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Reactions of the heterometallic cuboidal clusters Mo_3MS_4 (M = Co, Ni, Pd, Cu) and Mo_3NiSe_4 with CO: electron counts and kinetic/thermodynamic studies with M = Ni, Pd

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Contents

Abstract

The aqueous solution reactions of heterometallic cube derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$, written here as $[Mo_3MS_4(H_2O)_{10}]^{4+}$ (tetrahedral M = Fe, Co, Ni, Pd, Cu) with carbon monoxide are considered. Thermodynamically favourable reactions complete in 330 min are detected with M = Co (Group 9), and Ni and Pd (Group 10) containing cubes having 15 and 16 metal electrons, respectively, but no corresponding reactions are observed with M = Fe,

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Cu cubes having 14 and 17 metal electrons, respectively. A similar reaction is observed with the Se-containing cube $[Mo_3NiSe_4(H_2O)_{10}]^{4+}$, and with the higher oxidation state cube $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ (16 electrons) $[Mo_3S_4(H_2O)_9]^{4+}$ and $Cu(CO)^+$ are obtained as final products. On bubbling N_2 through the latter CO is removed, and approaching quantitative reformation of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ is observed. Greater difficulty is experienced in removing carbon monoxide from the other carbonyl adducts (M = Co, Ni, Pd) using N_2.

Keywords: Heterometallic cuboidal clusters; Kinetic thermodynamic studies; $[Mo_3MS_4(H_2O)10]^{4+}$

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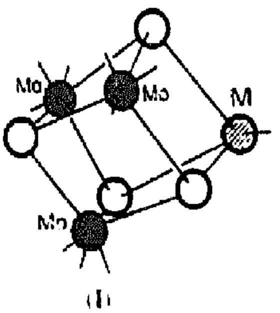
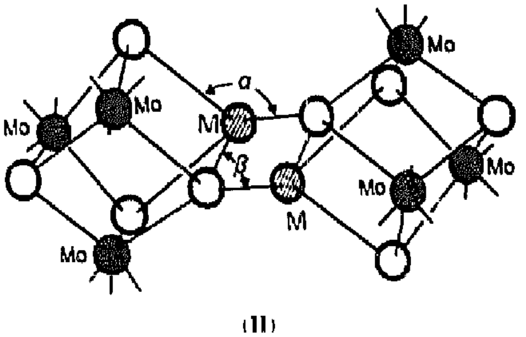
1. Introduction

Harris and colleagues have recently presented Fenske–Hall molecular orbital calculations for Mo_3MS_4 cuboidal core clusters, and considered variations in electronic structures when M is a transition metal (Co, Ni, Pd), or Main Group metal (Sn) [1]. While it is generally difficult to assign formal oxidation states to metal atoms in such clusters they have concluded that for M = Co, Ni, Pd, the heterometal is not oxidised, but instead shares electron density with the Mo_3S_4 unit by formation of Mo–M bonds. In other words, with Ni and Pd at least, the heterometal is best described as M^0 and the clusters can be regarded as $Mo_3S_4^{4+}M^0$ [2]. A similar formalism has been suggested for the single cubes $(Mo_3S_4^{4+})In^+$, $(Mo_3S_4^{4+})Ga^+$ (Group 13) and $(Mo_3S_4^{4+})Sn^{2+}$ (Group 14), where such assignments help in understanding the redox chemistry as well as interconversion of single and corner-shared double cubes [2]. The $[Mo_3CuS_4(H_2O)_{12}]^{5+}$ cube can be considered in this latter category as $(Mo_3S_4^{4+})Cu^+$.

In the present paper we consider reactions of Mo_3MS_4 cubes M = Fe, Co, Ni, Pd, Cu with CO and the ability of the heterometal atoms to give carbonyl products in aqueous solutions. The aim is to define by experiment the boundaries for the occurrence of such reactions and relate the findings to electron counts. The reactions of the Mo_3NiSe_4, Mo_3CoS_4 and Mo_3CuS_4 cubes as aqua ions are reported for the first time and allow an over-view of the combined data. We also consider kinetic and thermodynamic data for the reactions of the M = Ni, Pd cubes with CO and other ligands L. In the case of M = Co [3], Pd [4], Cu [5], the single cubes (I) give edge-linked double cubes (II) which have been identified by X-ray crystallography. Equilibria between I and II have to be taken into account.



