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Synthesis and characterization of tetranuclear hydroxocarbonyl complexes of molybdenum and tungsten, $[Et_4N]_4[Mo(CO)_3(\mu_3\text{-}OH)]_4$ and $[Et_4N]_4[W(CO)_3(\mu_3\text{-}OH)]_4$

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Abstract

Reaction of $M(CO)_3(PMTA)$ (M = W, Mo; PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) with a stoichiometric amount of hydroxide ion in aqueous THF solution yields $[M(CO)_3(\mu_3\text{-}OH)]_4^{4-}$ (**1**, M = W; **2**, M = Mo). These tetranuclear metal carbonyl complexes were isolated as their Et_4N^+ salts. The crystal structures of both complexes have been determined. Compounds **1** and **2** are isostructural; the crystals are monoclinic, space group $C2/c$, $Z = 4$, with unit cell dimensions a 23.86(3), b 12.317(7), c 23.21(1) Å, β 123.8(2)° for **1**; and a 23.888(7), b 12.300(2), c 23.254(3) Å, β 123.85(2)° for **2**. The anions consist of a distorted cubic A_4B_4 (A = metal, B = oxygen) core with triply bridging hydroxide groups and $M(CO)_3$ units. The M–M distances (average 3.59(6) Å for **1** and 3.58(6) Å for **2**) within the M_4O_4 core clearly show non-bonding between metal atoms which is consistent with a closed-shell metal configuration.

Introduction

Transition-metal oxide compounds are of fundamental importance in the catalytic oxidation of hydrocarbons, and in the polymerization and metathesis of olefins [1]. The catalytic activities of the metal oxides are thought to depend on their acid–base properties [2]. Polynuclear organometallic complexes containing hydroxyl groups are interesting not only because they could serve as models for the acid–base character of metal oxides, but also because they are closely related to the recently developed oxide-supported organometallic catalysts [3], such as $Mo(CO)_6$ + alumina $\rightarrow Mo(CO)_3(ads) + 3CO$. Polynuclear carbonyl clusters containing hydroxyl ligands

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are not very common. Of these complexes, $[Re(CO)_3(OH)]_4$ [4], $[Mo(CO)_2(NO)(OH)]_4$ [5], and $[Cr(CO)_3(OH)]_4^{4-}$ [6] all consist of four tetrahedral arrays of $M(CO)_2L$ (L = CO or NO) units held together by four triply-bridging OH groups. This cubic tetranuclear structure has also been observed in some closely related complexes containing organo-oxo or organo-thio ligands such as $[Cr(CO)_3(OC_6H_5)]_4$ [6], $[Cr(CO)_3(OMe)]_4^{4-}$ [7], and $[Re(CO)_3(SMe)]_4$ [8].

Protonation of the tri(μ-hydroxo) trianion $[M_2(\mu\text{-}OH)_3(CO)_6]^{3-}$ (M = Mo, W) [9] results in the formation of Hieber's acid, $[HM(CO)_3(\mu_3\text{-}OH)]_4$, originally formulated as $H_3M_2(\mu\text{-}OH)_3(CO)_6$. The presence of four triply bridging hydroxo groups and the tetrahedral array of $M(CO)_3$ units in Hieber's acids has been confirmed on the basis of the structural characterization of the tungsten derivatives $[HW(CO)_3(OH)(PPh_3O)]_4$ [10]. It is surprising that the "conjugate base" of Hieber's acid, $[M(CO)_3(\mu_3\text{-}OH)]_4^{4-}$, being iso-electronic with $[Re(CO)_3(\mu_3\text{-}OH)]_4$, remains elusive in the literature. There is no reason why these anions should not exist. The chromium cognate in this family, $[Cr(CO)_3(\mu_3\text{-}OH)]_4^{4-}$, has recently been successfully isolated [6]. Here we report our successful synthesis, and the characterization of the conjugate bases of two compounds, $[Et_4N]_4[M(CO)_3(\mu_3\text{-}OH)]_4$ (M = W, Mo).

Experimental

All manipulations were carried out under purified N_2 using standard Schlenk techniques, or in a Vacuum Atmosphere DL-08/85 drybox. THF was distilled from blue Na-benzophenone ketyl solution before use. Acetonitrile and methanol were purged thoroughly with dry N_2, refluxed over P_2O_5 and Mg/I_2, respectively, and distilled under N_2. All other solvents were stored over 4 Å molecular sieves and purged with N_2 before use. $Mo(CO)_6$ and $W(CO)_6$ were purchased from Strem Chemicals Inc.; 1,1,4,7,7-pentamethyldiethylenetriamine (PMTA) was purchased from Eastman Kodak; tetraethylammonium hydroxide (20 wt.% in H_2O) from Merck. $M(CO)_3(PMTA)$ (M = Mo, W) was prepared by a published procedure [1]. The IR spectra were recorded on a Perkin-Elmer 880 spectrometer. The NMR spectra were recorded on a Bruker MSL 200 spectrometer. Melting points were determined in N_2-filled capillaries using a Buchi 520 apparatus and are uncorrected. Elemental analyses were performed by Taipei Regional Instrumental Center.

