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Further studies on the chemistry of molybdenyl adducts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$; hydrolysis, condensation and ligand exchange processes

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Abstract

Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $[MoO_2(acac)_2]$ in methanol gives the known five-coordinate Mo(VI) adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$ isolated as its PF_6^-, BPh_4^- and $[Mo_8O_{26}]^{4-}$ salts; the latter was structurally characterised, the polymolybdate anion being the uncommon γ form. Hydrolysis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$ in wet dichloromethane initially produces $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OH)]^+$ and subsequently the bright yellow oxo-bridged dimolybdenum species $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O]^{2+}$, structurally characterised as its tetraphenylborate salt, and found to contain two five-coordinate molybdenum centres. $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O]^{2+}$ can be prepared directly from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and $[MoO_2(acac)_2]$ in wet MeCN. Slow reconversion to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$ occurs when $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O]^{2+}$ is dissolved in methanol. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$ undergoes alkoxide exchange in dichloromethane-alcohol solutions to give $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OR)]^+$ species (R = e.g. n-octyl). These reactions are easily monitored using electrospray ionisation mass spectrometry.

Keywords: Platinum complexes; Molybdenum complexes; Sulfide ligands; Crystal structure; Electrospray ionisation mass spectrometry; Ligand exchange reactions

Introduction

In some recent papers[1,2,3,4,5,6,7] we have reported continued explorations into new chemistry of the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ ("$\{Pt_2S_2\}$") metalloligand **1**,[8,9] which possesses highly nucleophilic sulfide centres. Our approach has been to use electrospray ionisation mass spectrometry (ESI MS)[10] as a screening technique, to characterise reaction mixtures and identify novel reaction products in an efficient manner.[11] While its preference is for coordination to soft metal centres, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ also reacts with a selection of oxophilic metal centres, namely molybdenum(VI), vanadium(V) and uranium(VI), forming 'hard-soft' sulfide-bridged trinuclear aggregates.[12] For example, reaction with sodium molybdate in methanol produced exclusively the ion $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$ **2**, which was isolated as its hexafluorophosphate salt **2a**.[12] Five-coordinate molybdenyl complexes with chelating sulfur ligands are of interest because of their similarity to the active sites in certain molybdenum-containing enzymes e.g. the *sulfite oxidase* family of enzymes[13,14,15] which has prompted interest in the synthesis and properties of molybdenyl thiolate complexes.[16]

The only other molybdenum and tungsten adducts of $\{Pt_2S_2\}$ systems known to date are the organometallic derivatives $[Pt_2(\mu_3\text{-}S)_2(PPh_3)_4MI(CO)_4][MI_3(CO)_4]$ (M = Mo, W), formed by reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $[MI_2(CO)_3(NCMe)_2]$,[17] and the heterometallic complex $[\{Mo_3PtS_4(H_2O)_9\}_2]^{8+}$ with sulfide-bridged cubes forming a dimer through a (phosphine-free) $\{Pt_2S_2\}$ unit.[18] In this contribution we describe further studies into the ligand exchange chemistry of the $\{Pt_2S_2\}$-Mo(VI) system, and the formation of a multimetallic complex containing the bridging $[Mo_2O_5]^{2+}$ moiety spanning two $\{Pt_2S_2\}$ metalloligands.

Results and discussion

Synthesis and spectroscopic characterisation

In molybdenum(VI) chemistry, the acetylacetonato complex $[MoO_2(acac)_2]$ (acac = $CH_3COCHCOCH_3^-$) is widely used as a convenient soluble source of the molybdenyl (MoO_2^{2+}) moiety.[19] Reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $[MoO_2(acac)_2]$ in methanol proceeds rapidly (*ca.* 10 min.) at room temperature, giving a pale yellow solution shown by positive-ion ESI MS to contain solely $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$ (*m/z* 1662), which we have previously obtained from the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with sodium molybdate in methanol.[12] The cation was isolated as its hexafluorophosphate salt **2·PF$_6$** as a pale yellow solid, with identical spectroscopic properties to the material previously reported, with the exception of the colour, which was previously erroneously reported as red.

A series of ligand interconversions on the Mo centre were then investigated, using the technique of ESI MS to identify the cationic species present. These interconversions are summarised in Scheme 1. When $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]PF_6$ **2·PF$_6$** is dissolved in a wet, alcohol-free solvent (e.g. dichloromethane or acetonitrile), or in a stirred two-phase dichloromethane-water mixture, the initial very pale yellow organic solution slowly becomes bright yellow. ESI MS showed a single species at *m/z* 1639, which is found from its isotope pattern to be a dication. This was subsequently identified as the dimolybdenum oxo-bridged species $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O]^{2+}$ **3**. Monitoring the hydrolysis reaction by ESI MS in a mixed CH_2Cl_2-CH_3CN-H_2O solvent system showed initial fairly rapid hydrolysis to the (pale yellow) hydroxo species $[Pt_2(\mu\text{-}$

$S)_2(PPh_3)_4MoO_2(OH)]^+$ **4** (*m/z* 1649) which then decreases in intensity and is replaced by $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O]^{2+}$ **3**. From these solutions, the PF_6^- salt **3·(PF$_6$)$_2$** can be crystallised from dichloromethane-ether as fine, bright yellow needles. The dimolybdenum complex can alternatively be synthesised directly, in reasonable yield, by reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** with $[MoO_2(acac)_2]$ in wet MeCN; the initial orange colour of **1** is smoothly converted to a bright yellow suspension of the product, subsequently isolated as its hexafluorophosphate salt.

The dimolybdenum complex **3·(PF$_6$)$_2$** gave a single peak at δ 20.2 in the $^{31}P\{^1H\}$ NMR spectrum, with a $^1J(PtP)$ coupling constant of 3217 Hz. By comparison, complex **2·PF$_6$** shows a $^{31}P\{^1H\}$ NMR resonance at δ 18.9, with a very similar $^1J(PtP)$ of 3197 Hz.[12] Complex **3·(PF$_6$)$_2$** shows a characteristic absorption in its UV-visible spectrum (CH_2Cl_2 solution) at 450 nm; this is absent in the complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$, which instead shows an absorption at *ca.* 380 nm as a broad shoulder on an intense charge transfer absorption occurring at <340 nm. Other mononuclear MoO_2 complexes of chelating sulfur donor ligands also give absorption maxima in the same region, e.g. $[MoO_2(S_2CNEt_2)_2]$ (380 nm) and $[MoO_2(S_2PPh_2)_2]$ (375 nm), shifted from complexes with oxygen donor ligands e.g. $[MoO_2(acac)_2]$ (320 nm).[19] The IR spectrum of **3·(PF$_6$)$_2$** showed two weak bands at 905 and 937 cm^{-1}, attributable to symmetric and asymmetric modes of the *cis*-MoO_2 unit, together with a band at 744 cm^{-1} which is tentatively assigned as the μ-oxo stretching band, by comparison with other dinuclear Mo complexes, where it normally occurs between 650-770 cm^{-1}.[20]

