

structure of $[(\text{MeCp})_2\text{ZrH}(\mu\text{-H})]_2^{14}$ as typical of the MeCp ligand, the methine protons in **1** are separated by over 2.6 Å whereas the carbon is only 0.92 Å from a proton. This ratio of 2.7 more than compensates for the 4-fold lower gyromagnetic ratio of carbon because the distance factor enters as the sixth power. The T_1 for the ipso carbon, 56 s, is longer than any of the proton T_1 's. This carbon, unlike the methines, does not show a full NOE and its relaxation is not dominated by the dipole–dipole interaction.

$(\text{RCp})_2\text{Zr}(\text{CD}_3)_2$. Proton and carbon-13 chemical shifts have not been previously reported for the higher homologues of **2**. The cyclopentadienyl chemical shifts (Table III) are not a function of the R substituent.

Experimental Section

NMR spectra were obtained on a Varian XL-400 spectrometer, operating at 400 MHz for ^1H , on solutions in CDCl_3 for **1** and **4** and in toluene- d_8 for all the other compounds. Proton chemical shifts are given relative to internal Me_4Si ; carbon chemical shifts were determined relative to CDCl_3 (76.91 ppm) or the para CD of toluene- d_8 (125.2 ppm). Resolution-enhanced proton spectra were obtained with acquisition times in excess of 5 s and pseudoecho weighting of the free induction decay. Resolution-enhanced uncoupled carbon spectra were obtained with acquisition times exceeding 2.5 s and a delay, during which the decoupler was on for a time equal to the acquisition time. The proton–carbon correlations were determined by single-frequency decoupling of the proton resonances. 2D INADEQUATE spectra of **1** were obtained by using a 4.0 M solution to which sufficient $\text{Cr}(\text{acac})_3$ was added to reduce the carbon relaxation times to less than 0.2 s. The spectra were acquired over 15 h with a 0.6-s repetition time, 3100-Hz spectral width, and 64 increments. The delays were optimized for $J(\text{CC}) = 49$ Hz. Approximate values of $J(\text{CC})$ were determined directly from the ^{13}C satellites on spectra run for several hours with a 4.0-s acquisition time and 55° pulses (8 μs) on concentrated solutions (>1 M). Spin–lattice (T_1) relaxation times were determined by using the inversion–recovery pulse sequence with at least eight values of τ , typically between 1 and 16 s, and a delay exceeding $4T_1$. Spin–spin relaxation times were determined by using the Carr–Purcell–Meiboom–Gill pulse sequence with the same delay as for the T_1 analyses. Proton T_1 relaxation times for **1** ranged from 4.4 to 6.5 s on an undegassed solution; the values in Table II were obtained on a solution degassed via the freeze–pump–thaw technique. Proton homonuclear NOE experiments were performed with single-frequency decoupling on the methyl protons. The spectrum was quantitatively compared to a spectrum obtained under identical conditions, but with the decoupler offset 1000 Hz upfield. Sixteen transients, obtained with a 2-min recycle time, were accumulated with 90° pulses, alternating the decoupler frequency every four pulses. The proton homonuclear NOE's were attenuated by competitive relaxation by paramagnetic oxygen and were only 2% in the undegassed solution of **1**.

Syntheses of $(\text{RCp})_2\text{ZrCl}_2$. A generalized preparation of (alkylcyclopentadienyl)metal complexes requires generation of RC_5H_4^- . In contrast to ref 15, we find that this is difficult to achieve by alkylation in THF of NaCp by alkyl halides. This is presumably because an equilibrium mixture of C_5H_5^- and its mono- and dialkylated derivatives is produced, which, when treated with ZrCl_4 , yields a complex mixture of products. A one-pot synthesis is possible when a highly reactive alkylating agent, such as ethyl trifluoromethanesulfonate, is used. Alternatively, NaCp in liquid ammonia can be cleanly alkylated by alkyl halides, a modification of the method of Alder and Ache.¹⁶

$(\text{EtCp})_2\text{ZrCl}_2$. A solution of 3.0 g (40 mmol) of LiCp (Aldrich) in 40 mL of glyme (1,2-dimethoxyethane) was added under nitrogen and with stirring to 7.17 g (40 mmol) of ethyl trifluoromethanesulfonate (Aldrich) in 25 mL of the same solvent at 0 °C. This mixture was stirred for 1 h at room temperature, recooled to 0 °C, and treated with 16 mL of 2.5 M *n*-BuLi (40 mmol) in hexane. After 2 h, a solution of 4.6 g (20 mmol) of ZrCl_4 in 40 mL of glyme was added. After overnight stirring, the mixture was filtered through celite and evaporated to dryness under vacuum. Recrystallization of the residue from hot hexane afforded 3.2 g (46%) of product as white needles, mp 106.5–107.0 °C. Anal. Calc (found): C, 44.4 (44.3); H, 5.6 (5.6). Use of glyme in this synthesis is preferred because some triflate salts can polymerize THF.

