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Synthesis and Characterization of Polynuclear Chromium Carbonyl Tetraanions

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Received January 23, 1985

Polynuclear chromium carbonyl complexes of the general formula $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OR})_4]^{4-}$ ($\text{R} = \text{H}, \text{C}_6\text{H}_5$) have been prepared as their Et_4N^+ salts. Reaction of $\text{Cr}(\text{CO})_6$ with excess hydroxide ion in aqueous THF solution yields $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]^{4-}$. The X-ray structure of $[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]$ has been determined. The structural features of the tetraanion consist of a cubane-like A_4B_4 ($\text{A} = \text{chromium}, \text{B} = \text{oxygen}$) arrangement with triply bridging μ_3 -hydroxide groups and $\text{Cr}(\text{CO})_3$ units. The Cr-Cr distance within the Cr_4O_4 core is nonbonding (3.33 (5) Å (average)), consistent with a closed-shell metal configuration. The crystals are monoclinic (space group $I2/a$) with cell constants $a = 21.827$ (7) Å, $b = 12.236$ (2) Å, $c = 22.899$ (4) Å, $\beta = 116.49$ (2)°, $V = 5474$ (5) Å³, and $Z = 8$. The μ_3 -phenoxide derivative, $[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OC}_6\text{H}_5)_4]$, has been prepared by treatment of $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ with $[\text{Et}_4\text{N}][\text{OC}_6\text{H}_5]$ in equimolar concentrations and characterized by spectroscopic methods.

Introduction

Nucleophilic additions of hydroxide ions to group 6^{1c} metal hexacarbonyls have been used in the synthesis of a variety of metal carbonyl anions. For example, $\text{K}[(\mu\text{-H})\text{M}_2(\text{CO})_{10}]$ ($\text{M} = \text{Cr}, \text{W}$) has been prepared in good yields by reaction of $\text{M}(\text{CO})_6$ and KOH in a methanol-tetrahydrofuran mixture containing water.² On the other hand, in aprotic solvent, cryptand- (Kryptofix-222-) solubilized KOH reacts with the group 6 hexacarbonyls to provide the mononuclear $\text{HM}(\text{CO})_5^-$ species.^{3,4} These hydride derivatives have been synthesized by protonation of the corresponding dianions, $\text{M}(\text{CO})_5^{2-}$, and have been fully characterized by X-ray crystallography.^{5,6} Much of the interest in these mononuclear anionic hydrides is centered around their intermediacy in water gas shift chemistry,^{4,7} carbon dioxide reductions,^{3,4,8,9} and the reduction of a large variety of organics (e.g. alkyl halides, ketones, and aldehydes).¹⁰⁻¹²

Several polynuclear metal carbonyl derivatives have also been synthesized via the reaction of hydroxide ions with group 6 metal hexacarbonyls. The tris(μ -hydroxo) trianion $[\text{W}_3(\mu\text{-OH})_3(\text{CO})_6]^{3-}$ can be prepared by alkaline hydrolysis of $\text{W}(\text{CO})_6$ and consists of two $\text{W}(\text{CO})_3$ fragments bridged by three hydroxo groups.¹³ Protonation of this dimer results in the formation of Hieber's acid $[\text{W}_4(\text{CO})_{12}(\mu_3\text{-OH})_4\text{H}_4]$, a complex containing triply bridging μ_3 -OH groups and a tetrahedral array of $\text{W}(\text{CO})_3$ units.¹⁴ It has been previously reported that these base reactions with $\text{Cr}(\text{CO})_6$, in addition to producing the above-mentioned hydridocarbonyl metalates, yield polynuclear carbonyl anions of uncertain formulation.¹⁵ However, one of us has recently been successful in

characterizing a polynuclear chromium tetraanion, $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OCH}_3)_4]^{4-}$, by reaction of $\text{Cr}(\text{CO})_6$ with excess hydroxide ion in methanol.¹⁶ This anion has a cubane-like structure consisting of four $[\text{Cr}(\text{CO})_3(\text{OCH}_3)]^-$ monomers. The Cr_4O_4 core is a distorted cube in which the chromium and methoxide oxygen atoms occupy alternate corners.

Because of the present interest in synthetic methods aimed at the preparation of such polynuclear group 6 species,¹⁷ principally in regard to their potential value as precursors to metal carbonyl clusters that may play a role in catalysis,¹⁸ we herein report the preparation and characterization of two related tetranuclear derivatives, $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OR})_4]^{4-}$ ($\text{R} = \text{H}, \text{C}_6\text{H}_5$). An X-ray structural analysis of $[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]$ has been performed, and a general route to these cubic tetraanions is presented whereby the CO-labilizing^{4,19} ability of the oxygen donor ligands is utilized to account for the formation of these high-nuclearity complexes. In addition, these efforts serve as model studies for analogous mechanisms operative on alumina surfaces where coordination of the metal center to one of the basic sites present on the surface, either an oxide or hydroxyl oxygen, results in labilization of CO ligands,²⁰ e.g. $\text{Mo}(\text{CO})_6 + \text{alumina} \rightarrow \text{Mo}(\text{CO})_3(\text{ads}) + 3\text{CO}$.

