Inorganic Chemistry, Vol. 15, No. 5, 1976 **1179**

Contribution from the Department of Chemistry,
University of North Carolina, Chapel Hill, North Carolina 27514

Synthesis and Structural and Magnetic Characterization of the Alkoxo-Bridged Chromium(III) Dimer Di-μ-methoxo-bis[bis(3-chloro-2,4-pentanedionato)chromium(III)]

EVA DIXON ESTES, RAYMOND P. SCARINGE, WILLIAM E. HATFIELD, and DEREK J. HODGSON*

Received October 31, 1975

AIC50784J

The complex di-μ-methoxo-bis[bis(3-chloro-2,4-pentanedionato)chromium(III)], $[Cr(3\text{-}Cl(acac))_2OCH_3]_2$, has been synthesized and its crystal structure has been determined from three-dimensional counter x-ray data. The material crystallizes in the monoclinic space group $P2_1/c$ with two dimeric formula units in a cell of dimensions a = 7.794 (6) Å, b = 18.189 (18) Å, c = 11.232 (8) Å, β = 112.82 (5)°. Least-squares refinement of 3092 independent data has led to a final R factor (on F) of 0.045. The complex consists of two chromium(III) ions which are symmetrically bridged by two methoxide groups, the remaining coordination sites being occupied by the oxygen atoms of two bidentate 3-Cl(acac) ligands. The coordination around each chromium center is roughly octahedral; the average Cr–O(ligand) bond length is 1.957 (5) Å while the Cr–Cr separation is 3.025 (2) Å and the Cr–O–Cr bridging angle is 101.07 (9)°. The 3–Cl(acac) ligands are approximately planar. The magnetic susceptibility of a powdered sample of the complex has been examined in the temperature range 4–78 K. The dimer exhibits an antiferromagnetic exchange interaction, with the best fit to the Van Vleck equation including biquadratic exchange yielding $2J = -7.34$ cm^{-1} and $j = +0.38$ cm^{-1} with $\langle g \rangle = 1.901$. These data lead to a singlet–triplet splitting of -9.82 cm^{-1}.

Introduction

The study of the magnetic interactions in hydroxo- and alkoxo-bridged dimers of copper(II) and chromium(III) has received extensive recent attention.[1,2] It has been demonstrated[3-6] for the simplest case, i.e. the dihydroxo-bridged dimers of copper(II), that the magnitude and sign of the exchange integral J are principally determined by the value of the Cu–O–Cu bridging angle ϕ, although other authors[7,8] have noted that distortions from planar geometry at the metal center also influence the magnitude of J.

For the analogous chromium(III) complexes the magnetic exchange is greatly complicated by the presence of more than one unpaired electron at each metal center, which leads to unpaired spin in the π system of the dimer in addition to that in the σ system. There is, however, one simplifying feature in that the geometry at chromium in all complexes of the types $[CrL_2OH]_2^{n+}$ and $[CrL_2OR]_2^{n+}$ (where L is a bidentate ligand) is pseudooctahedral and, therefore, approximately constant throughout the series. Hence, the probable influence[7] of changes in the geometry at the metal on the magnetic exchange does not intrude here.

We have, therefore, initiated studies on the structural and magnetic properties of chromium(III) dimers of these types and have reported elsewhere[2,9-12] the results of our studies of several hydroxo-bridged species. We here report the synthesis, structure, and magnetic properties of the first completely characterized dialkoxo-bridged dimer of chromium, the complex being di-μ-methoxo-bis[bis(3-chloro-2,4-pentanedionato)chromium(III)].