$(n\text{-BuCp})_2\text{ZrCl}_2$. Freshly distilled C_5H_6 was added with stirring at –78 °C under nitrogen to 1.43 g (62 mmol) of Na in 100 mL of liquid NH_3 until the blue color was discharged. Next, 11.4 g (62 mmol) of *n*- $\text{C}_4\text{H}_9\text{I}$ was added dropwise. The mixture was warmed to room tem-

perature overnight under a slow stream of N_2 . Pentane, 20 mL, was added, and the liquid residue was decanted and evaporated at room temperature under water aspirator vacuum. There remained 5.8 g (77%) of a ca. 80% pure 1:1 mixture of 1- and 2- $(n\text{-C}_4\text{H}_9)\text{C}_5\text{H}_5$; the ^1H NMR spectrum in CDCl_3 showed CH_2 multiplets at 2.95 and 2.90 ppm. This mixture need not be distilled or further purified. It was dissolved in THF and converted, by treatment with *n*-BuLi in hexane followed by ZrCl_4 in glyme (vide supra), to $(n\text{-BuCp})_2\text{ZrCl}_2$, mp 93 °C, as thin needles from heptane (68% yield based on *n*- $\text{C}_4\text{H}_9\text{I}$). Anal. Calc (found): C, 53.5 (53.6); H, 6.4 (6.3).

$(n\text{-PrCp})_2\text{ZrCl}_2$, mp 110–111 °C, was similarly prepared (74% yield). Anal. Calc (found): C, 51.1 (51.4); H, 5.9 (5.8).

The $(\text{RCp})_2\text{ZrCl}_2$ compounds were converted to their $(\text{RCp})_2\text{Zr}(\text{CD}_3)_2$ analogues by a literature method using LiCD_3 in diethyl ether followed by quenching of unreacted LiCD_3 by Me_3SiCl .¹⁷ After removal of solvents, the products were isolated by extraction with hexane. The substituted dimethylzirconocenes are liquids or low-melting solids; purity was verified by NMR and mass spectroscopy.

Supplementary Material Available: Figures S1 and S2, showing ^1H -resolved spectra of **1**, Figures S3 and S4, portraying uncoupled ^{13}C NMR spectra of Cp multiplets of **1**, and Figures S5–S10, giving unsymmetrized and symmetrized COSY spectra of **1** with recycle delays of 1.2 and 10.2 s (10 pages). Ordering information is given on any current masthead page.

(17) Samuel, E.; Rausch, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6263.

Contribution from the Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel, and Chemistry Department I, Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark

A New Tetranuclear Cr(III) Complex with a $[\text{Cr}_4\text{O}_2]$ Core: Synthesis, Structure, and Magnetic Properties of $[\text{Cr}_4\text{O}_2(\text{O}_2\text{CCH}_3)_7(\text{bpy})_2]\text{PF}_6$ (bpy = 2,2'-Bipyridine)

Avi Bino,*[†] Ruthie Chayat,[†] Erik Pedersen,*[†] and Andreas Schneider[†]

Received May 17, 1990

Introduction

Basic metal carboxylates with a $[\text{M}_3\text{O}]^{n+}$ core, in which three metal atoms in an equilateral triangle are bridged by an oxo ligand, are common in the coordination chemistry of many transition metals.¹ Chromium(III) compounds containing the $\{\text{Cr}_3\text{O}(\text{O}_2\text{CR})_6\}^+$ core were prepared a century ago, and their physical properties were extensively investigated in many laboratories. The $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]^+$ ion is the prototypical species for the study of antiferromagnetic interactions between the d^3 chromium(III) ions.¹

The structure of an unusual tetranuclear sulfur-centered chromium(III) complex, $[\text{Cr}_4\text{S}(\text{O}_2\text{CCH}_3)_8(\text{H}_2\text{O})_4]^{2+}$, was recently reported.² This complex, which is prepared by the reaction between chromium and sulfur in acetic acid, exhibits intramolecular ferromagnetic coupling with a ground state with spin $S = 6$.

