Hydroxo-Bridged *fac*-Tricarbonylmolybdenum(0) Complexes: Synthesis, ^{95}Mo NMR Spectroscopy, and Crystal Structure of Cs$_4$[Mo$_4$(μ_3-OH)$_4$(CO)$_{12}$]·nH$_2$O

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In 1959 Hieber, Englert and Rieger[1] showed that hexacarbonylmolybdenum reacts with potassium hydroxide in hot ethanol to give a yellow water-soluble compound which they formulated as the μ-triol K$_3$[Mo$_2$(μ-OH)$_3$(CO)$_6$]. This formulation is supported by an X-ray crystal structure determination[2] of the analogous tungsten compound K$_3$[W$_2$(μ-OH)$_3$(CO)$_6$]·2H$_2$O. By addition of cesium ions to an aqueous solution of the potassium salt obtained by Hieber's method, we have now prepared and structurally characterized the new compound Cs$_4$[Mo$_4$(μ_3-OH)$_4$-(CO)$_{12}$]·nH$_2$O. The presence in the cesium salt of the cubane-like tetranuclear anion [Mo$_4$(μ_3-OH)$_4$(CO)$_{12}$]$^{4-}$ ([1]$^{4-}$) rather than the expected μ-triol anion prompted us to undertake a closer examination of this class of compounds.

Experimental Section

Synthesis. Preparations were carried out under a dinitrogen atmosphere by using Schlenk techniques.[3]

K$_4$[1]·2H$_2$O. The method is essentially identical to that used by Hieber et al.[1] to prepare what they formulated as K$_3$[Mo$_2$(μ-OH)$_3$(CO)$_6$]. A 9.0-g sample of Mo(CO)$_6$ was added to a solution of 19 g of KOH in 150 mL of 96% ethanol from which carbonate had been removed with a few drops of Ba(OH)$_2$(aq). The mixture was magnetically stirred at 100 °C for 14 h in a Schlenk flask fitted with a reflux condenser. A bright yellow powder was formed without (or only very little) gas evolution. A reaction at 80 °C for 4 h gave the same product. The crude product was highly contaminated[1] with potassium formate and hydroxide. To purify the product, K$_4$[1] was extracted with liquid ammonia (30 mL).[1] No measures were taken to remove water from the commercial grade liquid ammonia. All traces of ammonia were evaporated from the product by using an oil pump. Yield: 5.9 g (70%). Anal. Calcd for K$_3$[Mo$_2$(μ-OH)$_3$(CO)$_6$]: K, 22.20; Mo, 36.32; C, 13.64; H, 0.57. Calcd for K$_4$[1]·2H$_2$O: K, 15.95; Mo, 39.15; C, 14.70; H, 0.82. Found: K, 17.56; Mo, 39.47; C, 14.79; H, 0.78; N, 0. IR (KBr, cm^{-1}): 3640 (w, sp), 3615 (s, sp), 3435 (s, b), 2400 (w), 2220 (w), 1870 (vs, sp), 1701 (vs, b), 1590 (sh), 1150 (w, d), 864 (w), 745 (m), 670 (vw), 643 (m), 521 (m). Recrystallization:[4] A 4-mL quantity of ethanol was added to a solution of 0.7 g of K$_4$[1]·2H$_2$O in 4 mL of water. The yellow precipitate formed on mixing was dissolved by temporarily warming the mixture. Crystals formed in the course of hours and were washed with ethanol. The recrystallization did not affect the IR spectrum.

