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# New Heterometallic Cubane-Like Clusters $[\{(\eta^5\text{-Cp})Mo\}_3S_4\{M'(CO)_3\}](pts)$ ($M' = Cr, Mo, W$; pts = *p*-Toluenesulfonate) Obtained by Ligand Substitution Reactions and Insertion of $\{M'(CO)_3\}$ Fragments

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A series of group 6 heterometallic sulfide clusters have been prepared to establish a route to potential models of hydrodesulfurization catalysts suitable for application in nonaqueous media. The cluster compound $[\{(H_2O)_3Mo\}_3S_4](pts)_4{\cdot}9H_2O$ (pts = *p*-toluenesulfonate) was treated with triethyl orthoformate in the presence of a catalytic amount of Hpts to yield an ethanol complex of the $[Mo_3S_4]^{4+}$ cluster core. The complex was subsequently converted in situ to acetonitrile and tetrahydrofuran complexes before treatment with thallium cyclopentadienide to yield the new cluster compound $[\{(\eta^5\text{-Cp})Mo\}_3S_4](pts)$ (**1**). Insertion of $\{M'(CO)_3\}$ fragments into **1** afforded the series of cubane-like, heterometallic clusters $[\{(\eta^5\text{-Cp})Mo\}_3S_4\{M'(CO)_3\}](pts)$ ($M'$ = Cr (**2a**), Mo (**2b**), W (**2c**)). Single-crystal X-ray analysis established the heterometallic $S_4$-capped tetrahedral cluster core in the structure of **2c**$\cdot{}^1/_2CH_3OH$.

## Introduction

Hydrodesulfurization (HDS) is an important refinery process for removing sulfur from crude oil fractions.[1] At elevated temperatures and in the presence of hydrogen at high pressure, the oil is placed into contact with a heterogeneous catalyst, whereby organosulfur compounds in the oil (e.g. thiols, sulfides, disulfides, thiophenes, benzo- and dibenzothiophenes) are converted into hydrocarbons and $H_2S$. The industrially used catalysts consist of $MoS_2$ crystallites that are promoted by Co or Ni and supported on a high-suface-area carrier such as, for example, alumina. Careful studies of the catalyst in its active state have shown that the promoter atoms are bonded to the sulfide atoms that constitute the $MoS_2$ crystallite edges.[1b,2,3]

On the basis of the expectation that molecular metal sulfide clusters may provide insight into the mechanism for catalytic HDS, such clusters have attracted considerable attention recently.[4] In this context, heterometallic CoMo and NiMo clusters are particularly relevant, and Curtis and co-workers have found that $[\{(\eta^5\text{-Cp}')Mo\}_2S_3\{Co(CO)_2\}_2]$ ($Cp' = CH_3Cp$) reacts with thiophene to yield a mixture of desulfurized hydrocarbons and $[\{(\eta^5\text{-Cp}')Mo\}_2S_4\{Co(CO)\}_2]$.[5] Reaction of acidic, aqueous solutions of $[\{(H_2O)_3Mo\}_3S_4]^{4+}$ with either metal powder alone or metal ions combined with a reducing agent have provided an extensive series of compounds $[\{\{(H_2O)_3Mo\}_3S_4\}_nM'_mL_p]^{q+}$ ($M'$ = Cr, Mo, Fe, Co, Ni, Pd, Cu, Hg, Ga, In, Tl, Sn, Pb, As, Sb, Bi; e.g. L = $H_2O$)[6]

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all containing the cubane-like $Mo_3S_4M'$ motif. These synthetic procedures are generally limited to application in *aqueous* solution, and the aim of this work is to establish the chemistry necessary to extend the study of such species into *nonaqueous* media.

We report herein that insertion reactions analogous to those established in the preparation of heterometallic cubane-like sulfide clusters in aqueous solution[6] can be made in organic media using the new compound $[\{(\eta^5\text{-Cp})Mo\}_3S_4](pts)$ (**1**; pts = *p*-toluenesulfonate) as a source of the $[Mo_3S_4]^{4+}$ cluster core. The cation of **1** has previously been isolated in 50% yield in $[\{(\eta^5\text{-Cp})Mo\}_3S_4][Sn(CH_3)_3Cl_2]$.[7] However, the synthesis from $[(\eta^5\text{-Cp})Mo(CO)_3Cl]$ and $[Sn(CH_3)_2]_2S$ is less well-established and the resulting complex counterion is likely to interfere in the development of further chemistry for these systems.