$[Et_4N]_4[W(CO)_3(\mu_3\text{-}OH)]_4$ (1). To a solution of $W(CO)_3(PMTA)$ (2.10 g, 4.76 mmol) in 60 ml of THF was added 40 ml of H_2O and 3.5 ml (4.76 mmol) of aqueous Et_4NOH (20 wt.%). The contents of the flask were heated at 85 °C for 5 h. The solution separated into two layers during the reaction. After cooling, the solution was evaporated to dryness. The yellow crystals so obtained were washed with MeOH (2 × 20 ml), THF (2 × 20 ml), and dried in vacuo. Yield: 1.74 g, 89% based on $W(CO)_3(PMTA)$. IR: (ν(CO), CH_3CN) 1868(s), 1727(vs) cm^{-1}; (ν(OH), Nujol mull) 3676(m) cm^{-1}. ^{13}C NMR (δ 0 ppm for TMS): (δ(CO), CD_3CN) 231 ppm. ^1H NMR (CD_3CN): δ 3.28 (q, J(H–H) 7.2 Hz, 8H, CH_2), 1.31(tt, J(H–N) 1.7 Hz, 12H, CH_3), 0.96 ppm (s, 1H, OH). The compound decomposes at 181 °C. Anal. Found: C, 31.55; H, 5.23; N, 3.09. $C_{44}H_{84}N_4O_{16}W_4$ calcd.: C, 31.82; H, 5.10; N, 3.37%. The μ_3-OD derivative of **1** was prepared similarly, except that Et_4NOD, D_2O, and CD_3OD were used in the reaction. Et_4NOD was prepared as follows: The solid Et_4NOH obtained by removal of water from the commercial aqueous Et_4NOH

was stirred with a 100-fold excess of D_2O. The process was repeated three times to ensure maximal H/D exchange. The μ_3-OD derivative of **1** has a ν(OD) band at 2712 cm^{-1}.

$[Et_4N]_4[Mo(CO)_3(\mu_3\text{-}OH)]_4$ (2). To a solution of $Mo(CO)_3$(PMTA) (500 mg, 1.42 mmol) in 25 ml of THF was added 25 ml of H_2O and aqueous Et_4NOH (1.0 ml, 1.42 mmol). The solution was heated at 85 °C for 2 h. After cooling, the solution was evaporated to dryness and the yellow crystals obtained were washed with MeOH (2 × 20 ml), THF (2 × 20 ml), and then dried in vacuo. Yield: 300 mg, 65% based on $Mo(CO)_3$(PMTA). IR: (ν(CO), CH_3CN) 1871(s), 1736(vs) cm^{-1}; (ν(OH), Nujol mull) 3691(m) cm^{-1}. ^{13}C NMR: (δ(CO), CD_3CN) 234 ppm. ^1H NMR (CD_3CN): δ 3.28 (q, J(H–H) 7.2 Hz, 8H, CH_2), 1.31 (tt, J(H–N) 1.7 Hz, 12H, CH_3), −0.27 ppm(s, 1H, OH). The compound decomposes at 189 °C. Anal. Found: C, 40.13; H, 6.68; N, 4.23. $C_{44}H_{84}Mo_4N_4O_{16}$ calcd.: C, 40.38; H, 6.47; N, 4.28%. The μ_3-OD derivative of **2** was prepared similarly. It has a ν(OD) band at 2712 cm^{-1}.

Crystallographic studies. Crystals of **1** and **2** suitable for X-ray diffraction measurements were grown by slow diffusion of THF into a concentrated solution of **1** or **2** in CH_3CN. Crystals were coated with Nujol and mounted in the thin-walled glass capillary tubes under nitrogen. Diffraction measurements were made on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation (λ 0.7107 Å) with the θ–2θ scan mode. Unit cells were determined from