Experimental Section

Synthesis. A saturated solution of the complex[13] tris(3-chloro-2,4-pentanedionato)chromium(III) in methanol was refluxed for several days. The fine green precipitate which formed was removed by filtration and recrystallized twice from benzene–heptane solutions, yielding the green desired complex, di-μ-methoxo-bis[bis(3-chloro-2,4-pentanedionato)chromium(III)]. This procedure is entirely analogous to that used by Kasuga et al.[14] for the synthesis of the 3-bromo analogue. Anal. Calcd for $C_{22}H_{30}Cl_4Cr_2O_{10}$: C, 37.71; H, 4.29; Cl, 20.29. Found: C, 37.96; H, 4.12; Cl, 20.46. 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 10000 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 to the monoclinic system. The observed systematic absences are $h0l$ for l odd and $0k0$ for k odd, which suggests that the space group is $P2_1/c$ (C_{2h}^5). The cell constants, obtained by least-squares method, are a = 7.794 (6), Å, b = 18.189 (18) Å, c = 11.232 (8) Å, and β = 112.82 (5)°. The observations were made at 20.5 °C with the wavelength assumed as λ(Mo Kα_1) = 0.7093 Å. A density of 1.585 g cm^{-3} calculated for two dimeric formula units in the cell compares well with a value of 1.57 (3) g cm^{-3} observed by flotation in aqueous zinc bromide solution. Hence, in space $P2_1/c$, the dimer is constrained to lie on a crystallographic inversion center.

Diffraction data were collected from an irregular shaped crystal with faces (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, (011), $(0\bar{1}\bar{1})$, $(01\bar{1})$, and $(0\bar{1}1)$. The separations between opposite pairs of faces were as follows: (100) and $(\bar{1}00)$, 0.092 cm; (010) and $(0\bar{1}0)$, 0.030 cm; (011) and $(0\bar{1}\bar{1})$, 0.041 cm; $(01\bar{1})$ and $(0\bar{1}1)$, 0.002 cm. The crystal was mounted on a glass fiber normal to the (100) planes, and in this orientation intensity data were collected on Picker four-circle automatic diffractometer equipped with a graphite monochromator and using Mo Kα radiation. The mosaicity of the crystal was examined by means of the narrow-source, open counter ω-scan technique[17] and was judged to be acceptable.

Twelve reflections, accurately centered through a narrow vertical slit at a takeoff angle of 1.0°, formed the basis for the least-squares refinement of cell parameters and orientation using the logic documented by Busing and Levy[18] for the PDP-8/L computer.

Intensity data were collected at a takeoff angle of 1.3°; at this angle the intensity of a typical reflection was approximately 85% of maximum as a function of takeoff angle. The receiving aperture was 5.0 mm high by 5.0 mm wide and was positioned 32.0 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 1.0°/min. Allowance was made for the presence of both Kα_1 and Kα_2 radiations, the peaks being scanned from $-0.75°$ in 2θ below the calculated Kα_1 peak position to $+0.75°$ in 2θ above the calculated Kα_2 position. Stationary-counter, stationary-crystal background counts of 10 s were taken at each end of the scan. The pulse height analyzer was set for approximately a 90% window, centered on the Mo Kα peak.

A unique data set having $2° \leq 2\theta \leq 58°$ was gathered; a total of 3980 intensities were recorded. The intensities of three standard reflections, measured after every 100 reflections, declined steadily throughout the run so that the average intensity had dropped by approximately 8% by the end of the data collection. This decline in intensity as a function of exposure time was allowed for in the structure refinement.[19]

Data processing was carried out as described by Corfield et al.[20] After correction for background, the intensities was assigned standard

Table I. Positional Parameters ($\times 10^4$) for $[Cr(3\text{-}Cl(acac))_2OCH_3]_2$

Atom	x	y	z
Cr	1067 (0)	224 (0)	1390 (0)
Cl1	5108 (1)	2498 (1)	2367 (1)
Cl2	465 (2)	−1200 (1)	5071 (1)
O1	1212 (3)	1137 (1)	2336 (2)
O2	3209 (2)	554 (1)	1024 (2)
O3	−984 (2)	−87 (1)	1867 (2)
O4	2784 (2)	−290 (1)	2922 (2)
OB	713 (2)	−623 (1)	242 (2)
C1A	1901 (8)	2323 (2)	3200 (5)
C2A	2280 (4)	1690 (1)	2481 (2)
C3A	3702 (4)	1713 (1)	2017 (3)
C4A	4121 (3)	1150 (1)	1319 (2)
C5A	5701 (4)	1220 (2)	873 (4)
C1B	−2820 (5)	−539 (2)	2930 (4)
C2B	−967 (4)	−436 (1)	2839 (2)
C3B	680 (4)	−725 (2)	3785 (2)
C4B	2454 (3)	−646 (1)	3778 (2)
C5B	4130 (5)	−994 (2)	4813 (3)
CME	839 (5)	−1361 (2)	629 (3)
H1A[a]	179 (8)	274 (4)	274 (5)
H2A	239 (9)	235 (4)	406 (8)
H3A	80 (10)	230 (4)	315 (6)
H4A	−468 (13)	167 (5)	1 (8)
H5A	589 (6)	75 (3)	50 (4)
H6A	695 (8)	120 (3)	168 (5)
H1B	−376 (6)	−28 (2)	208 (4)
H2B	304 (7)	398 (3)	173 (4)
H3B	312 (12)	465 (5)	156 (8)
H4B	−427 (8)	75 (3)	442 (6)
H5B	393 (7)	−146 (4)	482 (5)
H6B	474 (8)	407 (3)	45 (6)
HM1	−184 (8)	362 (3)	384 (5)
HM2	−79 (6)	169 (2)	6 (4)
HM3	40 (8)	348 (3)	435 (6)