The positive-ion ESI mass spectrum of isolated **3·(PF$_6$)$_2$** in dichloromethane-methanol shows the expected $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O]^{2+}$ cation as the base peak at

m/z 1639. A slow reaction of **3** occurs with methanol (*vide infra*), but the timescale is such that spectra can be recorded quickly without appreciable interference from the methoxy species. The fragmentation behaviour of $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O]^{2+}$ at elevated cone voltages was studied; we have previously reported the behaviour of the methoxy complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$, which fragments by loss of methanol with concomitant cyclometallation of a PPh_3 ligand.[12] At cone voltages up to around 65V, effectively no fragmentation of **3** is observed. At 80V, the spectrum is dramatically different, comprising predominantly an ion at *m/z* 1649, proposed to be the hydroxy species $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OH)]^+$ **4**, together with an ion at *m/z* 1368, which matches for $[Pt_2S_2(PPh_3)_4Mo(OMe)]^+$, and traces of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$ (*m/z* 1662), from the methanol co-solvent used together with $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O]^{2+}$. Reduction of high valent metal centres typically occurs under high energy collision conditions[10] e.g. $[ReO_4]^-$ fragments to the ions $[ReO_x]^-$ (x = 2,3).[21] At 100V, the *m/z* 1368 ion is the base peak, but at this higher cone voltage, an ion at *m/z* 718, assigned to the cyclometallated mono-platinum complex $[Pt(Ph_2PC_6H_4)(PPh_3)]^+$ is also observed, indicative of the breakup of the complex; this is typical behaviour for many other platinum-triphenylphosphine complexes at elevated cone voltages.[10, 22]

X-ray structural studies

In order to determine the coordination geometries around molybdenum, an X-ray structure determination on $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O](BPh_4)_2$ **3·(BPh$_4$)$_2$** was carried out. Crystals of the complex were obtained from a sample of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]BPh_4$ (**2·BPh$_4$**) that underwent slow hydrolysis in the solid state

over a period of several months, as shown by ESI MS and conversion of the initial pale yellow solid into a brighter yellow colour. The structure of the cation and the atom numbering scheme are given in Figure 1, while Table 1 gives a selection of bond distances and angles. The dication consists of two $\{Pt_2S_2\}$ metalloligands chelating the two molybdenum atoms of a bent MoO_2-O-MoO_2 unit. Both $\{Pt_2S_2Mo\}$ units have similar geometries with the same S-Mo-S bite angles [S(1)-Mo(1)-S(2) 71.92(13) and S(3)-Mo(2)-S(4) 71.67(13)°].

It is noteworthy that the molybdenum centres are five-coordinate, with a distorted geometry between that of a square pyramid and a trigonal bipyramid; the coordination geometry around one of the Mo atoms [Mo(1)] is shown in Figure 2. The τ_5 parameter defined by Addison, Reedijk and co-workers[23] has been extensively used to quantify transition metal complexes having five-coordinate geometries lying between the extremes of trigonal bipyramidal to square pyramidal.[24] In **3·(BPh$_4$)$_2$**, the τ_5 parameters for Mo(1) and Mo(2) are 0.305 and 0.508 respectively. By comparison, a regular trigonal bipyramid has $\tau_5 = 1$, and a regular square pyramid has $\tau_5 = 0$, so the Mo centres in **3** do indeed have geometries between the two extremes, with Mo(1) having a geometry somewhat closer to square pyramidal. If the geometry is considered as trigonal bipyramidal, this allows identification of one axial sulfide [i.e. S(1) on Mo(1)] and one equatorial sulfide [i.e. S(2)]. The coordination geometry is then completed by two terminal oxo ligands in equatorial positions, and the bridging oxygen in the other axial position.

The Mo atoms bond asymmetrically to the $\{Pt_2S_2\}$ units; the Mo-S bond distances are 2.479(4) and 2.576(4) Å to one $\{Pt_2S_2\}$ and 2.498(4) and 2.559(4) Å to the second. In each case the shorter of the two Mo-S bonds is *trans* to the axial bridging oxygen atom

O(1) in the Mo coordination sphere, as a consequence of the structural *trans*-influence of the MoO_2 group.[19] The terminal molybdenum-oxo bonds range from 1.696(11) to 1.702(10) Å, while the bond distances to the bridging oxo are Mo(1)-O(1) 1.912(10) and Mo(2)-O(1) 1.931(10) Å.

The Mo(1)-O(1)-Mo(2) angle is 129.3(5)°, significantly smaller than other crystallographically characterised complexes containing the $SMoO_2$-O-MoO_2S coordination motif with a single μ-oxo bridge, which range from around 144 to 180°.[16,25] This is noteworthy given the substantial steric bulk of the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ groups. The bridging Mo-O bond distances are also relatively long; in previous studies of other $Mo_2O_5^{2+}$ complexes with sulfur donor ligands this has been ascribed to the bridging oxygen being *trans* to sulfur, which is a strong σ donor and π acceptor, which weakens the *trans* Mo-O bond.[25] Together, the long bridging Mo-O bonds and the relatively acute Mo-O-Mo angle suggest decreased π-bonding involving the μ-oxo ligand. The Pt-S bond distances span a range from 2.336(4) to 2.373(4) Å though no definite pattern in the bond distances could be determined.

During one reaction between $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and $[MoO_2(acac)_2]$, slow partial evaporation of the reaction mixture (without addition of a precipitating anion such as hexafluorophosphate) resulted in the deposition of small light yellow crystals. In order to structurally characterise the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$ cation and provide a comparison with the structure of **3**, an X-ray crystal structure determination was carried out, which determined the crystal to be $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)][Mo_8O_{26}]_{0.25}\cdot 2H_2O$ [**2**$\cdot(Mo_8O_{26})_{0.25}\cdot 2H_2O$]. The structure of the cation is shown in Figure 3, and shows the expected $\{Pt_2S_2\}$ core attached *via* both S atoms to a $MoO_2(OMe)$ group, giving overall

five-coordination to the molybdenum(VI) centre, with a τ_5 parameter[23] of 0.447, again indicating a geometry approximately midway between trigonal bipyramidal and square pyramidal. The detailed bond parameters associated with the $\{Pt_2S_2\}MoO_3$ core (Table 2) are very similar to those for the same units in the dimeric complex **3**, though the Mo-OMe distance of 1.887(5) Å is slightly shorter than the Mo-O-Mo distances in the dimer (*av.* 1.92 Å). For example, the fold angles between the P_2PtS_2 planes are 129.9º for **2** compared with 129.8 and 127.2º for the two halves of **3**. Similarly the bite angle of the $\{Pt_2S_2\}$ ligand is 72.7º and the deviation from trigonal bipyramidal geometry of the Mo atom, shown by the angle involving the two axial ligands, is 154º in **2**, barely distinguishable from the equivalent parameters in **3**.

