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

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Received December 29, 1976 AIC609200

The crystal structures of the complexes di-μ-methoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)], $[Cr(3\text{-}Br\text{-}acac)_2OCH_3]_2$, and di-$\mu$-ethoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)], $[Cr(3\text{-}Br\text{-}acac)_2OC_2H_5]_2$, have been determined from three-dimensional counter x-ray data. The methoxy complex crystallizes in the monoclinic space group $P2_1/c$ with two dimeric formula units in a cell of dimensions a = 7.769 (7) Å, b 18.587 (21) Å, c = 11.353 (10) Å, and β = 112.99 (4)°. Least-squares refinement of 1366 independent data has led to a final R factor (on F) of 0.034; this complex is isomorphous with the 3-chloro analogue. The ethoxy complex also crystallizes in the monoclinic space group $P2_1/c$ in a cell of dimensions a = 8.428 (3) Å, b = 19.339 (7) Å, c = 11.376 (4) Å, and β = 109.10 (1)°. Least-squares refinement of 1151 data has led to an R factor (on F) of 0.046. Both complexes consist of two chromium(III) ions which are symmetrically bridged by two alkoxide groups, the remaining coordination sites being occupied by the oxygen atoms of two bidentate 3-Br-acac ligands. The coordination around each chromium center is roughly octahedral; in the methoxy complex the average Cr–O(ligand) bond length is 1.958 (5) Å, the Cr–Cr separation is 3.038 (3) Å, and the Cr–O–Cr bridging angle is 101.5 (2)° while the corresponding values in the ethoxy complex are 1.952 (8) Å, 3.027 (3) Å, and 101.8 (3)°. The 3-Br-acac ligands are approximately planar. The magnetic susceptibilities of powdered samples of the complexes have been examined in the temperature range 4–100 K. The dimers exhibit antiferromagnetic exchange interactions with the best fit to the Van Vleck equation including biquadratic exchange yielding $2J = -7.10$ cm^{-1} and $j = 0.22$ cm^{-1} with $\langle g \rangle = 1.932$ for the methoxy complex and $2J = -17.88$ cm^{-1}, $j = 0$, and $\langle g \rangle = 1.945$. The data for the methoxy complex are similar to those for the corresponding 3-chloro complex and lead to a singlet–triplet splitting of -8.53 cm^{-1}, but those for the ethoxy complex show stronger magnetic coupling which can be attributed to the greater electron density at the bridging oxygen atom in this case.

Introduction

In many recent communications, considerable experimental evidence has been presented supporting the contention that the isotropic exchange parameter, J, is correlated to the Cr–O–Cr bridging angle, ϕ, in dihydroxo bridged complexes of Cr(III).[2-11] These studies, however, have focused on only one property of the bridging unit, its geometry. A second property is the electron density at the bridging atoms, and it has been pointed out[2,12] that this should also influence J. More recently, Hoffmann[13] and his co-workers have supported this view through results obtained using molecular orbital theory. Experimentally, there are several ways of altering the electron density at the bridging atoms, and for the dihydroxo-bridged species hydrogen bonding to the hydroxo hydrogen atoms is an obvious possibility. This approach, however, has the disadvantage that locating hydrogen atoms with sufficient accuracy to determine "hydrogen-bond strengths" is beyond the scope of conventional x-ray techniques. A more practical approach is to investigate the analogous alkoxo-bridged systems, which avoids the necessity of accurately determining hydrogen atom positions. The electron density at the bridging oxygen atom in these systems can be changed by using alkoxides of various chain length or by substitution at the α carbon.

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

Experimental Section

Di-μ-methoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)]. Synthesis. This complex was prepared by the method of Kasaga[14] et al. Anal. Calcd for $C_{22}H_{30}Br_4Cr_2O_{10}$: C, 30.08; H, 3.42; Br, 36.42. Found: C, 30.21; H, 3.53; Br, 36.70. Single crystals for the crystallographic study (vide infra) were obtained by recrystallization from dichloromethane to which a few drops of ethanol had been added.

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

Collection and Reduction of the X-Ray Data. On the basis of Weissenberg and precession photographs, the crystals were assigned 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 methods,[17] are a = 7.769 (7) Å, b = 18.587 (21) Å, c = 11.353 (10) Å, and β = 112.99 (4)°. The observations were made at 21° with the wavelength assumed as λ(Mo Kα_1) 0.7093 Å. A density of 1.933 g cm^{-3} was calculated for two dimeric formula units in the cell. Hence, in space group $P2_1/c$, the dimer is constrained to lie on a crystallographic inversion center.

Diffraction data were collected from an irregularly shaped crystal with faces (100), ($\bar{1}00$), (010), ($0\bar{1}0$), (011), ($01\bar{1}$), and ($0\bar{1}1$). The separations between opposite pairs of faces were as follows: (100) and ($\bar{1}00$), 0.028 cm; (010) and ($0\bar{1}0$), 0.005 cm; (011) and ($0\bar{1}\bar{1}$), 0.017 cm; ($01\bar{1}$) and ($0\bar{1}1$), 0.018 cm. The crystal was mounted on a glass fiber normal to the (100) planes, and in this orientation intensity data were collected on a Picker four-circle automatic diffractometer equipped with a graphite monochromator and using Mo Kα radiation.