[a] Hydrogen atom parameters are $\times 10^3$.

deviations according to the formula[21]

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$$

and the value of p was selected as 0.050. The values of I and $\sigma(I)$ were corrected for Lorentz–polarization effects and for absorption factors. The absorption coefficent for this compound for Mo Kα radiation is 11.85 cm^{-1}, and for the crystal chosen the transmission coefficients[22] evaluated by numerical integration ranged from 0.637 to 0.741. Of the 3980 data collected, 3092 were greater than 3 times their estimated standard deviations; only these data were used in the subsequent structure analysis and refinement.

Solution and Refinement of the Structure. The position of the one independent chromium atom was determined from a three-dimensional Patterson function, and two cycles of least-squares refinement of this position were run. All least-squares refinements in this analysis were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o^2/\sigma^2(F_o^2)$. In calculations of F_c, the atomic scattering factors for Cr and Cl were from Cromer and Waber,[23] those for O and C from Ibers,[24] and those for H from Stewart, Davidson, and Simpson.[25] The effects of the anomalous dispersion of Cr and Cl were included in the calculation of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer and Liberman.[26] The remaining nonhydrogen atoms were located in subsequent difference Fourier maps. Isotropic least-squares refinement of these 19 atoms led to values of the conventional agreement factors

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$
$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$$

of 0.139 and 0.228, respectively. Anisotropic refinement of these atoms gave $R_1 = 0.073$ and $R_2 = 0.125$. The positions of 14 of the 15 hydrogen atoms were located in subsequent difference Fourier syntheses. The remaining hydrogen atom was placed in the position calculated on the basis of tetrahedral geometry at the carbon atom with a C–H distance 0.95 Å,[27] and a least-squares calculation in which all hydrogen atoms were refined isotropically while nonhydrogen atoms were refined anisotropically gave values of R_1 and R_2 of 0.045 and 0.058, respectively.

The value of R_2 showed some dependence on sin θ, and so the weighting scheme was modified by dividing the weights w for reflections with $2° \leq 2\theta \leq 20°$ by 1.80. In most cases in which we have used our graphite monochromator a similar correction has been necessary. The final values of F_o and F_c suggested that no correction for secondary extinction was necessary. In the final cycle of least-squares refinement no parameter underwent a shift in excess of 10% of its estimated standard deviation, which is taken as evidence that the refinement had converged. A final difference Fourier synthesis was featureless. The final values of R_1 and R_2 were 0.045 and 0.056, respectively.

The positional and thermal parameters derived from the final least-squares cycle are given in Tables I and II. A compilation of observed and calculated structure amplitudes is available.[28]

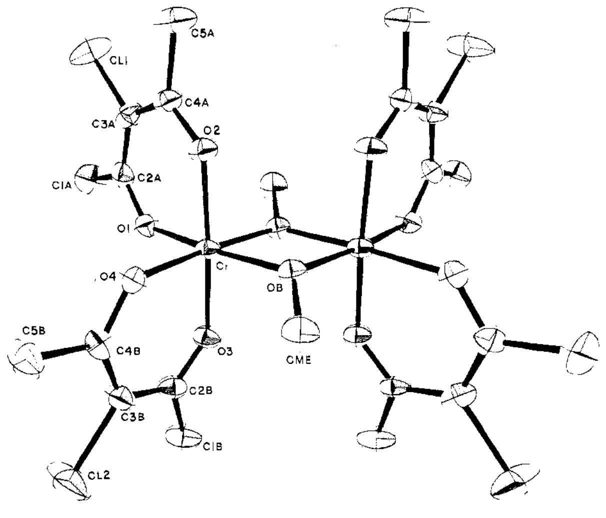

Figure 1. View of the dimeric $[Cr(3\text{-}Cl(acac))_2OCH_3]_2$ molecule. Hydrogen atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by the inversion center.

