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Synthesis and structural characterisation of a mixed Mo/Fe, mixed chalcogen, PhS-bridged cluster

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Abstract

Thermolytic reaction of $Cp_2Mo_2Fe_2STe(CO)_7$ and C_6H_5SH in benzene afforded two isomers of the new compound $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu_2\text{-}SPh)(\mu_3\text{-}H)(CO)_5$ in 23 and 21% yields. They were characterised by IR, ^1H- and ^{125}Te-NMR spectroscopy. The structure of one isomer was established by single crystal X-ray diffraction method. The structure consists of a Mo_2Fe_2 tetrahedron with μ_3-S and μ_3-Te face capping ligands. The Mo–Mo bond is bridged by a SPh group and one $MoFe_2$ face is bridged by a μ-H group. Each Fe atom has two terminal carbonyls and one CO group bridges the Fe–Fe bond. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum; Iron; Sulphur; Tellurium; Thiolato; Hydride; Cluster

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1. Introduction

The chemistry of transition-metal main-group clusters has undergone rapid developments in recent years [1]. The synthetic strategy of incorporating single atom main group element ligands in transition metal clusters, with a view of stabilising the cluster bonding network and hence facilitating cluster growth reactions, is now well established [2]. In general, the dinuclear compounds $Fe_2(CO)_6(\mu\text{-}E)_2$, and the trinuclear compounds $Fe_3(CO)_9(\mu_3\text{-}E)_2$ (E = S, Se, Te; M = Fe, Ru, Os) have been employed extensively for this purpose [3]. Using $Fe_3(CO)_9(\mu_3\text{-}E)_2$ as precursors, we have been able to synthesise, by thermolysis with $Cp_2Mo_2(CO)_6$ for 24 h and subsequent separation by column chromatography, the new class of mixed-metal heterochalcogen atom stabilised carbonyl clusters $Cp_2Mo_2Fe_2(CO)_7(\mu_3\text{-}E)(\mu_3\text{-}E')$ [4]. These compounds have served as convenient second generation starting materials for further cluster growth reactions. Recently we have examined the reactivity of $Cp_2Mo_2Fe_2(\mu_3\text{-}Te)_2(CO)_7$ with PhN_3 and have obtained a dimolybdenum complex with μ-NPh and μ-Te ligands [5]. We have also been able to synthesise some oxo-bridged dimolybdenum complexes with μ_2-S and μ_2-Te ligands, from $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(CO)_7$ [6].

Chemistry of bimetallic sulphido clusters continues to be the focus of considerable research activity due to their probable relevance to the chemistry underlying certain types of biological and industrial catalyses [7]. The FeMoCo cofactor of nitrogenase is one example of the many metal chalcogenide clusters in enzymes and proteins [8]. Sulphided clusters containing Mo and a group 8 metal, e.g. Fe, Co, Ni are also especially interesting as models for hydrodesulphurisation (HDS) catalysts.

Research into the synthesis, structure and properties of transition metal complexes of thiolate containing

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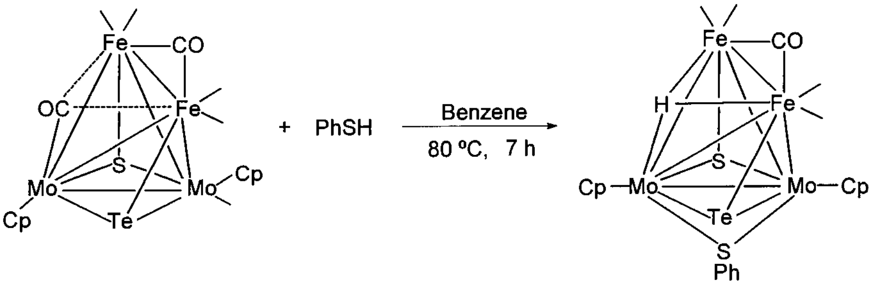

Scheme 1.

ligands is expected to shed light on the structure and mechanism of action of thiolate containing metalloproteins such as Fe–S cluster and Ni–Fe hydrogenase. As an extension of our interest in the reactivity of the mixed-metal mixed-chalcogenide carbonyl clusters towards thiophenol, we report here on the reaction of $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(CO)_7$ with C_6H_5SH, and isolation of the first example of a mixed Fe/Mo mixed-chalcogen complex containing a bridging thiolate group.

