The structure was readily solved with direct methods and Fourier techniques. Since most hydrogen atoms were apparent in a difference Fourier synthesis, final refinement included hydrogen atoms placed in fixed idealized positions[6] (d(C–H) = 0.95 Å, B_{iso} = 4.0 Å^2). Full-matrix anisotropic refinement converged to $R(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.042$ and $R_w(F) = \sum(w||F_o| - |F_c||)^2/\sum wF_o^2 = 0.053$. Weights, w, where calculated as $w(F_o) = \sigma(I)^{1/2}/2F_o$, where $\sigma(I)$ is based on counting statistics and an "ignorance factor" of 0.05. The goodness of fit for the last cycle was 1.22.

The [Co((py)$_3$tach)](ClO$_4$)$_2$ crystal used was an irregular shape with a maximum dimension of 0.25 mm. A total of 5235 reflections were measured for 4° ≤ 2θ ≤ 45° and reduced as before to 2943 unique amplitudes. Refinement was identical with that of the Zn((py)$_3$tach)$^{2+}$ sample and converged to $R(F) = 0.079$ and $R_w(F) = 0.033$. The goodness of fit for the final cycle was 1.76.

Fractional coordinates for non-hydrogen atoms are given in Table VI.

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Registry No. [Co((py)$_3$tach)](ClO$_4$)$_2$, 28849-62-9; [Zn((py)$_3$tach)](ClO$_4$)$_2$, 25765-80-4.

Supplementary Material Available: Complete lists of bonded distances and angles, hydrogen coordinates, anisotropic thermal parameters, and observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

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Structural and Magnetic Characterization of the Alkoxo-Bridged Chromium(III) Dimer Bis(μ-methoxo)bis[bis(2,4-pentanedionato)chromium(III)], [(acac)$_2$Cr(OCH$_3$)]$_2$

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The complex bis(μ-methoxo)bis[bis(2,4-pentanedionato)chromium(III)], [(acac)$_2$Cr(OCH$_3$)]$_2$, [CrC$_{11}$H$_{17}$O$_5$]$_2$, has been synthesized, and its crystal structure has been determined from three-dimensional counter X-ray data. The complex crystallizes in the triclinic space group $P\bar{1}$ with two binuclear formula units in a cell of dimensions a = 10.958 (4) Å, b = 12.769 (3) Å, c = 10.073 (2) Å, α = 96.65 (2)°, β = 95.04 (2)°, and γ = 97.00 (2)°. Least-squares refinement based on 1960 independent data has led to a final value of the weighted R factor (on F) of 0.048. The complex consists of two chromium(III) ions which are bridged by two methoxy groups, the remaining sites in the roughly octahedral coordination sphere being occupied by the oxygen atoms of two cis bidentate 2,4-pentanedionato ligands. The average Cr–O(ligand) bond length is 1.965 (10) Å while the Cr–Cr separation is 3.028 (2) Å and the Cr–O–Cr bridging angles are 100.8 (2) and 101.2 (2)°. The average value of the dihedral angle between the O–C bonds on the bridging methoxo groups and the bridging Cr$_2$O$_2$ least-squares plane is 29.8°. The isomer studied here is the racemic isomer in contrast with the meso form of analogous dimers previously studied. The temperature dependence of the magnetic susceptibility of the complex has been fitted to a model assuming independent triplet, quintet, and septet energies. The fit is consistent with the Heisenberg model corrected for biquadratic exchange and yields a triplet-state energy of 9.83 (6) cm^{-1} above the ground-state singlet.

Introduction

In recent years we[2-9] and others[10-14] have been studying the influence on the magnetic properties of chromium(III) dimers of small structural changes, with particular emphasis on the impact of changes in the bridging geometry of μ-hydroxo and bis(μ-hydroxo) chromium(III) dimers. While the bridging Cr–O–Cr angle (ϕ) and the Cr–O bond length (R) were quickly seen to be significant, perhaps in analogy with earlier work on simpler systems,[15] it is only relatively recently that the frequently overriding importance of the dihedral angle (θ) between the O–H vector and the bridging Cr$_2$O$_2$ (or Cr$_2$O for μ-hydroxo complexes) plane has been recognized.[2-5,16,17] Regrettably, this parameter is often poorly determined even in precise X-ray structural studies because of the small contribution of hydrogen atoms to the X-ray structure factors.