Experimental Section

General Methods. All manipulations involving air-sensitive compounds were performed with Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres inert-atmosphere chamber under prepurified argon. All solvents were distilled under prepurified nitrogen prior to use. Acetonitrile and methanol were distilled from calcium hydride, and tetrahydrofuran was distilled from lithium aluminum hydride. IR spectra were obtained on a Perkin-Elmer 283 spectrometer. ¹H NMR spectra were recorded on a Varian EM-360 spectrometer or Varian HFT-80 spectrometer. All NMR data are listed in ppm relative to internal Me_4Si . Chromium hexacarbonyl was purchased from Pressure Chemical Co.; tetraethylammonium hydroxide (40% (w/w) in H_2O), triethylammonium hydroxide (25% (w/w) in CH_3OH), and phenol were purchased from Alfa Products. Phenol was purified by vacuum sublimation prior to use. $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ was synthesized by a published method.²¹ Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

- (1) (a) Loyola College. (b) Texas A&M University. (c) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)
- (2) Grillone, M. D.; Kedzia, B. B. *J. Organomet. Chem.* **1977**, *140*, 161.
- (3) Darensbourg, D. J.; Rokicki, A. *ACS Symp. Ser.* **1981**, *No. 152*, 107.
- (4) Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685.
- (5) Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644.
- (6) Darensbourg, M. Y.; Bau, R.; Marks, M. W.; Burch, R. R., Jr.; Deaton, J. C.; Slater, S. *J. Am. Chem. Soc.* **1982**, *104*, 6961.
- (7) Darensbourg, D. J.; Darensbourg, M. Y.; Burch, R. R., Jr.; Froelich, J. A.; Incorvia, M. J. *Adv. Chem. Ser.* **1979**, *No. 173*, 106.
- (8) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223.
- (9) Darensbourg, D. J.; Ovalles, C. *J. Am. Chem. Soc.* **1984**, *106*, 3750.
- (10) Kao, S. C.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 646.
- (11) Kao, S. C.; Spillet, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83.
- (12) Kao, S. C.; Graus, P. C.; Darensbourg, M. Y. *Organometallics*, in press.
- (13) Albano, V.; Ciani, G.; Manassero, M. *J. Organomet. Chem.* **1970**, *25*, C55.
- (14) Albano, V.; Ciani, G.; Manassero, M.; Sansori, M. *J. Organomet. Chem.* **1972**, *34*, 353.
- (15) Hieber, W.; Beck, W.; Braun, G. *Angew. Chem.* **1960**, *72*, 795 and references cited therein.

- (16) McNeese, T. J.; Cohen, M. B.; Foxman, B. M. *Organometallics* **1984**, *3*, 552.
- (17) Darensbourg, D. J.; Zalewski, D. J., to be submitted for publication in *J. Am. Chem. Soc.*
- (18) Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225 and references cited therein.
- (19) (a) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398. (b) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudarowski, R. *Inorg. Chem.* **1982**, *21*, 1656. (c) Darensbourg, D. J.; Walker, N.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1980**, *102*, 1213; *Inorg. Chem.* **1981**, *20*, 1918. (d) Darensbourg, D. J.; Pala, M.; Waller, J. *Organometallics* **1983**, *2*, 1285.
- (20) (a) Brown, T. L. *J. Mol. Catal.* **1981**, *12*, 41. (b) Brenner, A.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 2565. (c) Brenner, A.; Burwell, R. L., Jr. *J. Catal.* **1978**, *52*, 353. (d) Brenner, A.; Hucul, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 2484. (e) Barth, R.; Gates, B. C.; Zhao, Y.; Knozinger, H.; Hulse, J. *J. Catal.* **1983**, *82*, 147.
- (21) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433.