## Experimental Section

**General Considerations.** All experiments were carried out under dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled before use (dichloromethane, acetonitrile, and chloroform-*d* from $P_2O_5$; methanol from magnesium; *n*-hexane, tetrahydrofuran (THF), and diethyl ether from sodium/benzophenone) and stored under nitrogen; triethyl orthoformate (Aldrich) was degassed and stored under nitrogen. $[\{(H_2O)_3Mo\}_3S_4](pts)_4\cdot 9H_2O$[8] and $[(CH_3CN)_3M'(CO)_3]$ ($M'$ = Cr, Mo, W)[9] were isolated by the methods described in the literature. Thallium cyclopentadienide (Aldrich) was sublimed prior to use and stored under nitrogen. Silica gel (70−230 mesh, 60 Å; Aldrich) was dried in vacuo at 180 °C for 14 h, deactivated with 5% distilled and degassed water, and stored under nitrogen. Products were purified by low-pressure liquid column chromatography under nitrogen; solvents for chromatography (dichloromethane and methanol: SPS quality, purchased from Romil) were degassed before use and stored under nitrogen. Elemental analysis were performed at DB-Lab, Dansk Bioprotein A/S, Odense, Denmark.

**Spectra.** Infrared spectra were recorded on a Bio-Rad FTS-60 spectrometer as solids in KBr disks. $^1H$ NMR spectra were recorded at room temperature on a Varian UNITY 300 MHz spectrometer and were referenced to the chemical shift of the nondeuterated part in the deuterated solvents relative to TMS. Mass spectra were obtained on a JEOL SX-102 spectrometer.

**Synthesis of $[\{(\eta^5\text{-Cp})Mo\}_3S_4](pts)$ (1).** A 423 mg (0.297 mmol) amount of $[\{(H_2O)_3Mo\}_3S_4](pts)_4\cdot 9H_2O$[8] was dissolved at room temperature (RT) in 12 mL of $(C_2H_5O)_3CH$, and in the presence of a catalytic amount (a few crystals) of Hpts the mixture was stirred. After 15 h a green solid had precipitated, the supernatant solution was removed, and the suspended solid was washed twice with 15 mL of diethyl ether and dried in vacuo. The solid was dissolved in $CH_3CN$ (10 mL) with stirring to give a green solution to which, after 15 min of stirring and vacuum evaporation of solvent, THF (25 mL) was added; this mixture was stirred for 10 min. The greenish brown solution obtained was added to 286 mg (1.061 mmol) of TlCp, and the color changed spontaneously to intense dark green. The mixture was stirred for 15 h, forming a brown suspension. All solvent was removed by evaporation, 100 mL of $CH_2Cl_2$ was added, and the mixture was stirred for 1 h, yielding a brownish green suspension. Filtration (P4) gave a green solution, which was evaporated to dryness, forming **1** as a brownish green solid. Yield: 196.4 mg (85%). Recrystallization from a saturated $CH_2Cl_2$ solution at −20 °C gave small black crystals. IR (KBr, $\nu$ in $cm^{-1}$): 3086 (m, $CH_{arom}$), 1425 (w, $CH_{arom}$). $^1H$ NMR ($CDCl_3$, $\delta$ in ppm): 7.79 (d, 2H, $CH_{arom}$, $^3J(H,H) = 8.1$ Hz), 7.11 (d, 2H, $CH_{arom}$, $^3J(H,H) = 8.1$ Hz), 6.22 (15 H, Cp), 2.31 (s, 3H, $CH_3$). $FAB^+$ mass spectrum (*m*/*z* (% abundance)): 609 ($M^+ - pts$, 14), 547 ($M^+ - pts - Cp$, 6). Anal. Calcd for $C_{22}H_{22}Mo_3O_3S_5\cdot CH_2Cl_2$: C, 31.84; H, 2.79; S, 18.48. Found: C, 32.19; H, 2.93; S, 18.65.