The structure of the $[Mo_8O_{26}]^{4-}$ anion is illustrated in Figure 4. There are five known variants of the $[Mo_8O_{26}]^{4-}$ anion[26] and the present example corresponds to the less common γ form,[27,28,29] though with a small distortion leading to two Mo-O bonds [Mo(3)-O(14) and the symmetry equivalent] being longer than usual (2.633 Å). As detailed in the Experimental section, there is evidence that the bulk sample contains predominantly the $[Mo_6O_{19}]^{2-}$ anion, and that the crystal chosen for the structural study may not have been representative. The source of these polymolybdate anions is clearly hydrolysis of the excess $[MoO_2(acac)_2]$ starting material by adventitious water (the methanol solvent used was not dried, and reactions were carried out under ambient conditions).

The five-coordination of the Mo centres in complexes **2** and **3** is noteworthy, given the strong preference of molybdenum dioxo complexes for six-coordination.[19] Other examples of structurally characterised complexes containing $Mo_2O_5^{2+}$ units with five-coordinate Mo are known in systems where the sulfur ligand is a strongly electron-

donating chelating bis(thiolate) ligand.[18,30] The strongly electron-donating and bulky $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ is known to promote the formation of lower coordination numbers in metal adducts, such as five-coordination in $[\{Pt_2S_2\}Rh(\eta^5\text{-}C_5Me_5)]^{2+}$,[31] $[\{Pt_2S_2\}Ru(\eta^6\text{-arene})]^{2+}$, [31] and $[\{Pt_2S_2\}Re(CO)_3]^+$,[17] four-coordination in $[\{Pt_2S_2\}PbX_2]$ (X = Br, I),[32] and two-coordination in $[\{Pt_2S_2\}Tl]^+$.[33] The molybdenum complexes **2** and **3** described herein represent additional structurally-characterised examples of this behaviour.

Alcohol exchange reactions

The esterification and transesterification reactions of these $\{Pt_2S_2\}Mo$ species have been explored, and are summarised in Scheme 1. Such reactions have generated interest, since the anionic dimolybdate species $[Mo_2O_6(OCH_2R)]^-$ and $[Mo_2O_6(OCHR_2)]^-$ formed through esterification of $[Mo_2O_6(OH)]^-$ with RCH_2OH or R_2CHOH, have been probed in detail by mass spectrometry and found to be the active catalyst for oxidation of primary and secondary alcohols.[34]

The dimolybdenum complex **3** can be slowly reconverted to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$ **2** (using monitoring by ESI MS) by stirring it with methanol which occurs with a concomitant fading of the reaction solution from bright yellow to pale yellow. A freshly prepared solution of **3·(PF$_6$)$_2$** in dichloromethane-methanol shows only a trace of **2**, allowing rapid analysis by ESI MS in this solvent mixture (*vide supra*). After 1 hour, around 18% relative intensity of **2** was observed, with complete conversion after around 24 hours. In this methanolysis reaction, only **3** and **2** were observed. The hydroxo species **4** might be expected to form as an intermediate, but is not observed, presumably because it reacts with methanol more rapidly than **3**.

Microscale reactions, probed by ESI MS, show that a number of primary and secondary alcohols ROH also react with **2** resulting in rapid and essentially complete alkoxide exchange, giving new $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OR)]^+$ cations, easily identified by their *m/z* values [R (*m/z*): ethyl (1677); 2-propyl (1691); 1-butyl (1705); 1-hexyl (1733); 1-octyl (1761); 1-decyl (1789)]. Both primary (1-octanol) and secondary (2-octanol) alcohols undergo ready exchange with $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$. It is noteworthy that the attempted reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]PF_6$ with (-)-menthol (a bulky secondary alcohol) resulted in the formation of only a small amount of the alcohol-exchanged product (at *m/z* 1787); instead the solution turned bright yellow due to hydrolysis and condensation with adventitious water, as described previously, and the dimolybdenum species **3** was the base peak observed. It therefore appears that primary and non-bulky secondary alcohols can result in effective alkoxide exchange reactions; ROH competes effectively with adventitious water, and the formation of the dinuclear oxo-bridged dimolybdenum species **3** is avoided. Reaction of **2·PF$_6$** with 1-octanol in dichloromethane solution, followed by evaporation of the solvent and washing to remove excess octanol produced pale yellow crystals of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OC_8H_{17})]PF_6$, which has $^{31}P\{^1H\}$ NMR data [δ 19.4, $^1J(PtP)$ 3210 Hz] similar to **2**.[12]

Experimental

ESI mass spectra were recorded on (low resolution) VG Platform II or (high resolution) Bruker MicrOTOF instruments. Solutions of isolated products (concentration *ca.* 0.1 mg mL^{-1}) were prepared by dissolution in a few drops of dichloromethane and

dilution with either methanol or acetonitrile. Methanol was frequently used as the mobile phase, except where alkoxide exchange was undesired, in which case acetonitrile or dichloromethane were used. Confirmation of species was facilitated by comparison of observed and calculated isotope distribution patterns, the latter obtained from the *Isotope* program.[35] Elemental analyses were obtained by the Campbell Microanalytical Laboratory at the University of Otago, Dunedin, New Zealand. UV-visible spectra were recorded in CH_2Cl_2 solution on a Perkin-Elmer Lambda 11 spectrophotometer.

The complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** [36] and $[MoO_2(acac)_2]$[37] were prepared by the literature procedures. 1-Octanol (BDH), ammonium hexafluorophosphate (Aldrich) and sodium tetraphenylborate (BDH) were used as supplied from commercial sources. Other alcohols were reagent grade and used as supplied from BDH. Reactions were carried out in methanol (LR grade) or acetonitrile (AR grade) in air.

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]PF_6$ 2·PF_6 from $[MoO_2(acac)_2]$

A mixture of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** (400 mg, 0.266 mmol) and $[MoO_2(acac)_2]$ (93 mg, 0.285 mmol) in methanol (35 mL) was stirred for 30 min. giving a clear light yellow solution. After filtering to remove a small quantity of insoluble matter, NH_4PF_6 (300 mg, 1.8 mmol) was added to the filtrate, giving a light yellow precipitate. After stirring for 30 min., water (20 mL) was added to assist precipitation, and the solid was filtered, washed with water (10 mL) and dried to give **2·PF_6** (380 mg, 79%). Found: C, 48.2; H, 3.3. $C_{73}H_{63}F_6MoO_3P_5Pt_2S_2$ requires C, 48.5; H, 3.5%. ESI MS (MeOH) $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]^+$ (*m/z* 1662, 100%).