(I)



(II)

The Co cube is in a different oxidation state to $[Mo_3(CoCo)S_4(Cp')_3]$ (Cp′ = methylcyclopentadyl), which was considered in reference [1].

2. Experimental

2.1. Preparation of clusters

The trinuclear Mo_3^{IV} clusters $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3Se_4(H_2O)_9]^{4+}$ were obtained in 2 M Hpts (*p*-toluenesulfonic acid) or 2 M HCl as previously described [6]. The details of UV–vis absorbance spectra are summarised in Table 1. Conversion to the heterometallic cuboidal $Mo_3MS_4^{4+}$ cores, M = Fe [7], Co [8], Ni [9], Pd [10], Cu [11], have been described using one or other of the procedures (1) and (2):

$$Mo_3S_4^{4+} + M \rightarrow Mo_3MS_4^{4+} \quad (1)$$

$$Mo_3S_4^{4+} + M^{II} + 2e^- \rightarrow Mo_3MS_4^{4+} \quad (2)$$

Table 1
Summary of UV–vis absorption spectra of trinuclear incomplete cubes, of heterometal derivatives as single edge-shared double cubes, and carbonyl complexes in 2 M acids as designated[a]

Cluster	Acid	Colour	λ nm (ε M^{-1}cm^{-1})	Ref.
$[Mo_3S_4(H_2O)_9]^{4+}$	Hpts	Green	366(5550); 603(362)	[2]
$[Mo_3Se_4(H_2O)_9]^{4+}$	Hpts	Yellow brown	427(5820); 646(595)	[6]
$[Mo_3FeS_4(H_2O)_{10}]^{4+}$	$HClO_4$	Grey-purple	503(730); 603(448); 970(122)	[7]
$[Mo_3CoS_4(H_2O)_{10}]^{4+}$	HCl	Brown	360(5370); 445(4260), 796(3360)	[3]
$[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$ [b]	Hpts	Brown	360(13 690); 447(9860); 790(6810)	This work
$[Mo_3(CoCO)S_4(H_2O)_9]^{4+}$	Hpts	Brown	555	This work
$[Mo_3NiS_4(H_2O)_{10}]^{4+}$	Hpts	Green blue	677(610)	[9]
$[Mo_3(NiCO)S_4(H_2O)_9]^{4+}$	Hpts		525(820)	[9]
$[Mo_3(PdCl)S_4(H_2O)_9]^{4+}$	HCl	Blue	450(1013); 580(1382)	[10]
$[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$	Hpts	Purple	456(2310); 572(2786)	[10]
$[Mo_3(PdCO)S_4(H_2O)_9]^{4+}$	Hpts	Yellow	415(1950); 470(1870)	[10]
$[Mo_3CuS_4(H_2O)_{10}]^{4+}$	Hpts	Brown red	325(3700); 470(1870); 975(473)	[11]
$[Mo_3CuS_4(H_2O)_{10}]^{5+}$	Hpts	Red brown	328(5130); 472(2200); 623(sh)(299)	[11]
$[Mo_3NiSe_4(H_2O)_{10}]^{4+}$	Hpts	Green	707(660)	This work
$[Mo_3(NiCO)Se_4(H_2O)_9]^{4+}$	Hpts	Brown	545(954)	This work

[a] ε's per Mo_3 (single) or Mo_6 (double) according to formulae given.
[b] Confirmation of these assignments is required.

Reactions (and storage) are generally in rigorous air-free conditions, although for M = Ni, Pd air sensitivity is minimal and not detected over ca. 30 min. In Eq. (2) the reducing agent used is either sodium borohydride, $NaBH_4$ or hypophosphorous acid, H_3PO_2. Purification was by Dowex 50W-X2 cation-exchange chromatography, and the single cubes were eluted with 2 M acid as required (Hpts, HCl or $HClO_4$). The $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ products appear tobe present always as single cubes [12,13]. On elusion with 4 M Hpts $Mo_3PdS_4^{4+}$ gives the edge-linked double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$, but the single cube $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ is eluted with 2 M HCl and forms with as little as 10 mM Cl^- [10]. X-ray crystal structures of both Pd forms have been reported [4]. We assume here that $Mo_3CoS_4^{4+}$ exhibits the same behaviour, with $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$ characterised by X-ray crystallography as the pts^- salt [3], and the single cube very likely present in 2 M HCl [8]. The crystal structure of $Mo_3CuS_4^{4+}$ is also that of an edge-linked double cube [5], but elusion characteristics and solution properties suggest that the single cube is present following Dowex chromatography [11]. The aqua ion $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, a second oxidation state of the Cu containing cube, is obtained by addition of Cu^+ to the incomplete cube

