Articles

Preparation and Crystal Structures of Formato Complexes of the $[M^{IV}{}_3O_4]^{4+}$ and $[M^{IV}{}_3S_4]^{4+}$ (M = Mo, W) Clusters. Convenient Precursors to the Corresponding Aqua Complexes

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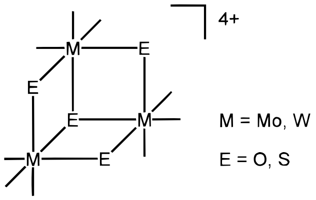
In the aqueous chemistry of molybdenum(IV) and tungsten(IV), trinuclear, incomplete cubane-like, oxo and sulfido clusters of the type $[M_3E_4]^{4+}$ (M = Mo, W; E = O, S) play a central role. We here describe how formato complexes of all these cluster cores can be prepared in high yields by crystallization from methanol−water or ethanol−water mixtures. Since potassium and ammonium formate are very soluble in these alcohol−water mixtures, high formate concentrations could be accomplished in the solutions from which the corresponding salts of cluster formato complexes crystallized. The $[Mo_3O_4]^{4+}$ compounds could be synthesized without requiring the use of noncomplexing acids in the process. Some $[M_3E_4]^{4+}$ compounds were characterized by single-crystal structure determinations. $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$ was triclinic, space group $P\bar{1}$ (No. 2) with $a = 11.011(2)$ Å, $b = 13.310(2)$ Å, $c = 9.993(1)$ Å, $\alpha = 106.817(7)°$, $\beta = 91.651(9)°$, $\gamma = 88.340(9)°$, and two formula units per cell. $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$ was monoclinic, space group $C2/m$ (No. 12) with $a = 19.605(6)$ Å, $b = 14.458(7)$ Å, $c = 13.627(5)$ Å, $\beta = 118.94(2)°$, and four formula units per cell. Generally, the nine coordination sites of $[M_3E_4]^{4+}$ were occupied either by a mixture of monodentate and μ_2-bridging formato ligands or by monodentate formato ligands only. By dissolution in noncomplexing strong acid, all the formato complexes immediately hydrolyzed to form $[M_3E_4(H_2O)_9]^{4+}$ aqua complexes. This allows, for example, high concentrations of $[Mo_3S_4(H_2O)_9]^{4+}$ in CF_3SO_3H to be obtained and these solutions to be used for the synthesis of bimetallic clusters containing the cubane-like motif $Mo_3M'S_4$.

Introduction

Molybdenum(IV) was recognized as a stable oxidation state in non-cyanide-containing aqueous solutions as late as 1966.[1,2] It occurs in the form of the trinuclear[3,4] cluster $[Mo_3O_4]^{4+}$, which was found to have the coordination number 9. Later, the analogous tungsten(IV) cluster $[W_3O_4]^{4+}$ was prepared[5] in aqueous solution and so were the two sulfido clusters $[Mo_3S_4]^{4+}$ (ref 6) and $[W_3S_4]^{4+}$ (ref 7). Mixed oxo−sulfido clusters[8] and mixed molybdenum−tungsten clusters[9] have also been prepared. The $[M_3E_4]^{4+}$ (M = Mo, W; E = O, S) type clusters play a central role in the aqueous chemistry[10] of molybdenum(IV) and tungsten(IV).



In acidic, aqueous solution and in the absence of strongly coordinating ligands, the clusters occur as aqua complexes: red $[Mo_3O_4(H_2O)_9]^{4+}$, orange $[W_3O_4(H_2O)_9]^{4+}$, green $[Mo_3S_4(H_2O)_9]^{4+}$, and purple $[W_3S_4(H_2O)_9]^{4+}$. The cluster cores are kinetically extremely inert; $[Mo_3S_4]^{4+}$ and $[W_3S_4]^{4+}$, for example, are stable in 2 M hydrochloric acid for several years. Even in concentrated sulfuric acid has $[Mo_3O_4]^{4+}$ been found to be stable for >2 years.[11] Both sulfido clusters are stable in 2 M H^+ with respect to oxidation by the air whereas $[Mo_3O_4(H_2O)_9]^{4+}$ oxidizes slowly and $[W_3O_4(H_2O)_9]^{4+}$ more rapidly under these conditions.