2. Results and discussion

When a benzene solution containing $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(CO)_7$ and C_6H_5SH was refluxed for 7 h, and subjected to chromatographic work-up on silicagel TLC plates using 50/50 (v/v) benzene/hexane mixture as eluent, a major red band was isolated. On repeated chromatography of this band using high performance TLC plates, two isomers (dark red **1a**, 34.3 mg, 23% and red **1b**, 31.3 mg, 21%) of a new compound $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu_2\text{-}SP\ h)(\mu_3\text{-}H)(CO)_5$ were separated Scheme 1. The compound $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu_2\text{-}SPh)(\mu_3\text{-}H)(CO)_5$ exists as two isomers because of the *syn* and *anti* orientation of the phenyl ring on the thiolate ligand [11]. The compounds **1a** and **1b** are stable both in solid state and in solution. They were characterised by IR and ^1H- and ^{125}Te-NMR spectroscopy. The IR spectra of both **1a** and **1b** display carbonyl stretching frequencies in the range 1800–2054 cm^{-1} indicating the presence of bridging as well as terminal carbonyls. The ^1H-NMR spectra of **1a** and **1b** each show two signals due to the presence of two non-equivalent Cp ligands as well as a multiplet in the range δ 7.1–7.3 ppm due to the phenyl ring. Occurrence of a single sharp peak in the high field region, in case of both **1a** and **1b**, confirmed the presence of a bridging hydride ligand. A single ^{125}Te-NMR signal was observed for both the compounds in the range typically that for μ_3-Te [4].

Formation of $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu_2\text{-}SPh)(\mu_3\text{-}H)(CO)_5$ can be envisaged to formally involve the replacement of two CO groups by a μ-H and a μ-SPh group, thus retaining the total cluster electron count. The reaction also produced several other compounds which were observed during chromatographic work-up, but they could not be characterised because of their insufficient yields.

To establish the structure of the new compound unequivocally, single crystal X-ray diffraction studies were undertaken. Dark red crystals of the compound **1a** were grown from hexane/dichloromethane solvent mixture at − 5°C, and its structure was elucidated by single crystal X-ray diffraction studies. The molecular structure is depicted in Fig. 1. The crystal data and details of measurement are given in Table 1. Fractional atomic coordinates are given in Table 2. Selected bond lengths and bond angles are listed in Table 3.

The basic cluster geometry consists of a Mo_2Fe_2 tetrahedron with one Mo_2Fe face capped by a μ_3-Te atom and the other by a μ_3-S atom. Each Fe atom has two terminally bonded carbonyl groups and one CO group which bridges the Fe–Fe bond. The Mo–Mo

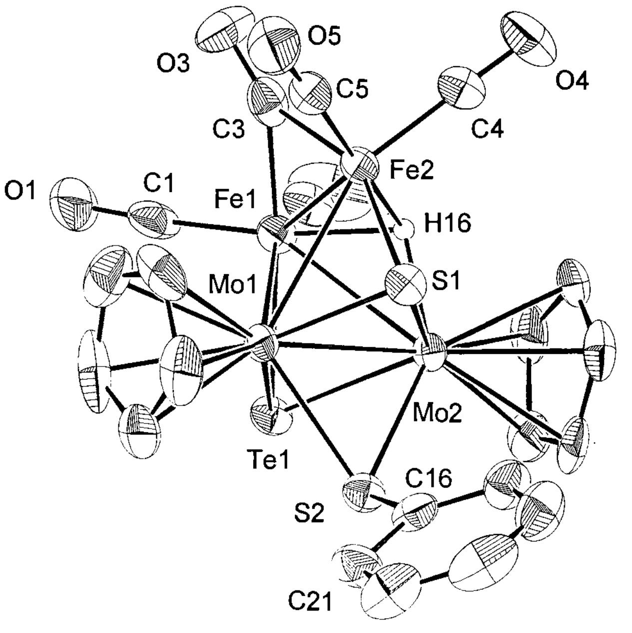

Fig. 1. ORTEP plot of $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu_2\text{-}SPh)(\mu_3\text{-}H)(CO)_5$ (**1a**). The atoms are drawn with 30% probability elipsoids. Ring hydrogen atoms are omitted for clarity.