$$Mo_3S_4^{4+} + Cu^+ \rightarrow Mo_3CuS_4^{5+} \tag{3}$$

An X-ray structure of the $Mo_3CuS_4^{5+}$ core has been reported [14]. There is as yet no evidence for other than a single cube of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ [11].

The dark green heterometal cube $Mo_3NiSe_4^{4+}$ has been prepared for the first time from yellow–brown $[Mo_3Se_4(H_2O)_9]^{4+}$. A like volume (1.5 ml) of concentrated HCl was added to $[Mo_3Se_4(H_2O)_9]^{4+}$ (13.3 mM) in 2 M HCl. Granules of Ni (18 g), the surface of which have been activated by immersion in conc. HCl for several minutes, were added, and the mixture heated (under nitrogen) in a water bath at ca. 90°C for 13 h. The resulting dark green solution was allowed to stand for 3 days at room temperature before purification. The solution was diluted to 0.5 M HCl and loaded onto a Dowex 50W-X2 column (30 × 1 cm). The purification was carried out under nitrogen. The column was washed with 0.5 M HCl when a pale green solution corresponding to Ni^{2+} was also eluted. An olive-green solution containing $Mo_3NiSe_4^{4+}$ followed by a small amount of $[Mo_3Se_4(H_2O)_9]^{4+}$ was then eluted with 1 M HCl. A brown band of unknown product remains on the upper part of the column which is difficult to remove in 4 M HCl. The yield was 40% based on the amount of $[Mo_3Se_4(H_2O)_9]^{4+}$ used. On heating a 0.7 mM solution in 2 M HCl in air for 2 h at ca. 90°C $[Mo_3Se_4(H_2O)_9]^{4+}$ reforms (Eq. (4)).

$$Mo_3NiSe_4^{4+} + \tfrac{1}{2}O_2 + 2H^+ \rightarrow Mo_3Se_4^{4+} + Ni^{2+} + H_2O \tag{4}$$

In 2 M HCl the UV–vis spectrum gives peaks at 265, 538(sh) and 729 nm. The spectrum of the product eluted in 2 M Hpts, peaking at 707nm (details Table 1), is shown in Fig. 2. The elusion behaviour is similar to that of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, indicating a single 4+ cube ion.

Solutions of the single cubes $[Mo_3InS_4(H_2O)_{12}]^{5+}$ and $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ in 2 M Hpts prepared by addition of In^I or Sn^{II} to $[Mo_3S_4(H_2O)_9]^{4+}$, as in Eq. (3), were also obtained [15,16].

2.2. *Preparation of CO*

This was obtained by drop-wise addition of concentrated formic acid, HCO_2H (80 ml), to concentrated sulfuric acid (80 ml), [17]. The sulfuric acid contained in a round-bottom flask was magnetically stirred and immersed in a water bath at 70–80°C. The apparatus was first flushed with N_2, and the CO produced bubbled through alkaline (KOH) pyrogallol to remove traces of O_2.

2.3. *Other Materials*

The strong acid *p*-toluenesulfonic acid (Hpts) was obtained as a white crystalline solid (Aldrich). The reducing agents hypophosphorous acid, H_3PO_2 (50% w/w H_2O solution), and sodium tetrahydroborate, $NaBH_4$, were from Aldrich. Stable and water soluble phosphines, 1,3,5-triaza-7-phophaadamantane (PTA) and tris(3-sulfonatophenyl phosphine tetrahydrate, $Na_3(3\text{-}SO_3C_6H_4)_3P{\cdot}H_2O$ (Strem; $TPPTS^{3-}$), were as previously described, [10]. Other reagents were of analytical grade purity.