The corresponding BPh_4^- salt **2·BPh$_4$** was similarly prepared from [$Pt_2(\mu$-$S)_2(PPh_3)_4$] **1** (150 mg, 0.100 mmol), [$MoO_2(acac)_2$] (90 mg, 0.276 mmol) and $NaBPh_4$ (200 mg, 0.585 mmol) in methanol (30 mL) to give **2·BPh$_4$** (143 mg, 72%).

Synthesis of [{$Pt_2(\mu$-$S)_2(PPh_3)_4MoO_2$}$_2$O](PF_6)$_2$ 3·(PF_6)$_2$

To a suspension of [$Pt_2(\mu$-$S)_2(PPh_3)_4$] **1** (376 mg, 0.250 mmol) and [$MoO_2(acac)_2$] (176 mg, 0.540 mmol) in acetonitrile (50 mL) was added 3 drops of water. The mixture was stirred, resulting in partial dissolution of the platinum complex, and formation of a bright yellow solution (with unreacted platinum complex), which then deposited a bright yellow precipitate. After stirring for 24h, dichloromethane (20 mL) was added to the yellow suspension, followed by NH_4PF_6 (300 mg, 1.84 mmol). After stirring for 20 min. the volume of the mixture was reduced to half (rotary evaporator), and water (30 mL) added, giving a bright yellow solid. This was isolated by filtration, washed with water (2 x 10 mL) and hexane (2 x 10 mL), and dried to give crude **3·(PF_6)$_2$**. Recrystallisation from dichloromethane-heptane gave bright yellow needles (258 mg, 58%). Found: C, 49.0; H, 3.3. $C_{144}H_{120}F_{12}Mo_2O_5P_{10}Pt_4S_4$ requires C, 48.5; H, 3.4%. $^{31}P\{^1H\}$ NMR, δ 20.2 [s, ^1J(PtP) 3217]. UV-vis (CH_2Cl_2) λ_{max} 450 nm. ESI MS (CH_2Cl_2-MeOH), *m/z* 1639 $[M]^{2+}$.

Ligand exchange of [$Pt_2(\mu$-$S)_2(PPh_3)_4MoO_2(OMe)]^+$ monitored using ESI MS

A solution of [$Pt_2(\mu$-$S)_2(PPh_3)_4MoO_2(OMe)]PF_6$ **2·PF$_6$** (*ca.* 10 mg) in dichloromethane (*ca.* 5 mL) was diluted with the appropriate alcohol (*ca.* 1 mL), or an excess of the solid

reagent (e.g. menthol) added. After shaking and centrifugation, the ESI mass spectrum was recorded, monitoring with time.

Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OC_8H_{17})]PF_6$ by ligand exchange from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]PF_6$ 2·PF_6

A solution of **2·PF_6** (97 mg, 0.054 mmol) in a mixture of dichloromethane (5 mL) and 1-octanol (2.5 mL) was stirred for 24 h. The resulting clear, light yellow solution was allowed to spontaneously evaporate, resulting in the formation of light yellow needles. The excess 1-octanol was decanted, and the crystals washed with 4 x 2 mL portions of heptane and dried. Found: C, 51.2; H, 4.1. $C_{80}H_{77}F_6MoO_3P_5Pt_2S_2$ requires C, 50.4; H, 4.1%. $^{31}P\{^1H\}$ NMR, δ 19.4 [s, $^1J(PtP)$ 3210].

X-ray structure determination on $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O](BPh_4)_2$ 3·$(BPh_4)_2$

On standing for several months, a solid sample of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)]BPh_4$ **2·BPh_4** gradually became more yellow coloured, and ESI MS showed conversion to mainly the dinuclear complex $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O]^{2+}$ **3** at *m/z* 1639. Recrystallisation of this solid by vapour diffusion of diethyl ether into a dichloromethane solution yielded bright yellow block crystals of **3·$(BPh_4)_2$**. These lost solvent very rapidly so crystallinity was less than ideal; the data set was weak beyond 2θ = 48°. X-ray data were collected on a Bruker Apex II CCD diffractometer, and corrected for absorption by a multi-scan procedure (SADABS).[38] The structure was solved and refined using the SHELX programs.[39] Crystal and refinement data are summarised in Table 3.

The solvent was modelled as three well defined CH_2Cl_2, one disordered CH_2Cl_2 and one very disordered, partially occupied site where only the two Cl atoms could be included. There were also other even-poorer defined solvent molecules that could not be modelled sensibly so were not accounted for. The combination of weak data, a very large number of atoms (which meant only the heavy atoms were treated anisotropically), together with disordered and un-modelled solvent, meant that the refinement was poorer than usual, with high R factors and significant residual electron density. However the cation was well behaved so the overall features are reliable.

Synthesis and X-ray structure determination of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)][Mo_8O_{26}]_{0.25}\cdot 2H_2O$ $[2\cdot 0.25Mo_8O_{26}\cdot 2H_2O]$

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (150 mg, 0.10 mmol) and $[MoO_2(acac)_2]$ (150 mg, 0.46 mmol) were stirred in methanol (30 mL) to give a clear pale yellow solution after several minutes. The solution was allowed to spontaneously evaporate under ambient conditions. After several days a small number of pale yellow crystals had formed, one of which was selected for X-ray analysis. Data were collected on a Bruker APEX II CCD diffractometer, and were corrected for absorption using a multi-scan method. Crystal and refinement details are in Table 3.

The structure was solved by direct methods and subsequent difference maps readily revealed the atoms of the cation. The remaining electron density could be assigned to an $[Mo_8O_{26}]$ anion, lying about an inversion centre, together with four associated H_2O molecules. However refinement was only reasonable if all of the anion atoms were assigned site-occupancy of 0.5. This makes sense based on the expected

charge of 4- for an $[Mo_8O_{26}]$ anion, since this would give the total unit cell contents in P-1 of two $[Pt_2S_2(PPh_3)_4MoO_2(OMe)]^+$ cations and one-half of an $[Mo_8O_{26}]^{4-}$ anion, (together with four H_2O molecules) giving overall charge neutrality. While this is crystallographically well-behaved and leads to a good refinement (R_1 0.047, wR_2 0.109, sensible U_{ij} values) the implication is that the anion site in the crystal is only 50% occupied, which would lead to unusually large voids in the lattice (possibly occupied by solvent molecules). Nevertheless we believe this is the correct interpretation since:

(i) refinement with site-occupance of 1.0 for the atoms of the anion (implying an $[H_2Mo_8O_{26}]^{2-}$ ion) leads to poor agreement indices (R_1 = 0.0995, wR_2 = 0.249) and very large thermal ellipsoids;

(ii) the density of other crystals from the same batch measured by flotation of 1.71 g cm^{-3} agrees better with the value calculated for the half-anion model (1.714 g cm^{-3}) than for the full anion model (1.99 g cm^{-3});

(iii) C, H microanalytical data (C 41.57, H 2.63%) are between the values calculated for the 2 cations:0.5 anion model (C 43.97, H 3.38%), and the 2 cations:1 anion version (C 38.90, H 2.81%) so cannot reliably distinguish between them (but see below).