Table 1
Crystal data and details of measurement for $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu_2\text{-}SPh)(\mu_3\text{-}H)(CO)_5$ (1a)

Formula	$C_{21}H_{16}O_5S_2Fe_2Mo_2Te$
Molecular weight	843.65
Colour	Dark red
Space group	$P2_1/c$
a (Å)	12.95(1)
b (Å)	10.069(9)
c (Å)	19.455(6)
β (deg)	106.70(4)
U (Å^3)	2429(2)
Z	4
ρ_{calc} (g cm^{-3})	2.31
F(000)	1608.00
$\mu_{(Mo\text{-}K\alpha)}$ (mm^{-1})	36.02
2θ max (deg)	50
Reflections measured	4763
Reflections observed	2911
No. parameters refined, N_p	298
Largest shift/esd in final cycle	0.001
Largest electron-density peak (e Å^{-3})	0.68
R^a	0.0373
R'^b	0.0281
GOF^c	1.53

[a] $R = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$.
[b] $R' = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$.
[c] $S = [\Sigma(|F_o|-|F_c|)/\sigma]/(N_o-N_p)$.

bond is bridged by a SPh group and one $MoFe_2$ face is capped by a hydride ligand. Each Mo atom is also attached to a cyclopentadienyl ligand. The Fe–Fe bond distance of 2.482(2) Å in **1a** is shorter than the Fe–Fe bond distance observed for the parent compound, $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(CO)_7$ (2.545(2) Å) [4]. The average Mo–SPh distance in **1a** is 2.429 Å which is comparable to other such Mo–SR bond distances found in literature (Mo–S(Me) = 2.411(4) Å in $Cp_2Mo_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}Cl)$ or average Mo–S(Me) = 2.453 Å in $[(CpMoCO)_2(S_2CH_2)(\mu\text{-}SMe)]^+$ or Mo–S(Pr^i) = 2.536(3) Å in $Mo_2Ru_2(\mu_3\text{-}S)_2(\mu\text{-}SPr^i)_2(CO)_4(\eta\text{-}C_5H_5)_2)$ [9,10]. The Mo(1)–S(2)–Mo(2) bond angle is 64.95(6)° which is again comparable to the Mo–S(Me)–Mo bond angle (64.99(11)° in $Cp_2Mo_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}Cl)$ but is larger than that (63.1(1)°) in $Mo_2Ru_2(\mu_3\text{-}S)_2(\mu\text{-}SPr^i)_2(CO)_4(\eta\text{-}C_5H_5)_2)$ [9,10]. As is evident from an examination of the following bond angles in **1a**, Mo(1)–S(2)–C(16) = 111.1(3)°, Mo(2)–S(2)–C(16) = 116.3(3)° and S(2)–C(16)–C(17) = 124.2(7)°, S(2)–C(16)–C(21) = 114.5(7)°, the phenyl ring attached to S(2) is bent slightly towards one of the Mo atoms.

The presence of the bridging SPh group shortens the Mo–Mo bond distance (Mo(1)–Mo(2) = 2.669(1) Å) in comparison to that in the parent cluster (Mo(1)–Mo(2) = 2.783(1) Å) [4]. Precedence of such shortening of metal–metal bond length under similar situations have been observed elsewhere too [9–11].

Although literature contains several examples of compounds containing the μ-SR group bridging two metal atoms [9,10,12], the compound $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu_2\text{-}SPh)(\mu_3\text{-}H)(CO)_5$ represents the first example of a mixed-metal cluster containing a μ-SR group supported by two different chalcogen atoms.