**Synthesis of $[\{(\eta^5\text{-Cp})Mo\}_3S_4\{Cr(CO)_3\}](pts)$ (2a).** A 338.2 mg (0.432 mmol) amount of $[\{(\eta^5\text{-Cp})Mo\}_3S_4](pts)$ (**1**) dissolved in 45 mL of $CH_2Cl_2$ was added to freshly isolated $[(CH_3CN)_3Cr(CO)_3]$ (prepared from 938.9 mg (4.267 mmol) of freshly sublimed $[Cr(CO)_6]$ by refluxing in 30 mL of MeCN for 16 h and evaporating to dryness[9]). The dark brownish green solution was stirred at RT for 3 h. The dark solution obtained was filtered (P3), and from the dark brownish green filtrate the solvent was completely evaporated; 40 mL of *n*-hexane was added to the dark residue, this mixture was stirred for 10 min, and the supernatant light green solution was removed; the procedure was repeated using 20 mL of *n*-hexane. The residue was dried in vacuo, giving **2a** as a brownish green solid. Yield: 277.0 mg (64%). IR (KBr, $\nu$ in $cm^{-1}$): 2012 (vs, C═O), 1984 (vs, C═O), 1960 (sh, C═O). $^1H$ NMR ($CDCl_3$, $\delta$ in ppm): 7.82 (d, 2H, $CH_{arom}$, $^3J(H,H) = 7.7$ Hz), 7.11 (d, 2H, $CH_{arom}$, $^3J(H,H) = 7.7$ Hz), 5.84 (s, 15 H, Cp), 2.31 (s, 3H, $CH_3$). $FAB^+$ mass spectrum (*m*/*z* (% abundance)): 661 ($M^+ - pts - 3CO$, 30). Anal. Calcd for $C_{25}H_{22}CrMo_3O_6S_5\cdot 2CH_2Cl_2$: C, 29.80; H, 2.41; S, 14.73. Found: C, 29.39; H, 2.98; S, 15.50.

**Synthesis of $[\{(\eta^5\text{-Cp})Mo\}_3S_4\{Mo(CO)_3\}](pts)$ (2b).** To a mixture of 228.4 mg (0.292 mmol) of $[\{(\eta^5\text{-Cp})Mo\}_3S_4](pts)$ (**1**) and 98.9 mg (0.326 mmol) of $[(CH_3CN)_3Mo(CO)_3]$[9] was added 20 mL of $CH_2Cl_2$, and the mixture was stirred for 15 h at RT. The solution was adsorbed on $SiO_2$ (5% $H_2O$) and separated by column chromatography (column 2.5 × 23 cm). With a mixture of $CH_2Cl_2$ and $CH_3OH$ (10:1) a purple fraction was obtained, which after evaporation to dryness gave **2b** as a dark solid. Yield: 120.8 mg (43%). Recrystallization at −20 °C from a saturated $CH_3OH$ solution gave dark needles. IR (KBr, $\nu$ in $cm^{-1}$): 2019 (vs, C═O), 1989 (s, C═O), 1972 (vs, C═O). $^1H$ NMR ($CDCl_3$, $\delta$ in ppm): 7.84 (d, 2H, $CH_{arom}$, $^3J(H,H) = 8.4$ Hz), 7.12 (d, 2H, $CH_{arom}$, $^3J(H,H) = 8.4$ Hz), 5.84 (s, 15 H, Cp), 2.31 (s, 3H, $CH_3$). $FAB^+$ mass spectrum (*m*/*z* (% abundance)): 790 ($M^+ - pts$, 14), 708 ($M^+ - pts - 3CO$, 50). Anal. Calcd for $C_{25}H_{22}Mo_4O_6S_5$: C, 31.20; H, 2.30; S, 16.66. Found: C, 31.55; H, 2.43; S, 16.75.

**Synthesis of $[\{(\eta^5\text{-Cp})Mo\}_3S_4\{W(CO)_3\}](pts)$ (2c).** Compound **2c** was prepared in the same manner as for **2b**: 579.6 mg (1.482 mmol) of $[(CH_3CN)_3W(CO)_3]$[9] and 201.8 mg (0.258 mmol) of **1** in 20 mL of $CH_2Cl_2$, 18 h at RT. Yield: 138.1 mg (56%). IR (KBr, $\nu$ in $cm^{-1}$): 2013 (vs, C═O), 1981 (s, C═O), 1960 (vs, C═O). $^1H$ NMR ($CDCl_3$, $\delta$ in ppm): 7.84 (d, 2H, $CH_{arom}$, $^3J(H,H) = 8.1$ Hz), 7.11 (d, 2H, $CH_{arom}$, $^3J(H,H) = 8.1$ Hz), 5.83 (s, 15 H, Cp), 2.31 (s, 3H, $CH_3$). $FAB^+$ mass spectrum (*m*/*z* (% abundance)): 878 ($M^+ - pts$, 6%), 796 ($M^+ - pts - 3CO$, 20%). Anal. Calcd for $C_{25}H_{22}Mo_3O_6S_5W\cdot CH_3OH$: C, 28.85; H, 2.42; S, 14.81. Found: C, 29.36; H, 2.49; S, 14.81.