$[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]$ (**1**). To $\text{Cr}(\text{CO})_6$ (10.0 g, 0.046 mol) in a 250-mL Schlenk tube with stirbar was added 40% (w/w) Et_4NOH (50.2 g, 0.139 mol OH^-) in H_2O . Approximately 100 mL of THF was added to the reaction flask via cannula. The Schlenk tube was then fitted with a reflux condenser and stopcock, and the contents of the flask were refluxed for 3 days. A gelatinous orange precipitate was produced during the course of reaction. After cooling, solidification of the gel was achieved by vigorous shaking of the flask and its reaction mixture. The orange solid so obtained was collected on a medium-porosity frit, washed with 30 mL of MeOH, and dried in vacuo. Crystallization from boiling CH_3CN gave bright red crystals of **1**. Yield: 4.0 g, 61.5% based on $\text{Cr}(\text{CO})_6$. IR: ($\nu(\text{CO})$, CH_3CN) 1861 (s), 1723 (vs) cm^{-1} ; ($\nu(\text{OH})$, Nujol mull) 3710 (m) cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{21}\text{CrNO}_4$: C, 46.63; H, 7.49. Found: C, 46.89; H, 7.78. ($\text{Et}_4\text{N})(\text{OC}_6\text{H}_5)$. The following method represents a modification of that recently published.²² A solution of phenol (6.4 g, 0.068 mol) in 50 mL of methanol was added via cannula to 25% (w/w) Et_4NOH (41.1 g, 0.068 mol) in methanol contained in a 250-mL Schlenk tube with stirbar. The reaction flask was then fitted with a reflux condenser and stopcock. With stirring, the reaction mixture was heated at 50 °C for 2 h. Following removal of the solvent by vacuum, the resulting white solid was crystallized from 35 mL of THF containing 5 mL of CH_3CN at -10 °C. The white needles were filtered and dried under vacuum, yielding 6.9 g (47%) of product; $^1\text{H NMR}$ (CD_3CN): anion δ 6.84 (2 H, t, $J = 8$ Hz), 6.30 (2 H, d, $J = 8$ Hz), 6.05 (1 H, t, $J = 7$ Hz); cation δ 3.15 (8 H, q, $J = 6$ Hz), 1.12 (12 H, t, $J = 6$ Hz).

$[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OC}_6\text{H}_5)_4]$ (**2**). Solid $\text{Et}_4\text{NOC}_6\text{H}_5$ (3.5 g, 0.016 mol) was added via a funnel to a 250-mL Airless-ware flask containing a 100-mL THF solution of $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (4.1 g, 0.016 mol). The reaction mixture was stirred at room temperature for a 12-h period. During this time a red solid formed, which was subsequently collected by filtration on a medium-porosity frit and dried under vacuum. The solid was crystallized from THF- CH_3CN (85%/15%) at room temperature affording 3.0 g (52%) of amber crystals of **2**. IR ($\nu(\text{CO})$, CH_3CN): 1870 (s), 1730 (vs) cm^{-1} . $^1\text{H NMR}$ (CD_3CN): anion δ 7.68 (2 H, d, $J = 9$ Hz), 7.00 (2 H, t, $J = 10$ Hz), 6.29 (1 H, t, $J = 9$ Hz); cation δ 3.02 (8 H, m), 1.07 (12 H, m). Anal. Calcd for $\text{C}_{17}\text{H}_{25}\text{CrNO}_4$: C, 56.80; H, 7.06. Found: C, 56.61; H, 7.38.

X-ray Experimental Data for $[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]$ (1**).** A red-orange crystal measuring 0.25 mm \times 0.20 mm \times 0.15 mm was sealed in epoxy and mounted inside a glass capillary tube for atmospheric protection. Intensity data were measured on an Enraf-Nonius CAD-4 computer-automated diffractometer by using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) by the θ - 2θ scan technique. Precise lattice parameters were determined from 25 well-centered reflections in the range $20^\circ < \theta < 24^\circ$ to give the following parameters: $a = 21.827$ (7) Å, $b = 12.236$ (2) Å, $c = 22.899$ (4) Å, $\alpha = 90.0^\circ$, $\beta = 116.49$ (2)°, $\gamma = 90.0^\circ$; $V = 5474$ (5) Å³. The space group was determined to be $I2/a$ with $Z = 8$. Intensity measurements for 4501 reflections in the range $0^\circ < \theta < 24^\circ$ were recorded ($h, k \geq 0, \pm l$) to give 2112 reflections with $E > 3\sigma(I)$. Data were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 8.7$ cm^{-1}).

Structure Solution and Refinement. The structure was solved by application of direct methods to yield the Cr atom positions. All other non-hydrogen atoms were located by subsequent least-squares and difference Fourier techniques. Hydrogen atoms were included in calculated positions with fixed temperature factors and were not refined. The structure was refined by weighted, full-matrix least squares ($w = 1/\sigma^2(F_o)$) treating all non-hydrogen atoms anisotropically, except those C atoms of the N(2) cation that were found to be disordered. Refinement converged for 2238 reflections ($I > 2.5\sigma(I)$) and 391 parameters at $R = 0.055$ ($R_w = 0.062$). The largest shift/esd for the final cycle of least squares was less than 0.07. A final difference Fourier map contained no residual peaks larger than 0.53 e/Å³. Details of the structure analysis are presented in Table I. Anisotropic temperature factors for the anion Cr, C, and O atoms, anisotropic temperature factors for the cation N and C atoms, including isotropic temperature factors for the disordered C atoms in the cation, a labeling scheme with selected bond distances and angles for the Et_4N^+ cations, and complete structure factor tables are provided as supplementary material.