A negative-ion ESI-MS examination of the solid dissolved in CH_2Cl_2 gave inconclusive results, indicating several different Mo containing species with only $[Mo_6O_{19}]^{2-}$ identifiable as a polyoxomolybdate anion in the mixture. This is clearly not the anion revealed in the structure analysis.

A repeat preparation gave a yellow, microcrystalline solid (yield 139 mg, from 150 mg of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$) which gave a very clean peak for $[Mo_6O_{19}]^{2-}$ in the ESI-MS, and microanalytical results (C 40.66, H 2.99%) which are close to those of the

original sample, and which correspond to $[Pt_2S_2(PPh_3)_4MoO_2(OMe)]_2[Mo_6O_{19}]$ (C 41.7, H 3.02%). Unfortunately this sample has not given crystals suitable for an X-ray determination.

We conclude that the preparation as detailed above leads predominantly to a $[Mo_6O_{19}]^{2-}$ salt. However in one preparation single crystals of a $[Mo_8O_{26}]^{4-}$ also formed and were hand-picked from the microcrystalline mass for the X-ray analysis, but were probably not representative of the bulk of the sample.

Supplementary material

Crystallographic data for the structures described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 783907 (**2**) and 783906 (**3**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 1 Selected bond lengths (Å) and angles (˚) for $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O](BPh_4)_2$ **3·(BPh$_4$)$_2$**

Pt(1)-P(2)	2.296(4)	Pt(1)-P(1)	2.307(5)
Pt(1)-S(1)	2.336(4)	Pt(1)-S(2)	2.360(4)
Pt(2)-P(3)	2.287(4)	Pt(2)-P(4)	2.313(4)
Pt(2)-S(1)	2.353(4)	Pt(2)-S(2)	2.359(4)
Pt(3)-P(6)	2.285(4)	Pt(3)-P(5)	2.299(5)
Pt(3)-S(4)	2.354(4)	Pt(3)-S(3)	2.373(4)
Pt(4)-P(8)	2.304(4)	Pt(4)-P(7)	2.311(4)
Pt(4)-S(3)	2.339(4)	Pt(4)-S(4)	2.354(4)
Mo(1)-O(2)	1.696(11)	Mo(1)-O(3)	1.701(11)
Mo(1)-O(1)	1.912(10)	Mo(1)-S(1)	2.479(4)
Mo(1)-S(2)	2.576(4)	Mo(2)-O(4)	1.696(11)
Mo(2)-O(5)	1.702(10)	Mo(2)-O(1)	1.931(10)
Mo(2)-S(4)	2.498(4)	Mo(2)-S(3)	2.559(4)

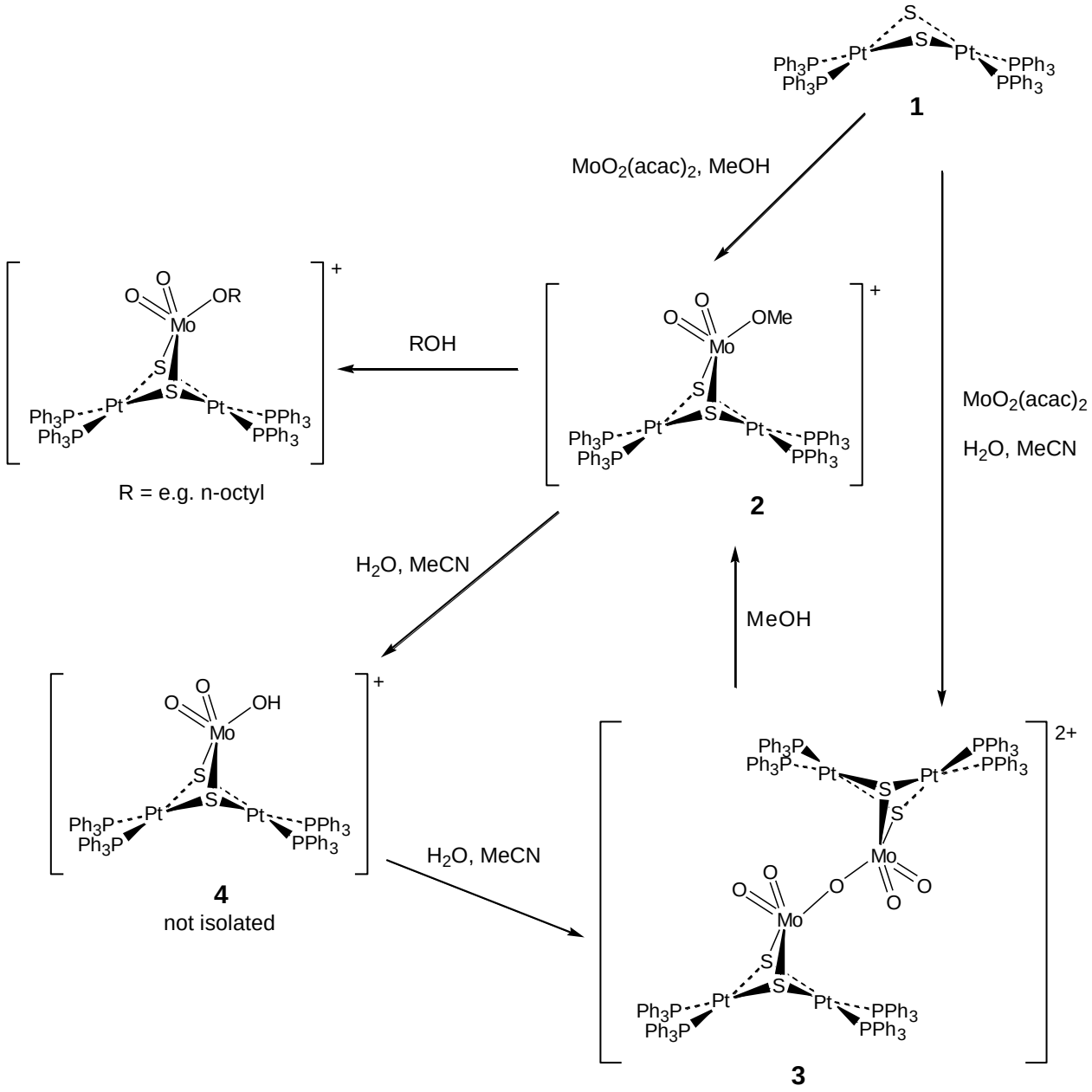
P(2)-Pt(1)-P(1)	95.81(16)	S(1)-Pt(1)-S(2)	78.46(14)
P(3)-Pt(2)-P(4)	99.56(16)	S(1)-Pt(2)-S(2)	78.13(14)
P(6)-Pt(3)-P(5)	98.64(16)	S(4)-Pt(3)-S(3)	77.55(14)
P(8)-Pt(4)-P(7)	100.40(16)	S(3)-Pt(4)-S(4)	78.22(14)
O(2)-Mo(1)-O(3)	109.6(5)	O(2)-Mo(1)-O(1)	100.8(5)
O(3)-Mo(1)-O(1)	104.8(5)	O(2)-Mo(1)-S(1)	89.3(4)
O(3)-Mo(1)-S(1)	97.8(4)	O(1)-Mo(1)-S(1)	150.3(3)
O(2)-Mo(1)-S(2)	132.0(4)	O(3)-Mo(1)-S(2)	116.4(4)
O(1)-Mo(1)-S(2)	80.8(3)	S(1)-Mo(1)-S(2)	71.92(13)
O(4)-Mo(2)-O(5)	111.1(5)	O(4)-Mo(2)-O(1)	103.2(5)
O(5)-Mo(2)-O(1)	100.7(5)	O(4)-Mo(2)-S(4)	93.1(4)
O(5)-Mo(2)-S(4)	91.6(4)	O(1)-Mo(2)-S(4)	154.2(3)
O(4)-Mo(2)-S(3)	122.9(4)	O(5)-Mo(2)-S(3)	123.7(4)
O(1)-Mo(2)-S(3)	82.7(3)	S(4)-Mo(2)-S(3)	71.67(13)
Mo(1)-O(1)-Mo(2)	129.3(5)		

