

# A New Series of Homologous Cluster Complexes $[\text{Mo}_3(\text{M}'\text{EPh}_3)\text{Q}_4\text{Cl}_4(\text{H}_2\text{O})_5]$ ( $\text{M}' = \text{Ni}, \text{Pd}$ ; $\text{E} = \text{P}, \text{As}, \text{Sb}$ ; $\text{Q} = \text{S}, \text{Se}$ )

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Cluster aqua complexes  $[\text{Mo}_3(\text{M}'\text{Cl})\text{S}_4(\text{H}_2\text{O})_9]^{3+}$  ( $\text{M}' = \text{Ni}, \text{Pd}$ ) react with  $\text{EPh}_3$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ) in  $\text{HCl}/\text{CH}_3\text{OH}$  to give neutral  $[\text{Mo}_3(\text{M}'\text{EPh}_3)\text{S}_4\text{Cl}_4(\text{H}_2\text{O})_5]$  ( $\text{M}' = \text{Pd}, \text{E} = \text{P}$  (**1**),  $\text{E} = \text{As}$  (**2**),  $\text{E} = \text{Sb}$  (**3**);  $\text{M}' = \text{Ni}, \text{E} = \text{P}$  (**4**),  $\text{E} = \text{As}$  (**5**);  $\text{E} = \text{Sb}$  (**6**)).  $[\text{Mo}_3(\text{PdPPh}_3)\text{Se}_4\text{Cl}_4(\text{H}_2\text{O})_5]$  (**7**) was also obtained. X-ray crystal structures were determined for **3**, **4** and **5**. The role of supramolecular interactions in crystal packing is discussed. ESI-MS spectra

were also studied and were used to follow the coordination of the solvent molecules at Mo sites and to assess relative strength of bonding in the clusters. Thermal properties were studied for **4** and **5**.

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## Introduction

The extensive family of cuboidal clusters with a tetrahedral  $\text{M}_4$  core,  $\text{M}_3\text{M}'\text{Q}_4$  (where  $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Q} = \text{S}, \text{Se}$ ;  $\text{M}'$  can be one of more than 20 transition or post-transition metals) has attracted interest because it provides a good opportunity to study how the metal-metal bonding and reactivity at metal centres are affected by changes in the nature of  $\text{M}$ ,  $\text{M}'$  and  $\text{Q}$ .<sup>[1]</sup> The bioinorganic significance of metal sulfide clusters is well known, and it has been put forward that the  $\text{Mo}_3\text{M}'\text{S}_4$  ( $\text{M}' = \text{Co}, \text{Ni}$ ) clusters in particular can constitute molecular models for the active sites of the industrial heterogeneous  $\text{Co}/\text{MoS}_2$  or  $\text{Ni}/\text{MoS}_2$  catalysts.<sup>[2]</sup> The  $\text{Mo}_3\text{PdS}_4^{4+}$  clusters catalyze nucleophilic addition to alkynes<sup>[3]</sup> and  $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$  has proved to be efficient in various heterogeneous catalytic processes.<sup>[4,5]</sup> Recently it was found that the heterometal in  $\text{M}_3\text{M}'\text{S}_4^{4+}$  clusters ( $\text{M} = \text{Mo}, \text{W}$ ; heterometal ( $\text{M}'$ ) =  $\text{Ni}, \text{Pd}$ ) stabilize very labile molecules of  $\text{P}(\text{OH})_3$ ,  $\text{RP}(\text{OH})_2$  ( $\text{R} = \text{H}, \text{Ph}$ ) and  $\text{Ph}_2\text{P}(\text{OH})$  by coordination at phosphorus<sup>[6–8]</sup>. Nonlinear optical properties of  $[\text{M}_3(\text{CuX})\text{Q}_4(\text{dmpe})_3\text{X}_3]\text{PF}_6$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{Q} = \text{S}, \text{Se}$ ) were also studied.<sup>[9]</sup>

A rational synthesis of these clusters is based on an addition of a heterometal in a low oxidation state (or even  $\text{M}'^0$ ) to the trinuclear complexes with the  $\text{M}_3\text{Q}_4^{4+}$  cores. Especially productive are incorporations into the aqua complexes  $[\text{M}_3\text{Q}_4(\text{H}_2\text{O})_9]^{4+}$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Q} = \text{S}, \text{Se}$ )<sup>[10]</sup> into the complexes with diphosphanes such as  $[\text{M}_3\text{Q}_4(\text{dmpe})_3\text{X}_3]^+$ ,<sup>[9,11]</sup> and  $[\text{M}_3\text{S}_4\text{Cp}'_3]^+$  ( $\text{Cp}' = \text{methylcyclopenta-}$

dienyl).<sup>[12–14]</sup> Dithiophosphates, dithiophosphinates, and dithiocarbamates  $[\text{M}_3\text{S}_4(\text{RO})_2\text{PS}_2)_4\text{L}]$ ,  $[\text{M}_3\text{S}_4(\text{R}_2\text{PS}_2)_4\text{L}]$ ,  $[\text{M}_3\text{S}_4(\text{R}_2\text{NCS}_2)_4\text{L}]$  were used for incorporation of  $\text{Cu}^{\text{I}}$  (and  $\text{d}^{10}\text{s}^2$ -post-transition metal ions).<sup>[15]</sup> Metal incorporation into the aqua complexes has been most widely used and it was found that even a noble metal, Pd (taken as Pd black), reacts with  $[\text{Mo}_3\text{Q}_4(\text{H}_2\text{O})_9]^{4+}$  in  $\text{HCl}$  to give  $[\text{Mo}_3(\text{PdCl})\text{Q}_4(\text{H}_2\text{O})_9]^{3+}$  ( $\text{Q} = \text{S}, \text{Se}$ ).<sup>[16,17]</sup> Extensive aqueous solution chemistry of these clusters has been reviewed.<sup>[10]</sup> The crystallization problems are efficiently dealt with by using *p*-toluenesulfonate as a counterion, and by formation of well-defined supramolecular complexes with cucurbit[6]-uril.<sup>[10]</sup> However, ligand substitution has not been widely used so far for the isolation of the heterometallic clusters from aqueous solutions. A few examples are transformation of  $[\text{Mo}_3(\text{PdCl})\text{S}_4(\text{H}_2\text{O})_9]^{3+}$  into  $[\text{Mo}_3(\text{PdCl})\text{S}_4(\text{tacn})_3]^{3+}$ <sup>[16]</sup> and  $[\text{Mo}_3(\text{Pd}(\text{dppe}))\text{S}_4(\text{dppe})_3\text{Cl}_3\text{Cl}]^{18}, and of  $[\text{Mo}_3(\text{NiCl})\text{S}_4(\text{H}_2\text{O})_9]^{3+}$  into  $[\text{Mo}_3(\text{NiCl})\text{S}_4(\text{dppe})_3\text{Cl}]^{18}. Substitution of water ligands by nitrylotriacetate ( $\text{nta}^{3-}$ ) is also possible and was used to prepare  $[\text{Mo}_3(\text{CuCl})\text{S}_4(\text{Hnta})_3]^{2-}$  and  $[\text{Mo}_3(\text{NiCl})\text{S}_4(\text{Hnta})(\text{nta})_2]^{5-}$ .<sup>[19,20]</sup> This scarcity may be attributed to enhanced lability of the cluster cores upon changing the coordination environment, which leads to the loss of the heterometal. Increasing of pH, necessary for complexation of various ligands, may have the same effect, as well as cause undesirable hydrolysis.$$