Results

Reaction of $\text{Cr}(\text{CO})_6$ with Et_4NOH in a 1:3 mole ratio in refluxing aqueous THF gave a red solid, which, on the basis of spectroscopic data, was formulated as $[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]$. The infrared carbonyl region exhibited a two-band pattern

Table I. Summary of the X-ray Diffraction Study of $[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]^a$

formula	$\text{C}_{44}\text{H}_{84}\text{Cr}_4\text{N}_4\text{O}_{16}$
formula wt	1133.3
a , Å	21.827 (7)
b , Å	12.236 (2)
c , Å	22.899 (4)
β , deg	116.49 (2)
cryst syst	monoclinic
space group	$I2/a$
Z	8
V , Å ³	5474 (5)
d_{calcd} , g/cm ³	1.37
cryst dims, mm	0.25 \times 0.20 \times 0.15
radiation	Mo K α ($\lambda = 0.71073$ Å)
abs. coeff, cm^{-1}	8.7
reflcs measd	$h, k \geq 0, \pm l$ (to $2\theta = 24^\circ$)
scan speed, deg/min	4 (θ - 2θ scan)
no. of reflcs measd	4501, 2238 with $I > 2.5\sigma(I)$
no. of variables	391
R	0.055
R_w	0.062

^aEstimated standard deviations in the least significant digits are given in parentheses.

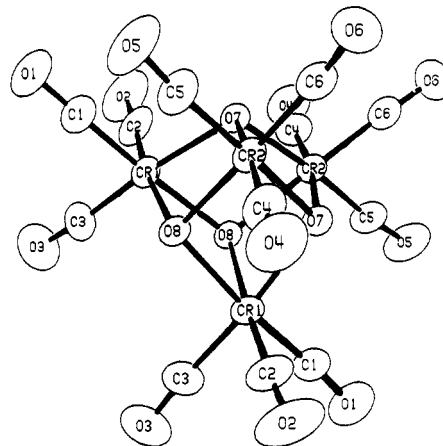


Figure 1. Structure of $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]^{4-}$ as its Et_4N^+ salt. Thermal ellipsoids show 50% probability levels.

($\nu(\text{CO})$ 1861 (s), 1723 (vs) cm^{-1}) characteristic of a $\text{Cr}(\text{CO})_3$ moiety and essentially identical with that found for $[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu\text{-OCH}_3)_4]$.¹⁶ The $^1\text{H NMR}$ (acetonitrile- d_3) spectrum of the μ_3 -hydroxide complex revealed peaks assignable to the tetraethylammonium cation; however, due to low solubility, the position of the $\mu_3\text{-OH}$ resonance could not be readily identified. Recrystallization of $[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]$ from hot CH_3CN gave crystals suitable for an X-ray structural determination. The structure of the tetraanion is shown in Figure 1. Selected bond distances and angles are presented in Table II, and atomic coordinates are listed in Table III.

$[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]^{4-}$ is composed of four $[\text{Cr}(\text{CO})_3(\text{OH})]^-$ units in a cubane-like arrangement with chromium and hydroxide oxygen atoms occupying alternate corners of a distorted Cr_4O_4 cube. The Cr_4O_4 core, shown in Figure 2, consists of a set of four chromium atoms and a set of four oxygen atoms positioned at the vertices of two concentric tetrahedra. These two nonbonding tetrahedra are different in size; the average Cr-Cr distance is 3.33 (5) Å while the average O-O distance is 2.57 (4) Å. Each Cr(O) atom, in addition to being bonded to three cis CO ligands, is coordinated to three O atoms of the hydroxide groups. Each approximately tetrahedral μ_3 oxygen atom is bonded to three chromium atoms and a hydrogen atom.