3. Results

3.1. *Formation of CO complexes*

The UV–vis absorption spectra relevant to these studies are summarised in Table 1. Solutions were in 2 M Hpts except in those cases where 2 M HCl was appropriate to retain the single cube structure. In all cases 3% methanol was added to the aqueous solution to increase the solubility of CO. Reactions with $[Mo_3(PdCl)S_4(H_2O)_9]^{4+}$ and $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ are rapid with colour changes as previously reported [10]. The reactions of $[Mo_3CoS_4(H_2O)_{10}]^{4+}$ (4 mM) under the conditions of 2 M Hpts, Fig. 1, and in 2 M HCl were also rapid, the resultant brown solutions having a peak at 559 nm with no peak at ca. 790 nm. The reactions of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, [9b], and $[Mo_3NiSe_4(H_2O)_{10}]^{4+}$ are slower and were allowed ~ 30 min. Relevant UV–vis absorbance changes for $[Mo_3NiSe_4(H_2O)_{10}]^{4+}$ (0.7 mM; 2 M Hpts) are shown in Fig. 2, with the appearance of a new peak at 545 nm. In 3 M HCl coordination of Cl^- to the Ni slows down the reactions with CO. The crystal structure of $[Mo_3(CoCO)S_4(Cp')_3]$, core $Mo_3CoS_4^{3+}$ [18], as well as $[Mo_3(NiCO)S_4(H_2O)_9]^{4+}$ [19], and $[Mo_3(PdCO)S_4(tacn)_3]^{4+}$ (tacn = 1,4,7 triazacyclo-nonane) [4], have established the nature of the carbonyl attachments. Relevant equations are as in Eqs. (5)–(7).

$$Mo_3NiS_4^{4+} + CO \rightarrow Mo_3(NiCO)S_4^{4+} \tag{5}$$

$$Mo_3(PdCl)S_4^{3+} + CO \rightarrow Mo_3(PdCO)S_4^{4+} \tag{6}$$

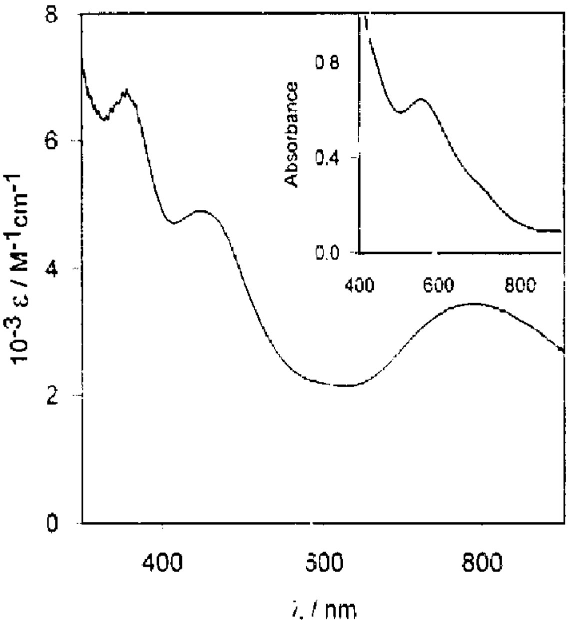


Fig. 1. UV–vis spectrum of $[Mo_3CoS_4(H_2O)_{10}]^{4+}$ in 2 M Hpts, (ε's per Mo_3) and the $[Mo_3Co(CO)S_4(H_2O)_9]^{4+}$ product (inset) in 2 M Hpts.

$$\{Mo_3PdS_4\}_2^{8+} + 2CO \rightarrow 2Mo_3(PdCO)S_4^{4+} \qquad (7)$$

On bubbling N_2 through the product solutions there is little or no reversal of the reactions within 15 min. No reaction of CO is observed at the heteroatoms of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ (1 mM; 2 M $HClO_4$) and $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ (7.9 mM; 2 M Hpts), or at the Mo's of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$ (both ca. 1 mM;