Here we report facile synthesis and structural characterization of a family of cluster complexes,  $[\text{Mo}_3(\text{M}'\text{EPh}_3)\text{Q}_4\text{Cl}_4(\text{H}_2\text{O})_5]$  ( $\text{M}' = \text{Ni}, \text{Pd}$ ;  $\text{E}' = \text{P}, \text{As}, \text{Sb}$ ;  $\text{Q} = \text{Se}$ ), obtained by adding  $\text{EPh}_3$  to solutions of  $[\text{Mo}_3(\text{M}'\text{Cl})\text{Q}_4(\text{H}_2\text{O})_9]^{3+}$  in  $\text{HCl}/\text{CH}_3\text{OH}$  mixtures. These products are air-stable, soluble in polar organic solvents and are convenient starting materials for introduction of various ligands into the cluster coordination sphere.

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## Results and Discussion

## Synthesis

Addition of methanolic solutions of  $\text{EPh}_3$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ) to the solutions of  $[\text{Mo}_3(\text{M}'\text{Cl})\text{S}_4(\text{H}_2\text{O})_9]^{3+}$  ( $\text{M}' = \text{Ni}, \text{Pd}$ ) in  $\text{HCl}$  produces characteristic color changes to brown in the case of  $\text{Pd}$ , and to various shades of blue in the case of  $\text{Ni}$ . Methanol enhances the ligand solubilities and is essential for the reaction, which does not take place without it. It is worth mentioning that under the employed conditions, no substitution at the  $\text{Mo}$  atoms takes place. Slow evaporation of methanol from resulting solutions leads to crystallization of the neutral complexes **1–7**. However, the  $^{31}\text{P}$  NMR spectroscopic monitoring of the complexation shows that in the reaction solutions of  $[\text{Mo}_3(\text{PdCl})\text{S}_4(\text{H}_2\text{O})_9]^{3+} + \text{PPh}_3$  (**1a**),  $[\text{Mo}_3(\text{PdCl})\text{Se}_4(\text{H}_2\text{O})_9]^{3+} + \text{PPh}_3$  (**7a**) and  $[\text{Mo}_3(\text{NiCl})\text{S}_4(\text{H}_2\text{O})_9]^{3+} + \text{PPh}_3$  (**4a**) three closely spaced singlets are observed in each case: at  $\delta = 31.6, 32.5$  and  $33.4$  ppm for **1a**,  $31.3, 32.2$  and  $33.3$  ppm for **7a**, and at  $\delta = 39.7, 40.7$  and  $41.9$  ppm for **4a**. This can be explained by the formation of either different isomers or of several species  $[\text{Mo}_3(\text{M}'\text{PPh}_3)\text{S}_4(\text{H}_2\text{O})_{9-x}\text{Cl}_x]^{(4-x)+}$  in solution, that are sufficiently kinetically inert in the NMR time-scale. Note the high-field shift on going from  $\text{Ni}$  to  $\text{Pd}$ , just as was observed for corresponding  $\text{Cp}$  derivatives.<sup>[12]</sup>

The electronic spectra show little, if any, dependence on the change of  $\text{EPh}_3$ , but there is a strong hypsochromic shift on going from  $\text{Ni}$  to  $\text{Pd}$ . The complexes are air stable, soluble in common organic solvents, and slowly, but completely soluble in water, apparently undergoing a hydrolytic decomposition.

ESI-MS Spectrum of  $[\text{Mo}_3(\text{M}'\text{EPh}_3)\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4]$  ( $\text{M}' = \text{Ni}, \text{Pd}$ ;  $\text{E} = \text{P}, \text{As}, \text{Sb}$ )

Electrospray mass spectrometry (ES-MS) is becoming a valuable tool for the investigation of coordination compounds allowing the study of solution speciation,<sup>[21]</sup> formation of aggregates,<sup>[22,23]</sup> or identification of major and minor products in solutions on a microscale,<sup>[24]</sup> since it allows pre-existing ions to be transferred into the gas phase with minimal fragmentation. Applications to a number of inorganic and organometallic systems have demonstrated the versatility of the technique.<sup>[25]</sup> In this work we have studied the family of cuboidal cluster complexes  $[\text{Mo}_3(\text{M}'\text{EPh}_3)\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4]$  ( $\text{M}' = \text{Ni}, \text{Pd}$ ;  $\text{E} = \text{P}, \text{As}, \text{Sb}$ ) by ESI-MS in the  $400\text{--}1100$   $m/z$  range in methanol. All compounds **1–7** show similar fragmentation pathways, although the relative intensities of the fragmentation peaks depend on the nature of the incorporated heterometal  $\text{M}'$ . Figure 1 shows the ESI-MS for compound **5** in methanol at different cone voltages.

The ionisation of these neutral complexes takes place by the loss of one chloride ligand and is accompanied by complete replacement of the coordinated water molecules by methanol except for compound **7** where only a partial substitution is found (see Table 1). A typical pattern is shown in Figure 1 (illustrated here by complex **5**): at low cone voltages a peak corresponding to the  $[\text{Mo}_3(\text{Ni}(\text{AsPh}_3))\text{S}_4(\text{CH}_3\text{OH})_6\text{Cl}_3]^+$  ion ( $m/z = 1078$  a.m.u.) is detected, where the vacant position left by the chloride ion is replaced by methanol keeping the octahedral environment around the molybdenum atoms. Additional peaks due to the sequential loss of methanol molecules are also present, even

