observed in the chloride perchlorate salt of this ion.[8]

A view of the dithionate anion is given in Figure 2.

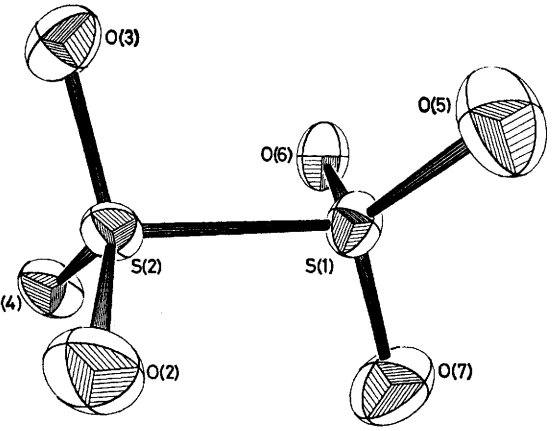

FIGURE 2 View of the dithionate anion, $[S_2O_6]^{2-}$. Thermal ellipsoids are drawn at the 40% level

The S–S bond length [2.127(3) Å] is consistent with values reported by earlier workers for this ion.[43-45] The S–O bonds [1.435(6)—1.460(5) Å] are again within the reported range[43-45] It is noteworthy that the longest S–O bonds involve atoms O(2), O(3), and O(5), which are involved in more hydrogen-bonding interactions than are the other oxygen atoms; all of the oxygen atoms, however, appear to participate in hydrogen bonding with the cation (see below). The geometry at each sulphur atom is distorted tetrahedral, with S–S–O angles in the range 102.6(3)—106.0(2)° and O–S–O angles in the range 112.0(3)—115.1(3)°. The conformation (Figure 2) is staggered. While the crystallographic symmetry is $C_1(1)$, the ion approximates to the idealized $D_{3d}(\bar{3}m)$ symmetry. Thus, for example, in idealized D_{3d} geometry, atom O(7) would lie in the plane defined by S(1), S(2), and O(3), while atoms O(5) and O(6) were equally disposed above and below this plane; we observe that O(7) lies only 0.16 Å below this plane, with O(5) 1.15 Å below it and O(6) 1.27 Å above it.

The hydrogen bonding in the crystals is extensive, with all the possible donor and acceptor atoms participating. The bridging hydroxo-group forms a strong hydrogen bond with atom O(5) of the dithionate anion, with an O(1) · · · O(5) distance and associated O(1)–H · · · O(5) angle of 2.724(9) Å and 178(8)°, respectively. All eight of the amine hydrogen atoms apparently also participate in hydrogen bonds with the oxygen atoms of the anion, with N · · · O distances and N–H · · · O angles in the ranges 2.91(1)—3.176(9) Å and 124(11)—159(9)°, respectively. Some of these hydrogen bonds, involving atoms N(1)H(1) and N(4)H(1), may be bifurcated. The probable hydrogen bonds in the complex are in Table 4.

TABLE 4

Probable A–H · · · B hydrogen bonds in $[\{Cr(en)_2(OH)\}_2][S_2O_6]_2$

			Bond/Å		Angle (°)
A	H	B	A · · · B	B · · · H	A–H · · · B
N(1)	N(1)H(1)	O(2)	3.122(11)	2.45(13)	143(11)
N(1)	N(1)H(1)	O(3)	3.084(10)	2.57(13)	124(11)
N(1)	N(1)H(2)	O(4)	2.997(9)	2.20(9)	153(7)
N(2)	N(2)H(1)	O(7)	2.912(12)	2.21(12)	156(10)
N(2)	N(2)H(2)	O(2)	3.176(9)	2.38(9)	154(7)
N(3)	N(3)H(1)	O(6)	2.978(10)	2.24(11)	159(9)
N(3)	N(3)H(2)	O(3)	2.971(8)	2.15(8)	146(7)
N(4)	N(4)H(1)	O(3)	3.151(9)	2.34(8)	143(6)
N(4)	N(4)H(1)	O(5)	3.115(10)	2.39(8)	133(6)
N(4)	N(4)H(2)	O(2)	3.037(9)	2.31(7)	155(7)
O(1)	H(1)	O(5)	2.724(9)	2.04(7)	178(8)

Magnetic Properties.—The magnetic susceptibility of a powdered sample of the complex was measured in the range 1.79—61.5 K using a Foner-type P.A.R. vibrating sample magnetometer as described elsewhere.[9] The expression for the magnetization of two exchange-coupled $S = \frac{3}{2}$ ions was derived in the usual manner,[9,46] and was expressed as in (1) where $G = g\beta H$ and the

$$\begin{aligned} M^{(c)} = Ng\beta\{&2\exp[(2J/\boldsymbol{k}T) - (6.5j/\boldsymbol{k}T)]\sinh(G/\boldsymbol{k}T) \\ &+ \exp[(6J/\boldsymbol{k}T) - (13.5j/\boldsymbol{k}T)][2\sinh(G/\boldsymbol{k}T) \\ &+ 4\sinh(2G/\boldsymbol{k}T)] \\ &+ \exp[(12J/\boldsymbol{k}T) - (9j/\boldsymbol{k}T)][2\sinh(G/\boldsymbol{k}T) \\ &+ 4\sinh(2G/\boldsymbol{k}T) \\ &+ 6\sinh(3G/\boldsymbol{k}T)]\}\{1 + \exp[(2J/\boldsymbol{k}T) \\ &- (6.5j/\boldsymbol{k}T)][1 + 2\cosh(G/\boldsymbol{k}T)] \\ &+ \exp[(6J/\boldsymbol{k}T) - (13.5j/\boldsymbol{k}T)][1 + 2\cosh(G/\boldsymbol{k}T)] \\ &+ 2\cosh(2G/\boldsymbol{k}\mathrm{T}) \\ &+ \exp[(12J/\boldsymbol{k}T) - (9j/\boldsymbol{k}T)][1 + 2\cosh(G/\boldsymbol{k}T) \\ &+ 2\cosh(2G/\boldsymbol{k}T) + 2\cosh(3G/\boldsymbol{k}T)]\}^{-1} \qquad (1) \end{aligned}$$