Cs$_4$[1]·4H$_2$O. A solution of 5.4 g (32 mmol) of CsOH·H$_2$O in 10 mL water was added to 3.9 g (4 mmol) of K$_4$[1]·2H$_2$O in 40 mL of water.[5] A yellow powder immediately precipitated. The mixture was cooled in

ice. After filtration, the product was washed, first quickly with ice-cold water and then with 96% ethanol. Yield: 4.4 g (80%). The salt may be recrystallized from warm water to produce large crystals. Prolonged exposure to warm water resulted in a brown discoloration of the otherwise bright yellow crystals. Anal. Calcd for Cs$_4$[1]·4H$_2$O: Mo, 27.58; C, 10.36; H, 0.87. Found: Mo, 28.87; C, 10.34; H, 0.74. IR (KBr, cm^{-1}): 3586 (s), 3500 (sh), 2400 (vw, d), 2230 (vw), 1861 (vs, sp), 1675 (vs, b), 1590 (s), 1150 (vw, d), 814 (vw), 734 (m), 665 (w), 647 (w), 540 (w), 511 (vw).[6] Solubility in water at room temperature is approximately 16 mg/mL. The crystal structure determination and microanalyses for C and H show that the tetrahydrate may lose some crystal water.

(NEt$_4$)$_4$[1] was prepared in the same manner as Cs$_4$[1]·4H$_2$O except for the use of 5.3 g of N(C$_2$H$_5$)$_4$Cl·xH$_2$O (Aldrich) instead of CsOH·H$_2$O. Yield: 4.5 g (84%). The yellow powder was pyrophoric. Large bright yellow shining crystals were obtained by recrystallization from warm water. Anal. Calcd for (NEt$_4$)$_4$[1]: Mo, 29.32; C, 40.38; H, 6.47; N, 4.28. Found: Mo, 31.50; C, 40.12; H, 6.71; N, 4.26. The X-ray powder diagram agreed with cell data from the single-crystal study.[7] IR (KBr, cm^{-1}): 3763 (w), 3734 (w), 3692 (s, sp), 3566 (w, sp), 3408 (m, b), 2400 (w), 2240 (m), 1869 (vs, sp), 1723 (vs) (NEt$_4$ bands not included).

K$_4$[W$_4$(μ_3-OH)$_4$(CO)$_{12}$]·2H$_2$O. The method of Hieber et al.[8] for preparing K$_3$[W$_2$(μ-OH)$_3$(CO)$_6$] was used. The crude product containing formate was dissolved in a volume of water, and the same volume of ethanol was added.[4] A yellow oil formed which in the course of a few days converted into large crystals. Anal. Calcd for K$_3$[W$_2$(μ-OH)$_3$(CO)$_6$]·2H$_2$O: K, 15.85; W, 49.68; C, 9.74; H, 0.95. Calcd for K$_4$[W$_4$(μ_3-OH)$_4$(CO)$_{12}$]·2H$_2$O: K, 11.74; W, 55.21; C, 10.82; H, 0.61. Found: K, 12.00; W, 54.60; C, 10.66; H, 0.72. IR (KBr, cm^{-1}): 3605 (w, sp), 3544 (s, b), 2405 (w), 2224 (w), 1866 (vs, sp), 1659 (vs, b), 1590 (sh), 1150 (w, d), 786 (m), 636 (m), 531 (m).

Analyses. K was determined by atomic emission. Prior to Mo analyses, the compounds were treated first with H$_2$O$_2$/NH$_3$ and then with hot concentrated HNO$_3$. Mo was determined gravimetrically with 8-hydroxyquinoline. W was determined spectrophotometrically[9] after the compound had been treated with H$_2$O$_2$. The Microanalytical Laboratory of the H. C. Ørsted Institute, University of Copenhagen, carried out the C, H, and N analyses.

Crystal Structure Determination of Cs$_4$[1]·2.25H$_2$O. A summary of the crystallographic data is given in Table I. Diffraction data were collected on a tabular brownish yellow crystal (0.08 × 0.20 × 0.36 mm) with an Enraf-Nonius CAD4 instrument. Three reflections were measured every 2.8 h to check for crystal decay, and there was found a 10% linear decrease during the data collection period. A total of 18 961 individual reflections were measured and reduced, including corrections for decay, Lorentz effects, polarization effects, and absorption (empirical using program DIFABS[10]), to values of $|F_o|$ and $\sigma(F_o)$ for 17525 unique reflections. A total of 11 946 reflections for which $I > 3\sigma(I)$ were included in the final structure analysis. The structure was solved using SHELXS-86[11] and refined with the SDP package.[12] Atomic scattering factors were taken from ref 13, except those for hydrogen.[14] Atomic coordinates for all atoms (except water hydrogens) and anisotropic thermal parameters for non-hydrogen atoms (except O18–O20), a total of 358 parameters, were refined. Some of the water of crystallization (O18–O20) appeared to be disordered with a total of 1.25 oxygen atoms occupying the three sites. After the final refinement cycle, the agreement factors were $R(F_o) = 0.028$ and $R_w(F_o) = 0.037$, and $S = 1.232$ and the maximum ratio (Δ/σ) was 0.02. A final