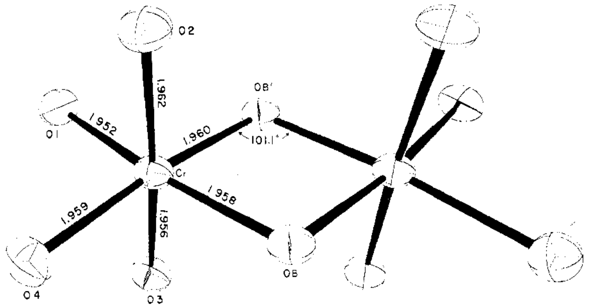

Figure 2. Coordination around the chromium centers in $[Cr(3\text{-}Cl(acac))_2OCH_3]_2$.

Description of the Structure

The structure consists of dimeric $[Cr(3\text{-}Cl(acac))_2OCH_3]_2$ (3-Cl(acac) = 3-chloro-2,4-pentanedione) units which are well-separated from one another. The geometry of the dimer is shown in Figure 1, and the inner coordination sphere around the chromium atoms is shown in Figure 2.

The geometry around the chromium atoms is roughly octahedral with two cis 3-chloro-2,4-pentanedione ligands and two cis methoxy groups occupying the coordination sites. The bond lengths and angles in the dimer are given in Tables III and IV. The Cr–O–Cr–O bridging unit is strictly planar, there being a crystallographic inversion center in the middle of the dimer. The methoxy carbon atom CME is considerably out of this plane, its deviation from the plane being 0.58 Å. For trigonal geometry at oxygen, this value would be zero, while for tetrahedral geometry it would be 1.15 Å. Hence,

Table II. Thermal Parameters (Å^2) for $[Cr(3\text{-}Cl(acac))_2OCH_3]_2$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	229 (2)	288 (2)	322 (2)	5 (1)	116 (1)	48 (1)
Cl1	720 (5)	470 (4)	1262 (9)	−282 (4)	401 (6)	−119 (5)
Cl2	788 (6)	1227 (9)	691 (5)	24 (6)	410 (5)	496 (6)
O1	420 (9)	372 (9)	433 (9)	−53 (7)	210 (8)	−45 (7)
O2	283 (8)	396 (9)	430 (9)	−34 (7)	170 (7)	23 (7)
O3	278 (8)	413 (9)	430 (9)	16 (7)	180 (7)	84 (7)
O4	263 (7)	483 (10)	343 (8)	20 (7)	100 (6)	98 (7)
OB	290 (7)	248 (7)	349 (7)	40 (5)	113 (6)	61 (6)
C1A	909 (30)	435 (17)	774 (25)	−70 (18)	446 (23)	−154 (18)
C2A	446 (13)	342 (12)	365 (12)	1 (10)	109 (10)	24 (9)
C3A	377 (12)	320 (12)	526 (14)	−67 (10)	109 (11)	52 (11)
C4A	235 (10)	378 (12)	420 (12)	−25 (9)	87 (9)	119 (10)
C5A	359 (14)	572 (19)	817 (22)	−7 (13)	318 (15)	159 (17)
C1B	449 (16)	628 (20)	774 (22)	−16 (14)	420 (16)	111 (17)
C2B	369 (12)	348 (11)	446 (12)	−12 (9)	247 (10)	12 (10)
C3B	457 (13)	491 (14)	395 (12)	−17 (12)	224 (11)	126 (11)
C4B	402 (12)	393 (12)	313 (10)	38 (10)	125 (9)	49 (9)
C5B	466 (16)	648 (20)	406 (14)	123 (14)	108 (12)	188 (14)
CME	624 (19)	293 (12)	483 (15)	92 (12)	155 (14)	133 (11)