3. Experimental

3.1. General procedures

All reactions and other manipulations were carried out using standard Schlenk techniques under an inert atmosphere of argon. All solvents were dried and distilled immediately prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FTIR spectrophotometer as dichloromethane solution in 0.1 mm pathlength NaCl cells. Elemental analyses were performed on a Carlo Erba automatic analyser. ^{1}H- and ^{125}Te-NMR spectra were recorded on a Varian VXR-300S

Table 2
Atomic coordinates and B(eq) of non-hydrogen atoms for $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu_2\text{-}SPh)(\mu_3\text{-}H)(CO)_5$ (**1a**)

Atom	x	y	z	B(eq)
Te(1)	0.39094(5)	0.04522(6)	0.28004(3)	2.25(2)
Mo(1)	0.32100(6)	0.06271(8)	0.13566(4)	1.89(3)
Mo(2)	0.21318(6)	−0.08728(7)	0.20491(4)	1.81(3)
Fe(1)	0.2350(1)	0.1950(1)	0.23432(7)	2.20(5)
Fe(2)	0.1033(1)	0.1265(1)	0.11985(6)	2.03(5)
S(1)	0.1603(2)	−0.0531(2)	0.0787(1)	2.20(9)
S(2)	0.3693(2)	−0.1727(2)	0.1679(1)	2.3(1)
O(1)	0.3618(5)	0.4361(7)	0.2489(4)	5.5(4)
O(2)	0.1782(6)	0.2383(8)	0.3676(4)	5.7(4)
O(3)	0.0969(5)	0.4113(6)	0.1539(3)	4.1(3)
O(4)	−0.1241(5)	0.0742(7)	0.1072(4)	4.3(3)
O(5)	0.0521(5)	0.2726(7)	−0.0141(4)	4.5(4)
C(1)	0.3151(7)	0.338(1)	0.2443(5)	3.4(4)
C(2)	0.1972(7)	0.225(1)	0.3133(5)	2.9(4)
C(3)	0.1255(7)	0.301(1)	0.1628(5)	2.9(4)
C(4)	−0.0348(7)	0.0964(9)	0.1125(4)	2.6(4)
C(5)	0.0705(7)	0.212(1)	0.0383(5)	3.0(4)
C(6)	0.466(1)	0.204(1)	0.1335(6)	4.9(6)
C(7)	0.375(1)	0.266(1)	0.0956(7)	4.4(6)
C(8)	0.3244(8)	0.188(1)	0.0349(6)	4.6(6)
C(9)	0.389(1)	0.075(1)	0.0375(5)	4.0(5)
C(10)	0.4767(8)	0.086(1)	0.0999(6)	4.0(5)
C(11)	0.0561(7)	−0.154(1)	0.2318(6)	3.3(5)
C(12)	0.1379(8)	−0.129(1)	0.2986(5)	3.6(5)
C(13)	0.2211(8)	−0.226(1)	0.3033(5)	3.3(4)
C(14)	0.1876(8)	−0.3056(9)	0.2412(5)	3.1(4)
C(15)	0.0869(8)	−0.261(1)	0.1970(5)	3.3(4)
C(16)	0.3376(7)	−0.2779(8)	0.0883(5)	2.6(4)
C(17)	0.2450(8)	−0.3542(9)	0.0650(5)	3.3(4)
C(18)	0.2345(9)	−0.438(1)	0.0068(5)	4.1(5)
C(19)	0.313(1)	−0.446(1)	−0.0273(5)	4.3(5)
C(20)	0.4065(9)	−0.370(1)	−0.0032(5)	4.0(5)
C(21)	0.4186(8)	−0.286(1)	0.0550(5)	3.4(5)

Table 3
Selected bond lengths (Å) and bond angles (deg) for $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu_2\text{-}SPh)(\mu_3\text{-}H)(CO)_5$ (**1a**)