While the use of neutron diffraction data provides, in principle, a solution to this problem, in practice a more valuable approach appears to be the synthesis and study of alkoxo-bridged rather than hydroxo-bridged complexes, since in the fomer the angle θ would be dependent only on chromium, oxygen, and carbon atomic parameters. The syntheses of several bis(μ-alkoxo) dimeric complexes of chromium(III) have been reported,[18-20] but unfortunately none of the three synthetic routes suggested has proved amenable to extension to large

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Table I. Crystallographic and Data Collection Parameters

formula: $[CrC_{11}H_{17}O_5]_2$	$D_{obsd} = 1.34\ (2)$ g cm^{-3}
$a = 10.958\ (4)$ Å	$Z = 2$
$b = 12.769\ (3)$ Å	$D_{calcd} = 1.352$ g cm^{-3}
$c = 10.073\ (2)$ Å	space group: $P\bar{1}$
$\alpha = 96.65\ (2)°$	$\mu = 8.69$ cm^{-1}
$\beta = 95.04\ (2)°$	max transmissn factor: 99.9%
$\gamma = 97.00\ (2)°$	min transmissn factor: 85.1%
$V = 1382\ (1)$ Å^3	data collected: $\pm h, \pm k, +l$
NO = 1960	data range: $2° \leqslant 2\theta(\mathrm{Mo}) \leqslant 55°$

numbers of analogous complexes; consequently, the only complexes whose structural and magnetic properties have been examined in detail are three bis(μ-alkoxo) complexes of chromium(III) with substituted acetylacetonate ligands, whose properties were reported by us several years ago.[21,22] We have now developed a modification of the synthetic route of Mehrotra and co-workers[20] which has permitted the extension of this scheme and which, we believe, will allow us to isolate an almost limitless array of bis(μ-alkoxo) chromium(III) dimers. We here report the use of this modified synthetic procedure for the preparation, isolation, and crystallization of the complex bis(μ-methoxo)bis[bis(2,4-pentanedionato)chromium(III)], $[(acac)_2Cr(OCH_3)]_2$, and the magnetic and structural properties of this dimeric species.

Experimental Section

Synthesis. To a solution of $CrCl_3 \cdot 3THF$ (7.5 g, 0.02 mol) in methanol (50 mL) were added 2,4-pentanedione (4.0 g, 0.04 mol) and sodium methoxide (3.24 g, 0.06 mol). The resulting green solution was refluxed for 10 min, benzene (150 mL) was added, and an azeotrope of benzene/methanol was distilled off. When 150 mL of azeotrope had distilled off, the temperature had risen to 80 °C and a green precipitate had formed. Most of the precipitate dissolved on the addition of further benzene (100 mL) and subsequent heating; the hot solution was filtered and the filtrate evaporated to 50 mL. This procedure represents a convenient modification of the method described by Mehrotra and co-workers.[20]

The product was crystallized by the slow addition of hexane to the solution and recrystallized by dissolution in benzene and subsequent addition of sufficient hexane to produce the first trace of precipitate. The solution was then allowed to stand for several days, and the green crystals which formed were hand selected and dried on filter paper. Some of these crystals were used for the subsequent magnetic and crystallographic measurements.

Magnetic Susceptibility Measurements. The magnetic susceptibility of a microcrystalline sample of the complex was measured by the Faraday method at a field strength of 12 000 Oe in the temperature range 4–260 K. Descriptions of the instrumentation and data analysis techniques are available elsewhere.[2,16]

Crystallographic Measurements. A green, prismatic crystal of the complex was mounted on an Enraf-Nonius CAD-4 diffractometer; preliminary analysis demonstrated that the complex belongs to the triclinic system, the cell chosen being consistent only with the space groups $P\bar{1}$ and $P1$. The centrosymmetric space group was chosen, and this assignment was justified by the successful refinement of the structure. The cell constants, observed and calculated densities, and data collection parameters are listed in Table I.