Table 1

Crystal data for compound **1** and **2**

	1	**2**
Formula	$C_{44}H_{84}N_4O_{16}W_4$	$C_{44}H_{84}N_4O_{16}Mo_4$
Formula wt	1660.6	1308.9
a, Å	23.86(3)	23.888(7)
b, Å	12.317(7)	12.300(2)
c, Å	23.21(1)	23.254(3)
β, deg	123.8(2)	123.84(2)
Cryst syst	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
Z	4	4
V, $Å^3$	5668.21	5674.37
d_{calcd}, g/cm^3	1.946	1.532
Cryst size, mm	0.65 × 0.65 × 0.65	0.35 × 0.35 × 0.43
Radiation	Mo-K_α (λ = 0.7107 Å)	Mo-K_α
μ (cm^{-1})	83.3	9.0
Transmission factors (max; min)	1.00; 0.79	1.00; 0.94
2θ range	0–50	0–50
Octants	$\pm h, +k, +l$ $-28 \sim 28, 0 \sim 14, 0 \sim 27$	$\pm h, +k, +l$ $-28 \sim 28, 0 \sim 14, 0 \sim 27$
No. of unique reflns	4978	4979
Reflns with $I > 3\sigma$	4147	3907
No. of variables	288	288
R; R_w	0.038; 0.046	0.041; 0.061
Extinction coeff	$2.7(4) \times 10^{-4}$	$5.4(4) \times 10^{-4}$

Table 2

Atomic coordinates and B_{eq} for $[W(CO)_3(\mu_3\text{-OH})]_4(NEt_4)_4$ esd's refer to the last digit

$$B_{eq} = \frac{8\pi^2}{3}\cdot\sum_{ij} u_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	B_{eq} [a]
W(1)	0.591436(18)	0.02476(3)	0.313239(18)	2.458(19)
W(2)	0.485650(18)	−0.17166(3)	0.319909(18)	2.372(18)
C(1)	0.6719(5)	0.0179(10)	0.3151(5)	4.2(6)
C(2)	0.6549(5)	0.0223(8)	0.4117(5)	3.8(6)
C(3)	0.6052(6)	0.1774(9)	0.3174(6)	4.4(7)
C(4)	0.5402(5)	−0.1711(8)	0.4199(5)	3.4(6)
C(5)	0.4082(5)	−0.1678(9)	0.3249(5)	3.5(6)
C(6)	0.4860(5)	−0.3253(8)	0.3349(5)	3.6(6)
O(1)	0.7242(4)	0.0161(9)	0.3186(5)	7.1(7)
O(2)	0.6943(4)	0.0227(8)	0.4726(4)	6.9(6)
O(3)	0.6159(5)	0.2725(7)	0.3201(5)	6.9(7)
O(4)	0.5710(4)	−0.1740(8)	0.4796(4)	5.9(5)
O(5)	0.3608(4)	−0.1691(7)	0.3277(4)	5.3(5)
O(6)	0.4855(4)	−0.4164(6)	0.3493(4)	5.7(5)
O(7)	0.4906(3)	0.0047(5)	0.2986(3)	2.5(3)
O(8)	0.5631(3)	−0.1514(5)	0.2951(3)	2.3(3)
N1A	0.2735(4)	0.4148(7)	0.6689(4)	3.9(5)
C1A	0.2015(6)	0.4451(11)	0.6283(6)	5.7(8)
C2A	0.1586(6)	0.3901(14)	0.6517(7)	7.1(10)
C3A	0.3061(7)	0.4780(11)	0.6392(6)	5.8(9)
C4A	0.3801(6)	0.4518(12)	0.6732(7)	6.1(9)
C5A	0.2827(7)	0.2955(12)	0.6649(8)	6.9(10)
C6A	0.2511(9)	0.2500(12)	0.5931(8)	8.4(12)
C7A	0.3080(6)	0.4445(13)	0.7445(6)	6.4(9)
C8A	0.3056(7)	0.5672(14)	0.7562(8)	8.5(12)
N1B	0.4086(5)	0.6886(7)	0.5117(5)	4.4(6)
C1B	0.4213(19)	0.786(3)	0.5523(19)	9.9(10)
C1B′	0.4423(10)	0.7687(17)	0.4919(10)	3.8(4)
C2B	0.4476(7)	0.8833(11)	0.5173(7)	6.2(3)
C3B	0.4005(18)	0.599(3)	0.5481(18)	9.2(9)
C3B′	0.4089(15)	0.577(3)	0.4813(15)	7.1(7)
C4B	0.3664(11)	0.4899(17)	0.4988(11)	11.4(6)
C5B	0.3336(18)	0.709(3)	0.4314(18)	9.3(9)
C5B′	0.3422(14)	0.7163(23)	0.5001(14)	6.3(6)
C6B	0.2835(12)	0.7345(20)	0.4356(12)	13.7(7)
C7B	0.449(3)	0.649(5)	0.487(3)	17.6(20)
C7B′	0.4499(13)	0.6934(21)	0.5973(13)	5.7(6)
C8B	0.524(3)	0.639(4)	0.568(3)	15.2(16)
C8B′	0.5213(20)	0.679(3)	0.6371(20)	10.2(11)
HO(7)	0.494(3)	0.052(6)	0.344(3)	6.3
HO(8)	0.406(4)	0.219(6)	0.681(4)	6.3

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid occupancy of C1B, C1B′, C3B, C3B′, C5B, C5B′, C7B, C7B′, C8B, C8B′ = 0.5.

