

Synthesis, Molecular Structure and Magnetic Properties of Di- μ -hydroxo-bis-(bis(1,3-bis(2-hydroxyphenyl)-1,3-propanedione)chromium(III)) Bistoluene

F. TEIXIDOR, J. COLOMER, J. CASABÓ*

Institut de Ciència dels Materials (C.S.I.C.) i Departament de Química, Universitat Autònoma de Barcelona, Campus de Bellaterra, Cerdanyola, 08193 Barcelona, Spain

E. MOLINS, C. MIRAVITLLES

Institut de Ciència dels Materials (C.S.I.C.), C/Marti i Franques s/n, Apartat de Correus 30102, 08028 Barcelona, Spain

and F. PALACIO

Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., Plaza S. Francisco s/n, 50009 Saragossa, Spain

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Abstract

The title compound $[\text{Cr}_2(\text{bhppH}_2)_4(\text{OH})_2] \cdot 2\text{C}_7\text{H}_8$ has been synthesized and isolated by chromatographic techniques from the reaction between 1,3-bis(2-hydroxyphenyl)-1,3-propanedione (bhppH_3) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Well formed single crystals were grown from toluene solutions and characterized by X-ray diffraction methods being triclinic, space group $P\bar{1}$, with $a = 12.692(2)$, $b = 13.423(2)$, $c = 21.983(4)$ Å, $\alpha = 102.24(1)$, $\beta = 92.04(1)$, $\gamma = 115.72(1)^\circ$, $V = 3.262(6)$ Å³, $Z = 2$, $D_x = 1.370$ g cm⁻³ and $\mu = 3.9$ cm⁻¹, $F(000) = 1.396$. Magnetic susceptibilities were measured from 50 down to 4.2 K and fitted using the simplest Hamiltonian for exchange coupled systems $\mathcal{H} = -2JS_1S_2$. The best results were obtained with $J = -4.1$ cm⁻¹ and $g = 1.85$. These values are compared with the Glerup, Hodgson and Pedersen (GHP) model.

Introduction

The compound 1,3-bis(2-hydroxyphenyl)-1,3-propanedione (bhppH_3) (Fig. 1) is an excellent ligand affording mononuclear complexes with divalent transition metal ions of formula $\text{M}(\text{bhppH}_2)_2$ [1]. Except for lithium, the metal ion is coordinated in a square planar mode by the two β -

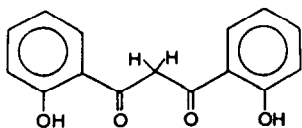


Fig. 1. The 1,3-bis(2-hydroxyphenyl)-1,3-propanedione (bhppH_3) ligand molecule.

* Author to whom correspondence should be addressed.

diketone moieties, corresponding to two bhppH_2^- ligands. The complex $[\text{Li}(\text{bhppH}_2)]^-$ displays a tetrahedral coordination [1d]. Usually the coordinated metal binds solvent molecules to achieve hexacoordination. This compound, bhppH_3 , is also a potentially trinucleating ligand with which we have been able to prepare linear trinuclear complexes of the type $\text{VO}-\text{VO}-\text{VO}$, $\text{UO}_2-\text{UO}_2-\text{UO}_2$, $\text{UO}_2-\text{M}-\text{UO}_2$ or $\text{Mn}-\text{M}-\text{Mn}$, M being one of the first row divalent transition metal ions [2].

Usually, the mononuclear complexes are scarcely soluble in organic solvents (except in tetrahydrofuran). For this reason we had planned to modify the original ligand via substitution at the methinic carbon atom. With these, *a priori*, more soluble mononuclear complexes, we expected a more feasible synthesis of the trinuclear compounds. For this reason we synthesized the Cr(III) mononuclear complex $\text{Cr}(\text{bhppH}_2)_3$ [3], and nucleophilic substitutions at the α -carbon of the β -diketone moieties were attempted.

The reaction of bhppH_3 with $\text{Cr}(\text{NO}_3)_3$ to afford $\text{Cr}(\text{bhppH}_2)_3$ revealed itself to be more complex than it had been first thought. Depending on the experimental conditions and reagents ratio the reaction produces different mixtures of compounds of which we have been able to isolate several chemicals by chromatographic techniques [3], one of them being the title dinuclear compound.

The magnetic properties of binuclear complexes of Cr(III) are very interesting from the superexchange point of view. A number of dinuclear di- μ -hydroxo-dicopper(II) complexes has been prepared and their magnetic properties studied. There is a simple semi-empirical model due principally to Hatfield and Hodgson which relates in a linear form the exchange constant J with the structural angle ϕ ($\text{Cu}-\text{O}-\text{Cu}$) [4a]. The results obtained, however, may not be applicable to exchange interactions between para-

magnetic centers with several unpaired electrons. As Hodgson has pointed out, the polynuclear Cr(III) complexes constitute an ideal choice for such a study [4b]. The ground state $^4A_{2g}$ of the monomeric Cr(III) ion being orbitally non-degenerate is, among others, one of the most important reasons for choosing polynuclear Cr(III) complexes in theoretical studies on exchange coupled systems, as well as their kinetic inertness which make easy their preparation. This is the reason for the large number of mono or polynuclear chromium(III) complexes reported in the literature.