**X-ray Crystallography.** Single crystals of $[\{(\eta^5\text{-Cp})Mo\}_3S_4\{W(CO)_3\}](pts)\cdot{}^1/_2CH_3OH$ ($\mathbf{2c}\cdot{}^1/_2CH_3OH$) were grown from a saturated methanol solution at −20 °C, and a selected specimen was mounted in a Lindemann tube under $N_2$. X-ray data were collected using a Stoe IPDS diffractometer ($\varphi$, 0−180°; sample-to-plate distance, 70 mm; 2 min exposure per 1.5° increment) with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods and refined[10] to convergence with all non-H atoms anisotropic (except the

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**Table 1. Crystal Data for $[\{(\eta^5\text{-Cp})Mo\}_3S_4\{W(CO)_3\}](pts)\cdot{}^1/_2CH_3OH$ ($2c\cdot{}^1/_2CH_3OH$)**

| | |
|---|---|
| empirical formula | $C_{25.5}H_{24}Mo_3O_{6.5}S_5W$ |
| fw | 1066.42 |
| source | $CH_3OH$, −20 °C |
| *a*, *b*, *c* (Å) | 9.6470(19), 10.900(2), 16.267(3) |
| α, *β*, *γ* (deg) | 107.96(3), 90.27(3), 99.53(3) |
| $V$ (Å$^3$) | 1601.9(6) |
| *Z*, calcd density (Mg/m$^3$) | 2, 2.211 |
| abs coeff (mm$^{-1}$) | 5.091 |
| *F*(000) | 1018 |
| *λ* (Å) | 0.71073 |
| temp (K) | 293(2) |
| radiation | Mo Kα |
| cryst syst, space group | triclinic, $P\bar{1}$ |
| cryst size (mm) | 0.39 × 0.31 × 0.08 |
| *θ* range for data collecn (deg) | 6.01−25.00 |
| limiting indices | $-10 \le h \le 10, -12 \le k \le 12, -19 \le l \le 19$ |
| no. of rflns collected/unique | 10084/5210 ($R_{int} = 0.0402$) |
| abs cor | empirical |
| max and min transmissn | 0.7671 and 0.3463 |
| refinement method | full-matrix least squares on $F^2$ |
| no. of data/restraints/params | 5210/55/374 |
| goodness-of-fit on $F^2$ | 0.998 |
| final *R* indices ($I > 2\sigma(I)$) | $R1(F)^a = 0.0506$, $wR2(F^2)^b = 0.1816$ |
| *R* indices (all data) | $R1(F)^a = 0.0570$, $wR2(F^2)^b = 0.1871$ |
| largest diff peak and hole (e/Å$^3$) | 2.414 (1.23 Å from W) and −1.463 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

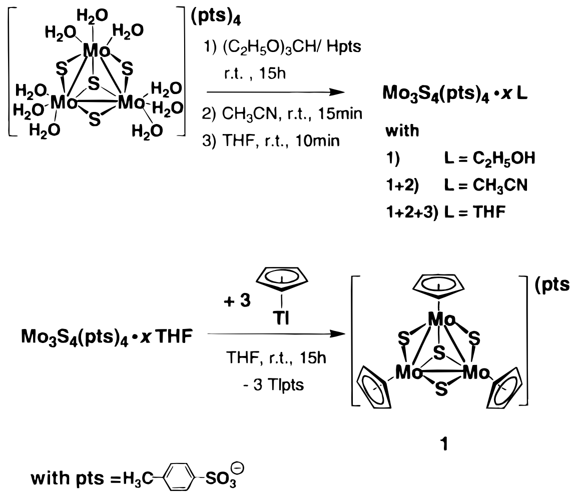
carbons of the two components of a disordered Cp ring) and H atoms in idealized positions with $U_{iso}(H^{methyl}) = 1.5U_{eq}(C)$ and $U_{iso}(H^{aromatic}) = 1.2U_{eq}(C)$. Crystallographic data are summarized in Table 1.