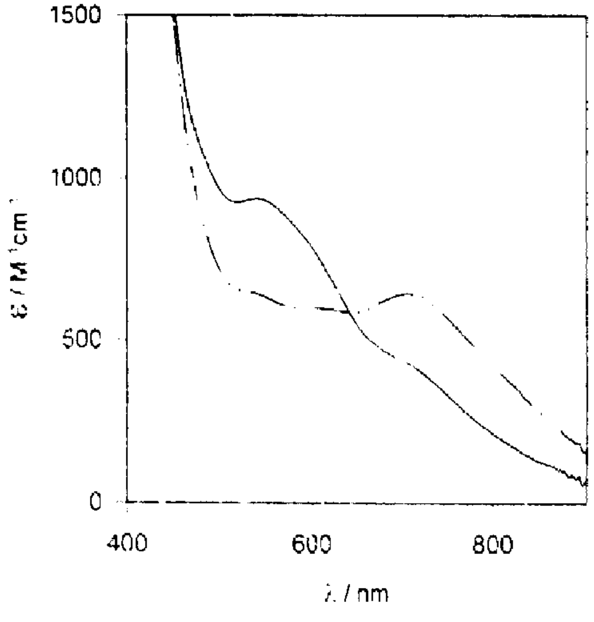


Fig. 2. UV–vis spectra of $[Mo_3NiSe_4(H_2O)_{10}]^{4+}$ in 2 M Hpts (- - -) and $[Mo_3Ni(CO)Se_4(H_2O)_{10}]^{4+}$ in 2 M Hpts ( ), ε's per Mo_3.

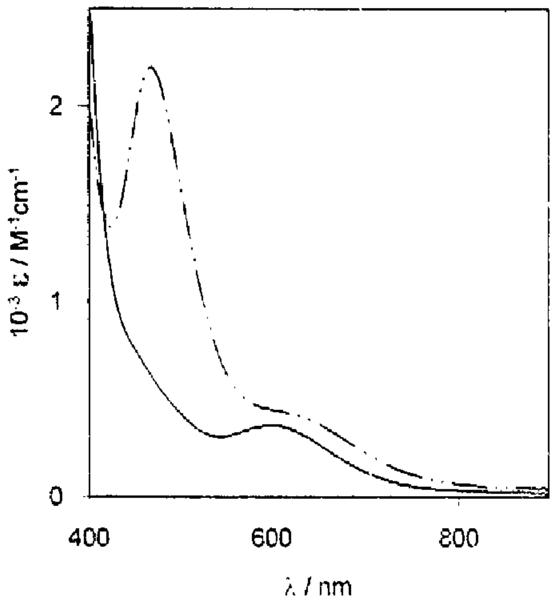


Fig. 3. UV–vis spectra of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ in 2 M Hpts (- · - ·) and the $[Mo_3S_4(H_2O)_9]^{4+}$ product (—) in 2 M Hpts obtained after bubbling CO through the solution for 5 min. ε's per Mo_3.

2 M $HClO_4$) [9b]. Similarly no reaction of CO at the Mo's of heterometallic clusters has been observed.

In the case of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ (1 mM; 2 M Hpts) a quite different reaction is observed. A colour change from red to brown to green is complete within 3–4 min of bubbling CO. From its UV–vis spectrum, Fig. 3, the green product is identified as $[Mo_3S_4(H_2O)_9]^{4+}$. When N_2 is bubbled through the solution for 15 min the red–brown colour of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ reforms. The removal of CO results in ca. 90% reformation of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, Fig. 3. The observations are explained by equilibria involving the formation of an aqua $Cu(CO)^+$ product, [20], which is no longer attached to the $[Mo_3S_4(H_2O)_9]^{4+}$ component. It has been reported that $Cu(CO)^+$ decomposes on pumping away CO to give Cu^+, [21], and this is in good agreement with our findings. The sequence of reactions is therefore as in Eqs. (8)–(10).

$$Mo_3CuS_4^{5+} + CO \rightarrow Mo_3S_4^{4+} + Cu(CO)^+ \qquad (8)$$

$$Cu(CO)^+ \xrightarrow{N_2} Cu^+ + CO \qquad (9)$$

$$Mo_3S_4^{4+} + Cu^+ \rightarrow Mo_3CuS_4^{5+} \qquad (10)$$

Checks carried out on $[Mo_3InS_4(H_2O)_{12}]^{5+}$ (2 mM) and $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ (0.5 mM) in 2 M Hpts gave no reaction (20 min) with CO.