Relevant bond distances and angles are as follows. The Cr-Cr mean distance within the Cr_4O_4 core is 3.33 (5) Å, and the average Cr-O $_{\mu_3}$ -Cr and O $_{\mu_3}$ -Cr-O $_{\mu_3}$ bond angles are 103.4 (2) and 74.61 (1)°, respectively. Within the chromium coordination sphere, the Cr-O $_{\mu_3}$ distance is 2.121 (4) Å while the Cr-CO $_{\text{CO}}$ distance is

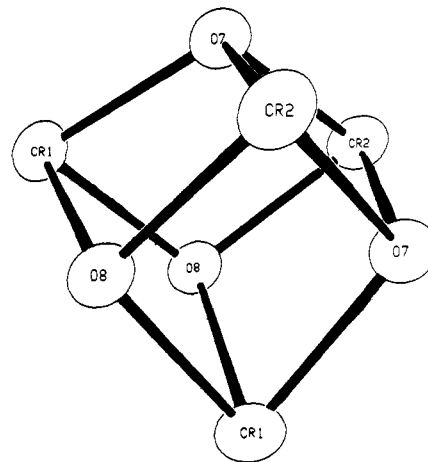
Table II. Selected Bond Distances (Å) and Angles (deg) for $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]^{4-}$ ^a

Cr-O _{μ₃}			
Cr(1)-O(7)	2.126 (4)	Cr(2)-O(7)	2.145 (3)
Cr(1)-O(8)	2.122 (4)	Cr(2)-O(7)	2.107 (3)
Cr(1)-O(8)	2.111 (3)	Cr(2)-O(8)	2.112 (4)
Cr-C			
Cr(1)-C(1)	1.787 (6)	Cr(2)-C(4)	1.770 (6)
Cr(1)-C(2)	1.787 (7)	Cr(2)-C(5)	1.791 (6)
Cr(1)-C(3)	1.803 (8)	Cr(2)-C(6)	1.798 (7)
C-O			
C(1)-O(1)	1.189 (7)	C(4)-O(4)	1.201 (6)
C(2)-O(2)	1.174 (7)	C(5)-O(5)	1.178 (7)
C(3)-O(3)	1.168 (8)	C(6)-O(6)	1.174 (7)
Cr-O _{μ₃} -Cr			
Cr(1)-O(7)-Cr(2)	100.5 (2)	Cr(1)-O(8)-Cr(1)	106.1 (2)
Cr(1)-O(7)-Cr(2)	102.7 (2)	Cr(1)-O(8)-Cr(2)	102.7 (2)
Cr(2)-O(7)-Cr(2)	106.5 (1)	Cr(1)-O(8)-Cr(2)	102.1 (2)
O _{μ₃} -Cr-O _{μ₃}			
O(7)-Cr(1)-O(8)	74.8 (1)	O(7)-Cr(2)-O(7)	72.7 (1)
O(7)-Cr(1)-O(8)	76.1 (1)	O(7)-Cr(2)-O(8)	75.7 (1)
O(8)-Cr(1)-O(8)	72.9 (2)	O(7)-Cr(2)-O(8)	75.4 (1)
Cr-C-O			
Cr(1)-C(1)-O(1)	174.0 (5)	Cr(2)-C(4)-O(4)	174.6 (6)
Cr(1)-C(2)-O(2)	174.3 (6)	Cr(2)-C(5)-O(5)	173.5 (6)
Cr(1)-C(3)-O(3)	173.7 (6)	Cr(2)-C(6)-O(6)	169.4 (6)

^a Estimated standard deviations in the least significant digits are given in parentheses.

1.789 (7) Å. The terminal carbonyl ligands have an average Cr-C-O bond angle of 173.3 (6)° with a carbonyl C-O distance of 1.181 (7) Å.

The $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OC}_6\text{H}_5)_4]^{4-}$ derivative was isolated as its Et_4N^+ salt from the room-temperature reaction of $\text{Cr}(\text{CO})_3(\text{C}-$

**Figure 2.** Structure of the Cr_4O_4 core.

$\text{H}_3\text{CN})_3$ and $\text{Et}_4\text{NOC}_6\text{H}_5$. This tetraanion can also be prepared from $\text{Cr}(\text{CO})_6$ and $\text{Et}_4\text{NOC}_6\text{H}_5$ in refluxing THF, however the yield is considerably lower (35% vs. 52% for **2** prepared from $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$). The complex shows the expected IR band pattern in the carbonyl region (1870 (s), 1730 (vs) cm^{-1}); its ^1H NMR (acetonitrile- d_3) spectrum, in addition to the Et_4N^+ protons, consists of three well-resolved resonances in the phenyl region integrating in the ratio of 2:2:1.