Solution and Refinement of the Structure. The locations of the two independent chromium atoms were deduced from a three-dimensional Patterson function, and all remaining non-hydrogen atoms were located in subsequent difference Fourier summations. Isotropic least-squares refinement of these 34 atoms gave values of the conventional agreement factors $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$ and R_2 (weighted R factor) $= [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ of 0.098 and 0.108, respectively. In all least-squares calculations refinement was carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$; the weights w were assigned as $4F_o^2/\sigma^2(F_o)^2$, where $\sigma(F_o)^2$ is given by $[\sigma^2(I) + (0.01I)^2]^{1/2}$ and $\sigma^2(I)$ is derived from counting statistics alone. Anisotropic refinement reduced the values of R_1 and R_2 to 0.072 and 0.078, respectively, and examination of a subsequent difference Fourier map revealed the location of all 34 hydrogen atoms. Attempts to refine the hydrogen atom parameters were unsuccessful, so all hydrogen atoms were assigned fixed isotropic thermal parameters of 8.0 Å^2 and were constrained to their observed locations. The final least-squares calculation, which involved anisotropic refinement of all non-hydrogen atoms but no refinement of any hydrogen atom parameter, gave values of R_1 and R_2 of 0.059 and 0.048, respectively; no parameter experienced a shift of more than 0.4σ, which was taken as evidence of convergence. A final difference Fourier was featureless, with no peak higher than 0.3 e Å^{-3}. All computer programs used were those provided by Enraf-Nonius in the CAD-4/SDP package.

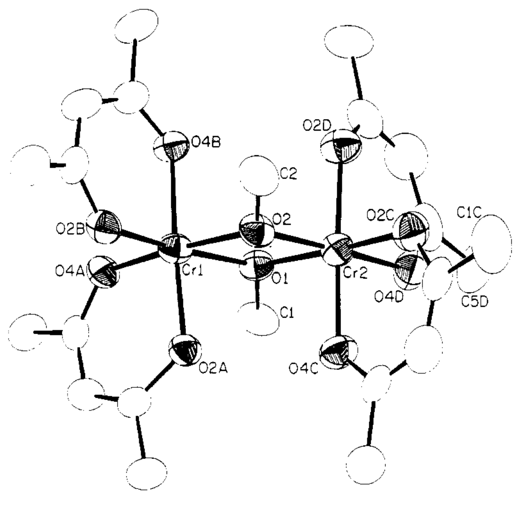

Figure 1. View of the dimeric $[(acac)_2Cr(OCH_3)]_2$ molecule. Carbon atoms are shown as open ellipsoids, while Cr and O atoms are shaded. The numbering scheme for C atoms that are not labeled follows the normal convention for pentane and its derivates, with the addition of a suffix (A, B, etc.) to designate the ring. The molecule shown here has the $\Delta\Delta$ configuration, but in this centrosymmetric space group there are an equal number of molecules exhibiting the $\Lambda\Lambda$ configuration.

The refined atomic positional parameters, along with their estimated standard deviations, are collected in Table II. The hydrogen atom coordinates, anisotropic librational parameters, and a listing of observed and calculated structure amplitudes are available as supplementary material.

Description of the Structure

The structure consists of dimeric $[(acac)_2Cr(OCH_3)]_2$ (acac = 2,4-pentanedionato) units, which are well separated from each other. The geometry of one dimer is shown in Figure 1, and the principal bond lengths and angles are displayed in Tables III and IV.

The geometry around each chromium center is roughly octahedral, the coordination sphere being occupied by two bidentate acac ligands and by two cis methoxo oxygen atoms. The Cr_2O_2 bridging unit is approximately planar, with no atom deviating from the unweighted least-squares plane by more than 0.012 Å. The methoxy carbon atoms C(1) and C(2) are considerably out of this plane, with C(1) lying 0.676 (8) Å above the plane while C(2) lies 0.729 (9) Å below it. With O(1)–C(1) and O(2)–C(2) bond lengths of 1.424 (7) and 1.409 (7) Å, respectively, these out-of-plane distances correspond to θ angles of 28.34 and 31.16°, respectively, or an average value for θ of 29.8°. As is shown in Table V, this value of θ is larger than those of 24.4 and 25.7° observed in the other methoxo-bridged dimers of chromium(III)[21,22] and is considerably larger than that of 18.3° in the only ethoxo-bridged complex whose structure has been reported.[22] The four independent bridging Cr–O bond distances (R) are in the range 1.951 (4)–1.973 (4) Å, with an average value of 1.962 (9) Å. The Cr–Cr separation in the dimer is 3.028 (2) Å, which is within the narrow range of 3.025 (2)–3.038 (3) Å in the other