## Results and Discussion

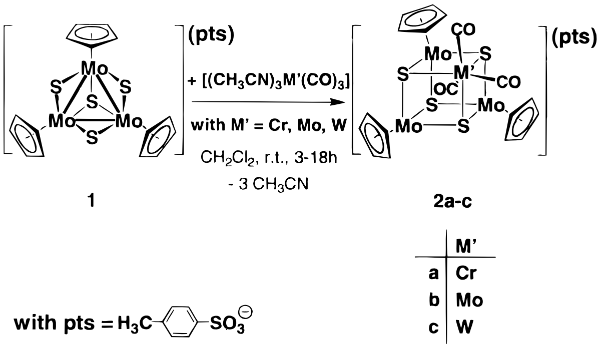
The crystalline aqua cluster $[\{(H_2O)_3Mo\}_3S_4](pts)_4\cdot 9H_2O$[8] was dissolved in triethyl orthoformate, forming an ethanol-substituted,[11] highly moisture-sensitive cluster salt. The compound thus obtained was reacted in situ with acetonitrile and, after the solvent was removed, with tetrahydrofuran (THF), giving a brownish green solution (Scheme 1). Treatment with acetonitrile before the THF complex was formed assured that traces of the triethyl orthoformate were removed and improved the final yield.

Reactions of the THF solution with sodium cyclopentadienide as the source of a carbocyclic ligand led to mixtures, probably because of the reducing ability[12] of NaCp. $^1H$ NMR spectra of the crude product indicated that the desired product *was* present in the mixture, but purification by chromatography and fractionated crystallization failed.

**Scheme 1**



**Scheme 2**



A much cleaner reaction with less reduction was performed with thallium cyclopentadienide.[13] The reaction of the brownish green THF solution with a slight stoichiometric excess of TlCp led to a spontaneous change of color to dark green. After a few minutes a brown suspension was formed, from which the new cluster salt $[\{(\eta^5\text{-Cp})Mo\}_3S_4](pts)$ (**1**) was isolated as a brownish green solid in 85% yield (Scheme 1).

The compound **1** was stable under a nitrogen atmosphere for at least several months and in the air for at least 1 day. It was soluble in polar organic solvents. Crystals could be obtained at −20 °C from a saturated dichloromethane solution.

The $^1H$ NMR spectrum showed two doublets at 7.79 and 7.11 ppm for the aromatic protons and a singlet at 2.31 ppm for the methyl group of the *p*-toluenesulfonate anion; additionally, a singlet at 6.22 ppm for the protons of the three Cp ligands was observed. This last chemical shift is consistent with the chemical shift of the Cp ligands in $[\{(\eta^5\text{-Cp})Mo\}_3S_4][Sn(CH_3)_3Cl_2]$.[7]

The FAB$^+$ mass spectrum of **1** showed the peak of the cluster cation $[\{(\eta^5\text{-Cp})Mo\}_3S_4]^+$ at *m*/*z* 609 with a relative intensity of 14%.

Tris(acetonitrile)tricarbonyl complexes[9] of Cr, Mo, and W were used to insert[14] $\{M'(CO)_3\}$ fragments into the $[\{(\eta^5\text{-Cp})Mo\}_3S_4]^+$ cluster cation, thereby forming three new cubane-like clusters $[\{(\eta^5\text{-Cp})Mo\}_3S_4\{M'(CO)_3\}](pts)$ (M′ = Cr (**2a**), Mo (**2b**), W (**2c**)), which are all soluble in common polar organic solvents (Scheme 2).

The compound **2a** was purified by washing with *n*-hexane and recrystallizing from dichloromethane. The compounds **2b**,**c** were isolated as dark solids after chromatography on silica gel. Dissolution of **2a** in

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dichloromethane or methanol gave a green solution, whereas **2b**,**c** gave purple solutions. All three compounds were stable in the air for at least a few days.