Intensity data were collected as described elsewhere.[8] A data set having 2° ≤ 2θ ≤ 45° was gathered; a total of 2175 intensities were recorded. The intensities of three standard reflections, measured after every 100 reflections, showed no noticeable decline as a function of total exposure time.

Data processing was carried out as described by Corfield et al.[18] After correction for background, the intensities were assigned standard deviations according to the formula[18]

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

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 coefficient for this compound for Mo Kα radiation is 59.98 cm^{-1}, and for the crystal chosen the transmission coefficients evaluated by numerical integration ranged from 0.399 to 0.748. Of the 2175 data collected, 1366 were greater than 3 times their estimated standard deviations; only these data were used in the subsequent structure analysis and refinement.[19]

Di-μ-ethoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)]. Synthesis. A small quantity of the complex was obtained by combining the crude products of several reactions following the method of Kasaga et al.[14] Single crystals suitable for x-ray work were obtained by slow evaporation of a benzene solution of the powdered material.

Magnetic Susceptibility. Data were collected in the temperature range 4–100 K in the manner described above for the methoxy complex.

Collection and Reduction of the X-Ray Data. The crystals were assigned to the monoclinic system after examination by precession and Weissenberg photography. Systematic absences were observed for $h0l$ with l odd and $0k0$ with k odd; this suggests that the space group is $P2_1/c$ (C_{2h}^5). The cell constants obtained were refined by least-squares methods[17] and found to be a = 8.428 (3) Å, b = 19.339 (7) Å, c = 11.376 (4) Å, and β = 109.10 (1)°. The radiation used for these measurements was Mo Kα_1 (λ 0.7093 Å). The observed density of 1.80 (2) g cm^{-3} measured in aqueous zinc bromide is in acceptable agreement with the calculated density of 1.804 g cm^{-3} calculated for two dimeric units in a cell. The dimers are, therefore, constrained to lie on inversion centers. This complex was found to crystallize as dark green truncated diamond-shaped plates bounded by faces (101), ($\bar{1}0\bar{1}$), ($10\bar{1}$), ($\bar{1}01$), (011), ($0\bar{1}\bar{1}$), ($01\bar{1}$), ($0\bar{1}1$). The distances between opposite faces for the small specimen selected for the collection of intensity data were 0.173, 0.151, 0.110, and 0.0755 mm, respectively. The crystal was glued to the end of a glass fiber approximately collinear with the a axis, and the data were collected using a Picker four-circle diffractometer, in a manner described above, equipped with a molybdenum tube and graphite monochromator. The takeoff angle used was 1.2°, the scan rate was 0.5°/min, and the scan range was from 0.5° below the calculated Kα_1 peak position to 0.5° above the calculated Kα_2 peak position, backgrounds being counted for 20 s at each end of the scan. A unique data set of 1996 reflections having 2θ(Mo) ≤ 44° was collected: 1021 of these were found to have intensities greater than 3 times their estimated standard deviation, while 1151 had intensities greater than twice their estimated standard deviation. The intensities of three standard reflections were measured after every 100 reflections, and no decline with cumulative exposure was observed. The data were processed in the manner described above and corrected for absorption effects. The linear absorption coefficient, μ, for this complex and Mo Kα radiation is 58.03 cm^{-1}, and the transmission coefficients for the particular specimen used for data collection ranged from 48.0% to 72.1%.

Table I. Positional Parameters (×10^4) for [Cr(3-Br-acac)$_2$OCH$_3$]$_2$

Atom	x	y	z
Cr	1076 (1)	226 (1)	1380 (1)
Br1	5274 (1)	2520 (0)	2338 (1)
Br2	426 (1)	−1214 (1)	5134 (1)
O1	1228 (7)	1131 (3)	2288 (4)
O2	3223 (6)	543 (2)	1011 (4)
O3	−969 (6)	−76 (2)	1849 (4)
O4	2798 (6)	−265 (2)	2922 (4)
OB	709 (6)	−609 (2)	251 (4)
C1A	1881 (27)	2304 (6)	3124 (15)
C2A	2303 (11)	1668 (4)	2434 (6)
C3A	3725 (10)	1682 (4)	1975 (6)
C4A	4138 (9)	1120 (4)	1278 (6)
C5A	5678 (12)	1188 (6)	828 (10)
C1B	−2850 (14)	−523 (7)	2867 (11)
C2B	−958 (10)	−425 (4)	2815 (6)
C3B	681 (11)	−700 (4)	3754 (6)
C4B	2451 (10)	−620 (4)	3768 (6)
C5B	4130 (13)	−946 (5)	4807 (8)
CME	796 (16)	−1335 (4)	652 (8)
H1A[a]	185 (10)	271 (4)	280 (6)
H2A	314 (28)	245 (10)	390 (18)
H3A	133 (25)	204 (9)	322 (18)
H4A	−399 (14)	168 (6)	61 (9)
H5A	572 (13)	79 (6)	43 (9)
H6A	699 (15)	119 (5)	160 (10)
H1B	−373 (13)	−39 (5)	207 (9)
H2B	−325 (13)	−101 (5)	287 (8)
H3B	−269 (17)	−40 (7)	359 (11)
H4B	414 (14)	−66 (6)	560 (10)
H5B	393 (14)	−146 (7)	501 (9)
H6B	−503 (11)	−103 (4)	457 (7)
HM1	193 (12)	−140 (4)	148 (8)
HM2	66 (10)	−169 (5)	−4 (7)
HM3	−17 (16)	−146 (6)	90 (10)

[a] Hydrogen atom parameters are ×10^3.