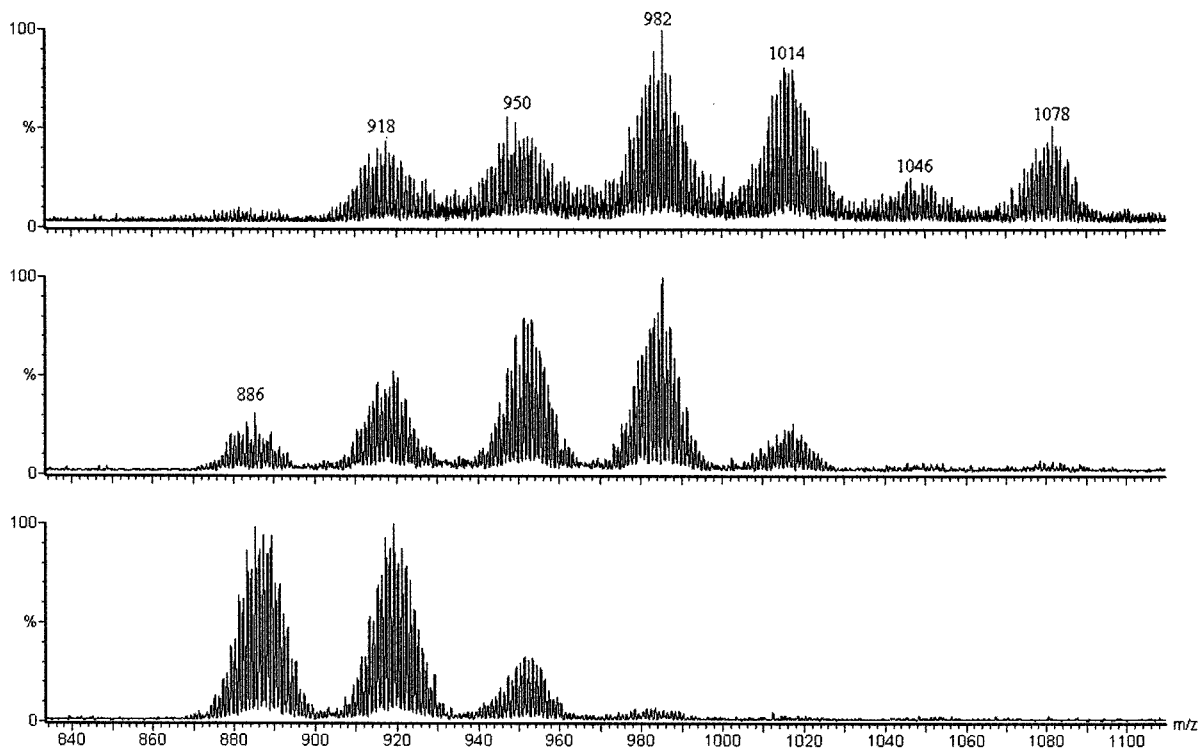


Figure 1. ESI-MS spectra of compound **5** at 10 V (top), 30 V (medium) and 50 V (bottom).

at 10 V (Figure 1 top). Increasing the cone voltage results in the consecutive losses of methanol molecules (Figure 1, bottom) up to 80 V, where the neutral  $\text{EPH}_3$  is also lost. The cluster core  $[\text{Mo}_3\text{M}'\text{S}_4]$  does not fragment under these experimental conditions as is also seen for the  $[\text{Mo}_3\text{Q}_4(\text{dmpe})_3\text{Cl}_3]^+$ ,  $[\text{Mo}_3\text{M}'\text{Q}_4(\text{dmpe})_3\text{Cl}_3]^+$  ( $\text{Q} = \text{S}, \text{Se}$ ;  $\text{M}' = \text{Ni}, \text{Co}$ ) complexes demonstrating robustness of the  $\text{Mo}_3\text{Q}_4$  and  $\text{Mo}_3\text{M}'\text{Q}_4$  cluster units.<sup>[11,26–28]</sup> Additional experiments using  $\text{CH}_3\text{CN}$  or THF as solvents resulted in substitution of water molecules by acetonitrile in the former case, analogously as described for methanol, whereas no substitution is observed for THF. Thus the qualitative order of substitution of coordinated water molecules in the large excess of another solvent is  $\text{CH}_3\text{OH} \approx \text{CH}_3\text{CN} \gg \text{THF}$ .

Table 1. Listing of the ions detected upon increasing the cone voltage for compounds 1–7.

	Chemical composition of the ions	Main ion peak (a.m.u.) and intensity at 50 V and 30 V
1	$[\text{Mo}_3(\text{PdPPh}_3)_4\text{Cl}_3]^+$	891 (100) (87)
	$[\text{Mo}_3(\text{PdPPh}_3)_4(\text{MeOH})\text{Cl}_3]^+$	923 (72) (100)
	$[\text{Mo}_3(\text{PdPPh}_3)_4(\text{MeOH})_2\text{Cl}_3]^+$	955 (34) (86)
	$[\text{Mo}_3(\text{PdPPh}_3)_4(\text{MeOH})_3\text{Cl}_3]^+$	987 (15) (28)
2	$[\text{Mo}_3(\text{PdAsPh}_3)_4\text{Cl}_3]^+$	934 (100) (51)
	$[\text{Mo}_3(\text{PdAsPh}_3)_4(\text{MeOH})\text{Cl}_3]^+$	966 (73) (100)
	$[\text{Mo}_3(\text{PdAsPh}_3)_4(\text{MeOH})_2\text{Cl}_3]^+$	998 (23) (84)
	$[\text{Mo}_3(\text{PdAsPh}_3)_4(\text{MeOH})_3\text{Cl}_3]^+$	1030 (27)
3	$[\text{Mo}_3(\text{PdSbPh}_3)_4\text{Cl}_3]^+$	982 (100) (49)
	$[\text{Mo}_3(\text{PdSbPh}_3)_4(\text{MeOH})\text{Cl}_3]^+$	1014 (59) (100)
	$[\text{Mo}_3(\text{PdSbPh}_3)_4(\text{MeOH})_2\text{Cl}_3]^+$	1046 (20) (70)
	$[\text{Mo}_3(\text{PdSbPh}_3)_4(\text{MeOH})_3\text{Cl}_3]^+$	1078 (20)
4	$[\text{Mo}_3(\text{NiPPh}_3)_4\text{Cl}_3]^+$	843 (84) (16)
	$[\text{Mo}_3(\text{NiPPh}_3)_4(\text{MeOH})\text{Cl}_3]^+$	875 (100) (41)
	$[\text{Mo}_3(\text{NiPPh}_3)_4(\text{MeOH})_2\text{Cl}_3]^+$	907 (39) (68)
	$[\text{Mo}_3(\text{NiPPh}_3)_4(\text{MeOH})_3\text{Cl}_3]^+$	939 (11) (100)
5	$[\text{Mo}_3(\text{NiPPh}_3)_4(\text{MeOH})_4\text{Cl}_3]^+$	971 (6) (25)
	$[\text{Mo}_3(\text{NiAsPh}_3)_4\text{Cl}_3]^+$	886 (98) (38)
	$[\text{Mo}_3(\text{NiAsPh}_3)_4(\text{MeOH})\text{Cl}_3]^+$	918 (100) (54)
	$[\text{Mo}_3(\text{NiAsPh}_3)_4(\text{MeOH})_2\text{Cl}_3]^+$	950 (35) (95)
6	$[\text{Mo}_3(\text{NiAsPh}_3)_4(\text{MeOH})_3\text{Cl}_3]^+$	982 (5) (100)
	$[\text{Mo}_3(\text{NiAsPh}_3)_4(\text{MeOH})_4\text{Cl}_3]^+$	1014 (32)
	$[\text{Mo}_3(\text{NiSbPh}_3)_4\text{Cl}_3]^+$	934 (76) (40)
	$[\text{Mo}_3(\text{NiSbPh}_3)_4(\text{MeOH})\text{Cl}_3]^+$	966 (100) (58)
7	$[\text{Mo}_3(\text{NiSbPh}_3)_4(\text{MeOH})_2\text{Cl}_3]^+$	998 (42) (54)
	$[\text{Mo}_3(\text{NiSbPh}_3)_4(\text{MeOH})_3\text{Cl}_3]^+$	1030 (11) (100)
	$[\text{Mo}_3(\text{NiSbPh}_3)_4(\text{MeOH})_4\text{Cl}_3]^+$	1062 (5) (52)
7	$[\text{Mo}_3(\text{PdPPh}_3)_4\text{Se}_4\text{Cl}_3]^+$	1078 (100) (98)
	$[\text{Mo}_3(\text{PdPPh}_3)_4\text{Se}_4(\text{MeOH})\text{Cl}_3]^+$	1010 (42) (100)
	$[\text{Mo}_3(\text{PdPPh}_3)_4\text{Se}_4(\text{MeOH})(\text{H}_2\text{O})\text{Cl}_3]^+$	1028 (60) (69)

