formed during the cathodic scan. Thus, $Fe(PhNO_2)_3$ by virtue of its highest formal potential can favorably (in the thermodynamic sense) receive[14] electrons from $Fe(EtMe)_3^-$, $Fe(EtMe)_2(PhNO_2)^-$, and $Fe(EtMe)(PhNO_2)_2^-$. On the other hand $Fe(PhNO_2)_3^-$ has no acceptor available. The effective concentration of $Fe(PhNO_2)_3^-$ available for oxidation at the electrode surface would thus increase, resulting in the observed effect.

Concluding Remarks. Facile ligand redistribution occurs in mixtures of triazene 1-oxide complexes of copper(II), cobalt(III), and iron(III). In ternary mixtures of iron(III) complexes, six closely spaced but clearly observable voltammetric responses occur. Such a system could act like a sponge for reversibly absorbing electrons over the applicable potential range. Whereas fast redistribution is not unexpected in the cases of the high-spin[5] iron(III) and copper(II) complexes, it is somewhat surprising[15] that the stereochemically rigid (meridional, ^1H NMR data[16]) low-spin cobalt(III) species also redistribute as readily. The redistribution reactions preclude the possibility of isolating mixed species in pure state.[17]

We are not aware of any other technique outside voltammetry by which the formation of the various mixed complexes could be established with such ease, authenticity, and generality. Virtually all previous voltammetric studies[3,4] on ligand redistribution concern dithiolenes, dithiocarbamates, and related species. To the best of our knowledge, the present work represents the first thorough and systematic report on O,N systems and on the effect of remote substituents (X) in mixed complexes.

Experimental Section

Materials. Complexes of types $Cu(RX)_2$, $Co(RX)_3$, $Fe(RX)_3$, and $Ru(RX)_3$ were synthesized as reported.[5,6] Solvents and supporting electrolyte for electrochemistry were purified as before.[5]

Formation of Mixed Complexes. Equimolar amounts ($\sim 10^{-3}$ M) of the two or three parent complexes together with the supporting electrolyte (tetraethylammonium perchlorate, TEAP) were allowed to equilibrate in the voltammetric vessel at 298 K in dimethylformamide ($Cu(RX)_2$ mixtures) or in acetonitrile ($Co(RX)_3$, $Fe(RX)_3$, and $Ru(RX)_3$ mixtures) for 2 h. Voltammetric examination however showed that redistribution equilibrium is achieved in most cases within the time of mixing. Only in the case of copper(II) species is a larger time needed. The equilibration time of 2 h was chosen to ensure that equilibrium is surely reached.

Electrochemical Measurements. A PAR Model 370-4 electrochemistry system, which includes the 174A polarographic analyzer, 175 universal programmer, and RE 0074 X-Y recorder, was used. The three-electrode measurements were carried out with either a Metrohm E 410 hanging-mercury-drop electrode (HMDE) or a G0021 glassy-carbon electrode, a platinum-wire counterelectrode, and a saturated calomel reference electrode (SCE). The cell was thermostated at 298 K. All measurements were carried out under a dinitrogen atmosphere. The results reported are uncorrected for junction potentials.

The formal potentials $E°_{298}$ were calculated as follows: (i) cyclic voltammetry, the average of the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials; (ii) differential-pulse voltammetry, $E_p = E°_{298} + 0.5\ \Delta E$, where E_p is the peak potential and ΔE is the modulation amplitude. A ΔE value of 25 mV was uniformly used.

The following σ values[5] for para substituents were used: Me, –0.17; H, 0.00; Cl, +0.23; CO_2Et, +0.45; NO_2, +0.78.