Solution and Refinement of the Structures. All least-squares refinements in this analysis were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o)^2$. In all calculations of F_c, the atomic scattering factors for Cr were from Cromer and Waber,[20] those for Br, O, and C from ref 21, and those for H from Stewart, Davidson, and Simpson.[22] 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.[23]

Di-μ-methoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)]. The initial positions of the nonhydrogen atoms were taken from the isomorphous chloro complex[8] [Cr(3-Cl-acac)$_2$OCH$_3$]$_2$, with Cl replaced by Br, and two cycles of least-squares refinement were run on these positions using isotropic thermal parameters. The usual agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and R_2 (or weighted R factor) = $(\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$ were 0.160 and 0.213, respectively. After correction for absorption, anisotropic refinement of the nonhydrogen atoms yielded values of 0.059 and 0.095 for R_1 and R_2.

At this point the hydrogen atoms were placed in the same positions as those in the corresponding chloro complex. A final least-squares calculation in which all hydrogen atoms were refined isotropically while nonhydrogen atoms were refined anisotropically yielded values of R_1 and R_2 of 0.034 and 0.041, respectively.

An examination of the values of $|F_o|$ and $|F_c|$ suggested to us that no correction for secondary extinction was necessary, and none was applied. In the final cycle of least-squares refinement no atomic parameter exhibited a shift of more than 0.7σ, which indicates that refinement had converged. A final difference Fourier synthesis contained a peak of 0.91 e Å^{-3} in the vicinity of atom Br(2); this peak must be ascribed to some minor error in our absorption correction. No other peak higher than 0.5 e Å^{-3} was present in the map. The position and thermal parameters derived from this final least-squares cycle, along with their standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A listing of observed and calculated structure amplitudes is available.[24]

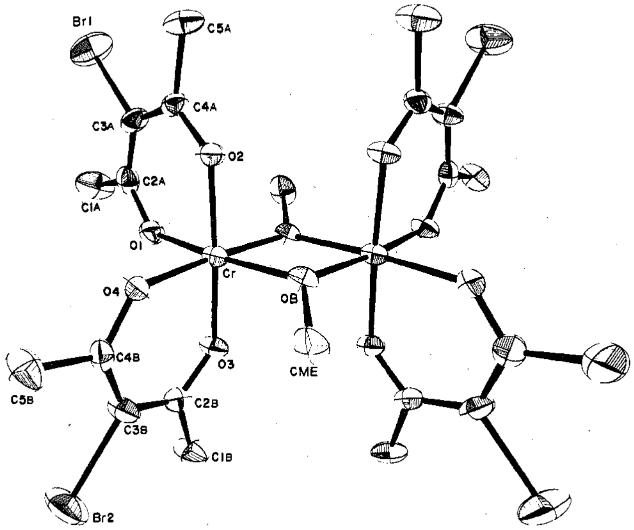


Figure 1. View of the dimeric $[Cr(3\text{-}Br\text{-}acac)_2OCH_3]_2$ molecule. Hydrogen atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by the inversion center.

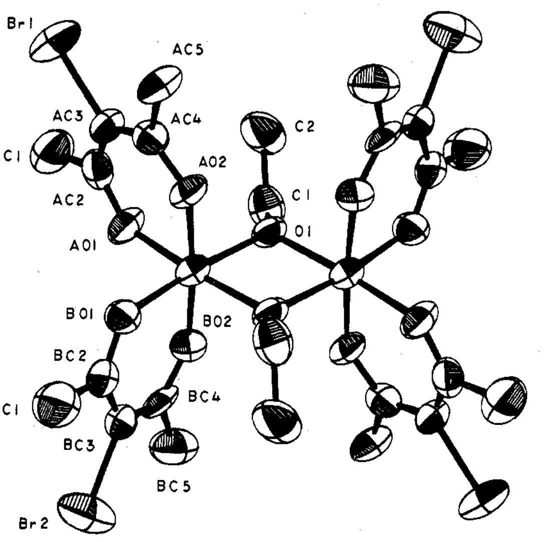


Figure 2. View of $[Cr(3\text{-}Br\text{-}acac)_2(OC_2H_5)]_2$.