Both the $\mu_3\text{-OH}$ and $\mu_3\text{-OC}_6\text{H}_5$ derivatives have a reactivity pattern similar to that of $[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OCH}_3)_4]^{4-}$.¹⁶ For example, acetonitrile solutions of these tetraanions react instantly at ambient temperature with hydrochloric acid to yield $\text{Cr}(\text{C}-\text{O})_3(\text{CH}_3\text{CN})_3$. Carbon monoxide-saturated solutions of the $\mu_3\text{-OH}$ complex yield allyl alcohol and $\text{Cr}(\text{CO})_5\text{Br}^-$ upon treatment with allyl bromide, while the phenoxide tetramer produces allyl phenyl ether and $\text{Cr}(\text{CO})_5\text{Br}^-$.²³

Table III. Atomic Coordinates for $[\text{Et}_4\text{N}]_4[\text{Cr}_4(\text{CO})_{12}(\mu_3\text{-OH})_4]^{4-}$

atom	x	y	z	atom	x	y	z
Anion							
Cr(1)	-0.16423 (5)	0.2296 (1)	0.02645 (5)	O(7)	-0.1864 (2)	0.3998 (3)	0.0179 (2)
Cr(2)	-0.23707 (5)	0.4141 (1)	0.07906 (5)	O(8)	-0.2591 (2)	0.2454 (3)	-0.0582 (2)
O(1)	-0.0607 (2)	0.2264 (5)	-0.0246 (2)	C(1)	-0.1047 (3)	0.2296 (6)	-0.0075 (3)
O(2)	-0.0342 (2)	0.2327 (6)	0.1478 (2)	C(2)	-0.0875 (3)	0.2323 (7)	0.1016 (3)
O(3)	-0.1376 (3)	-0.0085 (5)	0.0462 (3)	C(3)	-0.1519 (3)	0.0839 (6)	0.0362 (3)
O(4)	-0.1188 (2)	0.4162 (5)	0.2107 (2)	C(4)	-0.1651 (3)	0.4112 (6)	0.1566 (3)
O(5)	-0.3202 (2)	0.4264 (5)	0.1518 (2)	C(5)	-0.2892 (3)	0.4159 (7)	0.1212 (3)
O(6)	-0.2354 (2)	0.6469 (4)	0.1148 (3)	C(6)	-0.2369 (3)	0.5581 (6)	0.0949 (3)
Cation ^b							
N(1)	0.4773 (2)	0.1650 (5)	0.6460 (2)	C(27)	0.3011 (4)	0.6346 (7)	0.3186 (5)
N(2)	0.3425 (3)	0.4360 (5)	0.3536 (3)	C(28)	0.3023 (7)	0.5119 (14)	0.2931 (6)
C(7)	0.4444 (4)	0.1921 (8)	0.6915 (4)	H(1)	0.397 (3)	0.162 (5)	0.671 (3)
C(8)	0.4462 (4)	0.3129 (9)	0.7068 (5)	H(2)	0.508 (3)	0.126 (6)	0.728 (3)
C(9)	0.5509 (4)	0.1968 (9)	0.6760 (4)	H(3)	0.537 (3)	0.138 (5)	0.620 (3)
C(10)	0.5925 (4)	0.1369 (10)	0.7412 (5)	H(4)	0.516 (3)	0.289 (6)	0.666 (3)
C(11)	0.4644 (4)	0.0430 (8)	0.6313 (4)	H(5)	0.503 (3)	0.022 (5)	0.697 (3)
C(12)	0.4951 (5)	0.0020 (9)	0.5860 (5)	H(6)	0.411 (3)	0.128 (5)	0.616 (3)
C(13)	0.4409 (4)	0.2321 (8)	0.5820 (4)	H(7)	0.461 (3)	0.329 (5)	0.613 (3)
C(14)	0.3672 (4)	0.2082 (9)	0.5439 (4)	H(8)	0.479 (3)	0.188 (5)	0.564 (3)
C(15)	0.3018 (7)	0.4461 (16)	0.3984 (6)	H(9)	0.420 (3)	0.342 (5)	0.716 (3)
C(16)	0.2242 (7)	0.4128 (16)	0.3545 (12)	H(10)	0.489 (3)	0.354 (6)	0.703 (3)
C(17)	0.296 (1)	0.396 (3)	0.283 (1)	H(11)	0.431 (3)	0.371 (5)	0.668 (3)
C(18)	0.224 (2)	0.387 (3)	0.276 (2)	H(12)	0.626 (3)	0.132 (6)	0.742 (3)
C(19)	0.415 (1)	0.456 (3)	0.342 (1)	H(13)	0.579 (3)	0.140 (6)	0.775 (3)
C(20)	0.476 (2)	0.511 (3)	0.421 (2)	H(14)	0.600 (3)	0.063 (5)	0.736 (3)
C(21)	0.4149 (7)	0.4685 (13)	0.3964 (9)	H(15)	0.516 (3)	-0.051 (5)	0.618 (3)
C(22)	0.4680 (6)	0.4728 (14)	0.3915 (12)	H(16)	0.467 (3)	0.024 (5)	0.554 (3)
C(23)	0.3407 (9)	0.3167 (13)	0.3206 (10)	H(17)	0.548 (3)	0.030 (5)	0.612 (3)
C(24)	0.3815 (5)	0.2349 (9)	0.3818 (6)	H(18)	0.355 (3)	0.245 (5)	0.508 (3)
C(25)	0.359 (1)	0.345 (2)	0.403 (1)	H(19)	0.355 (3)	0.123 (6)	0.525 (3)
C(26)	0.326 (1)	0.541 (2)	0.379 (1)	H(20)	0.347 (3)	0.228 (5)	0.569 (3)