centering 25 reflections in the 2θ range 16.96–23.80 ° for **1** and 23.34–27.14 ° for **2**. Other relevant experimental details are listed in Table 1. Absorption corrections according to ψ scans of three reflections were applied. All the data processing was carried out on a PDP 11 and VAX 780 using the NRCC SDP program [12]. The coordinates of the tungsten or molybdenum atoms were obtained from Patterson syntheses. The coordinates of all the remaining atoms were obtained from a series of structure factor calculations and Fourier syntheses. The structures were refined by

Table 3

Atomic coordinates and B_{eq} for $[Mo(CO)_3(\mu_3\text{-}OH)_4(NEt_4)_4$ eds's refer to the last digit.

$$B_{eq} = \frac{8\pi^2}{3}\cdot\sum_{ij} u_{ij} a_i^{\star} a_j^{\star} a_i a_j$$

	x	y	z	B_{eq} [a]
MO(1)	0.591188(23)	0.02546(4)	0.312875(24)	2.422(23)
MO(2)	0.485675(23)	−0.17021(4)	0.319647(23)	2.342(23)
C(1)	0.6718(3)	0.0193(6)	0.3147(3)	4.0(4)
C(2)	0.6542(3)	0.0229(5)	0.4110(3)	3.6(4)
C(3)	0.6055(3)	0.1794(5)	0.3171(4)	3.9(4)
C(4)	0.5391(3)	−0.1707(5)	0.4184(3)	3.3(3)
C(5)	0.4089(3)	−0.1662(5)	0.3255(3)	3.3(3)
C(6)	0.4847(3)	−0.3221(5)	0.3348(3)	3.4(3)
O(1)	0.7243(3)	0.0174(6)	0.3200(3)	6.9(4)
O(2)	0.6960(3)	0.0233(5)	0.47107(24)	6.8(4)
O(3)	0.6185(3)	0.2722(4)	0.3212(3)	6.8(4)
O(4)	0.5706(3)	−0.1778(5)	0.47951(23)	5.9(3)
O(5)	0.36207(24)	−0.1686(5)	0.3296(3)	5.5(4)
O(6)	0.4841(3)	−0.4135(4)	0.3517(3)	5.6(3)
O(7)	0.49037(17)	0.0072(3)	0.29974(17)	2.42(19)
O(8)	0.56425(17)	−0.1523(3)	0.29593(18)	2.34(19)
N1A	0.27299(25)	0.4143(5)	0.6685(3)	3.7(3)
C1A	0.2016(4)	0.4460(7)	0.6274(4)	5.8(5)
C2A	0.1585(4)	0.3882(9)	0.6507(5)	6.8(6)
C3A	0.3069(4)	0.4767(7)	0.6395(4)	5.6(5)
C4A	0.3804(4)	0.4512(8)	0.6734(4)	6.0(6)
C5A	0.2831(4)	0.2919(8)	0.6664(5)	6.4(6)
C6A	0.2531(5)	0.2495(8)	0.5936(5)	7.7(7)
C7A	0.3074(4)	0.4415(8)	0.7446(4)	5.9(5)
C8A	0.3051(5)	0.5643(9)	0.7564(5)	7.5(7)
N1B	0.4096(3)	0.6889(5)	0.5129(3)	4.1(3)
C1B	0.4225(11)	0.7896(19)	0.5492(12)	8.7(6)
C2B	0.4478(4)	0.8844(8)	0.5180(5)	6.42(20)
C3B	0.3972(11)	0.5960(21)	0.5473(12)	9.4(6)
C4B	0.3709(6)	0.4890(10)	0.4994(6)	9.6(3)
C5B	0.3377(12)	0.7094(21)	0.4345(13)	9.9(6)
C6B	0.2845(7)	0.7327(12)	0.4333(8)	12.5(4)
C7B	0.4555(13)	0.6564(23)	0.4881(14)	11.6(8)
C8B	0.5292(13)	0.6411(23)	0.5743(14)	11.5(8)
C1B′	0.4441(7)	0.7704(12)	0.4920(7)	4.2(3)
C3B′	0.4107(9)	0.5773(16)	0.4843(9)	6.7(4)
C5B′	0.3421(9)	0.7174(15)	0.5005(9)	6.1(4)
C7B′	0.4510(8)	0.6975(14)	0.5980(9)	5.6(4)
C8B′	0.5235(12)	0.6731(19)	0.6340(12)	9.0(6)
HO(7)	0.494(3)	0.052(6)	0.344(3)	6.3
HO(8)	0.594(4)	−0.219(6)	0.319(4)	6.3

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid occupancy of C1B, C1B′, C3B, C3B′, C5B, C5B′, C7B, C7B′, C8B, C8B′ = 0.5.

minimizing $\Sigma_i w_i(F_i^{obs} - F_i^{cal})^2$, where w_i was calculated from the counting statistics. The atomic scattering factors f_0 and anomalous dispersion terms f', f'' were taken from ref. 13. All the non-hydrogen atoms, except the ethyl carbon atoms of NIB, were refined anisotropically. Hydrogen atoms in the anions were located in the final difference Fourier maps and refined. A secondary extinction correction was included in the refinement. One of the cations (NIB) was found to have some disorder atoms; namely all the α-carbon atoms and one of the β-carbon atoms. The disordered atoms, listed in Tables 2 and 3, are marked with an apostrophe (′).