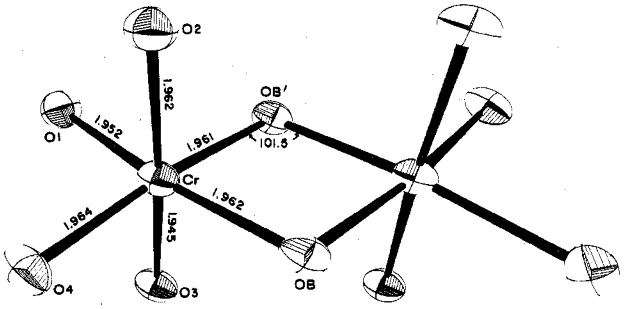


Figure 3. Coordination around the chromium centers in $[Cr(3\text{-}Br\text{-}acac)_2OCH_3]_2$.

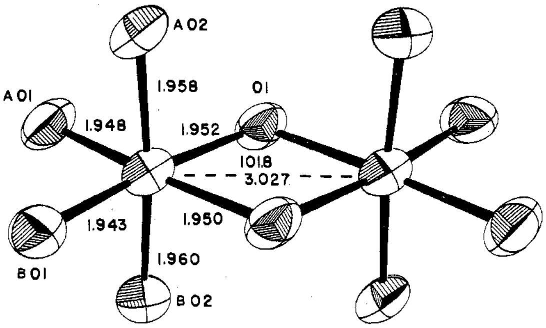


Figure 4. View of the inner coordination sphere in $[Cr(3\text{-}Br\text{-}acac)_2(OC_2H_5)]_2$.

Di-μ-ethoxy-bis[bis(3-bromo-2,4-pentanedionato)chromium(III)]. The positions of the two independent bromine atoms and the chromium atom were determined by the heavy atom technique.[25] These positions were refined by three cycles of least squares using variable isotropic thermal parameters. The resulting values of the residuals R_1 and R_2 were 0.33 and 0.41, respectively.

The subsequent difference synthesis indicated the positions of all remaining nonhydrogen atoms. Two cycles of least squares with these 20 positions, all with variable isotropic thermal parameters, yielded $R_1 = 0.175$ and $R_2 = 0.185$. The next difference Fourier synthesis revealed large portions of electron density close to the bromine atoms, and this was interpreted as being caused by neglecting the anisotropic motion of these heavy atoms. Two cycles of least-squares, with all nonhydrogen atoms being assigned anisotropic thermal parameters, yielded $R_1 = 0.058$ and $R_2 = 0.064$. From the subsequent difference map, all 17 hydrogen atoms were located, and with these positions fixed the following cycle of least-squares yielded $R_1 = 0.050$ and $R_2 = 0.051$. For the remainder of the refinement, hydrogen atom parameters and nonhydrogen atom parameters were varied in alternate cycles. At the end of this stage of the refinement, using 1021 data with 181 variables, the values of R_1 and R_2 were equal, both being 0.041. It was then decided to include all data whose intensities were greater than 2 times their esd; this had the effect of increasing the number of available data by about 10%. Thus, the final cycle of least squares involved the refinement of 181 variables based on 1151 independent intensities and yielded $R_1 = 0.046$, $R_2 = 0.042$. In the final cycle no parameter (all of which were nonhydrogen) exhibited a shift of more than 7% of its standard deviation, while in a previous cycle varying only hydrogen atom parameters there was no shift greater than 35%. The positional and thermal parameters are given in Tables III and IV. A listing of observed and calculated structure factors is available.[24]

Description of the Structures

Both complexes consist of dimeric $[Cr(3\text{-}Br\text{-}acac)_2OR]_2$ units (R = CH_3, C_2H_5) which are well separated from one another. The geometry about the chromium atoms is approximately octahedral, the six coordination sites being occupied by two cis alkoxy groups and two cis 3-Br-acac ligands. The molecules and labeling schemes are shown in Figures 1 and 2; the inner coordination spheres, in Figures 3 and 4. The present complexes are structurally very similar to the previously characterized[8] methoxy-bridged complex $[Cr(3\text{-}Cl\text{-}acac)_2(OMe)]_2$; the inner-coordination spheres of these three complexes are compared in Table V. Examination of Table V reveals that all of the bond lengths for any one complex are within 3 esd's of the comparable bond lengths for the other two complexes. The valence angles around the chromium atom are also very similar in the three complexes and in particular the differences in the Cr–O–Cr bridging angle, ϕ, are within experimental error for all three dimers. The average nonbridging Cr–O separations of 1.958 (5) (methoxy) and 1.952 (8) Å (ethoxy) are not significantly different from those found in complexes of the parent 2,4-pentanedione,[26,27] but as pointed out elsewhere,[8] the halogenated 2,4-pentanedione complexes of chromium(III) exhibit acute chelate angles while those for parent 2,4-pentanedione have been found to be obtuse.[26,27] These Cr–O separations are also quite similar to those found in a variety of carboxylate complexes of chromium(III). The average value here (vide supra) compares with 1.965 (2) Å found in $[Cr(gly)_3]\cdot H_2O$,[28] 1.964 (2) Å in $Na_4[Cr(mal)_2OH]_2\cdot 5H_2O$,[11] 1.974 (4) Å in $[Cr(gly)_2OH]_2$,[5] and 1.982 (11) Å in $Na_4[Cr(ox)_2OH]_2\cdot 6H_2O$.[9] Thus, the Cr–O separation seems to be insensitive to the detailed electronic properties of the chelating oxygen atom. The Cr–O separations of 1.952 (6) and 1.950 (6) Å in the bridging unit are similar to those found in several hydroxo-bridged dimers[5,9] but