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Table II. Positional Parameters for $[(acac)_2Cr(OCH_3)]_2$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cr(1)	0.0150 (1)	0.2571 (1)	0.2467 (1)	C4A	0.1363 (7)	0.1479 (6)	0.4494 (8)
Cr(2)	−0.2573 (1)	0.2455 (1)	0.1540 (1)	C5A	0.1946 (8)	0.1573 (6)	0.5903 (8)
O(1)	−0.1481 (4)	0.2334 (4)	0.3135 (5)	C1B	0.3299 (7)	0.3739 (7)	0.0646 (10)
O(2)	−0.0956 (5)	0.2729 (4)	0.0869 (5)	C2B	0.2322 (7)	0.3781 (6)	0.1584 (8)
O2A	0.0102 (5)	0.1051 (4)	0.1809 (5)	C3B	0.2152 (8)	0.4698 (6)	0.2330 (9)
O4A	0.1055 (5)	0.2343 (4)	0.4164 (5)	C4B	0.1134 (8)	0.4821 (6)	0.3062 (8)
O2B	0.1659 (5)	0.2868 (4)	0.1577 (5)	C5B	0.1023 (8)	0.5894 (6)	0.3820 (10)
O4B	0.0283 (5)	0.4093 (4)	0.3185 (5)	C1C	−0.4539 (9)	0.2289 (9)	−0.2334 (10)
O2C	−0.3505 (5)	0.2612 (4)	−0.0172 (6)	C2C	−0.3882 (7)	0.1865 (7)	−0.1120 (9)
O4C	−0.2698 (5)	0.0930 (4)	0.1005 (5)	C3C	−0.3787 (8)	0.0840 (7)	−0.1103 (9)
O2D	−0.2535 (5)	0.3980 (4)	0.2093 (6)	C4C	−0.3228 (7)	0.0401 (6)	−0.0044 (8)
O4D	−0.4098 (5)	0.2180 (4)	0.2405 (6)	C5C	−0.3185 (8)	−0.0788 (7)	−0.0165 (11)
C(1)	−0.1807 (8)	0.1599 (6)	0.4047 (9)	C1D	−0.2734 (9)	0.5572 (7)	0.3417 (10)
C(2)	−0.0696 (8)	0.3479 (7)	−0.0024 (9)	C2D	−0.3089 (8)	0.4424 (6)	0.2970 (9)
C1A	0.0382 (8)	−0.0757 (6)	0.1590 (8)	C3D	−0.4026 (8)	0.3893 (7)	0.3608 (9)
C2A	0.0582 (7)	0.0334 (6)	0.2406 (8)	C4D	−0.4476 (7)	0.2844 (7)	0.3271 (8)
C3A	0.1212 (7)	0.0529 (6)	0.3674 (8)	C5D	−0.5568 (8)	0.2289 (8)	0.3906 (10)

Table III. Principal Interatomic Distances (Å) in $[(acac)_2Cr(OCH_3)]_2$

Cr(1)–O(1)	1.967 (4)	Cr(2)–O(1)	1.951 (4)
Cr(1)–O(2)	1.973 (4)	Cr(2)–O(2)	1.957 (5)
Cr(1)–O2A	1.970 (4)	Cr(2)–O2C	1.969 (5)
Cr(1)–O4A	1.970 (4)	Cr(2)–O4C	1.945 (4)
Cr(1)–O2B	1.966 (5)	Cr(2)–O2D	1.956 (5)
Cr(1)–O4B	1.977 (4)	Cr(2)–O4D	1.965 (5)
O(1)–C(1)	1.424 (7)	O(2)–C(2)	1.409 (7)
C1A–C2A	1.515 (8)	C1C–C2C	1.550 (11)
C2A–O2A	1.290 (7)	C2C–O2C	1.271 (8)
C2A–C3A	1.379 (8)	C2C–C3C	1.328 (10)
C3A–C4A	1.370 (8)	C3C–C4C	1.391 (10)
C4A–O4A	1.264 (7)	C4C–O4C	1.242 (7)
C4A–C5A	1.490 (8)	C4C–C5C	1.517 (9)
C1B–C2B	1.490 (9)	C1D–C2D	1.476 (9)
C2B–O2B	1.296 (7)	C2D–O2D	1.238 (8)
C2B–C3B	1.358 (9)	C2D–C3D	1.405 (10)
C3B–C4B	1.405 (9)	C3D–C4D	1.363 (10)
C4B–O4B	1.258 (7)	C4D–O4D	1.277 (8)
C4B–C5B	1.514 (9)	C4D–C5D	1.542 (10)
Cr(1)–Cr(2)	3.028 (2)		