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Registry No. $Cu(EtMe)(EtNO_2)$, 93255-38-0; $Cu(EtH)(EtNO_2)$, 93255-39-1; $Cu(EtMe)(PhNO_2)$, 93255-40-4; $Cu(PhOMe)(PhNO_2)$, 93255-41-5; $Co(EtMe)_2(EtNO_2)$, 93255-42-6; $Co(EtH)_2(EtNO_2)$, 93255-43-7; $Co(EtMe)(EtNO_2)_2$, 93255-44-8; $Co(EtH)(EtNO_2)_2$, 93255-45-9; $Fe(EtMe)_2(EtCO_2Et)$, 93255-46-0; $Fe(EtMe)_2(PhH)$, 93255-47-1; $Fe(EtMe)_2(PhCl)$, 93255-48-2; $Fe(EtMe)_2(EtNO_2)$, 93255-49-3; $Fe(EtH)_2(EtNO_2)$, 93255-50-6; $Fe(EtMe)_2(PhNO_2)$, 93255-51-7; $Fe(EtMe)(EtCO_2Et)_2$, 93255-52-8; $Fe(EtMe)(PhH)_2$, 93255-53-9; $Fe(EtMe)(PhCl)_2$, 93255-54-0; $Fe(EtMe)(EtNO_2)_2$, 93255-55-1; $Fe(EtMe)(EtCO_2Et)(PhNO_2)$, 93255-56-2; $Fe(EtMe)(PhH)(PhNO_2)$, 93255-57-3; $Fe(EtH)(EtNO_2)_2$, 93255-58-4; $Fe(EtMe)(PhNO_2)_2$, 93255-59-5; $Fe(EtCO_2Et)_2(PhNO_2)$, 93255-60-8; $Fe(PhH)_2(PhNO_2)$, 93255-61-9; $Fe(EtCO_2Et)(PhNO_2)_2$, 93255-62-0; $Fe(PhH)(PhNO_2)_2$, 93255-63-1; $Cu(EtMe)_2$, 32425-23-3; $Cu(EtH)_2$, 32425-19-7; $Cu(PhOMe)_2$, 14647-29-1; $Cu(EtNO_2)_2$, 79972-14-8; $Cu(PhNO_2)_2$, 79972-17-1; $Co(EtMe)_3$, 79972-06-8; $Co(EtH)_3$, 77188-06-8; $Co(EtNO_2)_3$, 79972-10-4; $Fe(EtMe)_3$, 79971-92-9; $Fe(EtH)_3$, 77188-05-7; $Fe(PhCl)_3$, 79972-02-4; $Fe(EtNO_2)_3$, 79971-96-4; $Fe(PhNO_2)_3$, 79972-04-6; $Fe(EtCO_2Et)_3$, 79971-95-2; $Fe(PhH)_3$, 28660-76-6.

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(13) Pal, S.; Datta, D.; Chakravorty, A., unpublished results.

(14) It is reasonable to assume that the kinetic barrier to electron transfer between the closely related complexes would be small.

(15) The voltammetric solvent (acetonitrile, 0.1 M in TEAP) is however different from the ^1H NMR solvent[16] (neat $CDCl_3$).

(16) Chakravorty, A.; Behera, B.; Zacharias, P. S. *Inorg. Chim. Acta* **1968**, *2*, 85.

(17) Thus, when iron(III) acetate is reacted with 3 mol of an equimolar mixture of the ligands HEtMe and $HPhNO_2$, the crystalline material isolated has a voltammogram identical with that of mixture j.

Contribution from the Department of Chemistry,
The University of North Carolina,
Chapel Hill, North Carolina 27514,
and Chemistry Laboratory I, Inorganic Chemistry,
H. C. Ørsted Institute, University of Copenhagen,
DK-2100 Copenhagen Ø, Denmark

Synthesis and Characterization of the Alkoxo-Bridged Chromium(III) Dimer Bis(μ-methoxo)bis[bis(2,2,6,6-tetramethyl-3,5-heptanedionato)chromium(III)]

Helen R. Fischer,[1a] Derek J. Hodgson,*[1a] and Erik Pedersen*[1b]

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The effect of slight structural variations on the magnetic properties of chromium(III) dimers has been studied[2-13] with close attention paid to the impact of changes in the bridging geometry of μ-hydroxo- and bis(μ-hydroxo) chromium(III)

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(1) (a) The University of North Carolina. (b) University of Copenhagen.

(2) Michelsen, K.; Pedersen, E. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 847.

(3) Cline, S. J.; Kallesøe, S.; Pedersen, E.; Hodgson, D. J. *Inorg. Chem.* **1979**, *18*, 796.