A dinuclear, carboxylato-bridged, chromium(III) complex that results from the reaction of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and formic acid, $[\text{Cr}_2(\text{OH})(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_6]^{3+}$, was found to be an intermediate in the formation of trinuclear basic chromium carboxylates.³ This complex consists of two octahedrally coordinated Cr(III) ions bridged by an hydroxo ligand and two bidentate formate groups. An antiferromagnetic exchange coupling exists between the two Cr(III) centers with $J = -11.1$ (2) cm^{-1} .

Recently, research in Fe(III) and Mn(III) chemistry has revealed a new class of basic metal carboxylates containing a tet-

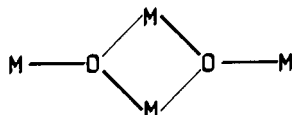
(14) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889.

(15) Lappert, M. F.; Pickett, C. J.; Riley, P. I.; Yarrow, P. I. W. *J. Chem. Soc., Dalton Trans.* **1981**, 805.

(16) Alder, K.; Ache, H.-J. *Chem. Ber.* **1962**, *95*, 503.

* The Hebrew University of Jerusalem.

† University of Copenhagen.

Figure 1. Structure of the M_4O_2 core.Table I. Crystallographic Data for $[Cr_4O_2(O_2CCH_3)_7(bpy)_2]PF_6$

formula: $C_{34}H_{37}Cr_4F_6N_4O_{16}P$	space group = $I2/c$ (No. 15)
fw = 1110.62	$T = 22$ °C
$a = 16.561$ (2) Å	$\lambda = 1.54178$ Å
$b = 11.825$ (2) Å	$\rho_{\text{calcd}} = 1.573$ g cm ⁻³
$c = 24.204$ (4) Å	$\mu = 84.58$ cm ⁻¹
$\beta = 98.32$ (3)°	$R(F_o) = 0.041$
$V = 4690$ (1) Å ³	$R_w(F_o) = 0.059$
$Z = 4$	

ranuclear core, $\{M_4O_2\}^{8+}$ (Figure 1). Planar and bent $\{Fe_4O_2\}^{8+}$ and $\{Fe_4(OH)_2\}^{10+}$ units occur as building blocks in several minerals and synthetic compounds.⁴ Similarly, $\{Mn_4O_2\}^{n+}$ appears in several complexes such as $[Mn_4O_2(OAc)_7(bpy)_2]^+$ and in higher aggregates of higher nuclearity.⁵ In most cases, the $\{M_4O_2\}$ core is produced by the conversion of other polynuclear species such as the dinuclear $[Fe_2OCl_6]^{2-}$ or the trinuclear $[Fe_3O(O_2CR)_6L_3]^+$ or $[Mn_3O(O_2CR)_6L_3]^+$.^{4,5}

This work is part of a project whose purpose is to elucidate the rationale behind the aggregation reactions that lead to the formation of polynuclear species. Here we investigate the role of the starting material nuclearity in the formation of tetranuclear $\{M_4O_2\}$ core.

We report the preparation, structure, and magnetic properties of the first Cr(III) complex containing the $\{Cr_4O_2\}^{8+}$ core, namely, $[Cr_4O_2(OAc)_7(bpy)_2]^+$ (**1**), and the various synthetic aspects associated with this tetranuclear moiety.

Experimental Section

Preparation of $[Cr_4O_2(O_2CCH_3)_7(bpy)_2]PF_6$. Mononuclear $[Cr(H_2O)_6](O_2CCH_3)_3$ (0.6 mmol) or, alternatively, trinuclear $[Cr_3O(O_2CCH_3)_6(H_2O)_3]Cl$ (0.2 mmol) was dissolved in molten bipyridine (2.2 mmol). The solution was stirred and kept at 80 °C for 4 h. A 20-mL aliquot of water was added, and the purple solution was filtered. KPF_6 (0.05 g) was added, and the resultant precipitate was filtered and washed with methanol; yield 0.08 g (0.07 mmol, 48%). Recrystallization from CH_3CN yielded purple prisms of (**1**) PF_6 .