Atom	U	Atom	U	Atom	U
H1A	11 (2)	H6A	10 (1)	H5B	10 (2)
H2A	14 (3)	H1B	7 (1)	H6B	11 (2)
H3A	13 (2)	H2B	8 (1)	HM1	10 (2)
H4A	19 (3)	H3B	17 (3)	HM2	8 (1)
H5A	9 (1)	H4B	11 (2)	HM3	11 (2)

[a] Anisotropic parameters are ×10^4; isotropic parameters, ×10^2. 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) in $[Cr(3\text{-}Cl(acac))_2OCH_3]_2$

Cr–Cr′	3.025 (2)	O2–C4A	1.269 (3)	C1B–C2B	1.499 (4)
Cr–OB	1.958 (2)	O3–C2B	1.258 (3)	C2B–C3B	1.412 (4)
Cr–OB′	1.960 (2)	O4–C4B	1.265 (3)	C3B–C4B	1.393 (4)
Cr–O1	1.952 (2)	C1A–C2A	1.500 (5)	C4B–C5B	1.510 (4)
Cr–O2	1.962 (2)	C2A–C3A	1.396 (4)	C3A–Cl1	1.749 (3)
Cr–O3	1.956 (2)	C3A–C4A	1.403 (4)	C3B–Cl2	1.747 (3)
Cr–O4	1.959 (2)	C4A–C5A	1.504 (4)	OB–CME	1.403 (3)
O1–C2A	1.275 (3)				

Table IV. Interatomic Angles (deg) in $[Cr(3\text{-}Cl(acac))_2OCH_3]_2$

Cr–OB–Cr′	101.07 (9)	O1–C2A–C3A	123.3 (2)
Cr–OB–CME	125.0 (2)	C1A–C2A–C3A	121.9 (3)
Cr′–OB–CME	125.7 (2)	C2A–C3A–C4A	125.3 (2)
OB–Cr–O1	172.6 (1)	C2A–C3A–Cl1	117.3 (2)
OB–Cr–O2	90.94 (8)	Cl1–C3A–C4A	117.4 (2)
OB–Cr–O3	91.84 (8)	C3A–C4A–O2	122.8 (2)
OB–Cr–O4	94.4 (1)	C3A–C4A–C5A	121.4 (2)
OB–Cr–OB′	78.93 (9)	C5A–C4A–O2	115.7 (3)
O1–Cr–O2	88.81 (8)	C4A–O2–Cr	130.0 (2)
O1–Cr–O3	88.72 (9)	Cr–O3–C2B	130.4 (2)
O1–Cr–O4	93.0 (1)	O3–C2B–C1B	115.8 (2)
O1–Cr–OB′	93.68 (9)	O3–C2B–C3B	122.8 (2)
O2–Cr–O3	176.4 (2)	C1B–C2B–C3B	121.4 (2)
O2–Cr–O4	89.05 (9)	C2B–C3B–C4B	124.9 (2)
O2–Cr–OB′	92.37 (9)	C2B–C3B–Cl2	117.1 (2)
O3–Cr–O4	88.52 (9)	Cl2–C3B–C4B	118.0 (2)
O3–Cr–OB′	90.35 (9)	C3B–C4B–O4	123.5 (2)
O4–Cr–OB′	173.2 (1)	C3B–C4B–C5B	121.1 (2)
Cr–O1–C2A	129.7 (2)	C5B–C4B–O4	115.4 (2)
O1–C2A–C1A	114.8 (3)	C4B–O4–Cr	129.8 (2)

in this complex the hybridization at the bridge cannot be described as either sp^2 or sp^3. The two independent bridging Cr–O bond distances are 1.960 (2) and 1.958 (2) Å which shows that the oxygen atoms are symmetrically bound to the two Cr atoms. These values are longer than those[11,12] in $[Cr(phen)_2OH]_2I_4{\cdot}4H_2O$ and $[Cr(phen)_2OH]_2Cl_4{\cdot}6H_2O$ and similar to those[10] in $[Cr(gly)_2OH]_2$. The Cr–Cr separation of 3.025 Å is longer than those found in these dihydroxo-bridged chromium dimers; however, the bridging Cr–O–Cr angle of 101.07 (9)° is intermediate between the values of 98.2 (2), 102.1 (3), and 102.7 (5)° found for the glycinato[10] and the iodide[12] and chloride[11] salts of the phenanthroline complex, respectively.