(4) Hodgson, D. J.; Pedersen, E. *Inorg. Chem.* **1980**, *19*, 3116.

(5) Cline, S. J.; Glerup, J.; Hodgson, D. J.; Jensen, G. S.; Pedersen, E. *Inorg. Chem.* **1981**, *20*, 2229.

(6) Scaringe, R. P.; Hodgson, D. J.; Hatfield, W. E., *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 340.

(7) Cline, S. J.; Hodgson, D. J.; Kallesøe, S.; Larsen, S.; Pedersen, E. *Inorg. Chem.* **1983**, *22*, 637.

(8) Glerup, J.; Hodgson, D. J.; Pedersen, E. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 161.

(9) Michelsen, K.; Pedersen, E.; Wilson S. R.; Hodgson, D. J. *Inorg. Chim. Acta* **1982**, *63*, 141.

(10) Beutler, A.; Güdel, H. U.; Snellgrove, T. R.; Chapuis, G.; Schenk, K. *J. Chem. Soc., Dalton Trans.* **1979**, 983.

(11) Kallesøe, S.; Pedersen, E. *Acta Chem. Scand., Ser. A* **1982**, *A36*, 859.

(12) Fischer, H. R.; Glerup, J.; Hodgson, D. J.; Pedersen, E. *Inorg. Chem.* **1982**, *21*, 3063.

(13) Hatfield, W. R.; MacDougall, J. J.; Shepherd, R. E. *Inorg. Chem.* **1981**, *20*, 4216.

0020-1669/84/1323-4755$01.50/0

Table I. Crystallographic and Data Collection Parameters

formula: $Cr_2O_{10}C_{46}H_{82}$
$a = 15.508$ (5) Å
$b = 10.862$ (3) Å
$c = 16.629$ (7) Å
$\beta = 111.86$ (3)°
$V = 2600$ (3) $Å^3$
NO = 1838 ($>3\sigma$)
$T = 20$ °C
$D_0 = 1.25$ (2) g cm^{-3}
$Z = 2$
$D_c = 1.154$ g cm^{-3}
space group: $P2_1/n$
$\mu = 4.88$ cm^{-1}
data range: $2° < 2\theta < 50°$
radiation: Mo Kα ($\lambda = 0.71073$ Å)
data collected: $\pm h, +k, +l$

dimers. Although initially the importance of the bridging Cr–O–Cr angle (ϕ) and the Cr–O bond length (R) were recognized, in analogy with earlier work on simpler systems,[14] it has only been recently that the greater importance of the dihedral angle (θ) between the O–H vector and the bridging Cr_2O_2 (or Cr_2O for μ-hydroxo complexes) plane has been recognized.[2–5,12,15–18] Unfortunately, due to the small contribution of hydrogen atoms to the X-ray structure factors, this parameter is rarely accurately determined even in precise X-ray structural studies.

Although, in principle at least, the use of neutron diffraction would provide a solution to this problem, in practice a simpler approach appears to be the synthesis and study of alkoxo-bridged rather than hydroxo-bridged complexes, since in the former 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[12,19–21] but the only synthetic route that promises to be readily extendable to a variety of complexes is our own recent report[12] of the synthesis of $[Cr(acac)_2(OCH_3)]_2$. We here report the use of this modified synthetic procedure for the preparation, isolation, and crystallization of the complex bis(μ-methoxo)bis[bis(2,2,6,6-tetramethyl-3,5-heptanedionato)chromium(III)], $[(tmhd)_2Cr(OCH_3)]_2$, and the magnetic and structural properties of this dimeric species.

Experimental Section

Synthesis. The synthetic procedure was as described previously.[12] To a solution of $CrCl_3 \cdot 3THF$ (10.0 g, 0.03 mol) in methanol (100 mL) were added 2,2,6,6-tetramethyl-3,5-heptanedione (16.0 g, 0.09 mol) and sodium methoxide (7.22 g, 0.13 mol). The resulting green solution was refluxed for 2 h, toluene (150 mL) was added, and an azeotrope of toluene/methanol was distilled off. When 150 mL of azeotrope had distilled off, the temperature had risen to 110 °C and a green precipitate had formed. Most of the precipitate dissolved on the addition of further toluene (150 mL) and subsequent heating; the hot solution was filtered and the filtrate evaporated to 50 mL. The product was crystallized by slow cooling.