It is well known that the efficiency of the ionization varies with the ion size and in our study only minor changes are expected based on the similar charge and size of the complexes 1–7. Therefore, we assume that the ratios of the apparent intensities of each peak are proportional to the relative abundance of the corresponding species. In order to obtain some insight into the energetics of the molybdenum–solvent bonds, we have analyzed the relative intensity of the different fragments obtained upon increasing the cone voltage from 30 V to 50 V to establish qualitatively how the nature of  $\text{M}'$ ,  $\text{E}$  and  $\text{Q}$  affects the binding energy of the  $\text{Mo}-\text{O}_{(\text{MeOH})}$  bond. Table 1 shows the ions detected and the

peak intensities at 30 and 50 V for sample solutions in methanol.

Clusters containing nickel (4–6) all show as base peaks  $[\text{Mo}_3(\text{NiEPH}_3)_4\text{S}_4(\text{MeOH})_3\text{Cl}_3]^+$  and  $[\text{Mo}_3(\text{NiEPH}_3)_4\text{S}_4(\text{MeOH})\text{Cl}_3]^+$  at 30 and 50 V, respectively, whereas the palladium derivatives 1–3,7 show  $[\text{Mo}_3(\text{PdEPH}_3)_4\text{S}_4(\text{MeOH})\text{Cl}_3]^+$  at 30 V and  $[\text{Mo}_3(\text{PdEPH}_3)_4\text{Q}_4\text{Cl}_3]^+$  at 50 V under identical conditions. These experimental observations clearly show that the binding  $\text{Mo}-\text{MeOH}$  energy is affected by the nature of the heterometal that is incorporated, which then interacts with the molybdenum atoms by direct metal–metal bonding. In particular the  $\text{Mo}-\text{MeOH}$  bond in the palladium derivatives is more prone to rupture than in the nickel analogs. In contrast, no clear tendency is observed upon substitution of either the  $\text{PPh}_3$ ,  $\text{AsPh}_3$  and  $\text{SbPh}_3$  nor the chalcogen atom (in the case of the  $\text{PdPPh}_3$  derivatives 1 and 7).

### Crystal Structures of $[\text{Mo}_3(\text{M}'\text{EPH}_3)_4\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4] \cdot n\text{H}_2\text{O}$ ( $\text{M}' = \text{Ni}, \text{Pd}$ ; $\text{E} = \text{P}, \text{As}, \text{Sb}$ )

The structures of the compounds 3, 4 and 5 have been determined by single-crystal X-ray diffraction. They all crystallize in the same triclinic space group  $P-1$  and share the structural features with previously reported  $[\text{Mo}_3(\text{PdPPh}_3)_4\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4] \cdot 3\text{H}_2\text{O} \cdot 0.5\text{CH}_3\text{OH}$  (1).<sup>[6]</sup> Figure 2 shows the structure of the neutral complex  $[\text{Mo}_3(\text{NiAsPh}_3)_4\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4] \cdot 3\text{H}_2\text{O}$  (5), with the atom numbering Scheme.

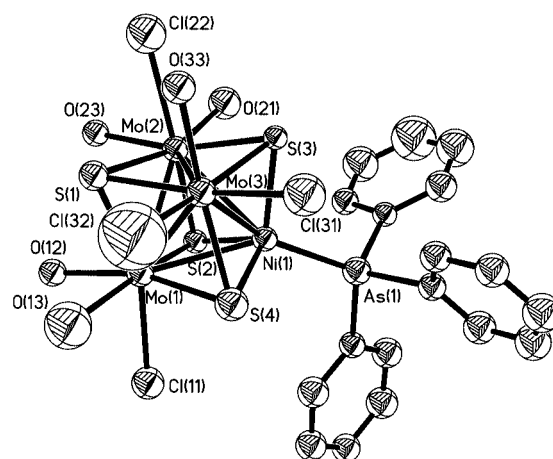


Figure 2. ORTEP representation (50% ellipsoid probability) of the neutral complex 5 with the atom numbering scheme.