^a Estimated standard deviations in the least significant digits are given in parentheses. ^b Labeling schemes for Et_4N^+ atoms are available as supplementary material.

Table IV. Core Bond Angles (deg) and Nonbonding M–M Distances (Å)^a for A₄B₄ Tetramers

compd	M–O _{μ₃} –M	O _{μ₃} –M–O _{μ₃}	M–M dist
[Cr ₄ (CO) ₁₂ (μ ₃ -OH) ₄] ⁴⁻ ^b	103.4 (2)	74.6 (1)	3.33 (5)
[Cr ₄ (CO) ₁₂ (μ ₃ -OCH ₃) ₄] ⁴⁻ ^c	102.86 (16)	75.30 (14)	3.31 (6)
[W ₄ (CO) ₁₂ (μ ₃ -OH) ₄ H ₄] ^d	104 (1)	74 (1)	3.48 (6)
[Mo ₄ (CO) ₈ (NO) ₄ (μ ₃ -OH) ₄] ^e	103 (1)	76 (1)	3.43 (6)
[Re ₄ (CO) ₁₂ (μ ₃ -OH) ₄] ^f	104.0 (5)	74.3 (1)	3.48 (4)

^a Estimated standard deviations in the least significant digits are given in parentheses. ^b This study. ^c Reference 16. ^d Reference 14. ^e Reference 24. ^f Reference 25.

Discussion

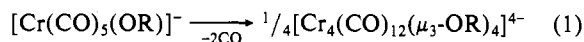
The structure observed for [Cr₄(CO)₁₂(μ₃-OH)₄]⁴⁻ is very similar to that of the recently characterized methoxide complex [Cr₄(CO)₁₂(μ₃-OCH₃)₄]⁴⁻¹⁶ and related polynuclear species of the alternating A₄B₄ type. The metal atoms within these tetramers consist of a closed-shell configuration with large metal–metal distances indicative of nonbonding interactions. Table IV contains a series of these A₄B₄ complexes for comparison and illustrates the obtuse Cr–O–Cr and acute O–Cr–O bond angles within the Cr₄O₄ core of [Cr₄(CO)₁₂(μ₃-OH)₄]⁴⁻. By contrast, short Cr–Cr distances ranging from 2.702 (6) to 2.900 (6) Å within the cubane-like Cr(III) cluster [Cr₄(η⁵-C₅H₅)₄(μ₃-O)₄]²⁶ result in acute Cr–O–Cr angles of 83.2 (2)–90.1 (1)° and imply the presence of Cr–Cr single bonds.

The metal atoms of the tetramers listed in Table IV are six-coordinate with the exception of [W₄(CO)₁₂(μ₃-OH)₄H₄]. In this complex, each tungsten atom is seven-coordinate; the presence of a metal hydride was detected by ¹H NMR²⁷ and confirmed structurally²⁴ by observing the opening of one of the C_{CO}–W–C_{CO} bond angles to 103° in order to accommodate the hydrogen atom within the coordination sphere. Our attempts to prepare the chromium analogue of this compound by protonation of [Cr₄(CO)₁₂(μ₃-OH)₄]⁴⁻ were unsuccessful and resulted in decomposition of the Cr₄O₄ core into mononuclear species. For example, reaction of [Et₄N]₄[Cr₄(CO)₁₂(μ₃-OH)₄] with HCl in CH₃CN gave only Cr(CO)₃(CH₃CN)₃, while the use of a weaker coordinating solvent, such as THF, yielded uncharacterizable solids that lacked discernable bands in the infrared metal carbonyl region.