Magnetic Susceptibility Measurements. The magnetic susceptibility of a microcrystalline sample of the complex was measured by the Faraday method at a field strength of 12000 Oe in the temperature range 4.8–260 K. Descriptions of the instrumentation and data analysis techniques are available elsewhere.[2,15]

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 monoclinic system, the cell chosen being consistent only with the space group $P2_1/n$. A total of 5006 data were collected, of which 1838 were independent data with $I \geq 3\sigma(I)$. Data were corrected for absorption, the maximum and minimum transmission coefficients being 99.99% and 94.61%, respectively. The cell constants, observed and calculated densities, and data collection parameters are listed in Table I.

Table II. Positional Parameters for $[Cr(tmhd)_2(OCH_3)]_2$

atom	x	y	z
Cr	0.48145 (6)	0.0615 (1)	0.07379 (6)
O(1)	0.4850 (2)	0.0981 (4)	−0.0402 (2)
O(3)A	0.4811 (2)	0.0062 (4)	0.1851 (2)
O(5)A	0.6105 (2)	0.1155 (4)	0.1331 (2)
O(3)B	0.3479 (2)	0.0202 (4)	0.0306 (2)
O(5)B	0.4503 (2)	0.2295 (4)	0.0930 (2)
C(1)	0.5191 (4)	0.2053 (6)	−0.0608 (4)
C(1)A	0.4295 (5)	0.0794 (11)	0.3334 (4)
C(2)A	0.5058 (4)	0.0007 (7)	0.3332 (4)
C(3)A	0.5342 (4)	0.0406 (7)	0.2597 (3)
C(4)A	0.6124 (4)	0.1114 (7)	0.2744 (4)
C(5)A	0.6467 (4)	0.1484 (6)	0.2109 (3)
C(6)A	0.7352 (4)	0.2249 (6)	0.2360 (4)
C(7)A	0.7250 (5)	0.3134 (7)	0.1637 (4)
C(8)A	0.8141 (4)	0.1393 (8)	0.2459 (5)
C(9)A	0.7570 (5)	0.2990 (7)	0.3187 (4)
C(10)A	0.4689 (6)	−0.1275 (10)	0.3181 (5)
C(11)A	0.5817 (5)	0.0025 (11)	0.4199 (4)
C(1)B	0.1288 (6)	0.0344 (13)	−0.0465 (6)
C(2)B	0.1975 (4)	0.0070 (7)	0.0369 (4)
C(3)B	0.2877 (4)	0.0723 (7)	0.0512 (3)
C(4)B	0.2985 (4)	0.1939 (7)	0.0833 (4)
C(5)B	0.3756 (4)	0.2685 (7)	0.1000 (4)
C(6)B	0.3778 (4)	0.4034 (7)	0.1249 (4)
C(7)B	0.2947 (5)	0.4441 (9)	0.1430 (5)
C(8)B	0.4620 (6)	0.4306 (9)	0.2032 (6)
C(9)B	0.3823 (7)	0.4780 (8)	0.0536 (5)
C(10)B	0.1616 (5)	0.0238 (11)	0.1029 (5)
C(11)B	0.2124 (6)	−0.1254 (10)	0.0369 (8)