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(5) Cs$_4$[1]·4H$_2$O and (NEt$_4$)$_4$[1] may also be prepared from solutions of *crude* potassium salt.
(6) The IR band patterns in the region 800–400 cm^{-1} are very similar for K$_4$[1]·2H$_2$O and Cs$_4$[1]·4H$_2$O. The same band pattern is not found for (NEt$_4$)$_4$[1], suggesting that it is due to the water of crystallization.
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Table I. Crystallographic Data

formula	$C_{12}H_{8.5}Cs_4Mo_4O_{18.25}$
fw	1360.07
space group	monoclinic, $P2_1/c$ (No. 14)
temp/K	122
$a/Å$	14.351 (3)
$b/Å$	17.481 (4)
$c/Å$	11.636 (6)
β/deg	93.10 (3)
$V/Å^3$	2914.4
Z	4
radiation λ(Mo Kα)/Å	0.710 69
abs coeff μ/cm^{-1}	66.25
max 2θ/deg	80
no. of reflcns measd	18 961
no. of unique data, $I > 3\sigma(I)$	11 946
$R(F_o)^a$	0.028
$R_w(F_o)^b$	0.037

^{a} $R(F_o) = \sum\|F_o| - |F_c\|/\sum|F_o|$. ^{b} $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

● Mo   ○ O

◎ C   ○ H
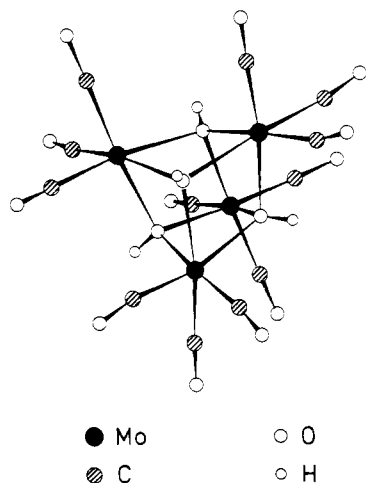
Figure 1. Computer drawing of $[Mo_4(\mu_3\text{-}OH)_4(CO)_{12}]^{4-}$ ($[1]^{4-}$) as found in $Cs_4[Mo_4(\mu_3\text{-}OH)_4(CO)_{12}]\cdot2.25H_2O$.

Fourier synthesis gave the highest and lowest residuals as 1.274 and -1.954 e Å^{-3}, respectively, mainly located around Cs sites.

NMR Spectra. The ^{95}Mo NMR spectra were recorded on a Bruker AC 300-MHz NMR spectrometer. A 10-mm broad-band probehead (^{109}Ag$-^{31}$P) with digital tuning was used for the measurements. A 2 M solution of Na_2MoO_4 in D_2O, basic, served as external standard. The ^{13}C and ^{1}H spectra were recorded on a Bruker AM 500-MHz NMR spectrometer.

Infrared Spectra. The IR spectra were obtained on a Perkin-Elmer 1710 FT-IR spectrometer using KBr pellets.