Electronic spectrum of **1** in CH_3CN , $\lambda_{\text{max}}/nm(\epsilon_{M/Cr}, L \text{ mol}^{-1} \text{ cm}^{-1})$: 440 sh (50), 507 sh (30), 562 (55).

X-ray Crystallography. Diffraction measurements on (**1**) PF_6 were made with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated $Cu K\alpha$ radiation. The unit cell dimensions were obtained by a least-squares fit of 22 reflections in the range $20 < \theta < 35^\circ$. Crystallographic data and other pertinent information are given in Table I. Intensity data were corrected for absorption (empirical), Lorentz, and polarization effects. The heavy-atom positions were obtained by using the results of the SHELX-86 direct-method analysis.^{6a} The structure was refined in space group $I2/c$ to convergence, using anisotropic thermal parameters for all non-hydrogen atoms.^{6b} Values of the atomic scattering factors and the anomalous terms were taken from the conventional sources.^{6c,d} All hydrogen atoms, except those of the central bridging

Table II. Positional Parameters and Estimated Standard Deviations for the Significant Atoms of $[Cr_4O_2(O_2CCH_3)_7(bpy)_2]PF_6$

atom	x	y	z
Cr(1)	0.10144 (4)	0.56820 (6)	0.16119 (2)
Cr(2)	-0.06744 (4)	0.48588 (6)	0.20837 (2)
O(1)	0.0472 (2)	0.4924 (2)	0.2118 (1)
O(11)	0.0410 (2)	0.7086 (2)	0.1665 (1)
O(12)	0.0233 (2)	0.5189 (2)	0.0955 (1)
O(13)	0.1931 (2)	0.6126 (2)	0.2196 (1)
O(21)	-0.0766 (2)	0.6528 (2)	0.1941 (1)
O(22)	-0.0897 (2)	0.4566 (3)	0.1266 (1)
O(23)	-0.0577 (2)	0.3168 (3)	0.2189 (1)
O(33)	0.1885 (2)	0.4902 (3)	0.2905 (1)
N(1)	0.1709 (2)	0.6414 (3)	0.1047 (1)
N(2)	0.1767 (2)	0.4359 (3)	0.1456 (1)

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Cr_4O_2(O_2CCH_3)_7(bpy)_2]PF_6$

Cr(1)-Cr(2)	3.3163 (9)	Cr(1)-Cr(2)'	3.4274 (8)
Cr(1)-O(1)	1.852 (3)	Cr(2)-Cr(2)'	2.7835 (8)
Cr(1)-O(11)	1.952 (3)	Cr(2)-O(1)	1.891 (3)
Cr(1)-O(12)	1.988 (3)	Cr(2)-O(1)'	1.914 (2)
Cr(1)-O(13)	1.989 (3)	Cr(2)-O(21)	2.005 (3)
Cr(1)-N(1)	2.098 (3)	Cr(2)-O(22)	1.990 (3)
Cr(1)-N(2)	2.069 (4)	Cr(2)-O(23)	2.019 (3)
		Cr(2)-O(33)'	2.009 (3)
Cr(1)-O(1)-Cr(2)	124.8 (1)	O(1)-Cr(2)-O(1)'	85.8 (1)
Cr(1)-O(1)-Cr(2)'	131.0 (1)	O(1)-Cr(2)-O(21)	91.0 (1)
Cr(2)-O(1)-Cr(2)'	94.0 (1)	O(1)-Cr(2)-O(22)	95.2 (1)
O(1)-Cr(1)-O(11)	93.8 (1)	O(1)-Cr(2)-O(23)	88.5 (1)
O(1)-Cr(1)-O(12)	93.8 (1)	O(1)-Cr(2)-O(33)'	175.0 (1)
O(1)-Cr(1)-O(13)	92.9 (1)	O(1)'-Cr(2)-O(21)	97.6 (1)
O(1)-Cr(1)-N(1)	174.5 (1)	O(1)'-Cr(2)-O(22)	172.2 (1)
O(1)-Cr(1)-N(2)	96.8 (1)	O(1)'-Cr(2)-O(23)	85.0 (1)
O(11)-Cr(1)-O(12)	91.3 (1)	O(1)'-Cr(2)-O(33)'	90.8 (1)
O(11)-Cr(1)-O(13)	94.3 (1)	O(21)-Cr(2)-O(22)	90.1 (1)
O(11)-Cr(1)-N(1)	91.5 (1)	O(21)-Cr(2)-O(23)	177.3 (1)
O(11)-Cr(1)-N(2)	169.4 (1)	O(21)-Cr(2)-O(33)'	85.8 (1)
O(12)-Cr(1)-O(13)	171.0 (1)	O(22)-Cr(2)-O(23)	87.3 (1)
O(12)-Cr(1)-N(1)	87.4 (1)	O(22)-Cr(2)-O(33)'	88.6 (1)
O(12)-Cr(1)-N(2)	88.4 (1)	O(23)-Cr(2)-O(33)'	94.9 (1)
O(13)-Cr(1)-N(1)	85.4 (1)		
O(13)-Cr(1)-N(2)	84.9 (1)		
N(1)-Cr(1)-N(2)	77.9 (1)		