Table 2 Selected bond lengths (Å) and angles (˚) for $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)][Mo_8O_{26}]_{0.25}\cdot 2H_2O$ **2**$\cdot(Mo_8O_{26})_{0.25}\cdot 2H_2O$

Pt(1)-P(2)	2.2898(18)	Pt(1)-P(1)	2.2877(18)
Pt(1)-S(1)	2.3578(17)	Pt(1)-S(2)	2.3383(17)
Pt(2)-P(3)	2.2935(18)	Pt(2)-P(4)	2.2757(19)
Pt(2)-S(1)	2.3560(17)	Pt(2)-S(2)	2.3577(17)
Mo(1)-O(2)	1.711(6)	Mo(1)-O(3)	1.698(5)
Mo(1)-O(1)	1.887(5)	Mo(1)-S(1)	2.5158(18)
Mo(1)-S(2)	2.5316(18)	C(1)-O(1)	1.430(11)
P(2)-Pt(1)-P(1)	98.16(7)	S(1)-Pt(1)-S(2)	79.10(6)
P(3)-Pt(2)-P(4)	97.94(7)	S(1)-Pt(2)-S(2)	78.75(6)
O(2)-Mo(1)-O(3)	111.8(3)	O(2)-Mo(1)-O(1)	99.8(3)
O(3)-Mo(1)-O(1)	102.7(3)	O(2)-Mo(1)-S(1)	90.5(2)
O(3)-Mo(1)-S(1)	95.28(19)	O(1)-Mo(1)-S(1)	154.04(18)
O(2)-Mo(1)-S(2)	127.2(2)	O(3)-Mo(1)-S(2)	119.1(2)
O(1)-Mo(1)-S(2)	82.21(18)	S(1)-Mo(1)-S(2)	72.66(6)

Table 3 Crystal, collection and refinement data for the X-ray structure determination of $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O](BPh_4)_2$ **3·(BPh$_4$)$_2$** and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)][Mo_8O_{26}]_{0.25}\cdot 2H_2O$ **2**$\cdot(Mo_8O_{26})_{0.25}\cdot 2H_2O$

Complex	**3**$\cdot(BPh_4)_2$	**2**$\cdot(Mo_8O_{26})_{0.25}\cdot 2H_2O$
Empirical formula	$C_{196}H_{169}B_2Cl_9Mo_2O_5P_8Pt_4S_4$	$C_{73}H_{67}Mo_3O_{11.5}P_4Pt_2S$
Formula weight	4293.22	1994.27
Temperature (K)	89(2)	83(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions		
a	19.7454(1)	10.8526(1)
b	20.7629(1)	17.4284(2)
c	26.6456(4)	20.9917(1)
α	89.440(1)	95.378(1)
β	76.429(1)	102.081(1)
γ	63.700(1)	90.438(1)
Volume (Å^3)	9463.9(2)	3863.90(6)
Z	2	2
D_c (g cm^{-3})	1.507	1.714
Absorption coeff. (mm^{-1})	3.365	4.273
F(000)	4256	1942
Crystal size (mm^3)	0.34x0.22x0.20	0.18x0.18x0.12
Reflections collected	74675	37119
Independent reflections	29617 [$R_{(int)}$ = 0.1168]	15617 [$R_{(int)}$ = 0.041]
Max. and min transmission	0.5526 and 0.3941	0.596 and 0.484
Data / restraints / parameters	29617 / 0 / 1054	15617 / 0 / 937
Goodness-of-fit on F^2	1.089	1.098
Final *R* indices [I > 2σ(I)]	R_1 0.0846, wR_2 0.1831	R_1 0.0473, wR_2 0.1004
R indices (all data)	R_1 0.1539, wR_2 0.2129	R_1 0.0668, wR_2 0.1092
Largest peak and hole (e Å^{-3})	3.997 and -1.418	1.986 and -1.452



Scheme 1 Some interconversions of the $\{Pt_2S_2\}$-Mo complexes.