Results

The yellow powder $K_4[1]\cdot2H_2O$, formed by the reaction of hexacarbonylmolybdenum with potassium hydroxide in hot ethanol, turns brown within a few minutes after exposure to air. After recrystallization from ethanol/water, $K_4[1]\cdot2H_2O$ seems to be even more air-sensitive. When potassium is replaced by the cesium or tetraethylammonium cation, the salts are more air-stable and can, when not in the form of powders, be handled in air for several minutes without any visual decomposition. Cs_4-$[1]\cdot4H_2O$ and $(NEt_4)_4[1]$ are also less soluble in water. $(NEt_4)_4$-$[1]$ has previously been prepared by a different method.[7]

The structure of $Cs_4[Mo_4(\mu_3\text{-}OH)_4(CO)_{12}]\cdot2.25H_2O$ was determined by X-ray crystallography. A computer drawing of the anion $[1]^{4-}$ is shown in Figure 1. Selected interatomic distances and angles are listed in Table II. Atomic coordinates and thermal parameters are given in Table III. The long Mo–Mo distance (3.54 Å) indicates that no metal bonds are present. The structure of $(NEt_4)_4[1]$ has been determined previously.[7] Both compounds contain the same cubane-like tetranuclear anion. These cubane-like tetranuclear structures have been found for a number of d^6

Table II. Selected Interatomic Distances (Å) and Angles (deg)^a

Distances	
Mo–(μ_3-O)	2.24 (2.203–2.261)
C–O	1.18 (1.173–1.193)
(μ_3-O)–(μ_3-O)′	2.66 (2.610–2.709)
Mo–C	1.92 (1.896–1.934)
Mo–Mo′	3.54 (3.4630–3.6110)

Angles	
(μ_3-O)–Mo–(μ_3-O)′	72.9 (71.03–74.90)
Mo–(μ_3-O)–Mo′	104.7 (100.22–107.81)
C–Mo–C′	84.2 (79.5–91.0)
Mo–C–O	175.0 (172.1–178.2)

^{a} Average values (minimum and maximum in parentheses) for the $[Mo_4(\mu_3\text{-}OH)_4(CO)_{12}]^{4-}$ ion.

Table III. Final Positional and Displacement Parameters (Å^2)