To the best of our knowledge, this is the first example of a dinuclear di- μ -hydroxodichromium(III) complex with β -diketone-like ligands, so we have undertaken its complete structural elucidation by X-ray diffraction methods and studied its magnetic properties from 50 down to 4.2 K. The results obtained are reported in this paper.

Experimental

All reagents and solvents were commercial grade materials and were used without further purification. 1,3-bis-(2-hydroxyphenyl)-1,3-propanedione (bhpp-H₃) was synthesized as previously described [1b]. Analyses (C, H) were performed in our microanalytical laboratory on a Perkin-Elmer 240 instrument. IR spectra were done on a Beckman IR-20 spectrophotometer as KBr pellets.

Synthesis of $Cr_2(OH)_2(bhppH_2)_4$

The reaction was conducted similarly as reported to produce $Cr(bhppH_2)_3$ [3], however the ratio of reagents was varied so that the dimer compound could be made in a larger yield.

To a warm solution of bhppH₃ (2.37 mmol, 0.7 g) in isopropanol (50 ml) was added with stirring $Cr(NO_3)_3 \cdot 9H_2O$ (1.65 mmol, 0.66 g) in the same solvent (20 ml). The resulting mixture was refluxed for 1 h. During this time, the color of the solution turned from pale red to dark brown. The solvent was stripped off in a rotavapor and the residue extracted with $CHCl_3$, washed with water (3 times) and dried ($MgSO_4$). After eliminating the $MgSO_4$, the chloroform was partially eliminated (rotavap) and the remaining solution chromatographed on silica gel ($CHCl_3$ /benzene, 1/1) to separate fractions 1 and 2; ($CHCl_3$) fraction 3 and 4; ($CHCl_3$ /acetone, 1/1) fraction 5 and finally with acetone (fraction 6).

A TLC at this stage (ALUGRAM SIL 6/UV254, benzene/ $CHCl_3$ 1/2 solvent) of the different fractions showed mainly one spot in fraction 1 due to $Cr(bhppH_2)_3$, R_f 0.555; fractions 2 and 3 a mixture of $Cr(bhppH_2)_3$ and other species; fraction 4 mainly $Cr_2(OH)_2(bhppH_2)_4$, R_f 0.180 and fractions 5 and 6 only 2'-hydroxyflavone [3].

Fraction 4 was chromatographed again under the same conditions (silica gel, $CHCl_3$). In this case the two final fractions did not contain the chromium compounds (TLC), but the central fraction did. These fractions were evaporated and the solid recrystallized with $OHCl_3$ /heptane to yield 200 mg of a crystalline compound.

Anal. Found: C, 60.4; H, 4.0; Cr, 8.7. Calc. for $C_{60}H_{46}O_{18}Cr_2 \cdot 2H_2O$: C, 60.30; H, 4.18; Cr, 8.71%.

Well formed crystals suitable for X-ray diffraction analysis were grown from toluene solutions and the structure elucidation revealed the presence of two toluenes as solvating molecules $C_{60}H_{46}O_{18}Cr_2 \cdot 2C_7H_8$.

X-ray Structure Determination

Single crystals, $C_{60}H_{46}O_{18}Cr_2 \cdot 2C_7H_8$ are triclinic, space group $P\bar{1}$, with $a = 12.692(2)$, $b = 13.423(2)$, $c = 21.983(4)$ Å, $\alpha = 102.24(1)$, $\beta = 92.04(1)$, $\gamma = 115.72(1)^\circ$, $V = 3.262(6)$ Å³, $Z = 2$, $D_x = 1.370$ g cm⁻³ and $\mu = 3.9$ cm⁻¹, $F(000) = 1.396$.

X-ray diffraction data at 293 K were collected with an Enraf-Nonius CAD-IV four circle diffractometer using graphite crystal monochromated Mo K α radiation ($\lambda = 0.71069$ Å) on a $0.2 \times 0.4 \times 0.4$ mm prismatic crystal. The number of collected reflections is 9904, 9611 of them were independent and 4502 were considered observed with $F > 2.5\sigma(F)$. The scan technique used was $\omega - 2\theta$, with $2\theta < 47^\circ$, and the range of hkl was $-14 < h < 14$, $-15 < k < 15$, $0 < l < 24$. The standard reflexion decay along the data measurement cycle was 1.1%. The intensities were corrected for Lorentz and polarization effects. The two chromium atoms were located with a straightforward application of MULTAN 11/84 [5], and all remaining non H atoms were obtained by successive cycles of refinement (isotropic full matrix least-squares) and difference Fourier synthesis.