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

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	289 (6)	306 (6)	308 (6)	−5 (5)	148 (5)	51 (5)
Br1	709 (7)	441 (5)	1197 (8)	−256 (5)	396 (6)	−77 (6)
Br2	813 (7)	1071 (9)	582 (6)	−54 (6)	376 (5)	396 (5)
O1	496 (33)	373 (29)	375 (27)	−76 (27)	254 (24)	−70 (23)
O2	316 (28)	358 (29)	368 (26)	−41 (25)	168 (23)	47 (22)
O3	331 (29)	393 (29)	390 (26)	3 (22)	213 (23)	105 (22)
O4	338 (29)	482 (29)	296 (25)	35 (24)	147 (23)	113 (23)
OB	309 (27)	225 (25)	331 (23)	94 (21)	137 (21)	92 (19)
C1A	1167 (99)	354 (64)	982 (92)	−206 (61)	726 (94)	−175 (57)
C2A	526 (51)	318 (43)	296 (39)	34 (41)	93 (37)	60 (33)
C3A	405 (47)	304 (43)	471 (43)	−136 (36)	117 (39)	27 (35)
C4A	298 (42)	332 (44)	360 (38)	−56 (37)	89 (33)	89 (34)
C5A	422 (55)	466 (60)	739 (60)	−130 (47)	345 (50)	62 (50)
C1B	490 (63)	709 (73)	644 (72)	−46 (56)	362 (59)	129 (56)
C2B	418 (48)	290 (41)	428 (42)	−25 (35)	286 (39)	−71 (34)
C3B	446 (51)	429 (48)	373 (39)	8 (40)	222 (38)	139 (34)
C4B	397 (47)	299 (39)	230 (34)	24 (35)	59 (34)	−24 (30)
C5B	508 (60)	631 (68)	421 (48)	130 (50)	238 (46)	95 (44)
CME	698 (68)	320 (47)	349 (47)	89 (44)	159 (51)	104 (38)

Atom	U	Atom	U	Atom	U
H1A	4 (2)	H6A	10 (4)	H5B	10 (4)
H2A	18 (11)	H1B	9 (3)	H6B	5 (3)
H3A	9 (9)	H2B	7 (3)	HM1	5 (3)
H4A	12 (4)	H3B	12 (5)	HM2	6 (2)
H5A	6 (4)	H4B	12 (4)	HM3	13 (5)

[a] Anisotropic parameters are $\times 10^4$; isotropic parameters, $\times 10^2$.

Table III. Positional Parameters in $[Cr(3\text{-}Br\text{-}acac)_2OEt]_2$[a]

Atom	x/a	y/b	z/c
Cr	10285 (20)	2038 (7)	14196 (13)
Br(1)	6100 (20)	−11829 (7)	51974 (12)
Br(2)	44444 (18)	25007 (6)	19879 (14)
O(1)	616 (8)	−588 (3)	257 (5)
C(1)	1747 (13)	−1154 (6)	483 (9)
C(2)	1109 (15)	−1768 (5)	988 (1)
AO(1)	2710 (8)	−277 (3)	2969 (6)
AO(2)	−875 (8)	−72 (3)	1869 (6)
AC(1)	4024 (16)	−938 (6)	4869 (11)
AC(2)	2400 (16)	−610 (5)	3809 (10)
AC(3)	772 (18)	−686 (5)	3793 (9)
AC(4)	−804 (15)	−408 (5)	2844 (11)
AC(5)	−2525 (16)	−513 (5)	2889 (9)
BO(1)	1222 (9)	1061 (3)	2363 (6)
BO(2)	3058 (8)	496 (3)	1131 (6)
BC(1)	1692 (17)	2208 (6)	2982 (11)
BC(2)	2054 (16)	1599 (6)	2389 (9)
BC(3)	3270 (14)	1650 (5)	1868 (9)
BC(4)	3762 (13)	1089 (6)	1319 (9)
BC(5)	5134 (15)	1156 (5)	851 (10)
1H(1)	163	−123	−27
1H(2)	297	−10	10
2H(1)	188	−203	84
2H(2)	5	−19	44
2H(3)	135	−163	199
A1H(1)	489	−87	475
A1H(2)	381	−144	501
A1H(3)	423	−83	551
A5H(1)	−346	−31	21
A5H(2)	−235	−46	367
A5H(3)	−283	−96	276
B1H(1)	66	221	315
B1H(2)	136	259	246
B1H(3)	234	227	363
B5H(1)	526	143	47
B5H(2)	545	73	63
B5H(3)	618	131	152

[a] Positional parameters are $\times 10^5$ for Cr, Br(1), and Br(2), $\times 10^4$ for all other nonhydrogen atoms, and $\times 10^3$ for hydrogen atoms.