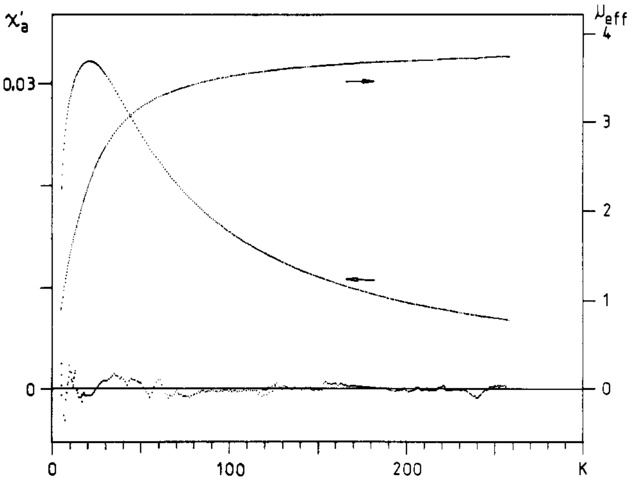

Figure 2. Temperature dependence of the magnetic susceptibility (left scale, cgs units) and effective magnetic moment (right scale, Bohr magnetons) of $[(acac)_2Cr(OCH_3)]_2$. The lower distribution of dots indicates the values of $(\chi_{obsd} - \chi_{calcd}) \times 100$, where χ_{calcd} is obtained from the parameters of model 3 in Table VI.

Cr(III) alkoxo-bridged dimers,[21,22] and the two independent Cr–O–Cr bridging angles (ϕ) are 100.8 (2) and 101.2 (2)° with a mean value of 101.0 (3)°. As is also shown in Table V, these *R* and ϕ values are again comparable to those in the analogues studied earlier.

Although the actual geometry of the dimer is C_1 (1), it approximates D_2 (222) rather than the equally possible C_{2h} (2/*m*). Thus, as is seen in Figure 1, the isomer studied here is the racemic form while the other alkoxo-bridged dimers studied were isolated as the centrosymmetric meso form. It is noteworthy that most of the dihydroxo-bridged chromium(III) dimers studied crystallographically have also been meso,[3,10,13,14] although the 1,10-phenanthroline complex $[Cr(phen)_2OH]_2^{2+}$ is only isolated as the racemic isomer.[23,24]