During these processes two toluene solvent molecules appeared in the Fourier synthesis map. Finally the structure was refined with anisotropic thermal parameters, although isotropic for the solvent molecules, in four blocks using the SHELX [6] program. The final R factor was 0.069 and $R_w = 0.076$ with $w = 1/[\sigma^2(F) + 0.00152F^2]$ where $\sigma(F)$ is derived from counting statistics. The maximum height in a final difference Fourier synthesis was 0.49 e Å⁻³ near a solvent molecule. The scattering factors were taken from ref. 7.

Magnetic Measurements

Magnetic susceptibility was measured from 4 to 50 K in a a.c. susceptometer at $H = 0$, the alternating field being about 1 Oe. Only 46 mg (3.97×10^{-5} mol) were available to make the measurements giving a rather weak signal at the secondary coils.

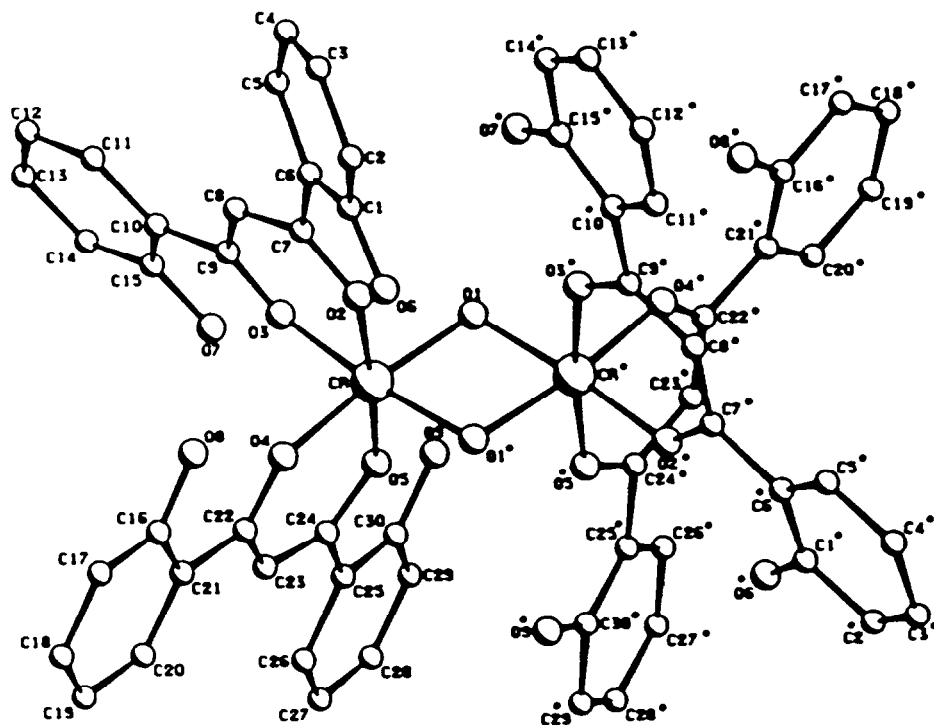


Fig. 2. Perspective view of the title molecule with the atom numbering.

No correction for ligand diamagnetism was made since it amounted to less than 1% of the experimental susceptibility values.

Results and Discussion

Description of the Structure

Figure 2 shows a perspective view of the molecule and the atom numbering [8]. The final parameters for all non-H atoms are given in Table I. Bond distances and angles and their e.s.d.s are given in Tables II and III. The two chromium(III) atoms are six-coordinated, forming two octahedrons which share one edge. This is constituted by two hydroxyl groups and the remaining sites correspond to oxygen atoms of the chelating ligands. The two Cr and the two oxygen atoms of the hydroxyl groups lie in a basal plane (r.m.s.d 0.012 Å), moreover the O₃, O₄, O₂', O₄' atoms are very close to this plane (range of out-of-plane distances 0.02–0.08 Å). The angles between the line bonds of Cr with axial oxygen atoms and basal plane are close to 90°.

The large distortion of these octahedrons is due to two bridging hydroxyl groups which produce a closing of the O₁–Cr–O₁' (78.5°) and O₁–Cr'–O₁' (78.7°) angles. The Cr...Cr' distance is 3.035 Å. The Cr–O bond distances are 1.96 Å except those with O₄, O₅, O₂', and O₄' which are about 1.94 Å.

The relative disposition of the chelating ligands is shown in Fig. 3, where it can be seen that the ligands at each side of the basal plane are parallel

and oriented in opposite directions (angles between mean planes of ligands in up and down hemispheres are 2.5 and 4.3°, respectively). The disposition suggests the presence of a pseudo-binary axis normal to the basal plane at the center of the Cr–Cr' segment.

Magnetic Properties

Magnetic measurements shown in Fig. 4, exhibit the typical behaviour of a dimer with two $S = 3/2$ Cr atoms interacting with each other through the μ -hydroxo bridges presenting a broad maximum at around 17 K. Due to the small amount of sample, with rather diluted magnetic moments, a certain scattering in the experimental points is present.