3.2. Removal of CO from cube products

It has been reported that in the case of the cubes $[M_3(NiCO)S_4(H_2O)_{10}]^{4+}$ (M = Mo, W), CO is replaced by Cl^- on addition of conc. HCl [22]. It is also known that the $Mo_3NiS_4^{4+}$ cube in HCl does not react with C_2H_4 [23]. It follows therefore that CO does not react with $Mo_3NiS_4^{4+}$ in concentrated HCl solutions. However we find that CO coordinates to $Mo_3CoS_4^{4+}$ at 6 M HCl levels. Also CO will bind to $[MO_3(PdCl)S_4(H_2O)_9]^{3+}$ in place of Cl^-.

No loss of CO is observed on bubbling N_2 through $[Mo_3(CoCO)S_4(H_2O)_9]^{4+}$ for 15 min. It has also been concluded that there is no reversibility of the reaction with $[Mo_3(PdCO)S_4(H_2O)_9]^{4+}$. In the case of $Mo_3NiS_4^{4+}$ the reaction with CO is non-reversible while the reaction with C_2H_4 is reversible. [23]. No loss of CO was observed on bubbling N_2 through $[Mo_3(NiCO)\,Se_4(H_2O)_9]^{4+}$ for 15 min. However in equilibration kinetic studies on $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ with CO ($t_{1/2} > 1$ min) a contribution from the reverse reaction has been observed [9b]. No similar step was detected in stopped-flow equilibration studies on $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ with CO [10]. These observations indicate formation of thermodynamically stable CO complexes.

3.3. *Air stability of carbonyl products*

Both the single and double cube forms of $Mo_3CoS_4^{4+}$ are very air-sensitive, and a 2 M Hpts solution undergoes 88% decay in 1 h (monitored at 790 nm). However $[Mo_3(CoCO)S_4(H_2O)_9]^{4+}$ was found to be much more stable, with no absorbance change in air over 15 min. The Pd > Ni containing cubes are much more stable in air, with the Pd double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ requiring several months for full decay, and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ oxidised only ca. 15% in 1 month [9,10]. It has been reported that the carbonyl complexes $[M_3(NiCO)S_4(H_2O)_9]^{4+}$ (M = Mo, W) are more stable than the parent aqua form in air [22]. These observations are consistent with binding of O_2 at the heteroatom becoming more difficult when CO is present. [24]. The coordinated CO is less readily replaced than H_2O.

4. Discussion

In studies reported herein an H_2O (or Cl^-) coordinated to Group 9 (Co) or Group 10 (Ni, Pd) heteroatoms of the single cubes, is displaced by CO and reactions are complete (Co and Pd) well within the ca. 30 min required by Ni The heteroatoms have tetrahedral coordination with Mo_3M outer electron counts of 15 (Co) and 16 (Ni, Pd) A similar reaction is observed at the Ni of $[Mo_3NiSe_4(H_2O)_{10}]^{4+}$, and has been reported also for $[W_3NiS_4(H_2O)_{10}]^{4+}$, [22]. In the case of M = Co and Pd edge-linked double cubes have been identified. Because of the greater stability in air in the Pd case, both the single and double cubes are well characterised. [4]. It has been demonstrated that the reactions with CO occur equally well with single and edge-linked double cubes. Thus the reactions of CO with $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ (the Cl^- serves to retain the single cube) and $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ (in 2 M Hpts) are both rapid. No reaction is observed of CO with the 14 electron $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ or 17 electron $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ cubes. However the Cu cube in the higher oxidation state $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ has

16 metal electrons, and reacts with CO. The reaction proceeds somewhat differently with the formation of $[Mo_3S_4(H_2O)_9]^{4+}$ and release of aqua $Cu(CO)^+$. The equilibrium (Eq. (11))

$$Cu(CO)^+ \rightleftharpoons Cu^+ + CO \tag{11}$$

shifts to the right on bubbling N_2 through the solution, and recombination of the d^{10} Cu^+ with $[Mo_3S_4(H_2O)_9]^{4+}$ is rapid (Eq. (12)),

$$Mo_3S_4^{4+} + Cu^+ \rightarrow Mo_3CuS_4^{5+} \tag{12}$$

with high yields (ca. 90%) observed for reformation of the original cube.