Mo(1)–Fe(1)	2.815(2)	Mo(2)–Fe(2)	2.836(1)
Mo(1)–Fe(2)	2.820(3)	Mo(2)–Fe(1)	2.897(1)
Mo(1)–Mo(2)	2.669(1)	Fe(1)–Fe(2)	2.482(2)
Mo(1)–S(1)	2.365(3)	Mo(2)–S(1)	2.377(2)
Mo(1)–S(2)	2.486(2)	Mo(2)–S(2)	2.486(3)
Mo(1)–Te(1)	2.6978(9)	Mo(2)–Te(1)	2.698(2)
Fe(1)–Te(1)	2.472(2)	Fe(2)–S(1)	2.190(3)
C(3)–O(3)	1.17(1)	S(2)–C(16)	1.823(9)
Mo(2)–Mo(1)–Fe(1)	63.71(4)	Mo(1)–Mo(2)–Fe(1)	60.60(3)
Mo(2)–Mo(1)–Fe(2)	62.15(4)	Mo(1)–Mo(2)–Fe(2)	61.54(5)
Mo(2)–Mo(1)–Te(1)	60.36(3)	Mo(1)–Mo(2)–Te(1)	60.35(4)
Mo(2)–Mo(1)–S(1)	55.95(6)	Mo(1)–Mo(2)–S(1)	55.53(6)
Fe(1)–Mo(1)–Fe(2)	52.26(4)	Fe(1)–Mo(2)–Fe(2)	51.29(4)
Fe(1)–Mo(1)–Te(1)	53.22(4)	Fe(1)–Mo(2)–Te(1)	52.28(3)
Fe(1)–Mo(1)–S(1)	94.92(8)	Fe(1)–Mo(2)–S(1)	92.57(6)
Fe(2)–Mo(1)–Te(1)	98.88(4)	Fe(2)–Mo(2)–Te(1)	98.48(4)
Fe(2)–Mo(1)–S(1)	49.01(7)	Fe(2)–Mo(2)–S(1)	48.71(6)
Te(1)–Mo(1)–S(1)	116.27(6)	Te(1)–Mo(2)–S(1)	115.84(6)
Mo(1)–Fe(1)–Mo(2)	55.69(3)	Mo(1)–Fe(2)–Mo(2)	56.31(3)
Mo(1)–Fe(1)–Fe(2)	63.98(6)	Mo(1)–Fe(2)–Fe(1)	63.76(5)
Mo(1)–Fe(1)–Te(1)	60.96(4)	Mo(1)–Fe(2)–S(1)	54.59(6)
Mo(2)–Fe(1)–Fe(2)	63.09(4)	Mo(2)–Fe(2)–Fe(1)	65.62(4)
Mo(2)–Fe(1)–Te(1)	59.71(4)	Mo(2)–Fe(2)–S(1)	54.63(6)
Fe(2)–Fe(1)–Te(1)	115.65(6)	Fe(1)–Fe(2)–S(1)	109.91(8)
Mo(1)–Te(1)–Mo(2)	59.30(2)	Mo(1)–S(1)–Mo(2)	68.52(6)
Mo(1)–Te(1)–Fe(1)	65.82(4)	Mo(1)–S(1)–Fe(2)	76.40(9)
Mo(2)–Te(1)–Fe(1)	68.01(5)	Mo(2)–S(1)–Fe(2)	76.66(8)
Mo(2)–Mo(1)–S(2)	57.53(6)	Mo(1)–Mo(2)–S(2)	57.52(6)
Fe(1)–Mo(1)–S(2)	113.52(6)	Fe(1)–Mo(2)–S(2)	110.81(7)
Fe(2)–Mo(1)–S(2)	114.58(6)	Fe(2)–Mo(2)–S(2)	114.03(7)
Te(1)–Mo(1)–S(2)	71.94(6)	Te(1)–Mo(2)–S(2)	71.93(7)
S(1)–Mo(1)–S(2)	76.80(8)	S(1)–Mo(2)–S(2)	76.59(8)

spectrometer in $CDCl_3$. The operating frequency for ^{125}Te-NMR was 94.705 MHz, with a pulse width of 9.5 μs and a delay of 1 s. The spectrum is referenced to Me_2Te ($\delta = 0$). The starting material $Cp_2Mo_2Fe_2STe(CO)_7$ was prepared as reported in literature [4]. Thiophenol was purchased from Fluka and used as such.