The simple exchange Hamiltonian

$$\mathcal{H} = -2JS_1S_2 + g\mu_B S'_z H_z$$

is usually adequate to describe the magnetic interaction, eigenvalues of $\mathcal{H}$ being

$$E(S') = -J[S'(S' + 1) - 2S(S + 1)] + g\mu_B m_s \times H_z$$

where $S = 3/2$ and $S' = 0, 1, 2, 3$ is the effective spin of each level in the pair.

The magnetic susceptibility data for the complex were fitted to the well known expression

$$\chi = \frac{Ng^2\mu_B^2}{kT} \times \frac{2\exp(2J/kT) + 10\exp(6J/kT) + 28\exp(12J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT)}$$

TABLE I. Fractional Coordinates ($\times 10^4$) for Non-hydrogen atoms^a and Equivalent Temperature Factors

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq}
Cr	5681(1)	2688(1)	6888(1)	4.35
Cr'	4973(1)	2462(1)	8175(1)	4.23
O1	3687(4)	7329(4)	2289(2)	4.40
O1'	5646(4)	7481(4)	2639(2)	4.51
O2	3686(5)	5642(4)	2880(3)	5.15
O3	2901(5)	7135(4)	3499(3)	5.27
O6	4450(8)	4127(7)	2621(4)	9.07
O7	2145(6)	8464(5)	4039(4)	8.34
C1	3308(13)	3374(8)	2569(5)	7.41
C2	3076(15)	2200(11)	2362(5)	10.08
C3	1885(21)	1392(12)	2281(7)	11.69
C4	990(15)	1680(10)	2398(6)	10.63
C5	1208(10)	2837(7)	2658(5)	8.04
C6	2421(10)	3682(7)	2744(4)	5.90
C7	2712(9)	4899(7)	3014(4)	5.23
C8	1944(8)	5140(7)	3384(4)	5.53
C9	2063(8)	6246(7)	3610(4)	5.17
C10	1197(8)	6443(8)	3993(4)	5.67
C11	273(9)	5513(10)	4158(5)	8.26
C12	-551(11)	5718(14)	4514(7)	10.48
C13	-424(12)	6840(15)	4715(6)	10.40
C14	485(10)	7779(11)	4550(6)	9.01
C15	1291(9)	7544(10)	4190(5)	7.09
O4	5131(5)	7356(4)	3888(2)	5.16
O5	4870(5)	8956(4)	3398(2)	4.69
O8	5386(6)	5917(5)	4372(3)	7.80
O9	4278(5)	10363(5)	3073(3)	5.87
C16	6092(8)	6806(7)	4852(4)	5.33
C17	6616(9)	6561(9)	5325(5)	6.72
C18	7373(9)	7461(9)	5845(5)	6.53
C19	7590(8)	8577(9)	5875(4)	6.07
C20	7044(7)	8824(7)	5394(4)	5.31
C21	6294(7)	7937(7)	4878(4)	4.50
C22	5750(7)	8215(7)	4375(4)	4.55
C23	5884(7)	9323(6)	4408(4)	4.79
C24	5449(6)	9651(6)	3938(4)	4.18
C25	5633(6)	10848(6)	4016(4)	4.10
C26	6412(7)	11716(6)	4544(4)	5.40
C27	6570(9)	12838(7)	4610(4)	6.29
C28	5973(8)	13113(7)	4183(5)	5.65
C29	5207(8)	12272(7)	3666(4)	5.65
C30	5051(7)	11143(7)	3586(4)	4.48
O2'	6430(5)	7765(4)	1437(3)	5.04
O3'	4413(4)	5890(4)	1472(2)	4.60
O6'	8207(5)	9478(4)	1276(3)	6.85
O7'	2423(5)	4135(5)	1337(3)	6.40
C1'	8529(8)	8705(7)	951(4)	5.14
C2'	9608(8)	9192(8)	718(5)	6.66
C3'	10051(9)	8469(9)	390(5)	8.03
C4'	9374(9)	7244(9)	275(5)	7.44
C5'	8300(8)	6805(7)	502(4)	5.82
C6'	7864(7)	7529(6)	841(4)	4.29
C7'	6708(7)	7040(6)	1070(4)	4.48
C8'	5949(7)	5853(6)	908(4)	4.72
C9'	4882(7)	5336(6)	1116(3)	3.82
C10'	4166(7)	4083(6)	940(4)	4.15
C11'	4655(8)	3378(7)	625(5)	6.55

(continued)