Table III. Principal Bond Angles (deg) in $[(tmhd)_2Cr(OCH_3)]_2$

O(1)–Cr–O(1)′	78.3 (2)	O(3)A–Cr–O(5)A	88.7 (1)
O(1)–Cr–O(3)A	173.6 (2)	O(3)A–Cr–O(3)B	84.4 (1)
O(1)–Cr–O(5)A	92.0 (1)	O(3)A–Cr–O(5)B	92.6 (1)
O(1)–Cr–O(3)B	95.6 (1)	O(5)A–Cr–O(3)B	170.3 (1)
O(1)–Cr–O(5)B	93.8 (1)	O(5)A–Cr–O(5)B	84.6 (1)
O(1)′–Cr–O(3)A	95.3 (1)	O(3)B–Cr–O(5)B	89.0 (1)
O(1)′–Cr–O(5)A	94.5 (1)	Cr–O(1)–Cr′	101.7 (2)
O(1)′–Cr–O(3)B	92.8 (1)	Cr–O(1)–C(1)	124.4 (3)
O(1)′–Cr–O(5)B	172.0 (1)	Cr′–O(1)–C(1)	120.9 (3)
Cr–O(3)A–C(3)A	127.6 (4)	Cr–O(3)B–C(3)B	126.1 (4)
Cr–O(5)A–C(5)A	125.7 (3)	Cr–O(5)B–C(5)B	127.9 (4)

Solution and Refinement of the Structure. The location of the chromium atom was 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 29 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 0.126 and 0.135, 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 0.076 and 0.088, respectively, and examination of a subsequent difference Fourier map revealed the location of all 41 hydrogen atoms. Attempts to refine the hydrogen atom parameters were unsuccessful, so all hydrogen atoms were assigned fixed isotropic thermal parameters in the range 6–15 $Å^2$, depending on the thermal parameters of the C atoms to which they were attached, 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 0.057 and 0.045, respectively; no parameter experienced a shift of more than 0.8σ, which was taken as evidence of convergence. A final difference Fourier was featureless, with no peak higher than 0.2 e $Å^{-3}$. All computer programs used were those provided by Enraf-Nonius in the CAD-4/SDP package. Atomic scattering factors and anomalous dispersion corrections were taken from ref 22.

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(14) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173.
(15) Josephesen, J.; Pedersen, E. *Inorg. Chem.* **1977**, *16*, 2534.
(16) Güdel, H. U.; Hauser, U. *J. Solid State Chem.* **1980**, *35*, 230.
(17) Decurtins, S.; Güdel, H. U.; Pfeuti, A. *Inorg. Chem.* **1982**, *21*, 1101.
(18) Decurtins, S.; Güdel, H. U. *Inorg. Chem.* **1982**, *21*, 3598.
(19) Vaughn, J. W.; Seiler, G. J.; Wierschke, D. J. *Inorg. Chem.* **1977**, *16*, 2423.
(20) Kasuga, K.; Itou, T.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1026.
(21) Mahendra, K. N.; Parashar, G. K.; Mehrotra, R. C. *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 213.
(22) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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

complex	R, Å	ϕ, deg	θ, deg	J, cm^{-1} obsd[a]	J, cm^{-1} calcd[b]	ref
$[Cr(3\text{-}Cl\text{-}acac)_2(OMe)]_2$	1.959 (2)	101.1 (1)	24.4	9.8	17.6	25
$[Cr(3\text{-}Br\text{-}acac)_2(OMe)]_2$	1.962 (4)	101.5 (2)	25.7	8.5	16.2	26
$[Cr(3\text{-}Br\text{-}acac)_2(OEt)]_2$	1.951 (6)	101.8 (3)	18.3	17.9	22.3	26
$[Cr(acac)_2(OMe)]_2$[c]	1.962 (9)	101.0 (3)	29.8	9.8	15.2	15
$[Cr(tmhd)_2(OMe)]_2$	1.954 (5)	101.7 (2)	31.2	8.9	18.0	this work

[a] Triplet-state energy as calculated from the observed susceptibility data. [b] Triplet-state energy calculated from the expression in ref 8. [c] The isomer here is the racemic form; all others are meso forms.

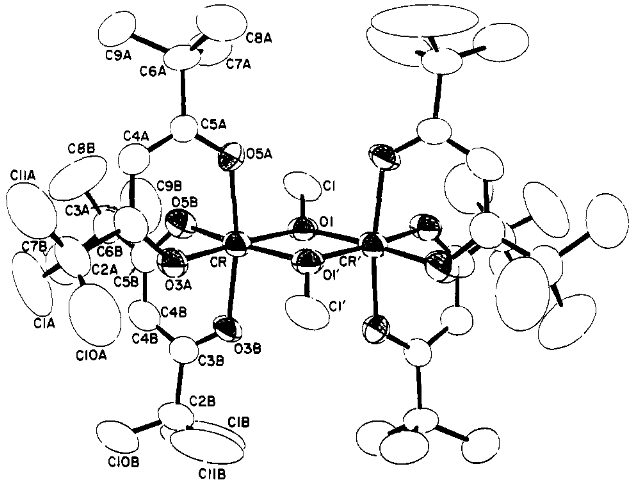

Figure 1. View of the dimeric $[(tmhd)_2Cr(OCH_3)]_2$ molecule. Hydrogen atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by the inversion center.