Although the actual geometry of the dimer is $C_i(\bar{1})$, it approximates C_{2h} $(2/m)$, rather than the apparently equally possible D_2 (222). In this respect it is similar to all related hydroxo-bridged dimers except the phenanthroline complexes; in these latter complexes, as has been noted elsewhere,[2] the C_{2h} conformer is unobtainable because of interligand H–H contacts.

The 3-chloro-2,4-pentanedionato ligands are nearly planar, with the greatest deviation of any atom from the best least-squares plane through the ligand atoms and the chromium atom being 0.04 Å for both the A ring and the B ring. The geometry of the ligand is similar to that found for the parent 2,4-pentanedionato ligand in variety of metal complexes.[29-31] The average O···O "bite" of 2.736 Å found here is slightly smaller than the values of 2.751 and 2.786 Å found in the manganese(III)[29] and chromium(III)[30] complexes $M(acac)_3$. The average Cr–O bond length of 1.957 (4) Å is not significantly longer than the values of 1.952 (8) and 1.952 (10) Å found in chromium(III) complexes of 2,4-pentanedione.[30,31] In the complex $Cr(3\text{-}Cl(acac))_3$, which is the precursor to the dimeric material studied here, however, it is apparent that the Cr–O bonds are weaker than in $Cr(acac)_3$ since, in the former, it is possible to remove one ligand in alcoholic medium to form the present dimer whereas $Cr(acac)_3$ is stable to refluxing in alcohol.[14] The chelating O–Cr–O angles of 88.5 and 88.7° are acute, whereas in reported[30,31] chromium(III) complexes of acac they are obtuse.

Discussion

The plot of molar magnetic susceptibility as a function of temperature exhibits a maximum at about 20 K, indicating antiferromagnetic coupling. The data were fitted to the expression

$$\chi_m = \frac{Ng^2\beta^2}{kT} \times \left\{ \frac{2e^{(2J-6.5j)/kT} + 10e^{(6J-13.5j)/kT} + 28e^{(12J-9j)/kT}}{1 + 3e^{(2J-6.5j)/kT} + 5e^{(6J-13.5j)/kT} + 7e^{(12J-9j)/kT}} \right\} \quad (1)$$

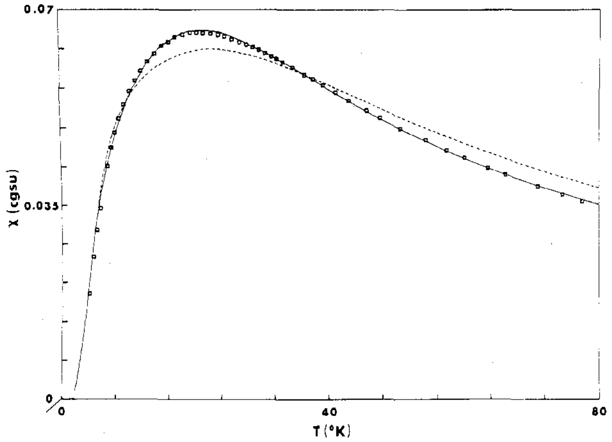

Figure 3. Temperature dependence of the magnetic susceptibility of $[Cr(3\text{-}Cl(acac))_2OCH_3]_2$. The experimental data are shown as squares. The dashed line represents the best fit to the dimer ($S = {}^3/_2, {}^3/_2$) equation in the absence of biquadratic exchange. The solid line represents the best fit to the dimer equation including biquadratic exchange.

where J and j are defined by the exchange Hamiltonian

$$\mathcal{H} = -2J\vec{S}_1\cdot\vec{S}_2 - j(\vec{S}_1\cdot\vec{S}_2)^2 \qquad (2)$$