TABLE I. (continued)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq}
C12'	3980(10)	2191(7)	444(5)	7.53
C13'	2620(9)	1693(7)	570(5)	6.58
C14'	2319(8)	2360(7)	865(4)	6.44
C15'	3001(8)	3546(6)	1050(4)	4.82
O4'	4219(5)	7593(4)	1074(2)	4.91
O5'	5741(5)	9214(4)	2099(2)	4.86
O8'	2907(5)	6159(5)	96(3)	6.16
O9'	7509(6)	10759(6)	2873(3)	8.09
C16'	7134(8)	2948(7)	72(4)	5.05
C17'	2164(9)	6802(9)	-641(5)	6.77
C18'	2081(9)	7674(10)	-859(5)	7.41
C19'	2689(9)	8818(9)	-489(5)	6.13
C20'	3400(8)	9060(7)	73(4)	5.38
C21'	6517(7)	1810(6)	-293(4)	4.28
C22'	4226(7)	8456(6)	898(4)	4.39
C23'	4898(7)	9606(6)	1256(4)	5.00
C24'	5595(7)	9921(6)	1817(4)	4.41
C25'	6310(8)	11150(6)	2161(4)	5.01
C26'	6063(9)	11978(7)	1972(5)	7.32
C27'	6728(12)	13147(8)	2290(6)	8.56
C28'	7629(11)	13446(8)	2776(6)	8.55
C29'	7909(9)	12673(9)	2964(5)	7.92
C30'	7205(9)	11483(7)	2646(5)	6.21
CT1	1114(10)	7293(10)	1880(10)	11.73
CT2	1234(10)	6718(10)	1317(10)	9.72
CT3	934(10)	5592(10)	1223(10)	12.55
CT4	495(10)	5009(10)	1700(10)	12.63
CT5	281(10)	5526(10)	2200(10)	12.37
CT6	649(10)	6730(10)	2371(10)	10.53
CT7	1527(10)	8515(10)	2015(10)	15.89
CT1'	8596(10)	8655(10)	3535(10)	14.15
CT2'	8017(10)	7632(10)	3652(10)	10.88
CT3'	7571(10)	6538(10)	3202(10)	14.89
CT4'	7783(10)	6554(10)	2617(10)	14.55
CT5'	8430(10)	7698(10)	2525(10)	12.01
CT6'	8830(10)	8788(10)	2884(10)	12.47
CT7'	8975(10)	9734(10)	3928(10)	16.83

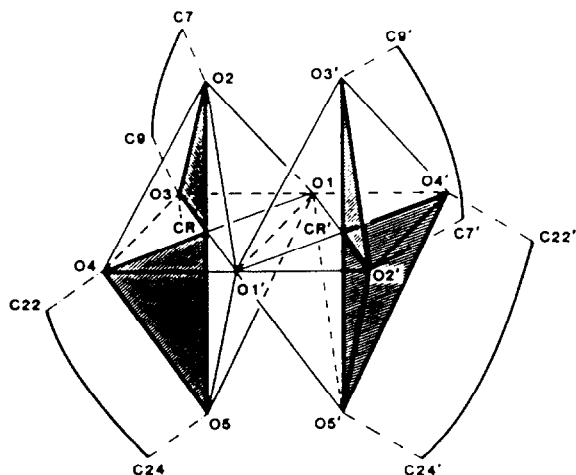
^ae.s.d.s given in parentheses.

Fig. 3. Relative dispositions of the chelating ligands about the two coordination octahedrons.

TABLE II. Bond Lengths (Å)^a

O1—Cr	1.961(4)	C30—C29	1.411(13)
O1'—Cr	1.966(4)	C7'—O2'	1.308(11)
O2—Cr	1.964(5)	C9'—O3'	1.300(11)
O3—Cr	1.960(5)	C1'—O6'	1.353(12)
O4—Cr	1.938(5)	C15'—O7'	1.374(12)
O5—Cr	1.947(5)	C2'—C1'	1.407(13)
O1—Cr'	1.960(4)	C6'—C1'	1.390(10)
O1'—Cr'	1.958(4)	C3'—C2'	1.407(17)
O2'—Cr'	1.934(5)	C4'—C3'	1.445(14)
O3'—Cr'	1.958(5)	C5'—C4'	1.389(14)
O4'—Cr'	1.945(5)	C6'—C5'	1.412(14)
O5'—Cr'	1.965(5)	C7'—C6'	1.480(11)
C7—O2	1.300(10)	C8'—C7'	1.412(9)
C9—O3	1.286(9)	C9'—C8'	1.373(11)
C1—O6	1.342(15)	C10'—C9'	1.476(9)
C15—O7	1.359(12)	C11'—C10'	1.423(14)
C2—C1	1.436(19)	C15'—C10'	1.391(12)
C6—C1	1.398(22)	C12'—C11'	1.397(11)
C3—C2	1.403(25)	C13'—C12'	1.395(15)
C4—C3	1.366(34)	C14'—C13'	1.380(16)
C5—C4	1.432(16)	C15'—C14'	1.397(11)
C6—C5	1.437(13)	C22'—O4'	1.293(11)
C7—C6	1.486(13)	C24'—O5'	1.309(12)
C8—C7	1.391(15)	C30'—O9'	1.364(15)
C9—C8	1.401(14)	C21'—C16'	1.410(10)
C10—C9	1.487(14)	C18'—C17'	1.397(20)
C11—C10	1.420(14)	C19'—C18'	1.418(14)
C15—C10	1.399(17)	C20'—C19'	1.394(14)
C12—C11	1.413(20)	C23'—C22'	1.423(15)
C13—C12	1.412(28)	C24'—C23'	1.364(17)
C14—C13	1.418(19)	C25'—C24'	1.497(16)
C15—C14	1.415(18)	C26'—C25'	1.412(18)
C22—O4	1.312(8)	C30'—C25'	1.378(18)
C24—O5	1.302(8)	C27'—C26'	1.416(14)
C16—O8	1.346(9)	C28'—C27'	1.394(15)
C30—O9	1.364(8)	C29'—C28'	1.366(15)
C17—C16	1.384(17)	C30'—C29'	1.443(16)
C21—C16	1.414(14)	CT2—CT1	1.363(23)
C18—C17	1.421(12)	CT6—CT1	1.445(22)
C19—C18	1.386(17)	CT7—CT1	1.445(25)
C20—C19	1.416(16)	CT3—CT2	1.354(23)
C21—C20	1.406(10)	CT4—CT3	1.427(22)
C22—C21	1.478(14)	CT5—CT4	1.275(21)
C23—C22	1.407(13)	CT6—CT5	1.430(24)
C24—C23	1.388(14)	CT2'—CT1'	1.334(22)
C25—C24	1.490(12)	CT6'—CT1'	1.504(23)
C26—C25	1.423(9)	CT7'—CT1'	1.382(25)
C30—C25	1.398(14)	CT3'—CT2'	1.441(23)
C27—C26	1.405(13)	CT4'—CT3'	1.327(22)
C28—C27	1.391(16)	CT5'—CT4'	1.457(24)
C29—C28	1.391(11)	CT6'—CT5'	1.363(22)