The cluster core consists of a slightly distorted tetrahedral arrangement of one nickel/palladium and three molybdenum atoms. Each tetrahedral face is capped by a  $\mu_3$ -coordinated sulfide ligand thus generating a cubanelike structure. The coordination sphere on one molybdenum atom is completed by one water molecule and two chlorine atoms while the two remaining molybdenum atoms fill their octahedral environment with two water molecules and one chlorine atom. Cl(31) and Cl(11) are *trans* to the unique S(1) atom, while Cl(32) and Cl(22) occupy *cis*-positions. It is re-

Table 2. Selected averaged bond lengths [ $\text{\AA}$ ] for compounds **1**, **3**, **4** and **5**.<sup>[a]</sup>

	Mo–Mo av.	Mo–M' av.	M'–E	Ref.
[Mo <sub>3</sub> Pd(PPh <sub>3</sub> ) <sub>4</sub> Cl <sub>4</sub> (H <sub>2</sub> O) <sub>5</sub> ] $\cdot$ 3 H <sub>2</sub> O ( <b>1</b> )	2.745[4]	2.81[1]	2.292(2)	[6]
[Mo <sub>3</sub> Pd(SbPh <sub>3</sub> ) <sub>4</sub> Cl <sub>4</sub> (H <sub>2</sub> O) <sub>5</sub> ] $\cdot$ 3 H <sub>2</sub> O ( <b>3</b> )	2.759[2]	2.788[8]	2.528(2)	this work
[Mo <sub>3</sub> Ni(PPh <sub>3</sub> ) <sub>4</sub> Cl <sub>4</sub> (H <sub>2</sub> O) <sub>5</sub> ] $\cdot$ 3 H <sub>2</sub> O ( <b>4</b> )	2.755[3]	2.68[1]	2.197(9)	this work
[Mo <sub>3</sub> Ni(AsPh <sub>3</sub> ) <sub>4</sub> Cl <sub>4</sub> (H <sub>2</sub> O) <sub>5</sub> ] $\cdot$ 2.5 H <sub>2</sub> O ( <b>5</b> )	2.763[2]	2.663[9]	2.272(2)	this work
[( $\eta^5$ -Cp') <sub>3</sub> Mo <sub>3</sub> Ni(AsPh <sub>3</sub> ) <sub>4</sub> ][pts]	2.833[5]	2.699[5]	2.255(1)	[12]
[( $\eta^5$ -Cp') <sub>3</sub> Mo <sub>3</sub> Ni(PPh <sub>3</sub> ) <sub>4</sub> ][pts]	2.831[4]	2.718[8]	2.160(2)	[13]
[( $\eta^5$ -Cp') <sub>3</sub> Mo <sub>3</sub> Pd(PPh <sub>3</sub> ) <sub>4</sub> ][pts]	2.836[4]	2.864[8]	2.277(1)	[13]

[a] Averaged values are given in square brackets.

markable that from several possible geometric isomers expected from various ways of occupying nine coordination sites available to four chloride ligands, only one is realised in **1**, **3**, **4** and **5**. This is most probably dictated by packing requirements, which lead to formation of large channels, defined by Cl $\cdots$ H<sub>2</sub>O hydrogen bonds (Figure 4, see the discussion below). Three bridging sulfur atoms and the EPh<sub>3</sub> ligand define the tetrahedral environment on the heterometal. The tetrahedral coordination is severely distorted due to a bending of EPh<sub>3</sub> ligands to one side. This distortion is strongest in **3**, where the angles around Pd vary from 103.3(2) to 118.3(4)°. The geometries of the cuboidal units [Mo<sub>3</sub>M'S<sub>4</sub>] (M' = Pd, Ni) in the crystal structures determined in this work are similar to those found in other related complexes. Table 2 shows the most relevant bond lengths within the cluster unit together with those of previously reported structures.

The Mo–Mo bond lengths are consistent with single bonds between metal atoms and no significant differences are detected upon changing either the heterometal M' or the EPh<sub>3</sub> fragment. However an increase of ca. 0.08  $\text{\AA}$  is observed by replacement of the Mo-bonded ligands, water and chloride, by the Cp' groups. The Mo–Ni and Mo–Pd bond lengths are slightly shorter on going from P to Sb, but again the largest difference is due to the substitution of the Mo-bonded ligands, the  $\eta^5$ -Cp' derivatives having the longest Mo–M' (by ca. 0.04  $\text{\AA}$ ) bonds. The Mo–M' and M'–E bonds regularly expand on going from nickel to palladium (0.18  $\text{\AA}$  for complexes **1** and **4**) and from P to Sb as expected, due to the increase in the covalent radii. The same tendency has been described previously for the isostructural family [M<sub>3</sub>(M'EPh<sub>3</sub>)<sub>4</sub>( $\eta^5$ -Cp')][pts] (M = Mo, W; M' = Ni, Pd, Pt; E = P, As).<sup>[12,13]</sup>

### Supramolecular Structure and Thermal Properties

A current challenge of crystal engineering is to control the assembly and orientation of solid-state structures in three dimensions.<sup>[29,30]</sup> This task is of a great complexity because the ionic/molecular building blocks can adopt a vast number of conformations in the crystal, thus making structural predictions extremely difficult. Covalent interactions or supramolecular connections (such as hydrogen bonds or  $\pi$ – $\pi$  interactions) have been widely used to prepare coordination polymers and much effort has been devoted to control and predict the assembled motifs.<sup>[31–33]</sup> In this

context it appears that compounds **1**, **3**, **4** and **5** are promising candidates to form supramolecular networks since they contain: a) five strong hydrogen-bond donors (water molecules); b) four strong electronegative atoms (chlorine) which are capable of propagating networks through Cl $\cdots$ Cl or Cl $\cdots$ H<sub>2</sub>O interactions;<sup>[34]</sup> c) an organic part consisting of three phenyl rings which can expand the network by  $\pi$ – $\pi$  interactions. These three potential sources of interactions, which can play a significant and predictable structure-determining role, can be grouped based on their hydrophilic (points a and b) or hydrophobic (point c) nature. Both functionalities (hydrophilic and hydrophobic) are located at opposite ends of the discrete molecular cluster, thus we can anticipate that the resulting supramolecular network will be expanded by bringing face to face ends of a similar nature.

A detailed analysis of the packing of neutral complexes **1**, **3**, **4** and **5** shows that all of them are expanded in the crystalline lattice through  $\pi$ – $\pi$  interactions (from the organic end) and short Cl $\cdots$ H<sub>2</sub>O contacts (both from the outer water ligands and water of crystallization) as will be described below. Regarding the organic part, it is well known that molecules containing PPh<sub>3</sub> ligands and PPh<sub>4</sub><sup>+</sup> cations commonly associate in crystals in different supramolecular patterns such as the sextuple phenyl embrace (SPE).<sup>[35,36]</sup> The source of the substantial attraction in these motifs is the interaction between phenyl groups where three types of pair-wise phenyl-phenyl configurations are recognized, namely the offset face-to-face **off**, edge-to-face **ef**, vertex-to-face **vf** and intermediate situations between these three configurations. The intermolecular structure of compounds **1**, **3**, **4** and **5** shows centrosymmetrical dimers formed by  $\pi$ – $\pi$  interactions involving the phenyl rings through one offset face-to-face and two vertex-to-face interactions as depicted in Figure 3, a) for compound **5**.