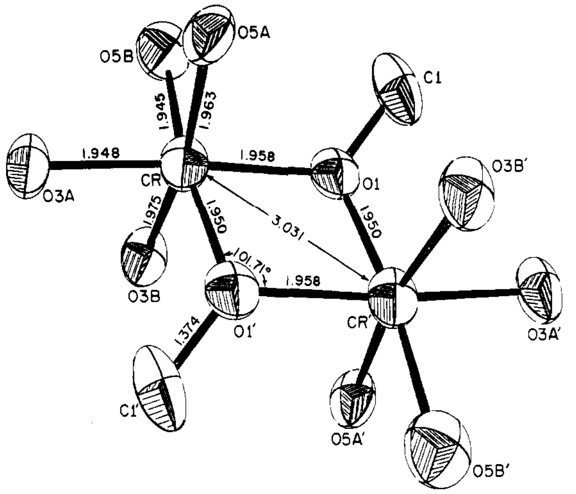

Figure 2. Coordination around the chromium centers in $[(tmhd)_2Cr(OCH_3)]_2$. Esd's on distances: Cr–Cr', 0.002 Å; Cr–O, 0.003 Å; C–O, 0.005 Å.

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 $[(tmhd)_2Cr(OCH_3)]_2$ (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionato) units which are well separated from each other. The geometry of one dimer is shown in Figure 1, and the coordination sphere around the chromium(III) centers is shown in Figure 2. The principal bond lengths and angles are displayed in Figure 2 and Table III, respectively.

The geometry around each chromium center is roughly octahedral, the coordination sphere being occupied by two bidentate tmhd ligands and by two cis methoxo oxygen atoms. The distortions from octahedral geometry are not severe, the trans angles falling in the range 170.3 (1)–173.6 (2)° while the cis angles, with the exception of the O(1)–Cr–O(1)' angle, are between 84.4 (1) and 95.6 (1)°. The O(1)–Cr–O(1)' angle subtended by the bridging methoxo groups is 78.3 (2)°.

The Cr_2O_2 bridging unit is constrained to be planar by the crystallographic inversion center. The methoxy carbon atom C(1) is considerably out of this plane, lying 0.711 (6) Å above the plane. With an O(1)–C(1) bond length of 1.374 (5) Å, this out-of-plane distance corresponds to a θ angle of 31.2 (4)°. As is shown in Table IV, this value of θ is similar to those of 24.4–29.8° observed in the other methoxo-bridged dimers of chromium(III)[12,23,24] but is considerably larger than that of 18.3° in the only ethoxo-bridged complex whose structure has been reported.[24] The two independent bridging Cr–O bond distances (R) are 1.950 (3) and 1.958 (3) Å, with an average value of 1.954 Å. The Cr–Cr separation in the dimer is 3.031 (2) Å, which is within the narrow range of 3.025 (2)–3.038 (3) Å in the other Cr(III) alkoxo-bridged dimers,[12,23,24] and the Cr–O–Cr bridging angle (ϕ) is 101.7 (2)°. As is also shown in Table IV, these R and ϕ values are again comparable to those in the analogues studied earlier.