^ae.s.d.s. given in parentheses.

by minimizing the function $\Sigma(\chi_{\text{found}} - \chi_{\text{calc}})^2$, assuming a fixed g value. The best fitting was accomplished using $J = -4.1 \pm 0.1 \text{ cm}^{-1}$ and $g = 1.85 \pm 0.01$.

Since the energies of the triplet, quintet and septet states are $-2J$, $-6J$ and $-12J$ respectively,

TABLE III. Bond Angles (°)^a

O1'—Cr—O1	78.5(0.3)	C22'—O4'—Cr'	130.4(0.8)
O2—Cr—O1	92.7(0.5)	C24'—O5'—Cr'	128.5(0.7)
O2—Cr—O1'	91.2(0.4)	C2—C1—O6	114.2(1.5)
O3—Cr—O1	95.3(0.5)	C6—C1—O6	123.8(1.0)
O3—Cr—O1'	173.8(0.4)	C6—C1—C2	121.8(1.2)
O3—Cr—O2'	88.8(0.5)	C3—C2—C1	115.6(1.8)
O4—Cr—O1	172.9(0.5)	C4—C3—C2	123.3(1.5)
O4—Cr—O1'	94.5(0.4)	C5—C4—C3	122.1(1.2)
O4—Cr—O2	88.8(0.5)	C6—C5—C4	115.6(1.2)
O4—Cr—O3	91.7(0.5)	C5—C6—C1	121.1(0.9)
O5—Cr—O1	89.7(0.5)	C7—C6—C1	120.4(0.8)
O5—Cr—O1'	93.2(0.4)	C7—C6—C5	118.5(1.1)
O5—Cr—O2	175.4(0.5)	C6—C7—O2	115.4(0.9)
O5—Cr—O3	87.0(0.5)	C8—C7—O2	126.3(0.8)
O5—Cr—O4	89.3(0.5)	C8—C7—C6	118.3(0.8)
O1'—Cr'—O1	78.7(0.3)	C9—C8—C7	123.2(0.8)
O2'—Cr'—O1	175.0(0.4)	C8—C9—O3	123.0(0.9)
O2'—Cr'—O1'	96.3(0.4)	C10—C9—O3	116.5(0.9)
O3'—Cr'—O1	92.4(0.4)	C10—C9—C8	120.5(0.8)
O3'—Cr'—O1'	93.1(0.4)	C11—C10—C9	120.0(1.0)
O3'—Cr'—O2'	88.6(0.5)	C15—C10—C9	120.0(0.8)
O4'—Cr'—O1	93.2(0.4)	C15—C10—C11	120.0(1.0)
O4'—Cr'—O1'	171.8(0.4)	C12—C11—C10	119.0(1.2)
O4'—Cr'—O2'	91.8(0.5)	C13—C12—C11	119.8(1.2)
O4'—Cr'—O3'	88.2(0.5)	C14—C13—C12	122.0(1.4)
O5'—Cr'—O1	93.5(0.4)	C15—C14—C13	116.7(1.4)
O5'—Cr'—O1'	90.6(0.4)	C10—C15—O7	122.6(1.0)
O5'—Cr'—O2'	85.7(0.5)	C14—C15—O7	115.0(1.1)
O5'—Cr'—O3'	173.5(0.5)	C14—C15—C10	122.4(1.0)
O5'—Cr'—O4'	89.0(0.5)	C17—C16—O8	116.8(0.9)
Cr'—O1—Cr	101.4(0.3)	C21—C16—O8	122.1(0.9)
Cr'—O1'—Cr	101.3(0.3)	C21—C16—C17	121.1(0.7)
C7—O2—Cr	127.3(0.7)	C18—C17—C16	119.6(1.1)
C9—O3—Cr	130.6(0.7)	C19—C18—C17	120.0(1.1)
C22—O4—Cr	130.4(0.7)	C20—C19—C18	120.3(0.8)
C24—O5—Cr	129.3(0.8)	C21—C20—C19	119.9(0.9)
C7'—O2'—Cr'	131.2(0.7)	C20—C21—C16	119.1(0.9)
C9'—O3'—Cr'	129.3(0.7)	C22—C21—C16	121.8(0.6)