In the solid state the infrared spectrum of **2a** contained two intense peaks at 2012 and 1984 cm$^{-1}$ as well as a shoulder at 1960 cm$^{-1}$. The spectra of the homologous compounds **2b**,**c** contained similar patterns consisting of three intense and discrete peaks for the three terminal *fac*-CO ligands[15] at 2019, 1989, and 1972 cm$^{-1}$ for **2b** and at 2013, 1981, and 1960 cm$^{-1}$ for **2c**. The relatively high wavenumbers are a reflection of the positive charge of the complex[16] and the predominant $\sigma$ character of the M−C bond.[16,17] This means that the inserted metal atoms M′ are relatively electron-poor.

The $^1$H NMR spectra showed the typical signals: two doublets at lowest field for the aromatic protons of the *p*-toluenesulfonate counterion, an intense singlet for the 15 protons of the three Cp ligands of the cluster cation, and a singlet at higher field for the methyl group of the *p*-toluenesulfonate anion. The chemical shifts were nearly identical for **2a**−**c**; the signals for the Cp ligands of **2a**−**c** were shifted to higher field relative to the peak for the Cp ligands in **1**. This indicates an increase in electron density at the connected molybdenum atoms in **2a**−**c** compared with those of **1**.

Both IR and $^1$H NMR spectroscopic data are in accordance with the results[17] from Fenske−Hall molecular orbital calculations on similar systems, namely $[\{L_xMo\}_3S_4\{M'(CO)\}]^{n+}$ (M′ = Co, Ni). The calculations predict an increase in electron density on the $Mo_3S_4$ fragment when a heterometal atom is inserted and a relatively electron-poor situation at the inserted metal atom.

The FAB$^+$ mass spectra of **2a**−**c** showed the peaks of the cluster cations $[(C_5H_5)_3Mo_3S_4M'(CO)_3]^+$ with relative intensities of 30, 14, and 6%, followed by intense signals from the peaks $[(C_5H_5)_3Mo_3S_4M']^+$ with intensities of 55, 50, and 20% for the Cr, Mo, and W derivative.

**Structural Study.** Single-crystal X-ray analysis of $[\{(\eta^5\text{-Cp})Mo\}_3S_4\{W(CO)_3\}](pts)\cdot{}^1/_2CH_3OH$ ($\mathbf{2c}\cdot{}^1/_2CH_3OH$) established the cubane-like cluster cation derived from three $\{(\eta^5\text{-Cp})Mo\}$ units, one $\{W(CO)_3\}$ fragment, and four sulfur atoms (Figure 1); selected bond lengths and angles are presented in Table 2. This is the first heterometallic $M_3M'$ group 6 cluster to be established unambiguously.[18] Previous examples have shown disorder of metal positions in the cluster core.[19]

The Mo−Mo and W−Mo distances are consistent with single bonds between the four metal atoms forming a tetrahedral framework (Figure 2), whose triangular faces are capped by four $\mu_3$-coordinating sulfur atoms, leading to a cubane-like cluster frame. The Mo−S and W−S bond lengths are within the usual range for single bonds,[19,20] where the average W−S bond with 2.475 Å is ca. 6% longer then the average Mo−S bond with 2.336 Å. The bond angles between the metal atoms (57.75(4)−61.46(4)°) correspond quite closely to a regular tetrahedron, although the smaller S−W−S angles are consistent with the longer W−S and W−Mo bond lengths and with a noticeable extrusion of the tungsten atom from the cluster core. The displacement of the tungsten can be further illustrated by comparing its height above the respective face of the $S_4$ tetrahedron (1.200(3) Å above the S(2),S(3),S(4) plane) with those observed for the Mo atoms (in the range 0.981(3) (for Mo(1) above S(1),S(2),S(3)) to 0.986(3) Å (for Mo(3) above S(1),S(3),S(4))). The extrusion of W cannot be attributed simply to size, and the more efficient acceptor character of its CO substituents in comparison to the Cp ligands attached to Mo[21] may play a role here. Further distortion of the overall cubane-like framework derives from considerably smaller dimensions of the metal tetrahedron with respect to the $S_4$ tetrahedron, and in this context, M−M bonds of ca. 2.9 Å compare with S···S distances of over 3.6 Å. The average S−M−S angles are relatively obtuse (98.46° at W and 103.49° at Mo), while the average M−S−M angles (76.18°) are much smaller than 90°; similar tendencies were observed for related compounds.[6,19,20,22] The distances from the Mo atoms to the centers of their connected Cp rings (between 2.023 and 2.026 Å) are very similar to the distances found in $[\{(\eta^5\text{-Cp})Mo\}_3S_4][Sn(CH_3)_3Cl_2]$.[7]