Results

Reaction of $M(CO)_3(PMTA)$ (PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) with one equivalent of Et_4NOH in aqueous THF at 85 °C, gave the yellow crystalline compound, $[Et_4N]_4[M(CO)_3(\mu_3\text{-}OH)]_4$ (**1**, M = W; **2**, M = Mo). The infrared carbonyl region of **1** and **2** exhibited the two-band pattern (ν(CO) 1868(s), 1727(vs) cm^{-1} for **1**, and 1871(s), 1736(vs) cm^{-1} for **2**) characteristic of a $M(CO)_3$ moiety. Only one carbonyl signal (δ 231 ppm for **1** and 234 ppm for **2**) in the ^{13}C NMR spectra was observed, indicating that all the carbonyl groups are equivalent in the solution. A ν(OH) band of medium intensity observed at 3676 cm^{-1} for compound **1**, and at 3691 cm^{-1} for compound **2** is indicative of the presence of a bridging hydroxide ligand. Peaks assignable to the μ_3-OH resonance appeared at δ 0.96 (compound **1**) and at − 0.27 ppm (compound **2**) in the ^1H NMR spectra. In order to characterize these species fully, single crystal structural determinations of **1** and **2** were undertaken. The structure of $[Mo(CO)_3(\mu_3\text{-}OH)]_4^{4-}$ is shown in Fig. 1. Atomic parameters are given in Table 2 and 3. Selected bond distances and angles are collected in Tables 4 and 5.

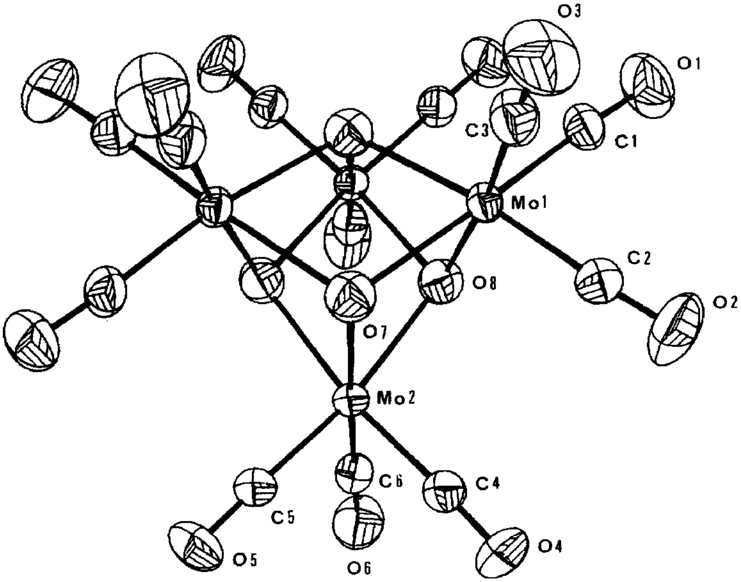

Fig. 1. ORTEP drawing of $[Mo(CO)_3(\mu_3\text{-}OH)]_4^{4-}$. Thermal ellipsoids are drawn with 50% probability boundaries.

Table 4

Selected interatomic distances (Å) and angles (deg) with esd's for $[W(CO)_3(\mu_3\text{-}OH)]_4^{4-}$ [a]