The data were fitted using a general nonlinear least-squares program written in our laboratory, the function minimized being $F = \sum_i w_i(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2$ with the weights being assigned $w_i = 1/\chi_i^{\text{obsd}}$. The best fit to the data, holding $j = 0$ and letting g and J vary, is displayed in Figure 3, where the final values were $g = 2.05$ (1) and $J = -5.04$ (6) cm^{-1}. The fit is at best unimpressive but this is not surprising since it has often been found necessary to include a term biquadratic in spin to obtain good fits for dimeric Cr(III) complexes.[7,32,33] The best fit, with the inclusion of the biquadratic exchange parameter, j, yielded $g = 1.901$ (4), $J = -3.67$ (3) cm^{-1}, and $j = 0.381$ (4) cm^{-1}, where the quantities in parentheses are the estimated standard deviations of the respective parameters from the last cycle of least-squares for which there were 50 observations and three variables. These data led to a singlet–triplet splitting of -9.82 cm^{-1}. The theoretical susceptibilities using these values for g, J, and j are also presented in Figure 3, and it can be seen that the comparison with experiment is greatly improved. The positive sign obtained for j in this study is significant in that it supports Kittel's exchange striction mechanism.[34] This point is discussed in some detail elsewhere.[35]

Registry No. $[Cr(3\text{-}Cl(acac))_2OCH_3]_2$, 58512-49-5.

Supplementary Material Available: Listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. J. Hodgson, *Prog. Inorg. Chem.*, **19**, 173 (1975), and references therein.
(2) D. J. Hodgson in "Extended Interactions between Metal Ions", L. V. Interrante, Ed., American Chemical Society, Washington, D.C., 1974, Chapter 9.
(3) D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **11**, 2216 (1972).
(4) 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).
(5) D. L. Lewis, K. T. McGregor, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **13**, 1013 (1974).
(6) E. D. Estes, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **13**, 1654 (1974).
(7) E. Sinn, paper presented at the American Crystallographic Association Meeting, Charlottesville, Va., March 1975.
(8) M. D. Glick and R. L. Lintvedt, paper presented at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974.
(9) D. J. Hodgson, J. T. Veal, W. E. Hatfield, D. Y. Jeter, and J. C. Hempel, *J. Coord. Chem.*, **2**, 1 (1972).
(10) J. T. Veal, W. E. Hatfield, D. Y. Jeter, J. C. Hempel, and D. J. Hodgson, *Inorg. Chem.*, **12**, 342 (1973).
(11) J. T. Veal, W. E. Hatfield, and D. J. Hodgson, *Acta Crystallogr., Sect. B*, **29**, 12 (1973).
(12) R. P. Scaringe, P. Singh, R. P. Eckberg, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **14**, 1127 (1975).
(13) J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).
(14) K. Kasaga, T. Itou, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.* **47**, 1026 (1974).
(15) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).
(16) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).
(17) T. C. Furnas, "Single Crystal Orienter Instruction Manual", General Electric Co., Milwaukee, Wis., 1957.
(18) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).
(19) E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, **14**, 334 (1975).
(20) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(21) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(22) For a description of the programs used, see E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, **12**, 2932 (1973).
(23) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(24) J. A. Ibers, "International Tables for X-Ray Crystallography", Vol. II, Kynoch Press, Birmingham, England, Talbe 3.31A.
(25) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(26) D. T. Cromer and D. Liberman, *J. Chem Phys.*, **53**, 1891 (1970).
(27) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
(28) Supplementary material.
(29) B. Morosin and J. B. Brathode, *Acta Crystallogr.*, **17**, 705 (1964).
(30) B. Morosin, *Acta Crystallogr.*, **19**, 131 (1965).
(31) C. E. Wilkes and R. A. Jacobson, *Inorg. Chem.*, **4**, 99 (1965).
(32) H. Ikeda, I. Kimura, and N. Uryu, *J. Chem. Phys.*, **48**, 4800 (1968).
(33) J. T. Veal, D. Y. Jeter, J. C. Hempel, R. P. Eckberg. W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **12**, 2928 (1973).
(34) C. Kittel, *Phys. Rev.* **120**, 35 (1960).
(35) J. C. M. Henning, J. H. den Boef, and G. G. P. van Gorkom, *Phys. Rev. B*, **7**, 1825 (1973). It should be noted that these authors obtained a negative value of j because they wrote the Hamiltonian $\mathcal{H} = JS_1\cdot S_2 + j(S_1\cdot S_2)^2$. Their result is, therefore, equivalent to a positive j using our Hamiltonian (eq 2).