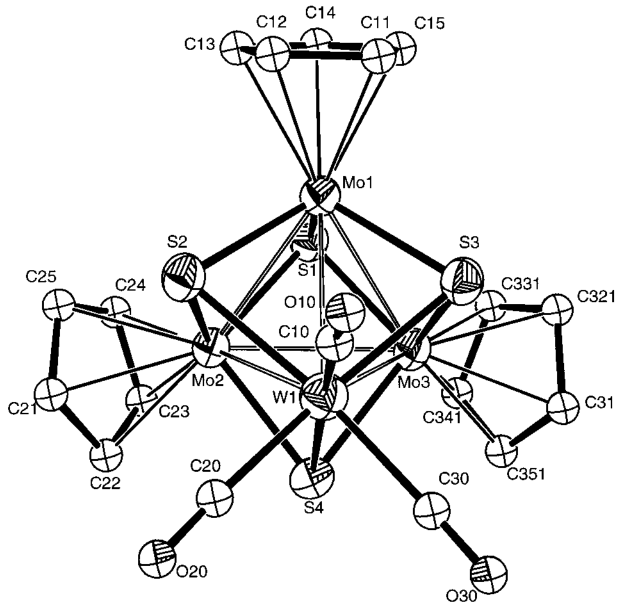

**Figure 1.** ORTEP plot of the $Mo_3W$ cluster cation in the crystal structure of $\mathbf{2c}\cdot{}^1/_2CH_3OH$ showing the numbering scheme adopted.

According to the Wade−Mingos rules for electron counting for polyhedra,[23] the cluster cation of **2c,** as well as its homologues in **2a**,**b**,[18] are all electron-precise tetrahedra.

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**Table 2. Selected Bond Lengths and Angles for $[\{(\eta^5\text{-Cp})\mathrm{Mo}\}_3\mathrm{S}_4\{\mathrm{W(CO)}_3\}](\mathrm{pts})\cdot {}^1/_2\mathrm{CH_3OH}$ ($\mathbf{2c}\cdot{}^1/_2\mathrm{CH_3OH}$)**

| Bond Lengths (Å) | | | | | |
|---|---|---|---|---|---|
| W(1)−Mo(1) | 2.9645(16) | W(1)−S(2) | 2.464(3) | Mo(2)−S(1) | 2.338(3) |
| W(1)−Mo(2) | 2.9753(13) | W(1)−S(3) | 2.478(3) | Mo(2)−S(2) | 2.333(3) |
| W(1)−Mo(3) | 2.9838(16) | W(1)−S(4) | 2.483(3) | Mo(2)−S(4) | 2.331(3) |
| Mo(1)−Mo(2) | 2.8770(17) | Mo(1)−S(1) | 2.337(3) | Mo(3)−S(1) | 2.332(3) |
| Mo(1)−Mo(3) | 2.8724(17) | Mo(1)−S(2) | 2.330(3) | Mo(3)−S(3) | 2.336(3) |
| Mo(2)−Mo(3) | 2.8811(15) | Mo(1)−S(3) | 2.337(3) | Mo(3)−S(4) | 2.346(3) |
| W(1)−C(10) | 2.047(17) | W(1)−C(30) | 2.068(18) | C(20)−O(20) | 1.104(19) |
| W(1)−C(20) | 2.038(16) | C(10)−O(10) | 1.118(19) | C(30)−O(30) | 1.11(2) |