are significantly longer than those found in $[Cr(phen)(OH)]_2I_4 \cdot 4H_2O$[7] and significantly shorter than those found in $Na_4[Cr(mal)_2OH]_2 \cdot 5H_2O$.[11]

The Cr–O–Cr–O units in the dimers are strictly planar owing to the inversion symmetry. In the methoxy complex the methoxy carbon atom CME is considerably out of this plane, its deviation being 0.61 Å; in the ethoxy complex the two ethoxide carbon atoms C(1) and C(2) are displaced on opposite sides of the bridging plane by 0.44 and 0.73 Å, respectively. These values for CME and C(1) (the α-carbon atom) lead us to the conclusion[8] that the hybridization at the bridging oxygen atom is intermediate between sp^2 and sp^3. In the ethoxy complex, the two symmetry-related chromium atoms are displaced similarly [at 1.56 and 1.46 Å] from the plane defined by the ethoxide group; this plane makes an angle of 93.2° with the bridge plane.

The bond lengths and angles within the ligands are given in Table VI; the chelates are in all respects similar to those of the closely related 3-chloro-2,4-pentanedionato complex.[8] The 3-bromo-2,4-pentanedionato rings are essentially planar, the largest deviations of any atom from the best least-squares plane through the chromium atom and the ligand atoms being 0.05 and 0.03 Å for the A and B rings, respectively, for the methoxy complex and 0.03 and 0.05 Å, respectively, for the ethoxy complex. The geometry of the ligand is similar to that found for the parent 2,4-pentanedionato ligand in a variety of metal complexes.[26,27,29] The average O···O "bite" of 2.724 Å in the methoxy complex, however, is smaller than the values of 2.751 and 2.786 Å found in the manganese(III)[29] and chromium(III)[26] complexes $M(acac)_3$.

Dicussion

The magnetic susceptibility data were fitted to the expression

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

where J and j are defined by the exchange Hamiltonian

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

Table IV. Thermal Parameters in $[Cr(3\text{-}Br\text{-}acac)_2OEt]_2$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	2047 (38)	286 (5)	814 (17)	−88 (11)	678 (21)	78 (8)
Br(1)	5044 (47)	618 (6)	1387 (16)	−205 (12)	1323 (23)	414 (7)
Br(2)	3705 (4)	394 (4)	2803 (27)	−447 (11)	1403 (3)	13 (8)
O(1)	209 (15)	21 (2)	81 (7)	6 (5)	58 (9)	12 (3)
C(1)	176 (26)	44 (4)	125 (14)	−1 (9)	29 (16)	−7 (6)
C(2)	328 (33)	26 (4)	181 (17)	−5 (9)	9 (20)	14 (6)
AO(1)	192 (16)	44 (2)	80 (8)	0 (5)	58 (9)	19 (4)
AO(2)	231 (17)	33 (2)	83 (7)	−1 (4)	87 (10)	10 (3)
AC(1)	325 (34)	56 (5)	129 (15)	−4 (10)	67 (20)	20 (7)
AC(2)	222 (32)	23 (3)	81 (14)	5 (8)	8 (19)	−3 (5)
AC(3)	239 (31)	27 (3)	75 (13)	0 (9)	54 (19)	10 (5)
AC(4)	205 (30)	30 (4)	106 (15)	−19 (8)	108 (19)	−16 (6)
AC(5)	360 (35)	47 (4)	108 (4)	−14 (9)	127 (18)	17 (6)
BO(1)	285 (19)	31 (2)	105 (8)	−29 (5)	111 (10)	−11 (4)
BO(2)	213 (17)	34 (2)	104 (8)	−21 (5)	78 (10)	0 (4)
BC(1)	477 (4)	45 (4)	171 (18)	−26 (11)	185 (23)	−13 (7)
BC(2)	279 (32)	31 (4)	75 (13)	−14 (10)	75 (17)	−8 (6)
BC(3)	198 (27)	27 (14)	74 (12)	−5 (8)	26 (15)	6 (5)
BC(4)	125 (26)	47 (5)	67 (11)	−3 (9)	51 (14)	27 (6)
BC(5)	262 (29)	41 (4)	181 (17)	−14 (9)	103 (20)	16 (7)

Atom	B, Å^2	Atom	B, Å^2	Atom	B, Å^2
1H(1)	10	A1H(2)	7	B1H(2)	4
1H(2)	5	A1H(3)	8	B1H(3)	9
2H(1)	16	A5H(1)	7	B5H(1)	8
2H(2)	11	A5H(2)	8	B5H(2)	6
2H(3)	12	A5H(3)	9	B5H(3)	5
A1H(1)	6	B1H(1)	4		

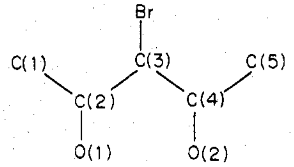
[a] Anisotropic thermal parameters are $\times 10^5$ for chromium and bromine and $\times 10^4$ for all others. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table V. Geometries of the Inner Coordination Sphere in Complexes of the Type $[Cr(3\text{-}X\text{-}acac)_2(OR)]_2$