While from X-ray crystallography it has been demonstrated that there is no Mo–M bonding in the single cubes Mo_3MS_4 (M = In [25], Ga [26], Sn [16]), or corner-shared double cubes Mo_6MS_8 (M = Hg [3], In [27], Sn [28], As [2], Sb [29]), with transition metals in that there is clearcut evidence for Mo–M bonding [2]. To obtain stable metal–carbonyl bonds σ-donation from the CO to the metal, and π-back bonding from the metal is normally required. Qualitative bonding schemes have been developed for the trinuclear $[Mo_3S_4(Cp')_3]^+$ and $[Mo_3S_4(CN)_9]^{5-}$ clusters [30,31]. Energy-level schemes have also been considered for transition-metal heterometal cubes $[Mo_3MS_4L_{10}]^{4+}$ containing MS_3L and $Mo_3S_4L_9$ fragments [1]. The d_{xz} and d_{yz} orbitals on M have a duel role and are involved in the formation of Mo–M bonds and in π backbonding to CO when the latter becomes coordinated. The metal framework of the cluster and CO are therefore in competition for electron density. It is this competition, and resultant weaker back donation to the carbonyl, that results in relatively high CO stretching frequencies [1]. Assignments $(Mo_3S_4^{4+})Ni^0$ and $(Mo_3S_4^{4+})Pd^0$ which are compatible with tetrahedral heteroatom geometries are therefore favoured rather than the earlier $(Mo_3S_4^{2+})Ni^{2+}$ and $(Mo_3S_4^{2+})Pd^{2+}$ assignments [4,19]. The behaviour of Co in $[Mo_3CoS_4(H_2O)_{10}]^{4+}$ is of interest because there are now only 15 metal electrons. This does not appear to decrease the affinity of the heterometal for CO binding. The cube reacts rapidly with both O_2 and CO. However in the case of the 14 electron cube $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ no CO binding to the Fe is observed.

Kinetic (k_f) and thermodynamic (K) data for the formation of $Mo_3(ML)S_4$ single cubes from the reaction of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ and $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ with L, including L = CO, provide interesting comparisons, Table 2 [9,10].Different reactions are implicated, as shown in Eqs. (13) and (14).

$$Mo_3(NiH_2O)S_4^{4+} + L \rightleftharpoons Mo_3(NiL)S_4^{4+} + H_2O \tag{13}$$

$$\{Mo_3PdS_4\}_2^{8+} + 2L \rightleftharpoons 2Mo_3(PdL)S_4^{4+} \tag{14}$$

with substitution of CO for H_2O occurring in Eq. (13), but cleavage of two inter-cube Pd–μ_3S bonds relevant in Eq. (14). Formation rate constants k_f for substitution of L = Cl^-, Br^-, I^- and NCS^- for H_2O in $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ lie in the narrow range 9.4–44 M^{-1} s^{-1} [9b]. Such behaviour is interpreted in terms of a dissociative interchange I_d mechanism [32]. The two water soluble phosphines PTA and $TPPTS^{3-}$ require a 3-fold extension of the above range. In contrast CO gives a value some 10 times smaller, attributed to its poor nucleophilic properties in competition with H_2O. All the results can be accounted for while retaining essential features of an I_d mechanism. The range of rate constants is ca. 10^3 times smaller than for the I_d water-exchange process on $[Ni(H_2O)_6]^{2+}$ [33] with every likelihood that an even bigger difference will hold for tetrahedral Ni^{II}, which has been little studied but is likely to be very labile. As far as Ni^0 substitution is concerned rate constants for ligand exchange on tetrahedral $[Ni(CO)_4]$ (2.0×10^{-2} M^{-1} s^{-1} in toluene) are much smaller [34]. An I_d mechanism is apparent for this reaction also. What emerges therefore from these studies is that Ni in the Mo_3NiS_4 cube has distinctive properties of its own and that the substitution rate constants k_f although supporting an I_d mechanism do not fall in any previously defined range for Ni. The Ni with its rather special coordination to three μ_3-S ligands behaves somewhere in the Ni^0 to Ni^{II} range. The properties displayed are quite acceptable for a Ni^0 assignment.