Although the actual geometry of the dimer is $C_i(\bar{1})$, it approximates $C_{2h}(2/m)$ rather than the equally possible $D_2(222)$. Thus, as is seen in Figure 1, the isomer studied here is the centrosymmetric meso form; the 2,4-pentanedionato (acac) analogue was crystallized as the racemic form,[12] but all other alkoxy-bridged dimers were also isolated as meso forms. Similarly, most of the dihydroxo-bridged chromium(III) dimers studied crystallographically have also been meso,[3,7,10,25,26] although some racemic isomers have been isolated.[27-29]

The five-membered chelating portions of the two tmhd ligands are approximately planar, the greatest deviations from the least-squares planes through the five atoms [O(3), C(3), C(4), C(5), O(5)] being 0.033 (7) and 0.040 (6) Å in the A and B ligands, respectively. The chromium atom is considerably out of these planes, lying 0.467 (1) Å above the A ring and 0.446 (1) Å below the B ring. The two planes are inclined at an angle of 61.6° to each other, which is close to the idealized value of 60°. The geometry of the ligands is similar to that found in a variety of metal complexes of β-diketonates.[12,23,24,30] The Cr–O bond lengths are in the range

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(23) Estes, E. D.; Scaringe, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1976**, *15*, 1179.

(24) Estes, E. D.; Scaringe, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1977**, *16*, 1605.

(25) Srdanov, G.; Herak, R.; Radanovic, D. J.; Velselinovic, D. S. *Inorg. Chim. Acta* **1980**, *38*, 37.

(26) Larsen, S.; Hansen, B. *Acta Chem. Scand., Ser. A* 1981, *A35*, 105.

(27) Veal, J. T.; Hatfield, W. E.; Hodgson, D. J. *Acta Crystallogr., Sect. B* **1973**, *B29*, 12.

(28) Scaringe, R. P.; Singh, P.; Eckberg, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 1127.

(29) Oki, H.; Yoneda, H. *Inorg. Chem.* **1981**, *20*, 3875.

(30) Morosin, B. *Acta Crystallogr.* **1965**, *19*, 131 and references therein.

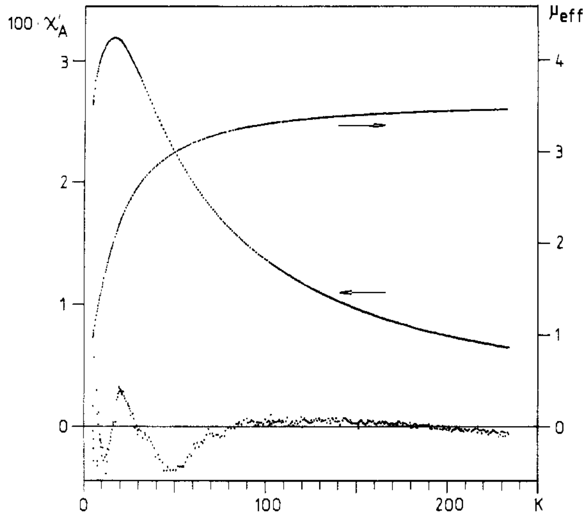

Figure 3. Temperature dependence of the magnetic susceptibility per chromium (left scale, cgs units) and effective magnetic moment (right scale, Bohr magnetons) of $[(tmhd)_2Cr(OCH_3)]_2$. The lower, almost random distribution of dots around the abscissa is $(\chi_{obsd} - \chi_{calcd}) \times 50$, where χ_{calcd} is based on the parameters in the text.

1.945 (4)–1.975 (3) Å with an average value of 1.958 (14) Å; these values are almost identical with those[12] in $[Cr(acac)_2(OCH_3)]_2$. It is noteworthy that the two bonds that are trans to the methoxy bridges [Cr–O(3)A and Cr–O(5)B] are significantly shorter than the other two, with lengths of 1.948 (3) and 1.945 (4) Å as compared to 1.963 (3) and 1.975 (3) Å. This apparent shortening does not occur[12] in $[Cr(acac)_2(OCH_3)]_2$. The chelating O–Cr–O angles of 88.7 (1) and 89.0 (1)° are comparable to the values of 89.4–90.1° found in the acac analogue.[12]

Magnetic Properties

The temperature dependence of the magnetic susceptibility and the effective magnetic moment of a powdered sample of the complex are shown in Figure 3.