Following the nomenclature introduced by Dance et al. this supramolecular motif belongs to the parallel quadruple phenyl embrace **PQPE** type. The values of the intercentroid distances between phenyl groups are 4.27 and 6.05  $\text{\AA}$  for the **off** and **vf** configurations (similar values are observed for complexes **1**, **3** and **4**) which are comparable to those published by Dance in his comprehensive structural report.<sup>[36]</sup> These dimers are further connected along the three crystallographic axes through weaker additional  $\pi$ – $\pi$  interactions with **off**, **vf** and **ef** configurations. Even though these secondary interactions are weaker than those of PQPE type, the intercentroid distances between the phenyl



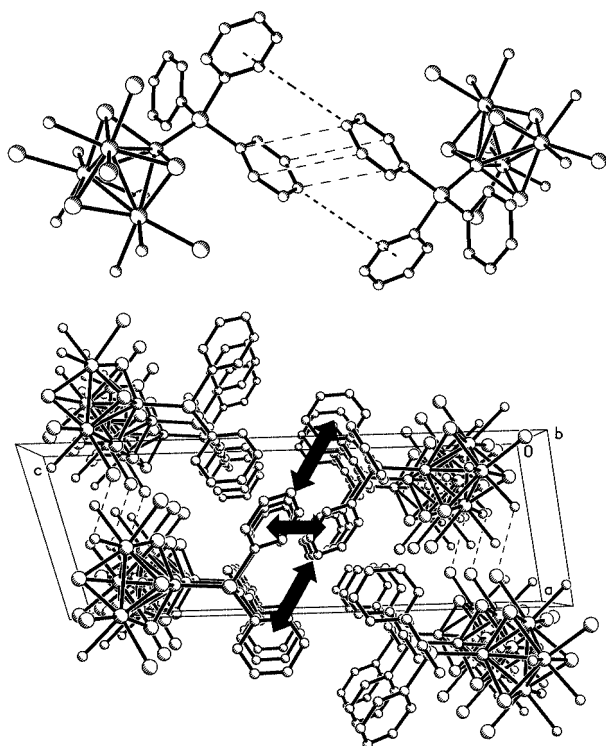


Figure 3. (a) PQPE type configuration of the phenyl rings where dashed lines show the **off** and the **vf** contacts. (b) View across the *ac* plane emphasizing the phenyl ring interactions (PQPE type contacts are shown by black narrows) which lead to the formation of organic columns along the *a* direction.

rings are below 8 Å and also contribute to the stabilization of organic columns as shown in Figure 3, b).

These well-defined  $\pi$ - $\pi$  interactions force the cluster discrete units to arrange one to each other forming columns, thus applying a key constraint for the accommodation of the remaining molecules in the solid-state structure. As a consequence of this constraint, the remaining molecules are also forced to reproduce this arrangement, and to direct the hydrophilic ends in such a way that additional short contacts between chlorine and water molecules, either of crystallization or coordinated to molybdenum atoms, arise. This arrangement also expands the solid structure through the three dimensions leaving hydrophilic cavities running along *a* and *b* axes. The complementarity of both packing principles leads to a supramolecular 3D network formed by segregated inorganic-organic columns where the water molecules of crystallization are accommodated in the hydrophilic cavities as shown in Figure 4.

Recently, the importance of preparing porous solids where labile terminal ligands are present pointing toward the center of the voids has been outlined. This makes them susceptible to both dissociation and evacuation from the pores, thereby producing periodically unsaturated open-metal sites to allow the study of metal site reactivity.<sup>[30,37]</sup> In order to evaluate this possibility, TGA-measurements for compounds **4** and **5**, representative of the whole family, were carried out in the 25–200 °C range (Figure 5), coupled with monitoring the peak at  $m/z = 18$  a.m.u. during the

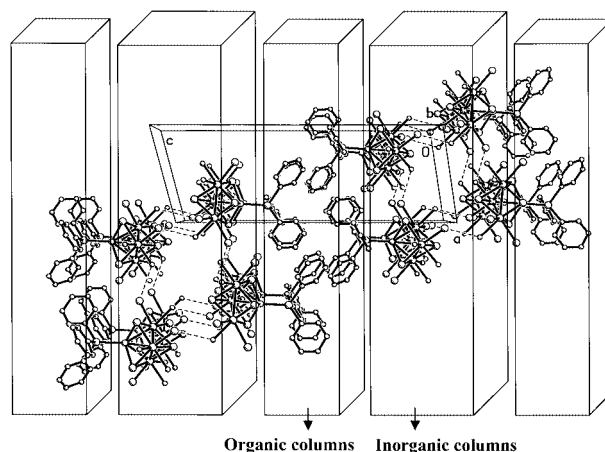


Figure 4. Supramolecular 3D network showing the alternate organic-inorganic columns and the voids left by the inorganic part.

thermal process by mass-spectroscopy. The first weight loss step (3.9% and 4.4% for **4** and **5**, respectively) at 25–80 °C corresponds to the loss of water of crystallization, which closely matches the percentage of water calculated from the X-ray structure determinations (4.6% and 5.3% for compounds **4** and **5**, respectively). The second weight loss of 8.1% and 7.8% (8.5% and 9.2% calculated from the X-ray analysis) for compounds **4** and **5**, respectively, between 100–150 °C is attributed to the loss of water molecules coordinated to molybdenum atoms. Simultaneously, XPD experiments at different temperatures for compound **5** showed a gradual lost of crystallinity from 25 to 250 °C to yield an amorphous solid above 150 °C clearly showing that the 3D network collapses. The low thermal stability of these compounds can be attributed to the evacuation of water molecules belonging to the cluster units, which as mentioned before connect the discrete molecular clusters along the three crystallographic axes and therefore are essential for the support of the 3D network. In this context it would be interesting to study the effect on the thermal stability upon replace-

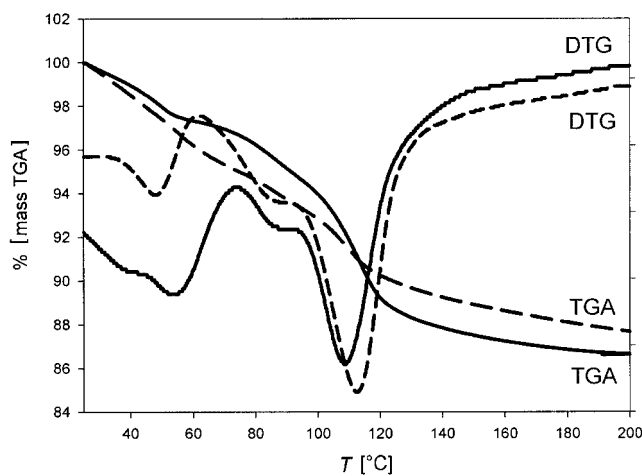


Figure 5. TGA and DTG curves for neutral complexes **4** and **5** (dashed lines) in the 25–200 °C range.

ment of the chlorine ligands by other monoanionic ligands with the aim to obtain more robust solid-state structures.