acetate group, were introduced as fixed contributions to F with $U = 0.05 \text{ \AA}^2$.

The discrepancy indices $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ are listed in Table I.

Physical Measurements. The magnetic susceptibility was measured on a powdered sample in the temperature range 2–300 K at 1.2 T. Preliminary descriptions of the instrument and the temperature calibration are found elsewhere.⁷ Diamagnetic corrections were applied as usual.

The UV-visible spectrum was recorded on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer.

Results and Discussion

Preparation. As mentioned, $\{Fe_4O_2\}^{8+}$ or $\{Mn_4O_2\}^{8+}$ cores were previously prepared by using $\{Fe_2O_2\}^{4+}$ or $\{Fe_3O_2\}^{7+}$ and $\{Mn_3O_2\}^{7+}$ units, respectively.^{4,5} Here, we show that $\{Cr_4O_2\}^{8+}$ is formed from $\{Cr_3O_2\}^{7+}$ or $\{Cr(H_2O)_6\}^{3+}$ units. The fact that the tetranuclear core in **1** is produced when a mononuclear species is used as the starting material suggests that di- or trinuclear units are not essential ingredients in the aggregation process. A possible mechanism for the formation of the M_4O_2 core from other polynuclear units involves degradation of the polynuclear complexes in a process in which mononuclear units are formed and

- (1) Cannon, R. D.; White, R. P. *Prog. Inorg. Chem.* **1988**, *36*, 195.
- (2) Bino, A.; Johnston, D. C.; Goshorn, D. P.; Halbert, T. R.; Stiefel, E. I. *Science*, **1988**, *241*, 1479.
- (3) Turowski, P. N.; Bino, A.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 811.
- (4) Lippard, S. J. *Agnew. Chem., Int. Ed. Engl.* **1988**, *27*, 344.
- (5) (a) Lis, T. *Acta Crystallogr., Sect. B* **1980**, *36*, 2042 (b) Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236 (c) Christmas, C.; Vincent, J. B.; Huffman, J. C.; Christou, G.; Chang, H.; Hendrickson, D. N. *Agnew. Chem., Int. Ed. Engl.* **1987**, *26*, 915.
- (6) (a) Sheldrick, G. M. *Crystallographic Computing 3*; Oxford University Press: Oxford, England, 1985; pp 175–189. (b) All crystallographic computing was done on a CYBER 855 computer at the Hebrew University with the SHELX 1977 structure determination package. (c) Cromer, D. T.; Weber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV. (d) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

- (7) (a) Josephson, J.; Pedersen, E. *Inorg. Chem.* **1977**, *16*, 2534 and references therein. (b) Anderson, P.; Damhus, T.; Pedersen, E.; Petersen, A. *Acta Chem. Scand.* **1984**, *A38*, 359.

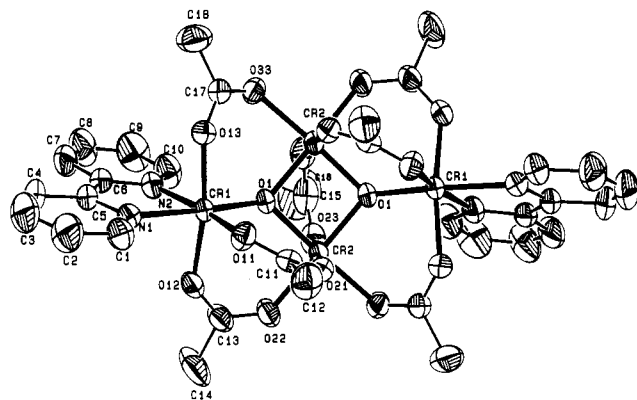


Figure 2. Structure of $[\text{Cr}_4\text{O}_2(\text{OAc})_7(\text{bpy})_2]^+$ and the atom numbering scheme. Each atom is represented by its ellipsoid of thermal displacement drawn at the 50% probability level.

reassembled to form a thermodynamically stable M_4O_2 . A mechanism in which mononuclear units aggregate stepwise and form di-, tri-, and finally tetranuclear complexes cannot be excluded at this stage. We are currently engaged in further investigation of related systems using mixed-metal $\{\text{M}'\text{M}_2\text{O}\}^{8+}$ units as starting materials.