atom	x/a	y/b	z/c	$B_{eq}{}^a$
Cs1	0.89130 (2)	−0.24419 (1)	−0.09761 (2)	2.055 (4)
Cs2	0.44977 (2)	−0.13613 (1)	0.34790 (2)	1.803 (3)
Cs3	0.64455 (1)	−0.33673 (1)	0.18167 (2)	1.527 (3)
Cs4	1.13473 (2)	−0.07525 (1)	0.21980 (2)	1.862 (3)
Mo1	0.82419 (2)	−0.04337 (1)	0.12586 (2)	0.824 (3)
Mo2	0.71263 (2)	0.13516 (1)	0.14108 (2)	0.858 (3)
Mo3	0.91454 (2)	0.10342 (1)	0.31977 (2)	0.804 (3)
Mo4	0.70881 (2)	−0.00059 (1)	0.37173 (2)	0.802 (3)
O1	0.8528 (2)	0.0823 (1)	0.1418 (2)	0.91 (3)
O2	0.6964 (2)	0.0117 (1)	0.1825 (2)	1.01 (3)
O3	0.8554 (2)	−0.0146 (1)	0.3126 (2)	0.94 (3)
O4	0.7584 (2)	0.1167 (1)	0.3279 (2)	0.97 (3)
O5	0.7275 (3)	−0.0761 (2)	−0.1130 (3)	3.50 (7)
O6	0.9976 (2)	−0.1006 (2)	0.0046 (2)	1.83 (4)
O7	0.7975 (2)	−0.2181 (1)	0.1505 (3)	2.13 (5)
O8	0.5036 (2)	0.1811 (2)	0.1245 (3)	2.02 (4)
O9	0.6724 (3)	0.1449 (2)	−0.1218 (2)	3.14 (6)
O10	0.7590 (2)	0.3062 (2)	0.0999 (3)	2.29 (5)
O11	0.9932 (2)	0.1092 (2)	0.5725 (2)	1.96 (4)
O12	1.1267 (2)	0.1028 (2)	0.2873 (3)	2.61 (6)
O13	0.9711 (2)	0.2742 (2)	0.3136 (3)	2.52 (5)
O14	0.5007 (2)	0.0402 (2)	0.3898 (2)	1.90 (4)
O15	0.6707 (2)	−0.1740 (2)	0.4045 (2)	1.89 (4)
O16	0.7084 (2)	0.0086 (2)	0.6382 (2)	1.50 (4)
O17	0.4339 (2)	0.7921 (2)	0.5997 (3)	2.80 (6)
O18	0.5795 (5)	−0.1515 (4)	0.1127 (6)	4.6 (1)*
O19	0.4975 (9)	−0.0130 (8)	0.109 (1)	2.7 (2)*
O20	0.463 (1)	0.4228 (8)	0.404 (1)	3.2 (2)*
C1	0.7670 (3)	−0.0610 (2)	−0.0247 (3)	1.66 (5)
C2	0.9355 (2)	−0.0766 (2)	0.0570 (3)	1.22 (4)
C3	0.8049 (2)	−0.1506 (2)	0.1436 (3)	1.22 (4)
C4	0.5839 (2)	0.1641 (2)	0.1375 (3)	1.28 (4)
C5	0.6885 (3)	0.1379 (2)	−0.0207 (3)	1.66 (5)
C6	0.7431 (2)	0.2417 (2)	0.1186 (3)	1.39 (4)
C7	0.9589 (2)	0.1065 (2)	0.4771 (3)	1.24 (4)
C8	1.0450 (2)	0.0976 (2)	0.2966 (3)	1.49 (5)
C9	0.9457 (2)	0.2100 (2)	0.3167 (3)	1.32 (4)
C10	0.5799 (2)	0.0234 (2)	0.3858 (3)	1.20 (4)
C11	0.6840 (2)	−0.1078 (2)	0.3907 (2)	1.17 (4)
C12	0.7150 (2)	0.0048 (2)	0.5373 (3)	1.08 (4)
H1	0.890 (3)	0.096 (3)	0.102 (4)	2.0*
H2	0.653 (3)	−0.019 (3)	0.148 (4)	2.0*
H3	0.890 (3)	−0.039 (3)	0.341 (4)	2.0*
H4	0.745 (4)	0.141 (3)	0.370 (4)	2.0*

^{a} Starred values indicate that atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab(\cos \gamma)\beta_{12} + 2ac(\cos \beta)\beta_{13} + 2bc(\cos \alpha)\beta_{23}]$.

metal ions: $(NEt_4)_4[M_4(\mu_3\text{-}OH)_4(CO)_{12}]$ (M = Cr,[15] W[7]), $[Os_4$-$(\mu_3\text{-}O)_4(CO)_{12}]$,[16] and $[Re_4(\mu_3\text{-}OR)_4(CO)_{12}]$ (R = H, OCH$_3$).[17]

The ^{95}Mo NMR data are listed in Table IV. The ^{13}C NMR spectra of $Cs_4[1]\cdot4H_2O$ in D_2O and $(NEt_4)_4[1]$ in CD_3CN showed single sharp peaks at 229.5 and 233.7 ppm. Otherwise, only peaks due to the solvent or the cation were observed.

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Table IV. ^{95}Mo NMR Data[a]

compound	solvent	δ[b]	line width/Hz
K$_4$[Mo$_4$(μ_3-OH)$_4$(CO)$_{12}$]·2H$_2$O	H$_2$O[c]	−870	90
	H$_2$O/EtOH[d]	−867	250
	NH$_3$(l), 225 K	−889	140
	dmso	−834	400
	dmf	−843	800
	dmf, 273 K	≈−857	≈1000
Cs$_4$[Mo$_4$(μ_3-OH)$_4$(CO)$_{12}$]·4H$_2$O	H$_2$O[e]	−870	90
	2 M NaOH[c]	−873	160
(NEt$_4$)$_4$[Mo$_4$(μ_3-OH)$_4$(CO)$_{12}$]	H$_2$O[f]	−869	100
	2 M NaOH[f]	−871	≈60
	CH$_3$CN	−829	80
	dmf	−827	180
	dmso	−828	230
[Mo(NH$_3$)$_3$(CO)$_3$]	NH$_3$(l), 225 K	−1162	60