exchange Hamiltonian is as in (2) with magnetic field

$$H_{\mathrm{ex}} = -2J\boldsymbol{S}_1\boldsymbol{S}_2 - j(\boldsymbol{S}_1\boldsymbol{S}_2)^2 \qquad (2)$$

strength H expressed[47] as in (3) where H_0 is the applied

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

magnetic field (10kG), $M^{(c)}$ is the calculated magnetization, and γ is a parameter which is varied in the fitting

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* The notation used is from *Inorg. Chem.*, 1970, **9**, 1.

[43] E. Stanley, *Acta Cryst.*, 1953, **6**, 187.

[44] S. Martinez, S. Garcia-Blanco, and L. Rivoir, *Acta Cryst.*, 1956, **9**, 145.

[45] E. Stanley, *Acta Cryst.*, 1956, **9**, 897.

[46] J. S. Smart, ' Effective Field Theories of Magnetism,' W. B. Saunders, Philadelphia, 1966.

[47] B. E. Meyers, L. Berger, and S. A. Friedberg, *J. Appl. Phys.*, 1969, **40**, 1149.

approximation and takes into account the existence of interdimer magnetic interactions within the system. The data were fitted to the theoretical expression (1) using a non-linear least-squares procedure written in these laboratories. The function minimized was $\sum_i w_i[M_i^{(o)} - M_i^{(c)}]$, where the weights w_i were assigned as $1/M_i^{(o)}$. The best least-squares fit to the data is shown in Figure 3, in which both the susceptibility (M/H_0 or χ) and the product of the calculated susceptibility and the temperature (MT/H_0 or χT) are plotted against temperature. In each case the full line represents the calculated values and the symbols represent the observed data. The parameters derived from the fitting process are $g = 1.947(7)$, $J = -1.08(2)$ cm^{-1}, $j = 0.234(7)$ cm^{-1}, and $\gamma = -0.37(8)$. These values of J and j lead to a singlet–triplet splitting (ΔE) of -3.68 cm^{-1}. Thus, the observed singlet–triplet splitting here is intermediate between the values reported[9,31] for the glycinato- and oxalato-dimers of this type, while the Cr–O–Cr bridge angle here is larger than those in both of these complexes. Hence, it is apparent that a more complex relation between ΔE and ϕ obtains for these chromium(III) complexes than for their copper(II) analogues. This complexity arises because J is the sum of several elementary contributions,[48] each of which responds independently to structural distortions of the bridging framework.[2] In the case of the copper(II) complexes, one contribution dominates all the others because there is only one unpaired electron formally associated with each metal centre, but this is not the case for the chromium(III) complexes under discussion here. The basic hypothesis, however, still holds: the magnetic behaviour of dimers of this general type is determined principally by the bridging angle, ϕ. Clearly, further systematic magnetic and structural studies are necessary before the details of the functional form of this dependence of J on ϕ can be evaluated; such work is proceeding in our laboratories.

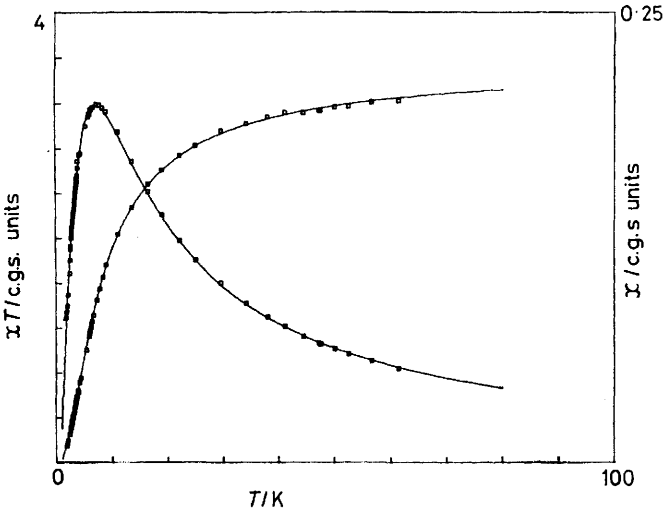

FIGURE 3 Temperature dependence of the magnetic susceptibility of a powdered sample of $[\{Cr(en)_2(OH)\}_2][S_2O_6]_2$. The curve which shows a maximum near T = 7K represents χ *versus* T. The other curve represents a plot of χT *versus* T. The observed data are shown as squares. The full lines represent the best fit to equation (1) with $J = -1.08$ cm^{-1}, $j = 0.234$ cm^{-1}, $g = 1.947$, and $\gamma = -0.37$

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[7/010 *Received, 4th January,* 1977]

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[48] J. C. M. Henning and H. van den Boom, *Phys. Rev.*, 1973, **B8**, 2255; G. G. P. van Gorkom, J. C. M. Henning, and R. P. van Stapele, *ibid.*, p. 955.