Structure. The atomic positional parameters of all chromium oxygen and nitrogen atoms are listed in Table II. Table III gives the important bond lengths and angles. Figure 2 shows the numbering scheme in 1. With $Z = 4$ in the cell of space group $I2/c$ there is only half a $[\text{Cr}_4\text{O}_2(\text{OAc})_7(\text{bpy})_2]^+$ ion in the asymmetric unit with the other half related to it by a crystallographic 2-fold axis. The two carbon atoms of the central OAc⁻ bridge, C(15) and C(16), reside on the axis itself. The structure and dimensions of the tetranuclear cation are similar to those found for the analogous $[\text{Mn}_4\text{O}_2(\text{OAc})_7(\text{bpy})_2]^+$.^{5b} The $\{\text{Cr}_4\text{O}_2\}^{8+}$ core with its seven bridging carboxylates in 1 is identical with that found in several Fe(III) and Mn(III) structures. It has a butterfly structure with a dihedral angle of 143.0° . The μ_3 -oxo atom O(1) lies 0.338 \AA below the Cr_3 plane defined by Cr(1), Cr(2), and Cr(2'). The central Cr(2)–Cr(2') distance, $2.7835(8) \text{ \AA}$, is shorter by ca. 0.064 \AA than the corresponding Mn–Mn distance in $\{\text{Mn}_4\text{O}_2\}^{8+}$.^{5b} The Cr(1)–Cr(2) and Cr(1)–Cr(2') distances, $3.3163(9)$ and $3.4274(8) \text{ \AA}$, respectively, are similar to the corresponding Mn–Mn distances in $\{\text{Mn}_4\text{O}_2\}^{8+}$ [$3.299(5)$ – $3.385(5) \text{ \AA}$].

Magnetic Properties. The measured magnetic susceptibility of the title compound corresponds to a calculated effective moment of the tetranuclear unit of $6.04 \mu_B$ at 281.5 K gradually falling to $2.44 \mu_B$ at 2.00 K . The susceptibility vs temperature plot shows no maximum. The susceptibility data were fitted to the expression

$$\chi'(T) = -\frac{N}{H} \frac{\sum_i \left(\frac{\partial E_i}{\partial H} \right) \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K \quad (1)$$

by minimization of

$$\sum_j \frac{[\chi_{\text{obsd}}(T_j) - \chi'(T_j)]}{\sigma^2(\chi(T_j)) + \left(\frac{\partial \chi_{\text{obsd}}}{\partial T} \right)^2 \sigma^2(T_j)} \quad (2)$$

Here χ_{obsd} is the measured susceptibility per formula unit corrected for diamagnetic contributions. The E_i in (1) are the energies of the components of the ground-state manifold of the complex as obtained by diagonalization of the isotropic Heisenberg-type model Hamiltonian

$$\hat{H} = \sum_{k<l} J_{kl} \hat{S}_k \cdot \hat{S}_l + \beta g \mathbf{H} \cdot \hat{S} \quad (3)$$

The adjustable parameters are J_{kl} , g , and K . K is an additive constant accounting for the temperature-independent paramagnetism and correction for the Pascal diamagnetism. The estimated

Table IV. Parameters for $[\text{Cr}_4\text{O}_2(\text{O}_2\text{CCH}_3)_7(\text{bpy})_2]\text{PF}_6$ Derived from Magnetic Susceptibility Data in the Temperature Range 2.00 – 281.5 K

param	model 1 ^c	model 2	model 3
$J_{12} = J_{23} = J_{34} = J_{41}/\text{cm}^{-1}$	31.4 (1)	28.74 (4)	29.42 (10)
J_{13}/cm^{-1}	50.9 (2)	48.39 (5)	49.41 (20)
J_{24}/cm^{-1}	0	7.12 (8)	6.80 (9)
K/cgsu	0	0	$+1.8(4) \times 10^{-4}$
f^a	184	183	182
v/f^b	24.4	0.89	0.87