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Richens et al. isolated $[Mo_3O_4(H_2O)_9]^{4+}$ (ref 12) and Shibahara and co-workers $[Mo_3S_4(H_2O)_9]^{4+}$ (ref 13) and $[W_3S_4(H_2O)_9]^{4+}$ (ref 14) as the very soluble *p*-toluenesulfonate (pts) salts. All were obtained by crystallization of *p*-toluenesulfonic acid (Hpts) supersaturated eluates of $[M_3E_4(H_2O)_9]^{4+}$ from cation exchange columns. Recently, a convenient high-yield method was reported for the isolation of such pts salts: By addition of a stoichiometric amount of Hpts to solutions of $[M_3NiS_4(H_2O)_{10}]^{4+}$ in aqueous CF_3COOH followed by complete removal of the solvent by rotary evaporation, crystalline pts salts of the M_3NiS_4 clusters could be isolated.[15]

We here report syntheses and structures of $[M_3E_4]^{4+}$ formato complexes. Formato complexes are excellent starting materials for the preparation of aqua complexes[10] by acid hydrolysis in noncomplexing acids. Previously, $Na_3[Mo^{III}(HCO_2)_6]$ [16,17] and $(NH_4)_3[Mo^{V}{}_2O_4(\mu\text{-}HCO_2)(HCO_2)_4]$[18,19] were thus used as precursors to the aqua complexes $[Mo^{III}(H_2O)_6]^{3+}$ and $[Mo^{V}{}_2O_4(H_2O)_6]^{2+}$. One of the new compounds reported in the present paper, $K_4Mo_3S_4(HCO_2)_8(H_2O)_3$, has already been used[20] for the preparation of the bimetallic cluster $[Mo_6PbS_8(H_2O)_{18}]^{8+}$;[20,21] here high concentrations of $[Mo_3S_4(H_2O)_9]^{4+}$ in CF_3SO_3H were required but the presence of pts^- undesired. This situation could *only* be accomplished by means of $K_4Mo_3S_4(HCO_2)_8(H_2O)_3$.

Experimental Section

Synthesis of Oxo Cluster Compounds. Due to the air-sensitivity of the oxo clusters, Schlenk techniques were used and preparations were carried out under a protective dinitrogen atmosphere with the use of deaerated solvents (by bubbling with N_2 for 15 min). For $[Mo_3O_4]^{4+}$ inert gas protection is important during the conproportionation reaction but is less important in other stages of the synthesis as $[Mo_3O_4]^{4+}$ in acidic solution is oxidized only slowly by atmospheric dioxygen at room temperature.

$[K]_4[Mo_3O_4(HCO_2)_8]\cdot nH_2O$. Literature methods[22,23] are available for preparation of the starting material $(NH_4)_2[MoCl_5(H_2O)]$; alternatively $(NH_4)_3[MoCl_6]$,[24] $K_2[MoCl_5(H_2O)]$,[25] or $K_3[MoCl_6]$[25] may be used.

While a flask containing 50 mL of O_2-free 2 M HCl was being flushed with N_2, $(NH_4)_2[MoCl_5(H_2O)]$ (9.82 g, 30 mmol) and $Na_2MoO_4\cdot 2H_2O$ (3.63 g, 15 mmol) were dissolved in the acid. The solution, which at first may contain some solid material, was stirred at 85 °C for 2 h under N_2. The dark red solution obtained was allowed to cool, diluted with 450 mL of O_2-free water, and set aside at room temperature (20 °C) for 18−20 h under N_2. Storing the solution for a shorter period made it difficult to chromatographically separate Mo^{V} and Mo^{IV}. If, on the other hand, the solution was stored for a longer period, extensive polymerization occurred (brown color).