		C22—C21—C20	119.1(0.8)
C21—C22—O4	115.5(0.8)	C13'—C12'—C11'	120.0(1.1)
C23—C22—O4	121.7(0.8)	C14'—C13'—C12'	120.7(0.8)
C23—C22—C21	122.8(0.6)	C15'—C14'—C13'	119.0(0.9)
C24—C23—C22	125.6(0.7)	C10'—C15'—O7'	122.9(0.7)
C23—C24—O5	123.3(0.7)	C14'—C15'—O7'	114.6(0.8)
C25—C24—O5	114.8(0.8)	C14'—C15'—C10'	122.4(0.9)
C25—C24—C23	121.8(0.6)	C19'—C18'—C17'	119.5(1.0)
C26—C25—C24	119.3(0.8)	C20'—C19'—C18'	119.4(1.0)
C30—C25—C24	121.7(0.6)	C23'—C22'—O4'	122.9(0.9)
C30—C25—C26	118.9(0.8)	C24'—C23'—C22'	124.3(0.7)
C27—C26—C25	118.5(0.9)	C23'—C24'—O5'	124.9(0.8)
C28—C27—C26	121.8(0.7)	C25'—C24'—O5'	113.4(0.9)
C29—C28—C27	120.2(0.9)	C25'—C24'—C23'	121.6(0.8)
C30—C29—C28	118.8(1.0)	C26'—C25'—C24'	118.6(0.8)
C25—C30—O9	122.7(0.8)	C30'—C25'—C24'	121.4(0.7)
C29—C30—O9	115.4(0.9)	C40'—C25'—C26'	120.0(0.9)
C29—C30—C25	121.8(0.7)	C27'—C26'—C25'	119.6(0.8)
C2'—C1'—O6'	114.1(0.7)	C28'—C27'—C26'	118.5(0.9)
C6'—C1'—O6'	124.1(0.8)	C29'—C28'—C27'	123.6(0.9)
C6'—C1'—C2'	121.8(0.9)	C30'—C29'—C28'	117.3(0.8)
C3'—C2'—C1'	119.1(0.8)	C25'—C30'—O9'	125.1(0.8)

(continued)

TABLE III. (continued)

C4'-C3'-C2'	119.9(0.9)	C29'-C30'-O9'	113.9(0.9)
C5'-C4'-C3'	118.7(1.1)	C29'-C30'-C25'	121.0(0.7)
C6'-C5'-C4'	121.5(0.8)	CT6'-CT1'-CT2	121.9(1.1)
C5'-C6'-C1'	119.0(0.8)	CT7'-CT1'-CT2	120.0(1.3)
C7'-C6'-C1'	120.6(0.8)	CT7'-CT1'-CT6	117.9(1.3)
C7'-C6'-C5'	120.5(0.7)	CT3'-CT2'-CT1	118.9(1.1)
C6'-C7'-O2'	116.4(0.6)	CT4'-CT3'-CT2	121.0(1.1)
C8'-C7'-O2'	121.5(0.7)	CT5'-CT4'-CT3	119.5(1.1)
C8'-C7'-C6'	122.1(0.8)	CT6'-CT5'-CT4	123.6(1.1)
C9'-C8'-C7'	125.3(0.8)	CT5'-CT6'-CT1	114.2(1.1)
C8'-C9'-O3'	123.9(0.6)	CT6'-CT1'-CT2'	122.0(1.1)
C10'-C9'-O3'	114.5(0.6)	CT7'-CT1'-CT2'	129.8(1.2)
C10'-C9'-C8'	121.6(0.8)	CT7'-CT1'-CT6'	107.8(1.3)
C11'-C10'-C9'	119.6(0.7)	CT3'-CT2'-CT1'	126.5(1.1)
C15'-C10'-C9'	122.9(0.8)	CT4'-CT3'-CT2'	116.5(1.1)
C15'-C10'-C11'	117.5(0.7)	CT5'-CT4'-CT3'	113.9(1.1)
C12'-C11'-C10'	120.3(0.9)	CT6'-CT5'-CT4'	136.2(1.1)
		CT5'-CT6'-CT1'	104.5(1.1)

^ae.s.d.s given in parentheses.