Table IV. Principal Bond Angles (Deg) in $[(acac)_2Cr(OCH_3)]_2$

O(1)–Cr(1)–O(2)	78.6 (2)	O(1)–Cr(2)–O(2)	79.4 (2)
O(1)–Cr(1)–O2A	92.4 (2)	O(1)–Cr(2)–O2C	173.6 (2)
O(1)–Cr(1)–O4A	94.0 (2)	O(1)–Cr(3)–O4C	90.3 (2)
O(1)–Cr(1)–O2B	172.0 (2)	O(1)–Cr(2)–O2D	90.9 (2)
O(1)–Cr(1)–O4B	89.3 (2)	O(1)–Cr(2)–O4D	94.5 (2)
O(2)–Cr(1)–O2A	89.6 (2)	O(2)–Cr(2)–O2C	94.2 (2)
O(2)–Cr(1)–O4A	172.4 (2)	O(2)–Cr(2)–O4C	92.8 (2)
O(2)–Cr(1)–O2B	93.5 (2)	O(2)–Cr(2)–O2D	90.0 (2)
O(2)–Cr(1)–O4B	93.2 (2)	O(2)–Cr(2)–O4D	173.8 (2)
O2A–Cr(1)–O4A	89.4 (2)	O2C–Cr(2)–O4C	90.1 (2)
O2A–Cr(1)–O2B	88.8 (2)	O2C–Cr(2)–O2D	89.1 (2)
O2A–Cr(1)–O4B	176.9 (2)	O2C–Cr(2)–O4D	92.0 (2)
O4A–Cr(1)–O2B	94.0 (2)	O4C–Cr(2)–O2D	177.1 (2)
O4A–Cr(1)–O4B	87.9 (2)	O4C–Cr(2)–O4D	87.8 (2)
O2B–Cr(1)–O4B	89.9 (2)	O2D–Cr(2)–O4D	89.5 (2)
Cr(1)–O(1)–Cr(2)	101.2 (2)	Cr(1)–O(2)–Cr(2)	100.8 (2)
Cr(1)–O(1)–C(1)	124.7 (4)	Cr(1)–O(2)–C(2)	124.5 (4)
Cr(2)–O(1)–C(1)	121.9 (4)	Cr(2)–O(2)–C(2)	122.9 (4)
Cr(1)–O2A–C2A	128.1 (4)	Cr(2)–O2C–C2C	125.5 (5)
Cr(1)–O4A–C4A	127.6 (4)	Cr(2)–O4C–C4C	128.2 (5)
Cr(1)–O2B–C2B	127.4 (5)	Cr(2)–O2D–C2D	128.4 (6)
Cr(1)–O4B–C4B	127.3 (5)	Cr(2)–O4D–C4D	124.4 (5)
O2A–C2A–C1A	113.9 (6)	O2C–C2C–C1C	111.2 (8)
O2A–C2A–C3A	123.7 (6)	O2C–C2C–C3C	126.5 (8)
C1A–C2A–C3A	122.4 (6)	C1C–C2C–C3C	122.2 (8)
C2A–C3A–C4A	125.3 (6)	C2C–C3C–C4C	125.5 (8)
O4A–C4A–C3A	125.6 (7)	O4C–C4C–C3C	124.1 (7)
O4A–C4A–C5A	113.6 (6)	O4C–C4C–C5C	116.0 (8)
C3A–C4A–C5A	120.9 (7)	C3C–C4C–C5C	119.9 (7)
O2B–C2B–C1B	112.8 (7)	O2D–C2D–C1D	119.2 (9)
O2B–C2B–C3B	124.9 (7)	O2D–C2D–C3D	123.7 (8)
C1B–C2B–C3B	122.2 (7)	C1D–C2D–C3D	117.1 (8)
C2B–C3B–C4B	124.5 (7)	C2D–C3D–C4D	123.6 (7)
O4B–C4B–C3B	125.5 (7)	O4D–C4D–C3D	127.1 (8)
O4B–C4B–C5B	114.8 (7)	O4D–C4D–C5D	109.7 (8)
C3B–C4B–C5B	119.7 (7)	C3D–C4D–C5D	123.2 (8)

The four independent acac ligands are approximately planar, the greatest deviations of any atom from the least-squares planes through the five central atoms being 0.034 (8), 0.043 (8), 0.024 (8), and 0.016 (9) Å for the A, B, C, and D ligands, respectively. The geometry of the acac ligand is substantially

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Table V. Structural and Magnetic Properties of Bis(μ-alkoxo) Chromium(III) Dimers

complex	R, Å	ϕ, deg	θ, deg	J_{obsd},[a] cm^{-1}	J_{calcd},[b] cm^{-1}	ref
$[Cr(3\text{-}Cl\text{-}acac)_2OMe]_2$	1.959 (2)	101.1 (1)	24.4	9.8	17.6	21
$[Cr(3\text{-}Br\text{-}acac)_2OMe]_2$	1.962 (4)	101.5 (2)	25.7	8.5	16.2	22
$[Cr(3\text{-}Br\text{-}acac)_2OEt]_2$	1.951 (6)	101.8 (3)	18.3	17.9	22.3	22
$[Cr(acac)_2OMe]_2$[c]	1.962 (9)	101.0 (3)	29.8	9.8	15.2	this work

[a] Since various magnetic models can be used, J here refers to the energy of the triplet state as calculated from the observed susceptibility data. [b] Calculated from the expression in ref 8. [c] The isomer studied here is the racemic form, while the other complexes studied were meso forms.

similar to that seen in a variety of metal complexes of acac.[25] The Cr–O(ligand) bond lengths are in the range 1.945 (4)–1.977 (4) Å with an average value of 1.965 (10) Å, which is again unremarkable. The four chelating O–Cr–O angles are in the very narrow range of 89.4 (2)–90.1 (2)°.