The following chromatographic operations, hydroxide precipitation and redissolution, should be carried out in noninterrupted succession (total time required is approximately 4 h). N_2 protection is not necessary. After the prescribed 18−20 h the 500 mL dark red solution was loaded onto a 17 cm × 3 cm column of Dowex 50W-X2 (100−200 mesh) cation exchange resin (H^+ form, packed in neutral water). The resin bed was washed with 1000 mL of 0.3 M HCl, which removed undesired byproducts: first orange $[Mo_2O_4]^{2+}$, then a small amount of a red species, probably a chloro complex of $[Mo_3O_4]^{4+}$. At the end, when the color of the washing liquid had become very weak, the desired $[Mo_3O_4]^{4+}$ was eluted with 2 M HCl. Only the first approximately 250 mL concentrated dark red eluate was used; subsequently the eluate became less concentrated and increasingly brownish in color. Without undue delay and while the eluate was being cooled in ice, small portions of 10 M KOH were added to the eluate until pH ≈ 10 was obtained (approximately 65 mL). This caused precipitation of dark-green $[Mo_3O_4]^{4+}$ hydroxide. The hydroxide was isolated as a concentrated slurry by centrifugation using an ordinary laboratory centrifuge. It was washed twice with water and then dissolved in 150 mL of an O_2-free buffer solution, which was 5 M in potassium formate and 10 M in formic acid (giving a total volume of approximately 225 mL). If not all hydroxide dissolved at once, the mixture was gently warmed while N_2 was bubbled through it. Then O_2-free ethanol (96%) was added in an amount equal to twice the volume of the aqueous solution. After standing for 10 min, a small amount of oily brown precipitate sometimes formed on the walls of the flask. This was removed, together with some fine dark brown particles, by filtering the solution through a Büchner funnel. Finally, the ethanolic solution was once again made O_2-free by bubbling N_2 through it for 15 min and then set aside for crystallization (N_2 protection, room temperature).

Complete crystallization of $[K]_4[Mo_3O_4(HCO_2)_8]\cdot nH_2O$ usually took place overnight. A white flocculent precipitate, which sometimes formed in the course of several days, should not be allowed to contaminate the product. The needle-shaped, maroon colored, air-stable crystals were isolated by filtration in air, washed several times with 96% ethanol, and thoroughly dried in the air. Yield: 6.4 g (46% based on total molybdenum; $n = 3$). Anal. Calcd for $[K]_4[Mo_3O_4(HCO_2)_8]\cdot 3H_2O$: K, 16.96; Mo, 31.20; C, 10.42; H, 1.53. Found: K, 17.2; Mo, 31.6; C, 10.31; H, 1.54. IR (cm^{-1}, KBr): 3520 (s, b), 2875 (m), 1610 (vs), 1544 (m, sp), 1377 (m, sp), 1354 (m, sp), 1300 (s), 1240 (s), 804 (s, sp, double), 767 (s, sp), 753 (s, sp), 723 (m, sp), 485 (m, sp). A single-crystal structure determination ($P2_1/c$, $a = 10.8748$ Å, $b = 6.6969$ Å, $c = 34.8815$ Å, $\beta = 91.3959°$)[26] gave $n = 1$, indicating that the crystal did not have the usual amount of water of crystallization which, according to elemental analyses, is $n \approx 3$. The air-dried product lost approximately 2 mol of water when kept over concentrated sulfuric acid. Magnetic susceptibility measurements showed that the compound had no unpaired electrons.

$[NH_4]_4[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$. This crystalline solid was prepared analogously to the potassium salt above. Aqueous ammonia was used instead of 10 M potassium hydroxide to precipitate the dark-green $[Mo_3O_4]^{4+}$ hydroxide and the formate/formic acid buffer solution should be 5 M in ammonium formate rather than potassium formate. Formation of the first crystals was sometimes slow. Yield: 3.0 g. Anal. Calcd for $[NH_4]_4[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$: Mo, 33.23; C, 12.48; H, 3.49. Found: Mo, 32.9; C, 12.47; H, 3.51. IR (cm^{-1}, KBr): 2875 (m), 1610 (vs), 1550 (m, sp), 1460 (m), 1399 (m, sp), 1275 (s), 1235 (m), 798 (s, sp), 752 (s), 717 (m, sp), 485 (m, sp).

$K_4W_3O_4(HCO_2)_8(H_2O)_3$. A solution of $[W_3O_4(H_2O)_9]^{4+}$ in 2 M *p*-toluenesulfonic acid was prepared from $K_2[WCl_6]$.[5] The concentration of the solution was determined spectrophotometrically by using the value[5] (λ_{max}, ϵ) = (455 nm, 375 $L\cdot mol^{-1}\cdot cm^{-1}$). An amount of 0.5 mmol of $[W_3O_4(H_2O)_9]^{4+}$ in 2 M *p*-toluenesulfonic acid was diluted 10 times with water and loaded onto a column (3 cm long, 13 mm diameter) of Dowex 50W-X2 (100−200 mesh) cation exchanger. The column was washed with water and run dry. Then 10 mL of 5 M potassium formate solution which was also 10 M with respect to formic acid was applied to the column. After the column had been soaked for 30 min, slow eluation (5 drops/min) was conducted. The dark red eluate