| Bond Angles (deg) | | | | | |
|---|---|---|---|---|---|
| Mo(1)−W(1)−Mo(2) | 57.94(4) | Mo(1)−S(1)−Mo(2) | 75.96(10) | S(2)−Mo(2)−S(1) | 101.74(12) |
| Mo(1)−W(1)−Mo(3) | 57.75(4) | Mo(3)−S(1)−Mo(1) | 75.93(10) | S(4)−Mo(2)−S(1) | 101.89(12) |
| Mo(2)−W(1)−Mo(3) | 57.83(3) | Mo(3)−S(1)−Mo(2) | 76.19(10) | S(4)−Mo(2)−S(2) | 106.70(12) |
| Mo(3)−Mo(1)−Mo(2) | 60.15(4) | Mo(1)−S(2)−Mo(2) | 76.17(10) | S(1)−Mo(3)−S(3) | 102.08(12) |
| Mo(2)−Mo(1)−W(1) | 61.22(4) | Mo(1)−S(2)−W(1) | 76.32(9) | S(1)−Mo(3)−S(4) | 101.63(11) |
| Mo(3)−Mo(1)−W(1) | 61.46(4) | Mo(2)−S(2)−W(1) | 76.60(10) | S(3)−Mo(3)−S(4) | 106.64(12) |
| Mo(1)−Mo(2)−Mo(3) | 59.85(4) | S(2)−W(1)−S(3) | 98.74(11) | Mo(3)−S(3)−Mo(1) | 75.86(10) |
| Mo(1)−Mo(2)−W(1) | 60.84(4) | S(2)−W(1)−S(4) | 98.30(11) | Mo(1)−S(3)−W(1) | 75.93(9) |
| Mo(3)−Mo(2)−W(1) | 61.24(4) | S(3)−W(1)−S(4) | 98.35(11) | Mo(3)−S(3)−W(1) | 76.54(10) |
| Mo(1)−Mo(3)−Mo(2) | 60.01(4) | S(1)−Mo(1)−S(3) | 101.88(12) | Mo(2)−S(4)−Mo(3) | 76.06(10) |
| Mo(1)−Mo(3)−W(1) | 60.79(4) | S(2)−Mo(1)−S(1) | 101.87(12) | Mo(2)−S(4)−W(1) | 76.28(10) |
| Mo(2)−Mo(3)−W(1) | 60.94(4) | S(2)−Mo(1)−S(3) | 106.97(12) | Mo(3)−S(4)−W(1) | 76.27(10) |

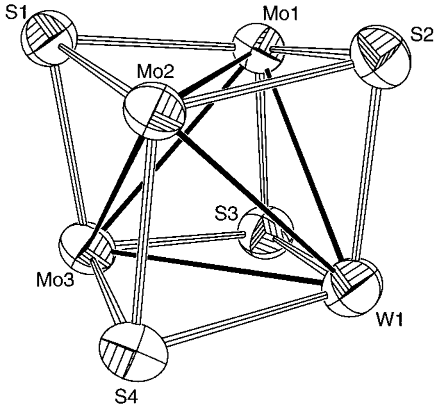

**Figure 2.** The cubane-like sulfide-capped cluster core of the cation of $\mathbf{2c}\cdot{}^1/_2\mathrm{CH_3OH}$.

## Conclusion

A new and convenient procedure for synthesis of a tris-Cp derivative of the $[\mathrm{Mo_3S_4}]^{4+}$ cluster core has been presented. Since no good and acceptable routes exist by which the cluster core $[\mathrm{Mo_3S_4}]^{4+}$ can be synthesized in nonpolar solvents, $[\{(\mathrm{H_2O})_3\mathrm{Mo}\}_3\mathrm{S_4}](\mathrm{pts})_4\cdot 9\mathrm{H_2O}$ was synthezised in aqueous solution by the established method and then, by a series of ligand substitutions, converted into the organically soluble compound $[\{(\eta^5\text{-Cp})\mathrm{Mo}\}_3\mathrm{S_4}](\mathrm{pts})$. From a geometrical point of view the $\mathrm{Mo_3S_4}$ cluster core is incomplete, and the possibility of introducing a heterometal atom to produce cubane-like $\mathrm{M'Mo_3S_4}$ cores is well-established in the aqueous chemistry of $[\mathrm{Mo_3S_4}]^{4+}$. We have now, in nonaqueous media, inserted $\{\mathrm{M'(CO)_3}\}$ (M′ = Cr, Mo, W) fragments into $[\{(\eta^5\text{-Cp})\mathrm{Mo}\}_3\mathrm{S_4}]^+$ and thus been able to produce the new series of heterometallic sulfide clusters $[\{(\eta^5\text{-Cp})\mathrm{Mo}\}_3\mathrm{S_4}\{\mathrm{M'(CO)_3}\}](\mathrm{pts})$ (M′ = Cr, Mo, W). Work is in progress with the aim of inserting other metallic elements, with particular focus on the hydrodesulfurization promoters Ni and Co.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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