Magnetic Properties. The temperature dependence of the average magnetic susceptibility of polycrystalline $[(acac)_2Cr(OCH_3)]_2$ is displayed as Figure 2. The susceptibility data were fitted to the generalized expression (1), where

$$\chi'_A = \frac{-N}{H}\left[\frac{\sum_i \frac{\partial E_i}{\partial H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}\right] \qquad (1)$$

H is the applied magnetic field strength, χ'_A is the observed susceptibility per chromium atom, the quantities E_i are the energies of the 16 components of the ground-state manifold, and the summations are taken over the 16 components. The data were fitted by using three different models (of varying levels of sophistication) for the exchange Hamiltonian.[2,7,9] In model 1 we used the simple Heisenberg Hamiltonian given by expression 2, where S' is $(S_1 + S_2)$ and the only variable

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

other than g is the exchange parameter J; this model gives rise to triplet, quintet, and septet energies of J, $3J$, and $6J$, respectively, relative to a singlet-state energy of zero. In model 2, the Hamiltonian was expanded to include a second-order (biquadratic) exchange term as in expression 3, where there

$$H = J\vec{S}_1\cdot\vec{S}_2 + j(\vec{S}_1\cdot\vec{S}_2)^2 + g\beta M_{S'} \qquad (3)$$

are now two variable exchange parameters, J and j. The triplet, quintet, and septet energies in this approximation are given by $(J + 6.5j)$, $(3J + 13.5j)$, and $(6J + 9.0j)$, respectively. Finally, in model 3, we used the generalized Hamiltonian given in expression 4, where the energies $E(S')$ of the triplet ($S' =$

$$H = E(S') + g\beta M_{S'} \qquad (4)$$

1), quintet ($S' = 2$), and septet ($S' = 3$) states are independent. Here, therefore, there are three variable exchange parameters, namely $E(1)$, $E(2)$, and $E(3)$. All three models assume the absence of any zero-field splitting term and an isotropic Zeeman effect. The data were fitted in each case by minimization of the function[2,9]

$$\sum_i(\chi'_i(\text{obsd}) - \chi'_A)^2/[\sigma^2(\chi) + (\partial\chi/\partial T)^2(\sigma^2(T))]$$

Table VI. Parameters Derived from Magnetic Susceptibility Data

parameter	model 1[a]	model 2	model 3
J, cm^{-1}	9.40 (2)	9.00 (1)	
j, cm^{-1}		0.145 (3)	
$E(1)$, cm^{-1}	9.40 (2)[b]	9.94 (1)[b]	9.83 (6)
$E(2)$, cm^{-1}	28.20 (6)[b]	28.96 (3)[b]	28.90 (4)
$E(3)$, cm^{-1}	56.4 (1)[b]	55.31 (6)[b]	55.1 (1)
g	1.991 (1)	1.9764 (6)	1.9758 (7)
var/f	5.09	1.06	1.05
% monomer	0.0070 (2)	0.0143 (2)	0.0131 (7)

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

In all cases, in addition to the parameters noted, we varied a temperature-independent susceptibility term and a term which allowed for the presence of a small quantity of monomeric impurity.

The results of the data fitting to these three models are displayed in Table VI. It is apparent that while all three models lead to approximately the same derived or calculated magnetic parmeters, the fit to model 1 is significantly inferior to that obtained with model 2; it would appear, however, that inclusion of an additional variable (in model 3) is not accompanied by any further improvement, since the variance per degree of freedom (var/f) is lowered by less than 1%. However, use of either of these models leads to the conclusion that in the present complex the triplet state lies approximately 9.8 (1) cm^{-1} higher in energy than the ground-state singlet.

The bridging geometry and magnetic properties of racemic $[(acac)_2Cr(OCH_3)]_2$ determined in the present study are compared with those found earlier for other bis(μ-alkoxo) dimers of chromium(III)[21,22] in Table V. It is apparent from this table that the structural and magnetic properties in the present complex are very similar to those observed in the other methoxo-bridged dimers but differ significantly in θ and (subsequently) in J from those of the ethoxo-bridged species. It is noteworthy that the trends in the observed J values in Table V are entirely consistent with those calculated from the Glerup–Hodgson–Pedersen (GHP) model[8] for the magnetism of chromium(III) dimers.

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Supplementary Material Available: Listings of H atom coordinates, anisotropic librational parameters, and observed and calculated structure amplitudes (17 pages). Ordering information is given on any current masthead page.

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