[a] Ambient temperature unless otherwise noted. EtOH = ethanol; dmso = dimethyl sulfoxide; dmf = N,N-dimethylformamide. [b] δ(Na$_2$MoO$_4$(aq)) = 0; ppm scale. [c] c_{Mo} ≈ 0.04 M. [d] Saturated in a 1:1 mixture. [e] c_{Mo} ≈ 0.025 M. [f] Saturated, c_{Mo} ≈ 0.01 M (estimated).

Aqueous solutions of K$_4$[1]·2H$_2$O, Cs$_4$[1]·4H$_2$O, and (NEt$_4$)$_4$-[1] were moderately basic (pH ≈ 10 for c_{Mo} ≈ 0.02 M).

Discussion

The elemental analysis shows that the product obtained by us from the reaction of hexacarbonylmolybdenum with potassium hydroxide in hot ethanol is K$_4$[1]·2H$_2$O. The discrepancies observed may be due to impurities or some decomposition during the analysis. For example, formate (IR, 1347 cm^{-1}) was still present in the purified compound obtained from the liquid ammonia extract.

Also, measurements of pH rule out that our product from the Mo(CO)$_6$–KOH reaction is K$_3$[Mo$_2$(μ-OH)$_3$(CO)$_6$]. A conversion of μ-triol to [1]$^{4-}$ by the reaction shown in (1) would be

$$2[Mo_2(\mu\text{-OH})_3(CO)_6]^{3-} \rightleftharpoons [Mo_4(\mu_3\text{-OH})_4(CO)_{12}]^{4-} +$$
$$2OH^- \quad (1)$$
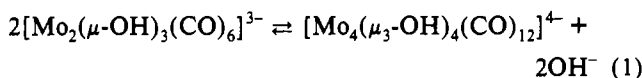
accompanied by an increase in pH. Solutions (c_{Mo} ≈ 0.02 M) of our product, Cs$_4$[1]·4H$_2$O, and (NEt$_4$)$_4$[1] all had pH ≈ 10. If our product were the μ-triol and reaction 1 occurred on dissolution, then a pH of ≈12 would be expected for the solution. Alternatively, if reaction 1 did not take place until Cs$_4$[1]·4H$_2$O or (NEt$_4$)$_4$[1] precipitated from a solution of our product, then the precipitation would be accompanied by an increase in the pH. This was not observed.

A ^{95}Mo NMR signal at approximately −830 ppm is observed when (NEt$_4$)$_4$[1] is dissolved in dmf, dmso, and CH$_3$CN (Table IV). This strongly suggests that the signal is due to [1]$^{4-}$. A signal at −834 ppm is also observed when K$_4$[1]·2H$_2$O is dissolved in dmso. In dmf, K$_4$[1]·2H$_2$O has a signal at −843 ppm, slightly more shielded than the other signals observed, but within error range,[18] considering the large line width. The difference in the line widths of all these signals is due to the different viscosities of the solvents used.[18]

In aqueous solution, a ^{95}Mo NMR signal at approximately −870 ppm is observed for all salts of [1]$^{4-}$ (Table IV). Assignment of the −870 ppm signal to [1]$^{4-}$ implies a large solvent effect, up to 40 ppm, but solvent effects of this magnitude have been observed.[18] (NEt$_4$)$_2$MoS$_4$, for example, has chemical shift differences up to 76 ppm, depending on the solvent.[19] The largest differences are between water and dmso, dmf, and CH$_3$CN,

the solvents used in this study. The almost identical chemical shifts observed for solutions of salts of [1]$^{4-}$ in neutral water and in 2 M NaOH show that reaction 1 does not proceed toward the left in strong base (within a couple of weeks at room temperature).