^a Degrees of freedom. ^b Variance per degree of freedom. ^c See text for description of the models.

standard deviations used in (2) are reported elsewhere⁸ as is the general computer program.^{7b} No attempt was made to include biquadratic coupling constants in the fittings for this compound. The natural choice of coupling parameters would be based on symmetry and would include $J_{12} = J_{34}$, $J_{23} = J_{41}$, J_{13} , and J_{24} . Such fittings diverged even when J_{24} was fixed at zero.

Convergent data fittings were performed by using three different models. In all cases g was fixed at 1.98. In model 1, the two parameters varied were $J_{12} = J_{23} = J_{34} = J_{41}$ and J_{13} ; J_{24} and K were both fixed at zero. In model 2, the three variable parameters were $J_{12} = J_{23} = J_{34} = J_{41}$, J_{13} , and J_{24} ; K was fixed at zero. In model 3, the four parameters were as in model 2, but K was allowed to vary. The results are shown in Table IV. Neither the numerical values of the initial parameters nor their signs were critical to the final results within wide ranges tried.

According to a V^2 test, model 1 is not in agreement with the observations, in contrast to models 2 and 3, which fit almost equally well. At zero magnetic field, the eigenvalues of (3) are grouped in 44 multiplets with spins ranging from $S = 0$ to $S = 6$. Their energies are very similar according to the calculations based on models 2 and 3 using the parameters in Table IV. In model 3, examples of energies in cm^{-1} and spins are as follows: $0.0 (S = 1)$, $18.9 (S = 2)$, $27.9 (S = 1)$, $30.6 (S = 0)$, $38.4 (S = 0)$, $43.7 (S = 0)$, $46.3 (S = 0)$, $53.1 (S = 1)$, ... $648.3 (S = 6)$. The ground state is thus calculated to be a spin triplet.

It is obvious to correlate $J_{12} = J_{23} = J_{34} = J_{41}$ with the interactions Cr(1)–Cr(2), Cr(2)–Cr(1'), Cr(1')–Cr(2'), and Cr(2')–Cr(1), assuming these to be equal, J_{13} with Cr(2)–Cr(2'), and J_{24} with Cr(1)–Cr(1'), although this is not required by any fundamentals. O(1) and O(1') are expected to be far most important contributors to the metal-to-metal π -overlaps than the μ -acetato groups.⁹ The J values in Table IV may be compared with values found for dinuclear chromium(III) complexes. $J_{13} = 49.41(20) \text{ cm}^{-1}$ is close to $J = 45.84(4) \text{ cm}^{-1}$ found for $[\text{2-picetam}]_4\text{Cr}_2(\text{OH})(\text{O})\text{Br}_3 \cdot 5\text{H}_2\text{O}$ having one of the bridging oxygen atoms with similar Cr–O distances.¹⁰ J_{12} , etc. is comparable to $J = 36.09(9) \text{ cm}^{-1}$ found for $[(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cr}(\text{OH})\text{Cr}(\text{N-H}_3)_5]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ having one bridging oxygen atom.¹¹ The nonzero value of J_{24} is reasonable in view of the possible long-distance π -overlap.

Acknowledgment. This research was supported by the Danish National Science Research Council through Grants Nos. 511-742, 511-3993 and 511-10516 (to E.P.). A.B. is grateful to the S.A. Schonbrunn Research Endowment for financial support.

Supplementary Material Available: Tables SI–SV, listing crystallographic data, positional parameters, derived hydrogen positions, bond angles, and bond distances (8 pages); a table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

- (8) Michelsen, K.; Pedersen, E. *Acta Chem. Scand.* **1978**, *A32*, 847.
- (9) Hodgson, D. J.; Glerup, J.; Pedersen, E. *Acta Chem. Scand.* **1983**, *A37*, 161.
- (10) Michelsen, K.; Pedersen, E.; Wilson, S. R.; Hodgson, D. J. *Inorg. Chim. Acta* **1982**, *63*, 141.
- (11) Cline, S. J.; Glerup, J.; Hodgson, D. J.; Jensen, G. S.; Pedersen, E. *Inorg. Chem.* **1981**, *20*, 2229.