Square-planar substitution reactions of Pd^{II} complexes are some 10^5 faster than those of Pt^{II}, [35]. In the case of square-planar $[M(CN)_4]^{2-}$ complexes M = Ni, Pd, Pt, rate constants (M^{-1} s^{-1}, 24°C) for CN^- exchange are Ni ($> 5 \times 10^5$) > Pd (120) > Pt (26) [36] The rate constants (Table 2) for identical reactants L indicate an opposite trend with the double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ reacting faster than $[Mo_3NiS_4(H_2O)_{10}]^{4+}$. Conversion of $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ to two single cubes $[Mo_3(PdL)S_4(H_2O)_9]^{4+}$ is observed with the in-coming ligands L = CO, PTA, $TPPTS^{3-}$, Cl^-, Br^- and NCS^-. As far as the reaction of L with $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ are concerned, these occur with cleavage of first one and then the second Pd–μ_3S bond in (II), with the first step rate determining. The latter is rapid and at the limit of the stopped-flow range. [10].

The structure of $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ (II) from X-ray crystallography indicates some distortion at the Pd's with angles α as large as 120°, and β as small as 69°, [4]. This appears to be a contributing factor to the ca. 10^3 times faster reactions of the

Table 2
Summary of rate constants k_{Ni} and equilibrium constants K_{Ni} (25°C) for formation of $[Mo_3(NiL)(H_2O)_9]^{4+}$ from $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, and corresponding parameters k_{Pd} and K_{Pd} for the formation of $[Mo_3(PdL)S_4(H_2O)_9]^{4+}$ from $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ [a]

L	k_{Ni} (M^{-1} s^{-1})[b]	K_{Ni} (M^{-1})[b]	k_{Pd} (M^{-1} s^{-1})[c]	K_{Pd} (M^{-1})[c]
CO	0.66	5150	1.11×10^3	$> 5 \times 10^3$
PTA	119	2040	27.8×10^3	
TPPTS	58	8900	9.6×10^3	
Cl^-	9.4	97	$> 10^3$	490
Br^-	14.6	150	Very fast	8040
I^-	32.3			
NCS^-	44	690	Very fast	630

[a] I = 2.00 M ($LiClO_4$) for Ni, and 2.00 M (Lipts) for Pd.

[b] Terms k_f and K are used in reference [9].

[c] Terms k_f and K are used in reference [10]; K_{Pd} is defined by the equation $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+} + 2L \rightleftharpoons 2[Mo_3(PdL)S_4(H_2O)_9]^{4+}$.

Pd double cube in Eq. (14). As with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ the rate constant for the reaction of CO is an order of magnitude slower than for other L ligands. Formation constants *K* for $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ with L indicate a preference for L complexing to Pd over H_2O which is not able to retain the single cube. Thus an order of stability $Mo_3(PdL)S_4^{4+} > \{Mo_3PdS_4\}_2^{8+} > Mo_3(PdH_2O)S_4^{4+}$ is indicated. In e.g. the Cl^- reaction cleavage of Pd–μ_3S inter-cube bonds and coordination of Cl^- occurs. This appears to conflict with the classic octahedral Co^{III} example (Eq. (15)),

$$[Co(NH_3)_5NO_3]^{2+} + NCS^- \rightarrow [Co(NH_3)_5NCS]^{2+} + NO_3^- \qquad (15)$$

in which reaction proceeds by replacement of NO_3^- by H_2O and then H_2O by NCS^-, with little or no direct replacement of one anion by another, [37]. The less crowded tetrahedral Pd is no doubt an important factor. The lack of information on single/double cube equilibria, as well as the high air sensitivity, has so far prevented kinetic studies on $Mo_3CoS_4^{4+}$.

To summarise, a comparatively narrow range of heterometal Mo_3MS_4 cubes with M = Co, Ni, Pd are able to bind CO and participate in the chemistry described. The higher oxidation state 16e$^-$ cube $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ also reacts with CO, but in a somewhat different way with release of $Cu(CO)^+$. Kinetic and thermodynamic studies on the single cube $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, and the edge-linked double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$, with CO and other ligands have been carried out. The stability and interconversion of the single and double cubes has been addressed in the case of $Mo_3PdS_4^{4+}$. The behaviour of the Ni clusters $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ and $\{MoNiSe_4(H_2O)_{10}]^{4+}$ is very similar.

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