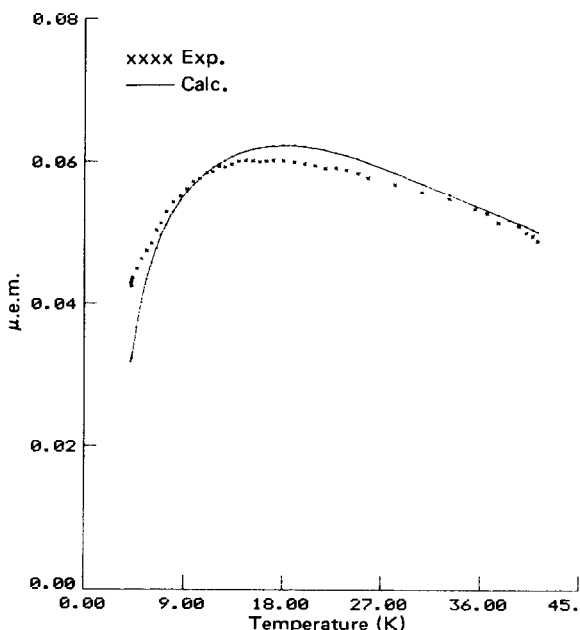


Fig. 4. Magnetic susceptibilities vs. temperature of the title compound.

the fitted value of J indicates a singlet ground state with

$$\Delta E = E(1) - E(0) = +8.2 \text{ cm}^{-1}$$

where $E(0)$ and $E(1)$ are the singlet and triplet energies, respectively.

Sometimes several authors have used a modified Hamiltonian including a second-order term called 'biquadratic exchange term'

$$\mathcal{H} = -2JS_1S_2 - j(S_1S_2)^2$$

which leads to energies of $-2J + 6.5j$, $-6J + 13.5j$ and $-12J + 9.0j$, respectively for the triplet, quintet and septet states. Finally, some authors have used an entirely generalized Hamiltonian in which the triplet, quintet and septet energies are independent [4b]. We have found it more reasonable to employ the first simplest model and to make use of the ΔE energy in the latter discussion.

The singlet-triplet energy distance, ΔE , has been related by means of an empirical model with the Cr-O bridge distance, (R), the Cr-O-Cr bridging angle, (ϕ), and the dihedral angle between the O-H vector and the Cr_2O_2 plane, (θ), by Glerup, Hodgson and Pedersen (GHP) [9]. The model has been fitted against a wide variety of Cr-Cr dimers [4b] and it provides a reasonably good agreement between observed and calculated ΔE values. Unfortunately it is not possible to make a comparison in the present case since positions of the hydrogen atoms in the μ -hydroxo bridges could not be determined in the X-ray diffraction study. However, the position of the hydrogen atoms has a rather large influence on the value of the Cr-Cr interaction [10, 11] in the sense that small values of θ indicate that the p orbital of the bridging oxygen atom perpendicular to the Cr_2O_2 plane is more available for π bonding to the Cr atoms. Antiferromagnetic superexchange through the O bridge is, thus, stronger for smaller values of θ , decreasing by increasing the angle θ , leading to positive ΔE values above 60° approximately. Therefore if the GHP model is assumed to be valid for the present case, it is possible to infer from the experimental values of R and ϕ and from the calculated value of ΔE , a value of 49.8° for θ . This compound seems to be among those that exhibit the smallest antiferromagnetic interactions, being between $[\text{Cr}(\text{NH}_3)_4\text{OH}]_2\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ ($\theta = 41^\circ$, $\Delta E = -9 \text{ cm}^{-1}$) $[\text{Cr}(\text{en})_2\text{OH}]_2(\text{S}_2\text{O}_6)_2$ ($\theta = 57^\circ$, $\Delta E = -3 \text{ cm}^{-1}$) and $\text{Na}_4[\text{Cr}(\text{mal})_2\text{OH}]_2 \cdot 5\text{H}_2\text{O}$ ($\theta = 54^\circ$, $\Delta E = -3 \text{ cm}^{-1}$), although there are no chemical similarities between them [4b]. It is difficult to infer anything about θ without structural evidence, because packing forces in the lattice seem to have great influence as is evidenced in the following pair of Cr(III) dimer compounds: $[\text{Cr}(\text{en})_2\text{OH}]_2(\text{S}_2\text{O}_6)_2$ ($\theta = 57(3)^\circ$), $[\text{Cr}(\text{en})_2\text{OH}]_2\text{Cl}_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\theta = 2(3)^\circ$) [4b], their corresponding ΔE values are -3 and -27 cm^{-1} respectively. In conclusion the magnetic behaviour of our Cr(III) dimer seems to be in accord with the GHP model.

Supplementary Material

Tables of observed and calculated structure factors and anisotropic thermal parameters for non-hydrogen atoms of $\text{C}_{60}\text{H}_{46}\text{O}_{18}\text{Cr}_2 \cdot 2\text{C}_7\text{H}_8$ are available from the authors on request.

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