Atoms	X = Br, R = Et[a]	X = Br, R = Me[a]	X = Cl, R = Me[b]
	Bond Lengths, Å		
Cr–Cr	3.027 (3)	3.038 (3)	3.025 (3)
Cr–AO(1)	1.948 (6)	1.952 (5)	1.952 (2)
Cr–AO(2)	1.958 (6)	1.962 (5)	1.962 (2)
Cr–BO(1)	1.943 (6)	1.945 (5)	1.956 (2)
Cr–BO(2)	1.960 (6)	1.964 (5)	1.959 (2)
Cr–O(1)	1.952 (6)	1.962 (4)	1.960 (2)
Cr–O(1)′	1.950 (6)	1.961 (4)	1.958 (2)
	Bond Angles, Deg		
O(1)–Cr–O(1)′	78.2 (3)	78.5 (2)	78.93 (9)
O(1)–Cr–AO(1)	94.7 (2)	93.5 (2)	93.68 (9)
O(1)–Cr–AO(2)	92.3 (2)	92.1 (2)	92.37 (9)
O(1)–Cr–BO(1)	172.1 (3)	173.5 (2)	173.2 (1)
O(1)–Cr–BO(2)	91.3 (3)	90.6 (2)	90.35 (9)
O(1)′–Cr–AO(1)	172.7 (3)	172.0 (2)	172.6 (1)
O(1)′–Cr–AO(2)	92.6 (2)	91.0 (2)	90.94 (8)
O(1)′–Cr–BO(1)	93.9 (3)	95.1 (2)	94.4 (1)
O(1)′–Cr–BO(2)	91.5 (2)	91.4 (4)	91.84 (8)
AO(1)–Cr–AO(2)	89.4 (3)	88.5 (2)	88.81 (8)
AO(1)–Cr–BO(1)	93.2 (3)	92.9 (2)	93.0 (1)
AO(1)–Cr–BO(2)	86.9 (3)	89.5 (3)	88.72 (9)
AO(2)–Cr–BO(1)	88.2 (3)	89.4 (2)	89.05 (9)
AO(2)–Cr–BO(2)	175.0 (3)	176.7 (3)	176.4 (2)
BO(1)–Cr–BO(2)	88.7 (3)	88.1 (2)	88.52 (9)
Cr–O(1)–Cr′	101.8 (3)	101.5 (2)	101.07 (9)

[a] This work. [b] Reference 8.

Table VI. Interatomic Distances (Å) and Angles (deg) in 3-Br-acac and Alkoxide Ligands



Atoms	Methoxide		Ethoxide	
	Ligand A	Ligand B	Ligand A	Ligand B
C(1)–C(2)	1.523 (12)	1.505 (11)	1.512 (13)	1.455 (13)
C(2)–C(3)	1.394 (10)	1.400 (10)	1.372 (13)	1.394 (13)
C(3)–C(4)	1.420 (10)	1.376 (10)	1.402 (13)	1.403 (13)
C(4)–C(5)	1.478 (10)	1.502 (11)	1.487 (13)	1.475 (13)
C(2)–O(1)	1.270 (8)	1.272 (7)	1.271 (11)	1.247 (11)
C(4)–O(2)	1.257 (8)	1.280 (7)	1.265 (10)	1.266 (11)
C(3)–Br	1.912 (7)	1.910 (6)	1.920 (9)	1.894 (9)
C(1)–C(2)–C(3)	122.7 (8)	122.6 (7)	121.1 (11)	118.8 (10)
C(1)–C(2)–O(1)	114.5 (8)	114.7 (7)	113.6 (11)	117.2 (11)
O(1)–C(2)–C(3)	122.8 (6)	122.7 (6)	125.2 (9)	124.0 (10)
C(2)–C(3)–C(4)	125.4 (6)	125.3 (6)	125.1 (9)	123.4 (9)
C(2)–C(3)–Br	117.3 (6)	116.9 (5)	118.5 (9)	119.3 (9)
Br–C(3)–C(4)	117.3 (5)	117.8 (5)	116.4 (9)	117.2 (9)
C(3)–C(4)–C(5)	121.3 (7)	121.5 (7)	122.1 (10)	121.6 (11)
C(3)–C(4)–O(2)	122.2 (6)	123.3 (6)	122.5 (9)	124.6 (9)
O(2)–C(4)–C(5)	116.5 (7)	115.1 (7)	115.3 (10)	113.7 (10
	Alkoxide			
O(1)–C(1)	1.418 (9)		1.399 (11)	
C(1)–C(2)			1.517 (13)	
O(1)–C(1)–C(2)			110.9 (9)	

using a general nonlinear least-squares program; the function minimized was $F = \sum_i w_i(\chi_i^{obsd} - \chi_i^{cald})^2$ with the weights being assigned $w_i = 1/\chi_i^{obsd}$. The best fit to the data for the methoxy complex in the absence of biquadratic exchange (i.e., holding $j = 0$ and letting g and J vary) is displayed in Figure 5, where the final values were $g = 2.05$ (1) and $J = -5.04$ (6) cm^{-1}. The best fit, with the inclusion of the biquadratic exchange parameter, j, yielded $g = 1.932$ (3), $J = -3.55$ (2) cm^{-1}, and $j = 0.218$ (6) cm^{-1} as compared to values of 1.901 (4), −3.67 (3) cm^{-1}, and 0.381 (4) cm^{-1}, respectively, for the chloro complex.[8] These data lead to a singlet–triplet splitting of −8.53 cm^{-1}. The theoretical susceptibilities using these values for g, J, and j are also presented in Figure 5, and it can be seen that the comparison with experiment is greatly improved. As expected, in view of the similarities in their bridging geometries, the magnetic properties of the chloro and bromo methoxy complexes are not significantly different from one another. This work, therefore, supports our general