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was collected, twice its volume of methanol was added, and the mixture was set aside at 5 °C for 2 days. A dark red oil formed. This was separated from the mother liquor and then converted into a dark red, glassy, amorphous material by treatment with 25 mL of absolute ethanol with magnetic stirring. The solid was isolated by filtration, washed with ethanol, and dried in a vacuum. Yield: 0.38 g (64%). Anal. Calcd for $K_4W_3O_4(HCO_2)_8(H_2O)_3$: C, 8.10; H, 1.19. Found: C, 8.23; H, 0.71. IR (cm^{-1}, KBr): 3415 (s, b), 2872 (m), 1631 (vs), 1389 (m, sp), 1348 (w), 1303 (s), 799 (m, sp), 759 (w), 735 (w), 697 (w).

Synthesis of Sulfido Cluster Compounds. Solutions of the aqua ions $[M_3S_4(H_2O)_9]^{4+}$ (M = Mo, W) in hydrochloric acid were prepared by reduction of $(NH_4)_2MS_4$ with $NaBH_4$.[14] Their concentrations were determined spectrophotometrically in 1 M HCl [$(\lambda_{max}, \epsilon)_{Mo}$ = (620 nm, 315 L·mol^{-1}·cm^{-1}) and $(\lambda_{max}, \epsilon)_W$ = (570 nm, 480 L·mol^{-1}·cm^{-1})]. All operations with the sulfido clusters can be carried out in air, and none of the products are air-sensitive.

$K_4Mo_3S_4(HCO_2)_8(H_2O)_3$. An amount of 0.5 mmol of $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M hydrochloric acid was diluted 10 times with water and then loaded onto a column (5 cm long, 13 mm diameter) of Dowex 50W-X2 (100−200 mesh) cation exchanger. The column was washed with 100 mL of distilled water and green product eluted with 50 mL 2 M *p*-toluenesulfonic acid. After 1 day at room temperature the eluate was diluted 10 times and reloaded onto the cation exchange column. The column was washed with water and then run dry to avoid dilution in the following step. Then 10 mL of 5 M potassium formate solution which was also 5 M with respect to formic acid was applied to the column. The column was soaked for 10 min, and slow eluation was conducted (5 drops/min). The bottle green eluate was collected. The soaking and elution process was repeated with another 10 mL quantity of formate/formic acid buffer solution. The amount of $[Mo_3S_4]^{4+}$ present on the column after this treatment was small and was discarded. To the approximately 20 mL of eluate was added 40 mL of 96% ethanol, and quickly thereafter the solution was filtered on a Büchner filter. The clear dark green solution was set aside at 5 °C, and after 1 day crystals were usually observed. After 2 days the crystals were collected by filtration on a G3 glass frit, washed with 50 mL of absolute ethanol, and dried in the air. Yield: 0.30 g (61%) of small, needle-shaped, dark yellowish green crystals. Anal. Calcd for $K_4Mo_3S_4(HCO_2)_8(H_2O)_3$: K, 15.85; Mo, 29.17; C, 9.74; H, 1.43. Found: K, 15.95; Mo, 28.1; C, 9.60; H, 1.18. IR (cm^{-1}, KBr): 3450 (m, b), 2944 (w), 2858 (m), 1596 (vs), 1537 (m), 1391 (m), 1369 (m), 1341 (m, sp), 1275 (s), 793 (s, sp), 774 (m, sp), 492 (m, sp), 457 (m).

$[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 3H_2O$. The preparative procedure was similar to that adopted for $K_4Mo_3S_4(HCO_2)_8(H_2O)_3$ apart from the use of $[W_3S_4(H_2O)_9]^{4+}$ instead of $[Mo_3S_4(H_2O)_9]^{4+}$. The eluate from the column was green. Yield: 0.35 g (49%) usually as a green powder, occasionally as small dark bluish green crystals. Anal. Calcd for $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 3H_2O$: C, 8.47; H, 1.14. Found: C, 8.43; H, 1.33. IR (cm^{-1}, KBr): 3480 (s, b, double), 2845 (m), 1617 (vs), 1399 (m, sp), 1389 (m, sp), 1303 (s), 801 (s, sp), 796 (s, sp), 762 (m), 550 (m, b), 471 (m, sp).

Magnetic Measurements. The magnetic susceptibility of powdered samples was determined by means of a Sherwood Scientific magnetic susceptibility balance.