Distances			
W(1)–W(1)a	3.661(9)	W(1)–W(2)	3.5616(24)
W(1)–W(2)a	3.530(4)	W(2)–W(2)a	3.6709(24)
W(1)–C(1)	1.899(10)	W(1)–C(2)	1.915(11)
W(1)–C(3)	1.902(11)	W(2)–C(4)	1.928(10)
W(2)–C(5)	1.915(10)	W(2)–C(6)	1.924(10)
W(1)–O(7)	2.250(6)	W(1)–O(7)a	2.231(8)
W(1)–O(8)	2.241(6)	W(2)–O(7)	2.245(6)
W(2)–O(8)	2.236(6)	W(2)–O(8)a	2.254(6)
C(1)–O(1)	1.205(13)	C(2)–O(2)	1.184(13)
C(3)–O(3)	1.193(14)	C(4)–O(4)	1.152(11)
C(5)–O(5)	1.169(12)	C(6)–O(6)	1.172(12)
O(7)–O(7)a	2.535(11)	O(7)–O(8)	2.618(8)
O(7)–O(8)a	2.639(8)	O(8)–O(8)a	2.537(12)
Angles			
W(1)–O(7)–W(1)a	109.6(3)	W(1)–O(7)–W(2)	104.83(23)
W(1)a–O(7)–W(2)	104.13(24)	W(1)–O(8)–W(2)	105.41(23)
W(1)–O(8)–W(2)a	103.47(22)	W(2)–O(8)–W(2)a	109.7(3)
O(7)–W(1)–O(7)a	68.91(24)	O(7)–W(1)–O(8)	71.32(21)
O(7)a–W(1)–O(8)	72.32(21)	O(7)–W(2)–O(8)	71.52(20)
O(7)–W(2)–O(8)a	71.81(20)	O(8)–W(2)–O(8)a	68.80(24)
W(1)–C(1)–O(1)	177.4(9)	W(1)–C(2)–O(2)	178.9(9)
W(1)–C(3)–O(3)	177.6(10)	W(2)–C(4)–O(4)	177.1(9)
W(2)–C(5)–O(5)	177.8(10)	W(2)–C(6)–O(6)	173.4(9)

[a] Atoms, W(1)a, W(2)a, O(7)a, O(8)a, are symmetry equivalent.

Complexes **1** and **2** are isostructural, and have the same structure as the chromium analogue. Thus they all crystallize in the same space group *. The anions of **1** and **2** are composed of four $[M(CO)_3(OH)]^-$ units in a cubane-like arrangement with metal and hydroxide oxygen atoms located at alternate corners of a distorted M_4O_4 cube. In **1**, the average W–W distance is 3.59(6) Å, and the average O–O distance is 2.60(5) Å. In **2**, the average Mo–Mo distance is 3.58(6) Å while the average O–O distance is 2.65(5) Å. The coordination geometry of each metal is a distorted octahedron. Each metal is bonded to three *cis*-CO ligands and three O atoms of the hydroxide groups. Each μ_3-oxygen atom is bonded to three metal atoms and a hydrogen atom. Although such hydrogen atom positions cannot be ascertained from X-ray diffraction, the IR spectra (vide supra) do indicate the existence of hydroxide groups.

Other relevant bond distances and angles are as follows. The average W–O(μ_3)–W, [Mo–O(μ_3)–Mo] and O(μ_3)–W–O(μ_3), [O(μ_3)–Mo–O(μ_3)] bond angles are 106(3)° [105(3)°] and 71(1)° [72(2)°], respectively. Within the tungsten (molybdenum) coordination sphere, the W–O(μ_3) distance is 2.24(1) Å (2.25(1) Å) and the $W\text{–}C_{CO}$ ($Mo\text{–}C_{CO}$) distance is 1.92(1) Å (1.91(1) Å). The terminal carbonyl

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* *I2/a* in ref. 6 can be transformed into *C2/c*, a correction has to be made for $Z = 4$ according to the formula given.

Table 5

Selected interatomic distances (Å) and angles (deg) with esd's for $[Mo(CO)_3(\mu_3\text{-}OH)]_4^{4-}$ [a]

Distances			
Mo(1)–Mo(1)a	3.6524(17)	Mo(1)–Mo(2)	3.5513(9)
Mo(1)–Mo(2)a	3.5153(9)	Mo(2)–Mo(2)a	3.6644(10)
Mo(1)–C(1)	1.905(7)	Mo(1)–C(2)	1.910(6)
Mo(1)–C(3)	1.917(7)	Mo(2)–C(4)	1.908(6)
Mo(2)–C(5)	1.912(6)	Mo(2)–C(6)	1.903(6)
Mo(1)–O(7)	2.264(4)	Mo(1)–O(7)a	2.241(3)
Mo(1)–O(8)	2.251(4)	Mo(2)–O(7)	2.246(4)
Mo(2)–O(8)	2.243(4)	Mo(2)–O(8)a	2.264(3)
C(1)–O(1)	1.188(8)	C(2)–O(2)	1.181(8)
C(3)–O(3)	1.172(8)	C(4)–O(4)	1.183(7)
C(5)–O(5)	1.177(7)	C(6)–O(6)	1.195(8)
O(7)–O(7)a	2.598(7)	O(7)–O(8)	2.672(5)
O(7)–O(8)a	2.695(5)	O(8)–O(8)a	2.585(7)
Angles			
Mo(1)–O(7)–Mo(1)a	108.36(15)	Mo(1)–O(7)–Mo(2)	103.91(14)
Mo(1)a–O(7)–Mo(2)	103.17(14)	Mo(1)–O(8)–Mo(2)	104.44(14)
Mo(1)–O(8)–Mo(2)a	102.28(14)	Mo(2)–O(8)–Mo(2)a	108.83(14)
O(7)–Mo(1)–O(7)a	70.43(13)	O(7)–Mo(1)–O(8)	72.59(13)
O(7)a–Mo(1)–O(8)	73.74(13)	O(7)–Mo(2)–O(8)	73.08(13)
O(7)–Mo(2)–O(8)a	73.40(13)	O(8)–Mo(2)–O(8)a	70.01(13)
Mo(1)–C(1)–O(1)	175.9(6)	Mo(1)–C(2)–O(2)	176.1(6)
Mo(1)–C(3)–O(3)	175.7(6)	Mo(2)–C(4)–O(4)	175.6(6)
Mo(2)–C(5)–O(5)	177.0(6)	Mo(2)–C(6)–O(6)	171.3(6)