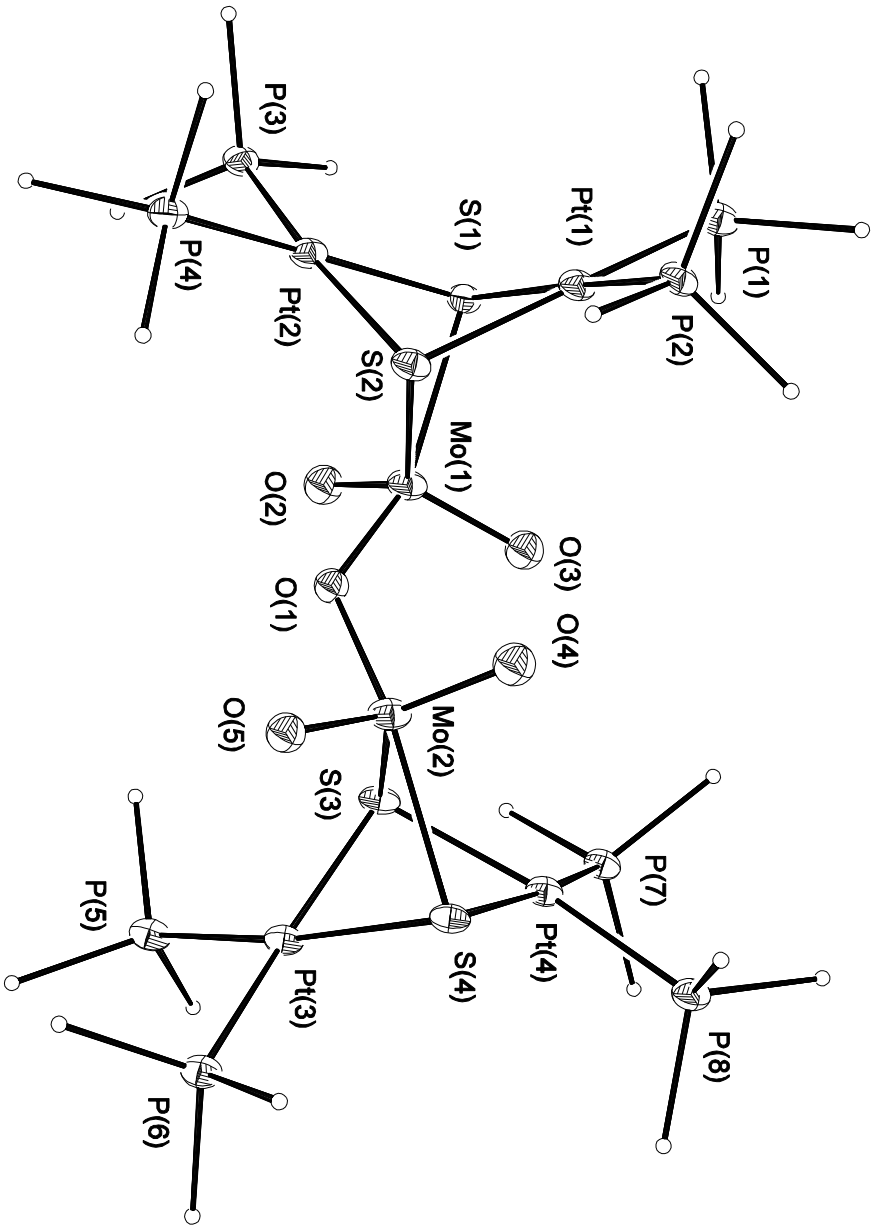


Figure 1 Structure of the cation of $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O](BPh_4)_2$ **3·(BPh$_4$)$_2$** with only *ipso* carbons of the triphenylphosphine ligands shown as small circles for clarity.

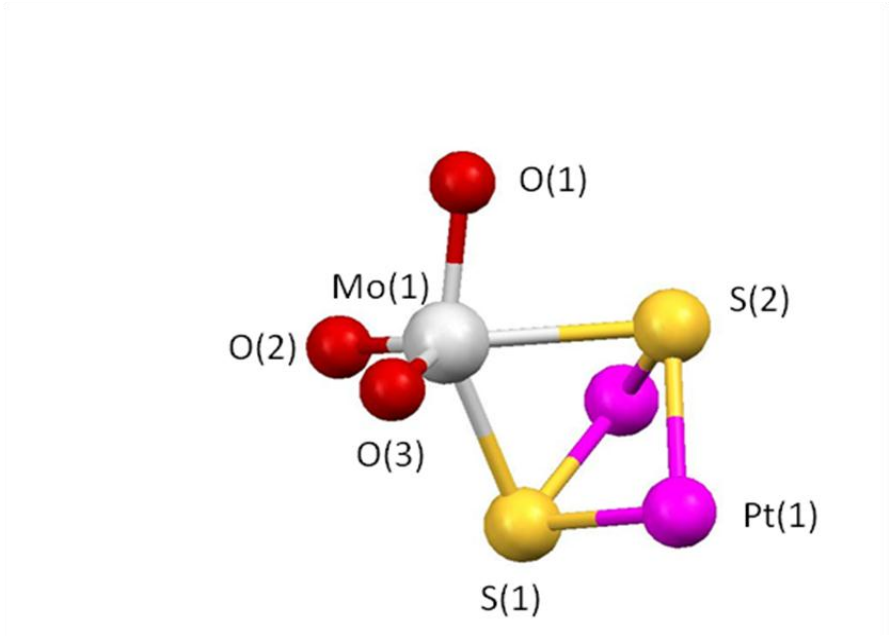


Figure 2 The coordination geometry of one of the molybdenum atoms in $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2\}_2O](BPh_4)_2$ **3·(BPh$_4$)$_2$**