## Experimental Section

### General Procedures

The solutions of  $[\text{Mo}_3(\text{PdCl})\text{S}_4(\text{H}_2\text{O})_9]^{3+}$  and  $[\text{Mo}_3(\text{NiCl})\text{S}_4(\text{H}_2\text{O})_9]^{3+}$  were prepared by published procedures<sup>[16,38]</sup> and concentrated by absorption on a cation-exchange Dowex 50W-X2 column, followed by elution with 4 M HCl. Triphenylphosphane (CHEMA-POL) was recrystallized from ethanol.  $\text{AsPh}_3$  (Aldrich),  $\text{SbPh}_3$  (Aldrich) and other reagents were used as purchased.

The electronic spectra were recorded with a UV-2201 "Shimadzu" UV/Vis spectrophotometer. The  $^{31}\text{P}$  NMR spectra were measured with a Bruker 250 MHz spectrometer using 85%  $\text{H}_3\text{PO}_4$  as external standard. A Quattro LC (quadrupole-hexapole-quadrupole) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, UK) was used. The drying gas, as well as nebulizing gas, was nitrogen at flow rates 400 L/h and 80 L/h, respectively. Sample solutions in methanol (ca.  $10^{-4}$  M) were infused via syringe pump directly to the interface at a flow rate of 6  $\mu\text{L}/\text{min}$ . The temperature of the source block was set to 120 °C and of the interface to 150 °C. A capillary voltage of 3.5 kV was used in the positive scan mode and the cone voltage varied between +10 and +80 V. The signal intensities were obtained by averaging approximately 40 scans and measuring the intensities of the three most intense peaks within the isotopic pattern of each signal. The chemical composition of each peak was assigned by comparison of the experimental and calculated isotopic patterns using the MassLynx 3.5 program. TGA/SDTA analysis were measured on a Mettler Toledo 851e instrument in the 25–300 °C range at 20 °C/min coupled to a ThermoStar Balzers GSD300T mass spectrometer. XPD pictures were obtained at 25, 100, 200 and 250 °C on a SIEMENS D5000 diffractometer using  $\text{Cu-K}_\alpha$  radiation.

**Preparation of  $[\text{Mo}_3(\text{PdPPh}_3)\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4]\cdot 0.5\text{CH}_3\text{OH}\cdot 3\text{H}_2\text{O}$  (1):** The complex was prepared as described in ref.<sup>[6]</sup>

**Preparation of  $[\text{Mo}_3(\text{PdAsPh}_3)\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4]$  (2):** A solution of  $\text{AsPh}_3$  (30 mg, 0.09 mmol) in methanol (5 mL) was added to 10 mL of a solution of  $[\text{Mo}_3(\text{PdCl})\text{S}_4(\text{H}_2\text{O})_9]^{3+}$  (4 mM, 0.04 mmol) in 2 M HCl. The solution rapidly turned from blue to brown. Keeping it in an open vial for 2 days gave a crop of brown crystals, which were filtered off. Yield quantitative. The compound was kept in a vacuum desiccator over  $\text{P}_4\text{O}_{10}$  to remove all solvent molecules. Electronic spectrum [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$  in  $\text{CHCl}_3$ ): 308 (15412), 441(4077), 480 (sh, 3378).

**Preparation of  $[\text{Mo}_3(\text{PdSbPh}_3)\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4]\cdot 3\text{H}_2\text{O}$  (3):** In the same manner, brown complex **3** was prepared from 10 mL of a 4 mM solution of  $[\text{Mo}_3(\text{PdCl})\text{S}_4(\text{H}_2\text{O})_9]^{3+}$  (0.04 mmol) in 2 M HCl and a solution of  $\text{SbPh}_3$  (30 mg, 0.08 mmol) in methanol (5 mL) in quantitative yield. The compound was kept in a vacuum desiccator over  $\text{P}_4\text{O}_{10}$  overnight before elemental analysis in order to remove all solvent molecules. For  $\text{C}_{18}\text{H}_{25}\text{Cl}_4\text{O}_5\text{SbS}_4\text{Mo}_3\text{Pd}$ : calcd. C 19.52, H 2.28, S 11.58; found C 19.60, H 2.36, S 11.53. Electronic spectrum [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$  in  $\text{CHCl}_3$ ): 311 (16227), 438 (4776), 473 (sh, 3846).

**Preparation of  $[\text{Mo}_3(\text{NiPPh}_3)\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4]\cdot 3\text{H}_2\text{O}$  (4):** A solution of  $\text{PPh}_3$  (62 mg, 0.238 mmol) in MeOH (11 mL) was added to a solution of  $[\text{Mo}_3(\text{NiCl})\text{S}_4(\text{H}_2\text{O})_9]^{3+}$  (8.5 mL, 14 mM, 0.119 mmol) in 2 M HCl. The reaction mixture was heated while stirring at 40 °C for 30 min. The color slowly changed from olive-green to wine-red.

Blue-violet crystals appeared after a few days of slow evaporation. Yield 60%. For  $\text{C}_{18}\text{H}_{25}\text{Cl}_4\text{O}_5\text{PS}_4\text{Mo}_3\text{Ni}$ : calcd. C 20.75, H 3.17, S 12.30, found C 21.16, H 2.96, S 12.40 (after drying). Electronic spectrum [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$  in  $\text{CHCl}_3$ ): 316 (15369), 488 (1667), 574 (940).

**Preparation of  $[\text{Mo}_3(\text{NiAsPh}_3)\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4]\cdot 2.5\text{H}_2\text{O}$  (5):** A solution of  $\text{AsPh}_3$  (30 mg, 0.09 mmol) in methanol (5 mL) was added to 10 mL of a solution of  $[\text{Mo}_3(\text{NiCl})\text{S}_4(\text{H}_2\text{O})_9]^{3+}$  (4 mM, 0.04 mmol) in 2 M HCl. The color slowly turned from green to purple. Keeping the solution in an open vial for 2 days gave a crop of dark blue crystals, which were filtered off. Yield quantitative. The compound was kept in a vacuum desiccator over  $\text{P}_4\text{O}_{10}$  overnight before elemental analysis to remove all solvent molecules. For  $\text{C}_{18}\text{H}_{25}\text{Cl}_4\text{O}_5\text{AsS}_4\text{Mo}_3\text{Ni}$ : calcd. C 21.34, H 2.49, S 12.66; found, C 21.75, H 2.55, S 12.59. Electronic spectrum [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$  in  $\text{CHCl}_3$ ): 313 (13879), 491 (1405), 573 (898).