3.2. Thermolytic reaction of $Cp_2Mo_2Fe_2STe(CO)_7$ and C_6H_5SH

To a benzene solution (30 ml) of $Cp_2Mo_2Fe_2STe(CO)_7$ (140 mg, 0.177 mmol), C_6H_5SH (0.4 ml, 3.636 mmol) was added slowly with the help of a microsyringe. The solution was refluxed with constant stirring for 7 h. The reaction was closely monitored by TLC. The solution was filtered through Celite to remove insoluble material. After removal of the solvent from the filtrate, the residue was dissolved in dichloromethane and subjected to chromatographic work-up using silica gel TLC plates. The major red band that was isolated was again subjected to repeated chromatography on high performance TLC plates using 50/50 (v/v) benzene/hexane mixture as eluent. Thereby, two red compounds (**1a** and **1b**) were isolated. The dark red compound **1a**, $Cp_2Mo_2Fe_2(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu_2\text{-}SPh)(\mu_3\text{-}H)(CO)_5$ was characterised spectroscopically as well as structurally (yield 34.3 mg (23%)). IR: ν(CO) 2054 (sh), 2007 (vs), 1981 (vs), 1949 (vs), 1800 (br, m) cm^{-1}. ^1H-NMR: δ 4.98 (C_5H_5), 5.36 (C_5H_5), 7.2–7.3 (C_6H_5), −23.30 ppm (μ_3-H). ^{125}Te-NMR: δ 1214.7 ppm (μ_3-Te). Anal. Found: C, 29.6; H, 2.01. $C_{21}H_{16}Mo_2Fe_2S_2TeO_5$ Calc.: C, 29.9; H, 1.89%. The red coloured compound **1b**, (yield 31.3 mg, 21%) was found to be an isomer of **1a** with identical carbonyl stretching frequencies and slight variations in the ^1H-NMR: δ 4.90 (C_5H_5), 5.402 (C_5H_5), 7.2–7.1 (C_6H_5), −23.18 ppm (μ_3-H); and ^{125}Te-NMR spectra: δ 1361.5 ppm (μ_3-Te). Anal. Found: C, 29.7; H, 2.04. $C_{21}H_{16}Mo_2Fe_2S_2TeO_5$ Calc.: C, 29.9; H, 1.89%.

3.3. Crystallography

A dark-red block crystal of $Cp_2Mo_2(H)Fe_2(CO)_5(Te)(S)SPh$, **1a** was mounted on a glass fibre and sealed with epoxy glue. Data was collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-K_α radiation operating at 50 kV and 35 mA. Cell constants and an orientation matrix for data collection, obtained from 25 carefully centred reflections in the range $10.41 < 2\ \theta < 21.42°$, corresponded to a primitive monoclinic cell whose dimensions are given in Table 1. On the basis of statistical analyses of intensity distributions and successful solution and refinement of the structure, the space group was determined to be $P2_1/c$.

The data were collected at a temperature of 23 ± 1°C using the $\omega - 2\theta$ scan technique to a maximum 2θ value of 50.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.27° with a take-off angle of 6.0°. Scans were made at a speed of 16.0° min − 1 (in omega). The weak reflections ($I < 10.0\ (I)$) were rescanned (maximum of four scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1.

Of the 4763 reflections which were collected, 4551 were unique. The intensities of three representative reflections that were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo-K_α radiation is 36.02 cm − 1. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.68 to 1.00. The data were corrected for Lorentz and polarisation effects.

The structure was solved by direct methods [13]. All non-hydrogen atoms were refined anisotropically. The hydride in the cluster was located from the difference map by using only the low-angle data. Its position was then fixed. The remaining hydrogen atoms were included in their idealised positions with C–H set at 0.95 Å and with their isotropic thermal parameters set at 1.2 times that of the atom to which they were attached. The final cycle of full-matrix least-squares refinement [14] was based on 2911 observed reflections ($I > 3.00\ (I)$) and 298 variable parameters and converged (largest parameter shift was 0.001 times its esd) with unweighted and weighted agreement factors of $R = \|F_o| - |F_c\|/|F_o| = 0.0373$ and $R' = [w(|F_o| - |F_c|)^2/wF_o^2]^{1/2} = 0.0281$.

The standard deviation of an observation of unit weight [15] was 1.53. The weighting scheme was based on counting statistics and included a factor (p = 0.004) to downweight the intense reflections. Plots of $\Sigma w(|Fo| - |Fc|)^2$ versus $|Fo|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.68 and -70 eÅ^{-3}, respectively.

Neutral atom scattering factors were taken from Cromer and Waber [16]. Anomalous dispersion effects were included in F_{calc} [17], the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [18]. All calculations were performed using the TEXSAN [19] crystallographic software package of Molecular Structure Corporation.

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