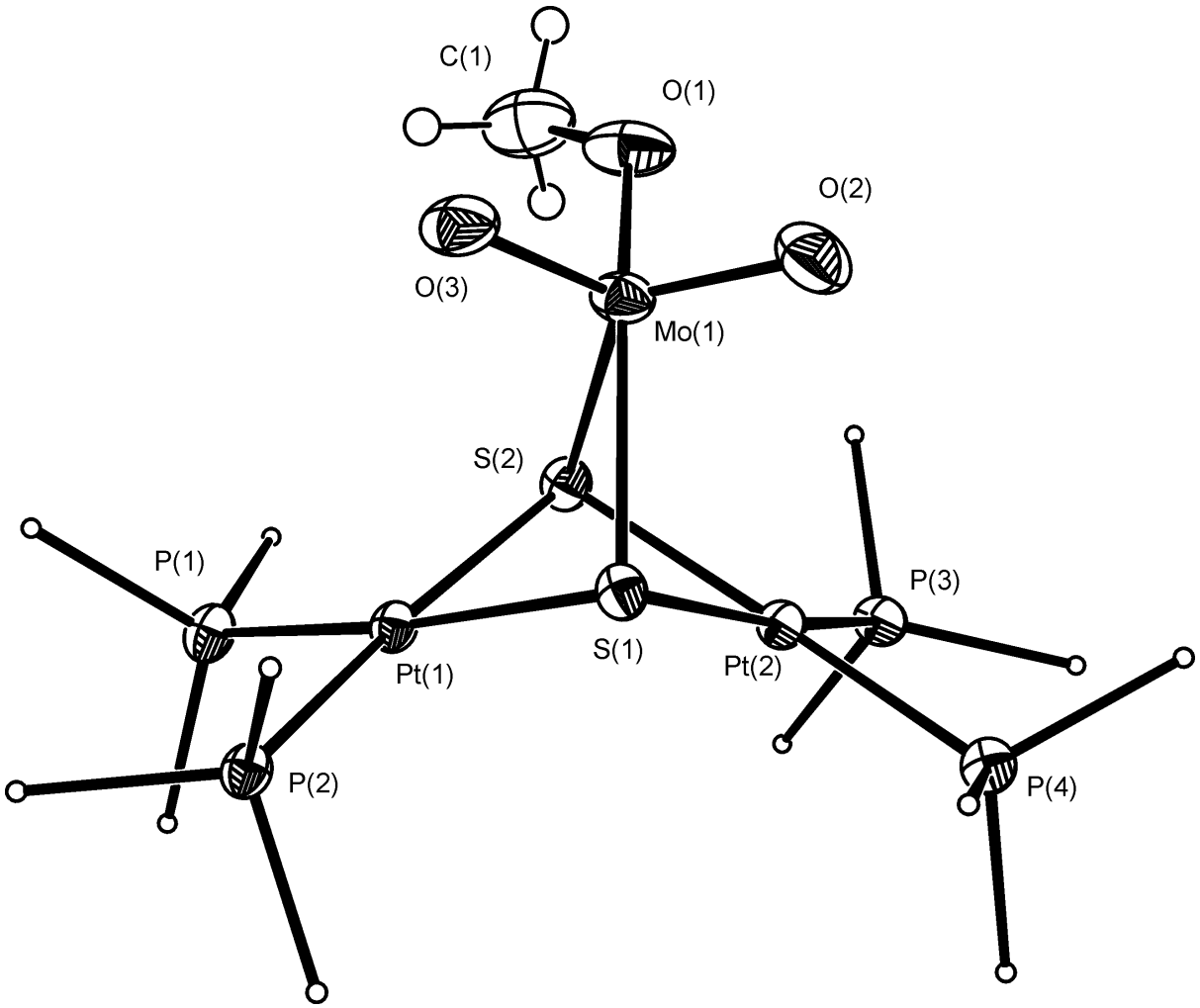


Figure 3 Structure of the cation of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)](Mo_8O_{26})_{0.25}\cdot 2H_2O$ **2**$\cdot(Mo_8O_{26})_{0.25}\cdot 2H_2O$ with only *ipso* carbons of the triphenylphosphine ligands shown as small circles for clarity.

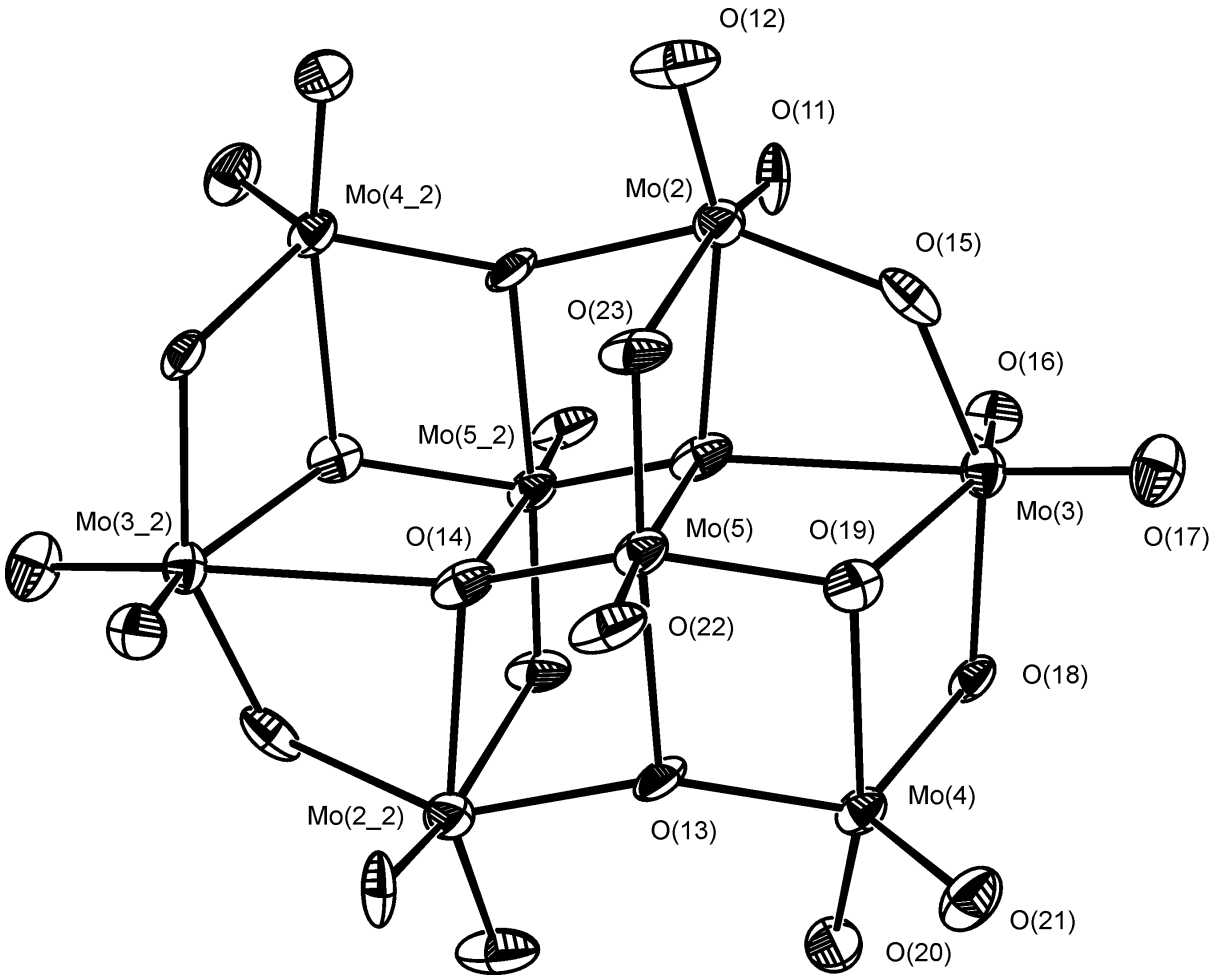


Figure 4 Structure of the $[Mo_8O_{26}]^{4-}$ anion of the complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4MoO_2(OMe)](Mo_8O_{26})_{0.25}\cdot 2H_2O$ (**2**$\cdot(Mo_8O_{26})_{0.25}\cdot 2H_2O$)

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