The observed susceptibility data were fitted to the simple Van Vleck Hamiltonian

$$\mathcal{H} = JS_1 \cdot S_2$$

by using the fitting procedure described earlier.[5,12] The fit to this model, while generally good, is only approximate, the variance per degree of freedom being 4.07. Inclusion of a second-order term (biquadratic exchange) in the Hamiltonian[10]

$$\mathcal{H} = JS_1 \cdot S_2 - j(S_1 \cdot S_2)^2$$

gave a markedly improved fit, the variance/degree of freedom falling to 1.12. The parameters derived from this model are $g = 1.980$ (1), $J = 8.18$ (2) cm^{-1}, and $j = 0.105$ (8) cm^{-1}. The calculated energies of the triplet, quintet, and septet states relative to the singlet ground state are, therefore, 8.86 (5), 25.96 (9), and 50.0 (2) cm^{-1}, respectively.

Agreement between the observed structural and magnetic properties and those calculated from our empirical model[8] is not entirely satisfying; the value calculated by using the present structural parameters and the values for *a*, *b*, and *c* in the expression[8]

$$J = [\exp(-ar')](bJ_{AF} - cJ_F)$$

where $r' = R - 1.8$ Å, J_{AF} is the antiferromagnetic contribution to J (dependent on θ and ϕ), and J_F is the ferromagnetic contribution (dependent on ϕ), is 18 (8) cm^{-1}. The parameters *a*, *b*, and *c* can be improved only by the advent of additional precise data for θ and ϕ, such as are available from the present experiment and the other studies in alkoxo-bridged systems. Regretably, the five structures of this type are all in the same ϕ and θ range, and consequently while an excellent fit $[|J_{obsd} - J_{calcd}| < 1$ cm$^{-1}]$ to the magnetic properties of these complexes can be obtained by using only these five data, the esd's on the derived parameters are so large as to render the results meaningless. We are, therefore, attempting to design, synthesize, and characterize complexes of this type that will have structural parameters markedly different from those observed here.

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Supplementary Material Available: Tables of hydrogen atom positional and thermal parameters, anisotropic thermal parameters, bond lengths and angles in the tmhd ligands, and observed and calculated structure amplitudes (19 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University
of Southern California, Los Angeles, California 90089,
Dipartimento di Chimica Generale, Università di Milano,
Milano 20133, Italy, Centro di studio sulla sintesi e la
struttura dei composti dei metalli di transizione nei bassi
stati di ossidazione, Milano 20133, Italy,
and Chemistry Department, Brookhaven National Laboratory,
Upton, New York 11973

X-ray and Neutron Diffraction Study of $[P(CH_2C_6H_5)(C_6H_5)_3]^+[HIr_4(CO)_{11}]^-$

Robert Bau,*[†] Michael Y. Chiang,[†] Chiau-Yu Wei,[†]
Luigi Garlaschelli,*[‡] Secondo Martinengo,[§]
and Thomas F. Koetzle*[⊥]

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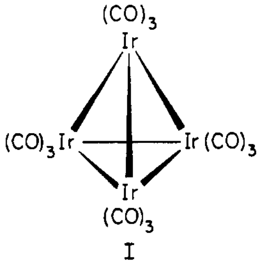
The monohydride anion $[HIr_4(CO)_{11}]^-$ was first prepared by Malatesta and co-workers in 1967 by treatment of $Ir_4(CO)_{12}$ with base.[1] It was subsequently shown that the compound can also be be made via the hydrolysis of $[Ir_4(CO)_{11}(COOR)]^-$ (R = Me, Et).[2a] There has been no report in the literature of the crystal structure of $[HIr_4(CO)_{11}]^-$ in spite of intensive structural interest in the parent compound $Ir_4(CO)_{12}$ (I)[3,4] and its derivatives. As opposed to configuration II of



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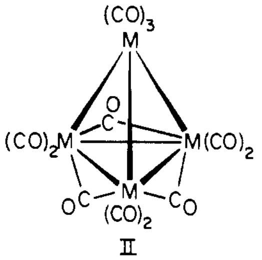

II

M = Co, Rh

[†] University of Southern California.

[‡] Università di Milano.

[§] Centro di studio sulla sintesi e la struttura dei composti dei metalli di transizione nei bassi stati di ossidazione.

[⊥] Brookhaven National Laboratory.

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