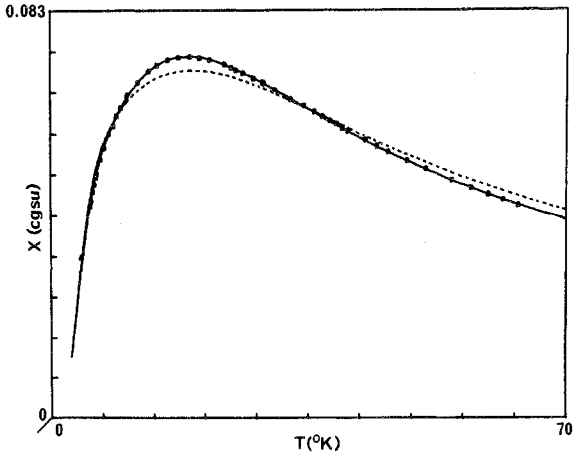


Figure 5. Temperature dependence of the magnetic susceptibility of $[Cr(3\text{-}Br\text{-}acac)_2OCH_3]_2$. The experimental data are shown as squares. The dashed line represents the best fit to the dimer ($S = {}^3/_2, {}^3/_2$) equation in the absence of biquadratic exchange. The solid line represents the best fit to the dimer equation including biquadratic exchange.

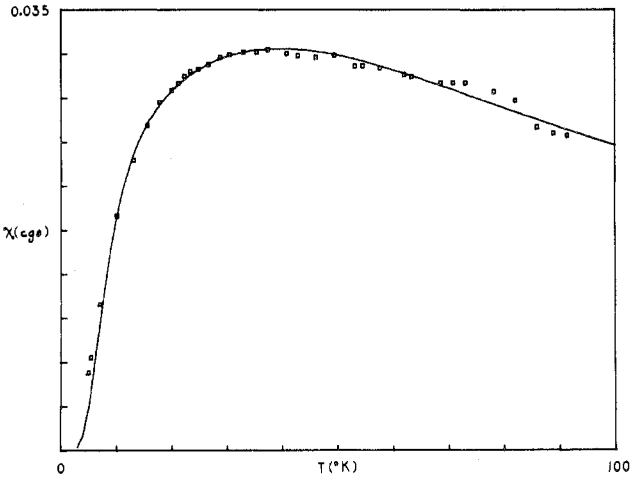


Figure 6. Temperature dependence of the magnetic susceptibility of $[Cr(3\text{-}Br\text{-}acac)_2(OC_2H_5)]_2$. Experimental points are shown as squares; the best fit is shown as the full line.

contention[2,3,30] that the magnetic properties of dimers of this general type are determined by the geometry of the bridging unit.

The magnetic data for the ethoxy complex are substantially different from those discussed above for the methoxy complexes; while the data for the present methoxy complex (Figure 5) show a maximum at approximately 18 °C, the ethoxy data maximize at approximately 35 °C. The best two-parameter ($j = 0$) fit to the data for the ethoxy complex yielded $g = 1.945$ (7) and $J = -8.94$ (6) cm^{-1}. Including j as a parameter in the fitting process produced no noticeable improvement in the fit and yielded a small value for j which was not significantly different from zero. The experimental and theoretical temperature dependence of the magnetic susceptibility are shown in Figure 6, and it can be seen that eq 1 (with $j = 0$) is in acceptable agreement with experiment. Hence, for the ethoxy complex the singlet–triplet splitting is $-17.88\ cm^{-1}$, which is substantially higher than the value of $-8.53\ cm^{-1}$ found for the methoxy complex above. These results indicate that the strength of the exchange interaction for the present complex is much greater than in the case of the two methoxy-bridged complexes (these both had $J = -3.6\ cm^{-1}$), despite the fact that the complexes are virtually identical in all respects except for the bridging group. It would seem that this datum strongly supports the contention[2,12,13] that the strength of the exchange interaction is influenced by the electron density at the bridging atom. Moreover, it has been shown in general[13] that the more electron rich the bridging atom is, the stronger the antiferromagnetic interaction should be; this of course is precisely the case here. To our knowledge, this work represents the most direct evidence regarding this subject yet to be reported.

Acknowledgment. This work was supported by the National Science Foundation through Grant No. CHE7606704.

Registry No. $[Cr(3\text{-}Br\text{-}acac)_2OCH_3]_2$, 52649-67-9; $[Cr(3\text{-}Br\text{-}acac)_2OC_2H_5]_2$, 52682-25-4.

Supplementary Material Available: Listings of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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