X-ray Crystallography. Crystal Preparation. The crystal used to determine the structure of the ammonium $[Mo_3O_4]^{4+}$ formate compound was produced by the synthetic procedure described above. However, since KOH rather than NH_3 had been used to precipitate the $[Mo_3O_4]^{4+}$ hydroxide, some potassium ions had isomorphously replaced ammonium ions in the product. X-ray powder diffraction showed that the obtained $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$ and the pure ammonium compound were isomorphous. The latter is thus formulated as $[NH_4]_4[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$. Crystals of $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$ were produced by replacing ethanol with methanol as precipitating agent in the normal synthetic procedure for the potassium $[W_3S_4]^{4+}$ formate compound. Macrocrystalline potassium $[Mo_3S_4]^{4+}$ formate compound could be obtained in the same way. However, the growing habit prohibited determination of its single-crystal structure.

Structure Solution. Data were collected for $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$ and $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$ using a Huber four-circle diffractometer. Crystal data and experimental parameters are listed in Table 1.

Table 1. Crystallographic Data for $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$ (**1**) and $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$ (**2**)

	1	**2**
formula	$C_9H_{26.8}N_{3.20}O_{24}K_{0.80}Mo_3$	$C_{10.73}H_{17.46}O_{23}S_4K_6W_3$
fw, g/mol	883.06	1428.92
space group	$P\bar{1}$ (No. 2)	$C2/m$ (No. 12)
a, Å	11.0111(2)	19.605(6)
b, Å	13.310(2)	14.458(7)
c, Å	9.993(1)	13.627(5)
α, deg	106.817(7)	90
β, deg	91.651(9)	118.94(2)
γ, deg	88.340(9)	90
V, Å^3	1401.0(3)	3381(2)
Z	2	4
T, °C	21	21
radiation	Mo Kα	Ag Kα
ρ_{calcd}, g/cm^3	2.088	2.807
μ, cm^{-1}	15.03	61.21
R $(R_w)^a$	0.026 (0.034)	0.046 (0.055)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ where $w = 1/\sigma^2(|F_o|)$.

Data for a crystal of $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$ (coated with epoxy resin) were collected using graphite-monochromated Mo Kα radiation; 5370 reflections were corrected for Lorentz and polarization effects and for absorption (transmission 0.740−0.941) which on averaging (R_{int} = 0.021) gave 4926 reflections of which 3972 had $I > 3\sigma(I)$ and which were used in subsequent calculations. The structures were solved using SIR92[27] and refined, on F, by the method of least-squares using a modification of ORFLS.[28] At an early stage in the refinement of $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$ it became clear that two of the sites (K1 and K2) initially believed to be occupied by ammonium ions were in fact partially substituted by potassium ions. In the refinement these two ammonium ions (K1′ and K2′) were assumed to be free rotors and the sum of the occupation factors for each site was constrained to be unity. X-ray fluorescence confirmed the presence of potassium in the bulk sample. All non-hydrogen atoms were refined anisotropically; hydrogen atoms other than those of the free rotors were located on a difference electron density map and were refined with isotropic displacement parameters. Absorption corrections were repeated during the refinement to fit with the potassium-containing formulation. The final chemical formula was found to be $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$.

Data for $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$ were collected using graphite-monochromated Ag Kα radiation; 4989 reflections were corrected for Lorentz and polarization effects and for absorption (transmission 0.326−0.513) which on averaging (R_{int} = 0.046) gave 4664 reflections of which 2656 had $I > 3\sigma(I)$ and which were used in subsequent calculations. The structure of $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$ was solved and refined in the centrosymmetric space group $C2/m$, with a potassium ion disordered over two sites (K4 and K5); maxima in a difference density map were modeled by disordered solvent molecules H_2O/CH_3OH. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were kept fixed in calculated positions with C−H = 0.95 Å and with isotropic displacement factors 20% larger than U_{eq} of the atom to which they are attached. The chemical formula for the crystal studied was found to be $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$.

Atomic scattering factors and anomalous dispersion corrections were taken from ref 29.