**Preparation of  $[\text{Mo}_3(\text{NiSbPh}_3)\text{S}_4(\text{H}_2\text{O})_5\text{Cl}_4]\cdot 2.5\text{H}_2\text{O}$  (6):** Prepared in the same way as **5**. Yield quantitative. Electronic spectrum [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$  in  $\text{CHCl}_3$ ): 315 (18315), 491 (1745), 578 (958). For  $\text{C}_{18}\text{H}_{25}\text{Cl}_4\text{O}_5\text{SbS}_4\text{Mo}_3\text{Ni}$ : calcd. C 19.10, H 2.92, S 11.31; found C 19.16, H 2.99, S 12.03.

**Preparation of  $[\text{Mo}_3(\text{PdPPh}_3)\text{Se}_4(\text{H}_2\text{O})_5\text{Cl}_4]$  (7):** A solution of  $\text{PPh}_3$  (70 mg, 0.27 mmol) in methanol (10 mL) was added to 10 mL of a solution of  $[\text{Mo}_3(\text{PdCl})\text{Se}_4(\text{H}_2\text{O})_9]^{3+}$  (25 mM, 0.25 mmol) in 4 M HCl.<sup>[17]</sup> The color of the solution rapidly turned to brown. Excess  $\text{PPh}_3$  precipitated and was filtered off. Keeping the solution in an open vial for 2 days gave a crop of brown crystals which were filtered off and thoroughly washed with diethyl ether to remove any  $\text{PPh}_3$ . Electronic spectrum [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$  in  $\text{CHCl}_3$ ): 326 (10659), 473 (3588).

**X-ray Crystallography:** The data collection on **4** was performed with a Bruker Smart CCD diffractometer using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a nominal crystal-to-detector distance of 40 mm. A hemisphere of data was collected based on three  $\omega$ -scan runs (starting  $\omega = -28^\circ$ ) at values  $\varphi = 0^\circ$ ,  $90^\circ$  and  $180^\circ$  with the detector at  $2\theta = 28^\circ$ . At each of these runs, frames (606, 435 and 230, respectively) were collected at  $0.3^\circ$  intervals and 25 seconds per frame. The diffraction frames were integrated using SAINT, and corrected for absorption with the SADABS package. The data collection for **3** and **5** was performed on a Bruker–Nonius X8APEX CCD diffractometer using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a nominal crystal-to-detector distance of 37.5 mm. The data was collected based on a full range  $\varphi$ -scan run (739 frames were collected at  $0.5^\circ$  intervals and 30 seconds per frame). The diffraction frames were integrated using the program SAINT package and corrected for absorption with SADABS.<sup>[39,40]</sup> The crystal parameters and basic information relating to the data collection and structure refinement for the three compounds are summarized in Table 3.

The positions of the heavy atoms were determined by direct methods and successive difference electron density maps using the SHELXTL 5.10 software package were calculated to locate the remaining atoms.<sup>[41]</sup> Refinement was performed by the full-matrix least-squares method based on  $F^2$ . All cluster atoms in compounds **3**, **4** and **5** were refined anisotropically except phenyl carbon atoms in compound **4**. Hydrogen atoms of the phenyl groups and water molecules were refined geometrically except for the water molecules in compound **4** which were not included in the refinement. Although the crystal quality of **4** was poor, the bond length analysis and the packing diagram enabled comparisons to be made.

CCDC-251550, -252539 and -252540 contain the supplementary crystallographic data for this paper (for **3**, **4** and **5**, respectively).

Table 3. Crystallographic Data for  $[\text{Mo}_3(\text{PdSbPh}_3)_4 \text{S}_4\text{Cl}_4(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O}$  (**3**),  $[\text{Mo}_3(\text{NiPPh}_3)_4 \text{S}_4\text{Cl}_4(\text{H}_2\text{O})_6] \cdot 3\text{H}_2\text{O}$  (**4**) and  $[\text{Mo}_3(\text{NiAsPh}_3)_4 \text{S}_4\text{Cl}_4(\text{H}_2\text{O})_6] \cdot 2.5\text{H}_2\text{O}$  (**5**).

Compound	<b>3</b>	<b>4</b>	<b>5</b>
Empirical formula	$\text{C}_{18}\text{H}_{31}\text{Cl}_4\text{Mo}_3\text{O}_8\text{PdS}_4\text{Sb}$	$\text{C}_{18}\text{H}_{31}\text{PCl}_4\text{Mo}_3\text{NiO}_8\text{S}_4$	$\text{C}_{18}\text{H}_{30}\text{AsCl}_4\text{Mo}_3\text{NiO}_{7.50}\text{S}_4$
Formula mass	1161.44	1022.97	1057.91
Crystal system	triclinic	triclinic	triclinic
$a$ [Å]	8.9799(18)	9.263(5)	9.1050(11)
$b$ [Å]	9.2193(18)	9.287(5)	9.2248(11)
$c$ [Å]	24.487(5)	23.121(11)	23.332(3)
$\alpha$ [°]	79.90(3)	92.747(11)	91.274(2)
$\beta$ [°]	99.58(3)	101.260(12)	100.074(2)
$\gamma$ [°]	117.21(3)	118.510(10)	117.328(2)
$V$ [Å <sup>3</sup> ]	1766.4(6)	1691.0(14)	1702.3(4)
$T$ [K]	173(2)	293(2)	293(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$Z$	2	2	2
$\mu(\text{Mo}-K_\alpha)$ [mm <sup>-1</sup> ]	2.865	2.283	3.184
Reflections collected	7523	9349	7244
$\varphi$ range for data collection	2.50 to 23.28	0.91 to 25.00	2.50 to 23.26
Unique reflections/ $R_{\text{int}}$	5018 [ $R(\text{int.}) = 0.0516$ ]	5889 [ $R(\text{int.}) = 0.1405$ ]	4795 [ $R(\text{int.}) = 0.0243$ ]
Goodness-of-fit on $F^2$	0.998	1.429	1.130
$R_1^{[\text{a}]} / wR_2^{[\text{b}]}$	$R_1 = 0.0696, wR_2 = 0.1566$	$R_1 = 0.1504, wR_2 = 0.2919$	$R_1 = 0.0613, wR_2 = 0.1674$
$R_1^{[\text{a}]} / wR_2^{[\text{b}]}$ (all data)	$R_1 = 0.1216, wR_2 = 0.1792$	$R_1 = 0.2725, wR_2 = 0.3309$	$R_1 = 0.0743, wR_2 = 0.1760$
Residual $\rho$ [e Å <sup>-3</sup> ]	1.65 and -1.28	2.67 and -2.42	1.97 and -1.01

[a]  $R_1 = \sum ||F_o| - |F_c|| / \sum F_o$ . [b]  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]\}^{1/2}$ .

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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