[a] Atoms, Mo(1)a, Mo(2)a, O(7)a, O(8)a, are symmetry equivalent.

ligands have an average W–C–O (Mo–C–O) bond angle of 177(2)° (175(2)°) and a C–O distance of 1.18(2) Å (1.18(1) Å).

Discussion

The structures observed for $[W(CO)_3(\mu_3\text{-}OH)]_4^{4-}$ and for $[Mo(CO)_3(\mu_3\text{-}OH)]_4^{4-}$ are the same as that of $[Cr(CO)_3(\mu_3\text{-}OH)]_4^{4-}$ [6]. The symmetry of the anion is C_2, which coincides with the crystallographic 2-fold axis. Other polynuclear complexes of the alternating A_4B_4 type have similar symmetry or even more symmetric geometries, e.g. $[Cr(CO)_3(\mu_3\text{-}OMe)]_4^{4-}$ has D_2 [7] and $[Mo(CO)_2(NO)(OH)]_4$ [5] has T_d. The observed W–W (Mo–Mo) mean distance of 3.59(6) Å (3.58(6) Å) indicates the absence of metal–metal bonds in such anions, since it is much longer than the W–W single bonds reported elsewhere 3.222(1) Å in $[C_5H_5W(CO)_3]_2$ [14], 3.155 Å in $I_2W_2(CO)_4$ [15], and 3.0256(4) Å in $W_2(CO)_8(\mu\text{-}PPh_2)_2$ [16]. The non-bonding between the metal atoms or ions are also formally in accord with the 18-electron rule, where μ_3-OH group is normally considered to be a five-electron donor. The obtuse M–O–M angles of 106(3)° for **1** and 105(3)° for **2**, and the acute O–M–O angles of 71(1)° for **1** and 72(2)° for **2** as well as the large metal separation are similar to those found for a series of cubane-like A_4B_4 complexes [17]. The average core bond angles and non-bonding M–M distances of these complexes are listed in Table 6 for comparison. In contrast, shorter metal–metal

Table 6

Core bond angles (deg) and M–M distances (Å) for A_4B_4 tetramers

Compound	$M–X_{\mu_3}–M$	$X_{\mu_3}–M–X_{\mu_3}$	M–M dist	Ref.
Compounds without M – M bonds				
$[Cr(CO)_3(\mu_3\text{-}OH)]_4^{4-}$	103.4(2)	74.6(1)	3.33(5)	6
$[Cr(CO)_3(\mu_3\text{-}OMe)]_4^{4-}$	102.9(2)	75.3(1)	3.31(6)	3
$[Re(CO)_3(\mu_3\text{-}OH)]_4$	104.0(5)	74.3(1)	3.480(2)	18
$[Re(CO)_3(\mu_3\text{-}SMe)]_4$	101.8(4)	76.8(3)	3.853(3)	19
$[Mo(CO)_2(NO)(\mu_3\text{-}OH)]_4$	103(1)	76(1)	3.429(3)	5
$[HW(CO)_3(\mu_3\text{-}OH)]_4$	104(1)	74(1)	3.479(3)	10
$[Os(CO)_3(\mu_3\text{-}O)]_4$	102(2)	77(1)	3.222(4)	20
$[PtMe_3(\mu_3\text{-}OH)]_4$	101.2(6)	77.6(6)	3.430(2)	21
Compounds with M – M bonds				
$[Cr(C_5H_5)(\mu_3\text{-}O)]_4$	93.1(3)	86.5(3)	2.81(9)	22
$[Fe(NO)(\mu_3\text{-}S)]_4$	73.4(1)	104.4(1)	2.634(1)	23
$[Fe(NO)(\mu_3\text{-}Se)]_4$	70.3	106.6	2.705	24

distances are also found in the cubane-like clusters, which normally have much smaller M–X–M angles (see Table 6) than those without metal–metal bonds.