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Results and Discussion

The $[Mo_3O_4]^{4+}$ cluster is prepared in hot strong acid ($[H^+] = 1-2$ M) by conproportionation of a low ($<+4$) and a high ($>+4$) oxidation state molybdenum compound.[1,2,30-32] The $[Mo_3O_4]^{4+}$ formate compounds were obtained by the following procedure, which does not involve the use of noncomplexing acids: The 2 M HCl solution in which the conproportionation had taken place was diluted to 0.2 M HCl and left overnight in order to aquate chloro complexes of $[Mo_3O_4]^{4+}$. Combined with the subsequent precipitation and wash of the $[Mo_3O_4]^{4+}$ hydroxide,[1,2] this was sufficient to obtain a chloride-free final product. Nonoptimized synthetic procedures led to the presence of KCl in the final product. Addition of excess KOH should be avoided as $[Mo_3O_4]^{4+}$ hydroxide dissolves in strong base.[2]

In the syntheses of the $[M_3S_4]^{4+}$ formate compounds care also has to be taken in order to avoid chloride impurities in the final products; hence the $[M_3S_4]^{4+}$ solutions were subjected to ion exchange chromatography after having been allowed to fully aquate in 2 M Hpts for 1 day. Precipitation of $[M_3S_4]^{4+}$ hydroxides is not an option, as substantial decomposition of the $[M_3S_4]^{4+}$ clusters was observed to take place in basic solution.

The present preparative procedures for $[M_3E_4]^{4+}$ formato complexes utilize the fact (e.g., ref 18) that addition of ethanol to 5 M ammonium, potassium, or cesium formate solutions does not precipitate the (pseudo) alkali formates even when 2 volumes of ethanol are added. Potassium and ammonium salts of the $[M_3E_4]^{4+}$ formato complexes could therefore be selectively grown from a medium containing a high concentration of free ligand. The potassium salts of the $[M_3S_4]^{4+}$ clusters could be prepared in good yields, but because of their higher solubilities, the corresponding ammonium salts could only be prepared in very low yields and as amorphous powders. Cesium salts of $[Mo_3S_4(HCO_2)_x]^{(x-4)-}$ and $[W_3S_4(HCO_2)_y]^{(y-4)-}$ were precipitated from a cesium formate/formic acid buffer (5 M $CsHCO_2$/10 M HCO_2H) by the addition of methanol. A cesium molybdenum compound precipitated as needle-shaped crystals, and a cesium tungsten material precipitated as a mixture of needle-shaped and cubic crystals, which did not have identical X-ray powder diffractograms. These well-crystallizing compounds were not further investigated. Preparation of $[W_3O_4]^{4+}$ formate compounds were generally difficult. The potassium salt was obtained as a glassy, amorphous material; chemical analysis results were not inconsistent with it being completely analogous to $[K]_4[Mo_3O_4(HCO_2)_8]\cdot 3H_2O$.

Whereas the oxo clusters only displayed minor changes in color upon exchange of aqua ligands with formato ligands, the sulfido clusters displayed more pronounced shifts in color: bottle green to yellow-green for $[Mo_3S_4]^{4+}$ and purple to dark green for $[W_3S_4]^{4+}$. When the formate compounds were dissolved in 2 M Hpts or CF_3SO_3H, rapid protonation of the formato ligands resulted in the immediate formation of the respective aqua ions $[M_3E_4(H_2O)_9]^{4+}$ (M = Mo, W; E = O, S). This demonstrates the presence of the trinuclear clusters also in the less well-characterized formate compounds. If the presence of formic acid is undesirable in the aqua complex solutions, it may be avoided by treating the solid formate compounds (e.g., $[K]_4[Mo_3O_4(HCO_2)_8]\cdot 3H_2O$) with concentrated CF_3SO_3H or H_2SO_4 and letting the carbon monoxide escape before dilution in water.

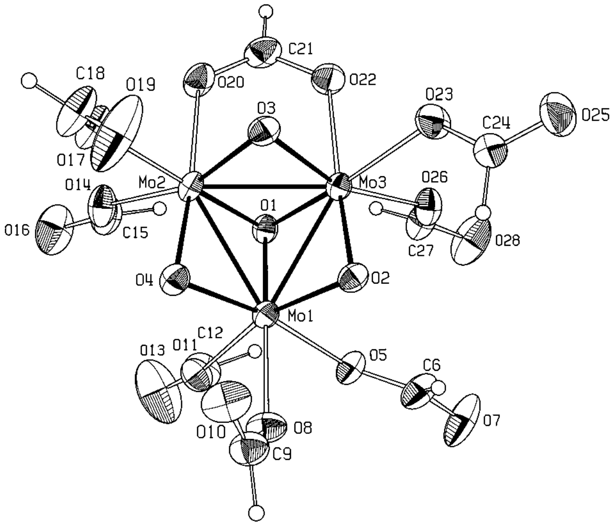

Figure 1. ORTEP[33] representation at the 50% probability level of the $[Mo_3O_4(HCO_2)_8]^{4-}$ cluster formato complex in $[NH_4]_{3.20}[K]_{0.80}[H_3O]$-$[Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$.