When K$_4$[1]·2H$_2$O is dissolved in liquid ammonia at 225 K, a ^{95}Mo signal at −889 ppm is observed. Since the compound[1] [Mo(NH$_3$)$_3$(CO)$_3$] has a signal at −1162 ppm (Table IV), a transformation of [1]$^{4-}$ to [Mo(NH$_3$)$_3$(CO)$_3$] in liquid ammonia can be ruled out. The −889 ppm signal is very likely due to [1]$^{4-}$. The upfield chemical shift change can be attributed to the lower temperature. Increased shielding was also observed for a solution of K$_4$[1]·2H$_2$O in dmf upon cooling (Table IV).

The results show that we have not been able to prepare the μ-triol K$_3$[Mo$_2$(μ-OH)$_3$(CO)$_6$] by the method of Hieber et al.[1] This raises the question as to whether K$_3$[Mo$_2$(μ-OH)$_3$(CO)$_6$] exists at all. The available evidence for its existence originates from two sources: the analytical data of Hieber et al.[1] and a statement in the (poorly documented) crystal structure report[2] for K$_3$[W$_2$(μ-OH)$_3$(CO)$_6$]·2H$_2$O saying that "the molybdenum compound is strictly isomorphous...but very unstable". A sample of the tungsten compound prepared[4,8] by us gave analytical results in agreement with the formula K$_4$[W$_4$(μ_3-OH)$_4$(CO)$_{12}$]·2H$_2$O. It should be noted, however, that a triply bridged structure is well-established in (NEt$_4$)$_3$[W$_2$(μ-OPh)$_3$(CO)$_6$]·3CH$_3$CN and that the anion of this salt has been produced from [W$_4$(μ_3-OPh)$_4$(CO)$_{12}$]$^{4-}$.[20]

In addition to the directly synthesized K$_3$[Mo$_2$(μ-OH)$_3$(CO)$_6$], Hieber et al.[1] described K, [Cr^{III}(en)$_3$], [Ni^{II}(en)$_3$], and NMe$_4$ salts that may be prepared from aqueous solutions of K$_3$[Mo$_2$(μ-OH)$_3$(CO)$_6$]. On the basis of elemental analyses, these salts were all formulated as containing the singly protonated μ-triol [Mo$_2$(μ-OH)$_3$(CO)$_6$H]$^{2-}$. In light of our present findings, the isomeric formulations as hydrated salts of [1]$^{4-}$ seem much more likely.

The product of the reaction between hexacarbonylchromium and potassium hydroxide in ethanol is formulated by Hieber et al.[21] as the singly protonated μ-triol K$_2$[Cr$_2$(μ-OH)$_3$(CO)$_6$H]. Since in the case of the chromium system there is no evidence at all to suggest a μ-triol structure, the isomeric formulation K$_4$[Cr$_4$(μ_3-OH)$_4$(CO)$_{12}$]·2H$_2$O must clearly be preferred. This is substantiated by the crystal structure of (NEt$_4$)$_4$[Cr$_4$(μ_3-OH)$_4$(CO)$_{12}$].[15] However, the synthetic route[15] to the tetraethylammonium salt is quite different from that to the potassium salt.

Conclusion

The compound K$_3$[Mo$_2$(μ-OH)$_3$(CO)$_6$] first described by Hieber et al.[1] in 1959 and later repeatedly cited in the literature[22] could not be prepared by us. The preparative method[1] invariably gave K$_4$[Mo$_4$(μ_3-OH)$_4$(CO)$_{12}$]·2H$_2$O. Either Hieber's μ-triol formulation is incorrect or the formation of the μ-triol rather than the μ_3-tetraol depends on yet unidentified experimental conditions. Twenty years ago it was found that the hydride species

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obtained from Hieber's potassium salt by addition of strong acid was not $[Mo_2(\mu\text{-}OH)_3(CO)_6H_3]$ as originally claimed[1] but was instead $[Mo_4(\mu_3\text{-}OH)_4(CO)_{12}H_4]$.[23,24] Were it not for the crystal structure[2] of $K_3[W_2(\mu\text{-}OH)_3(CO)_6]\cdot2H_2O$, the existence of the molybdenum μ-triol would be very doubtful.

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