A qualitative bonding description by Dahl [24] of 72-electron metal cluster system, $[Fe(CO)_3(\mu_3\text{-}X)]_4$ (X = S, Se), rationalized the completely non-bonding iron tetrahedron. These cubane-like iron tetramers, consisting of four d^6-Fe^{II}, four six-electron donor X^{2-} ligands, and twelve two-electron donor CO ligands, are electronically equivalent to **1** and **2**. Thus, the absence of a metal–metal bond in **1** or **2** is also in accord with Dahl's description.

The mean bond distances within the metal coordination sphere of **1** or **2** are normal. The W–O(μ_3) distance of 2.24(1) Å is comparable to that in $[HW(CO)_3(\mu_3\text{-}OH)]_4$ [10] (2.21(5) Å) and Mo–O(μ_3) distance of 2.25(1) Å is comparable to that in $[Mo(CO)_2(NO)(\mu_3\text{-}OH)]_4$ [5] (2.20(1) Å). The bond lengths of 1.92(1) Å for W–C(CO) and 1.91(1) Å for Mo–C(CO) are shorter than those reported for other trisubstituted $M(CO)_6$ derivatives [25], which are consistent with the negative charge on the anion. The average C–O distances, 1.18 Å, for the orthogonal carbonyl ligands are in agreement with metal carbonyl complexes in general. The terminal carbonyl ligands are almost linearly coordinated in both complexes.

The presence of the μ_3-OH groups was confirmed by isotopic studies. Firstly, the μ_3-OD derivative of **1** (**2**) gives a ν(OD) band at 2712 cm^{-1} (2723 cm^{-1}) but no high frequency band at 3676 cm^{-1} (3691 cm^{-1}). It is interesting that the ν(OH) bands of **1**, **2**, and $[Cr(CO)_3(\mu_3\text{-}OH)]_4^{4-}$ (3695 cm^{-1}) all appeared at unusually high frequency. For comparison, ν(OH) appears as a sharp double band at 3550 cm^{-1} for $[Re(CO)_3(\mu_3\text{-}OH)]_4$ [4] and as a double band at 3640/3625 cm^{-1} for $[Mn(CO)_3(\mu_3\text{-}OH)]_4$ [26]. Secondly, the peaks assignable to μ_3-OH in the ^1H NMR spectra (δ 0.96 ppm for **1** and -0.27 ppm for **2**) disappeared upon addition of excess D_2O to CD_3CN a solution of **1** or **2**. In addition the μ_3-OD derivative of **1** (**2**) does not have a peak at 0.96 (-0.27) ppm in D_2O solution.

It is important to note that our spectroscopic data, together with elemental analyses, and X-ray structural analyses did not allow us to eliminate the possibility that $[M(CO)_3(OH)]_3^{3-}$ is in equilibrium with $[M(CO)_3(OH)]_4^{4-}$ in the solution.

However, our ^1H NMR spectroscopic data strongly disfavor the existence of $(\mu\text{-H})W_2(CO)_{10}^-$ [27], $HW(CO)_5^-$ [28], and $W_2(\mu\text{-OH})_3(CO)_6^{3-}$ [9,29]. These complexes were reported to form from reaction of $W(CO)_6$ with OH^- under different conditions. We presently do not know why no discernible $M_2(\mu\text{-OH})_3(CO)_6^{3-}$ were detected in our case. When $M(CO)_3(PMTA)$ was allowed to react with an excess (more than five-fold) of Et_4NOH or KOH, the tetrameric $[M(CO)_3(OH)]_4^{4-}$ was contaminated with unidentified materials. No peaks assignable to $M_2(\mu\text{-OH})_3(CO)_6^{3-}$ [29] were detected, however. A speculative mechanism for the formation of **1** and **2** from $M(CO)_3(PMTA)$ involves a reversible ring opening (with scission at the M–N bond) followed by nucleophilic attack by OH^-. Such a mechanism has been proposed in the reaction of $Mo(CO)_3(PNP)$ ($PNP = Ph_2PCH_2CH_2N(Et)CH_2CH_2PPh_2$) with CO [30].

The large upfield shift of the hydroxide ligand in the ^1H NMR spectra is consistent with their basic character, i.e., the hydrogen atoms in $[M(CO)_3(\mu_3\text{-OH})]_4^{4-}$ are readily replaced by deuterium with D_2O (10-fold excess) within 30 minutes, the reaction product being $[M(CO)_3(\mu_3\text{-OD})]_4^{4-}$. Our preliminary results indicate that **1** reacts with electrophiles such as $NO^+BF_4^-$, Ph_3PAuCl and iodine. Further studies on the reactions of **1** and **2**, as well as the extension of similar synthetic strategy to other cubane type complexes are in progress.

Supplementary material available: Tables SI and SII listing anisotropic temperature factors and hydrogen atom coordinates and isotropic thermal parameters (6 pages); tables of calculated and observed structure factors (66 pages); Table SIII listing all bond distances and angles (6 pages), are all available from the authors.

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