Table 2. Selected Bond Lenghts (Å) and Angles (deg) for the $[Mo_3O_4(HCO_2)_8]^{4-}$ Cluster Formato Complex in $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$

Mo1−Mo2	2.506(1)	Mo1−Mo3	2.489(1)
Mo2−Mo3	2.488(1)	Mo1−O1	2.032(3)
Mo1−O2	1.939(2)	Mo1−O4	1.936(3)
Mo1−O5	2.105(3)	Mo1−O8	2.117(3)
Mo1−O11	2.067(3)	Mo2−O1	2.030(2)
Mo2−O3	1.918(3)	Mo2−O4	1.898(3)
Mo2−O14	2.068(3)	Mo2−O17	2.118(3)
Mo2−O20	2.193(3)	Mo3−O1	2.020(3)
Mo3−O2	1.910(3)	Mo3−O3	1.933(3)
Mo3−O22	2.199(3)	Mo3−O23	2.118(3)
Mo3−O26	2.054(3)		

Mo2−Mo1−Mo3	59.76(2)	Mo1−Mo2−Mo3	59.78(1)
Mo1−Mo3−Mo2	60.46(1)	O1−Mo1−O2	100.4(1)
O1−Mo1−O4	99.2(1)	O2−Mo1−O4	97.3(1)
O1−Mo2−O3	101.4(1)	O1−Mo2−O4	100.5(1)
O3−Mo2−O4	96.1(1)	O1−Mo3−O2	101.8(1)
O1−Mo3−O3	101.2(1)	O2−Mo3−O3	93.7(1)
Mo1−O1−Mo2	76.18(9)	Mo1−O1−Mo3	75.79(8)
Mo2−O1−Mo3	75.80(8)	Mo1−O2−Mo3	80.56(9)
Mo1−O4−Mo2	81.6(1)	Mo2−O3−Mo3	80.5(1)

Clear solutions could not be obtained by dissolving the formate compounds in neutral water: The initially formed clear solutions became cloudy in the course of minutes, presumably due to formation of basic formate compounds.

Crystals of $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$ consisted of trinuclear $[Mo_3O_4(HCO_2)_8]$,$^{4-}$ a noncoordinated formate ion, ammonium, potassium, and hydroxonium cations and a water of crystallization. Principal bond lengths and angles for the complex anion (Figure 1)[33] are given in Table 2. The Mo_3O_4 cluster core is similar to that in $[Mo_3O_4(H_2O)_9]^{4+}$,[12] i.e., an incomplete cube with mean dimensions Mo−Mo = 2.494(6) Å, Mo−(μ_3-O) = 2.027(4) Å, and Mo−(μ_2-O) = 1.922(7) Å (the standard deviations of average values are sample standard deviations of the mean). The cube is deformed along the diagonal so that the mean Mo−(μ_3-O)−Mo angle is 75.9(1)°. Seven monodentate formato ligands and one bridging bidentate formato ligand are coordinated to the

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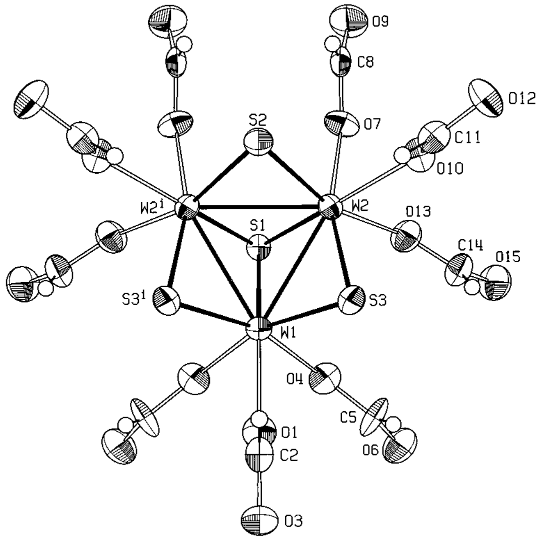