Although the hydrogen atoms of the triply bridging hydroxide groups within the Cr₄O₄ core of [Cr₄(CO)₁₂(μ₃-OH)₄]⁴⁻ were not located in the crystallographic study, their presence is implied by the following results. As mentioned earlier, the μ₃-OH derivative has a reactivity pattern identical with that of [Cr₄(CO)₁₂(μ₃-OCH₃)₄]⁴⁻. That is, reaction of CO-saturated solutions of the μ₃-OH tetraanion with allyl bromide yields allyl alcohol and Cr(CO)₃Br.²³ Furthermore, a ν(OH) band of medium intensity

at 3695 cm⁻¹ (Nujol mull) was observed, indicative of the presence of a bridging hydroxide ligand. Because of the unusually high frequency for such a mode (for comparison, ν(OH) appears as a sharp double band at 3550 cm⁻¹ in [Re₄(CO)₁₂(μ₃-OH)₄]²⁸), the μ₃-OD derivative of **1** was prepared by reaction of Cr(CO)₆ with base in D₂O/THF. This complex exhibits a spectrum featuring a ν(OD) band at 2720 cm⁻¹ while lacking the high frequency band at 3695 cm⁻¹. We do not, however, have an explanation for the presence of the ν(OH) stretch at such a high frequency, nor is there sufficient data available to draw a conclusion from other related μ₃-OH tetramers.

It appears that a general route to these tetranuclear species from Cr(CO)₆ is available as a result of the CO-labilizing ability of oxygen donor ligands.¹⁹ That is, the reaction solution reveals the presence of [(μ-H)Cr₂(CO)₁₀]⁻ which, under basic conditions, probably serves as a precursor to mononuclear [Cr(CO)₅(OR)]⁻ (R = H, CH₃) or their solvated analogues [Cr(CO)_{5-n}(solvent)_n(OR)]⁻. Loss of carbon monoxide or solvent ligand can then lead to clusterification (eq 1). Indeed, [Cr₄(CO)₁₂(μ₃-OR)₄]⁴⁻



(R = H, CH₃)¹⁶ can be directly prepared from aqueous (R = H) or methanolic (R = CH₃) alkaline solutions containing only the bridging hydride.

In independent experiments, we observed that a methanolic solution of [HCr(CO)₅]⁻²⁹ readily reacts to produce only [(μ-H)Cr₂(CO)₁₀]⁻⁵ and H₂ and that deprotonation of the bridging hydride to yield [Cr₂(CO)₁₀]²⁻³⁰ does not occur. Although we have thus far been unable to demonstrate the presence of [Cr(CO)₅(OR)]⁻ species during the course of reaction, it has been shown that fragmentation of [(μ-H)Cr₂(CO)₁₀]⁻ into monomers does occur,^{7,31} albeit slowly, which is entirely consistent with the reaction times required for the production of [Cr₄(CO)₁₂(μ₃-OR)₄]⁴⁻. The synthesis of [Cr₄(CO)₁₂(μ₃-OC₆H₅)₄]⁴⁻ from Cr(CO)₃(CH₃CN)₃ apparently involves aggregation of the preformed Cr(CO)₃(CH₃CN)₂(OC₆H₅)⁻ unit by successive displacement of acetonitrile ligands within the coordination sphere by phenoxide ion. Continued efforts to characterize reaction intermediates afforded during the synthesis of these tetranuclear derivatives are ongoing in our laboratories.

Acknowledgment. This research was supported by a grant from the Research Corp. (T.J.M.). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research (T.J.M.). Special thanks to Joe Cousins of Johns Hopkins University for technical assistance (80-MHz ¹H NMR).

Registry No. 1, 97879-17-9; 2, 97879-19-1; Cr(CO)₆, 13007-92-6; (Et₄N)(OC₆H₅), 32580-85-1; Cr(CO)₃(CH₃CN)₃, 16800-46-7.

Supplementary Material Available: Tables of selected bond distances and angles for the cations including a labeling scheme, anisotropic and isotropic temperature factors for all atoms, and structure factors (13 pages). Ordering information is given on any current masthead page.

(23) Detailed procedures may be found in the experimental section of ref 16.

(24) Albano, V.; Bellon, P.; Ciani, G.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1969**, 1242.

(25) Nuber, B.; Oberdorfer, F.; Ziegler, M. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, B37, 2062.

(26) Bottomley, F.; Paez, D. E.; White, P. S. *J. Am. Chem. Soc.* **1982**, 104, 5651.

(27) Sartorelli, U.; Gariascelli, L.; Ciani, G.; Bonora, G. *Inorg. Chim. Acta* **1971**, 5, 191.

(28) Heberhold, M.; Suss, G. *Angew. Chem., Int. Ed. Engl.* **1975**, 14, 700.

(29) Gibson, D. H.; Ahmed, F. U.; Phillips, K. R. *Organometallics* **1982**, 1, 679.

(30) Hayter, R. J. *J. Am. Chem. Soc.* **1966**, 88, 4376.

(31) Karn, F. S.; Shultz, J. F.; Anderson, R. B. *Ind. Eng. Chem. Prod. Res. Dev.* **1965**, 4, 265.