Figure 2. ORTEP[33] representation at the 50% probability level of the $[W_3S_4(HCO_2)_9]^{5-}$ cluster formato complex in $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$.

cluster, the Mo−O−CH═O moieties are close to planar, five are trans (Mo−O parrallel to C═O), and two are cis. Oxygen-17 NMR measurements on $[Mo_3O_4(H_2O)_9]^{4+}$ [12] showed four types of Mo−O bonds (a) Mo−(μ_3-O), (b) Mo−(μ_2-O), (c) bond trans to a, (d) bond trans to b; we were able to distinguish four different Mo−O distances that were not of the Mo−O(μ_2-formate) type: (a) 2.027(4) Å, (b) 1.922(1) Å, (c) 2.118(2) Å, and (d) 2.074(11) Å, i.e., b < a < d < c the reverse order of that found[12] for the ^{17}O chemical shifts in $[Mo_3O_4(H_2O)_9]^{4+}$. The Mo−O(μ_2-formate) distance is 2.196(2) Å.

Crystals of $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$ consisted of trinuclear $[W_3S_4(HCO_2)_9]^{5-}$, a noncoordinated formate ion, potassium ions, and water and methanol of crystallization. The complex cluster anion (Figure 2) is on a crystallographic mirror plane and forms an incomplete cube with dimensions W−W = 2.749(1) Å, W−(μ_3-S) = 2.348(2) Å and W−(μ_2-S) = 2.313(2) Å (cf. Table 3). The cube is slightly more deformed than Mo_3O_4 having a mean W−(μ_3-S)−W angle of 71.6(1)°. In contrast to $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$, nine monodentate formato ligands are coordinated to the cluster core, all of which bond in the trans configuration. The mean W−O 2.138(5) Å, bonds of types c and d did not differ significantly.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the $[W_3S_4(HCO_2)_9]^{5-}$ Cluster Formato Complex in $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$

W1−W2	2.744(1)	W2−W2^{i}	2.754(2)
W1−S1	2.349(5)	W1−S3	2.311(4)
W2−S1	2.351(4)	W2−S2	2.321(4)
W2−S3	2.305(4)	W1−O1	2.146(15)
W1−O4	2.124(10)	W2−O7	2.141(9)
W2−O10	2.147(10)	W2−O13	2.130(10)
W2−W1−W2^{i}	60.25(4)	W1−W2−W2^{i}	59.87(2)
S1−W1−S3	106.3(1)	S3−W1−S3^{i}	96.8(2)
S1−W2−S2	106.3(1)	S1−W2−S3	106.4(1)
S2−W2−S3	96.5(2)	W1−S1−W2	71.4(1)
W2−S1−W2^{i}	71.7(1)	W2−S2−W2^{i}	72.8(2)
W1−S3−W2	72.9(1)		

[a] (i) Symmetry code: *x*, −*y*, *z*.

The $[M_3E_4]^{4+}$ clusters have a coordination number of 9. It is not obvious why $[W_3S_4]^{4+}$ prefers to crystallize with nine monodentate formato ligands while $[Mo_3E_4]^{4+}$ (E = O, S) crystallize with only eight formato ligands. In $[NH_4]_4[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$ all nine cluster coordination sites are occupied by formato ligands as one of the eight is bridging. Exactly the same arrangement was found by an X-ray single-crystal structure determination of the (nonisomorphous) compound $[K]_4[Mo_3O_4(HCO_2)_8]\cdot H_2O$.[26]

The formate salts are easily prepared in high yields and constitute a new, well-defined, class of stable $[M_3E_4]^{4+}$ compounds. They have potential as starting materials as the formato ligands are weakly bonded and thus easily substituted. Once substituted, the formate ions are generally not likely to interfere with the chemistry of a synthesis; the bimetallic cluster $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ was, for example, synthesized[20] in a solution obtained by dissolving $K_4Mo_3S_4(HCO_2)_8(H_2O)_3$ in aqueous CF_3SO_3H.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $[NH_4]_{3.20}[K]_{0.80}[H_3O][Mo_3O_4(HCO_2)_8][HCO_2]\cdot H_2O$ and $[K]_6[W_3S_4(HCO_2)_9][HCO_2]\cdot 2.27H_2O\cdot 0.73CH_3OH$. This material is available free of charge via the Internet at http://pubs.acs.org.

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