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Transition metal incorporation into seleno-bridged cubane type clusters of molybdenum and tungsten. X-Ray crystal structures of the first [Mo_3CuSe_4] derivatives†

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Trinuclear clusters of formula [$M_3Se_4X_3$(dmpe)$_3$]PF_6, M = Mo with X = Cl (**1**), M = Mo with X = Br (**2**) and M = W with X = Br (**3**) have been synthesized by excision of polymeric $\{M_3Se_7X_4\}_x$ phases with dmpe in acetonitrile. Cu(I) is readily incorporated into the molybdenum selenide clusters in organic solvents to give [$Mo_3CuSe_4Cl_4$(dmpe)$_3$]PF_6 (**4**) and [$Mo_3CuSe_4Br_4$(dmpe)$_3$]PF_6 (**5**). These are the first reported complexes with [Mo_3CuSe_4] units. No reaction with Cu(I) has been observed for the tungsten cluster. In contrast with the aquo cuboidal seleno derivatives these trinuclear, **1**–**3**, and tetranuclear, **4** and **5**, clusters are air stable making easier their full characterization. X-Ray structural analysis of complexes **1** and **3** shows that the overall geometry of the [M_3Se_4] core is basically the same as for the [Mo_3S_4] units. Structures **1** and **3** do not present the weak dimerization through Se–Se bonds observed for the previously reported [M_3Se_4] cyano and thiocyanato cluster complexes. The addition of a Cu atom to [Mo_3Se_4] results in cluster compounds with single cube type structures. The six intermetallic distances within the [Mo_3Cu] tetrametallic unit in **4** are statistically the same. The Mo–Cu bond distance in **5** is 0.02 Å longer than the Mo–Mo bond length. Electrochemical reduction processes of compounds **1**–**5** have been investigated by cyclic voltammetry. Cu insertion into complexes **1** and **2** to give **4** and **5** results in an anodic shift potential of 0.25 V for the first reduction process.

Introduction

Cubane type sulfido clusters have been extensively investigated and for molybdenum and tungsten, a large number of heterobimetallic complexes has been prepared with the incorporation of transition metals and "p block" elements into the [M_3(μ_3-S)(μ-S)$_3$] incomplete cuboidal unit.[1] This chemistry has been mainly developed in aqueous media and the major advances have been found for molybdenum where the heterometals incorporated range from group 6 to 15 elements.[2] For tungsten the number of heterometals is more restricted, a fact that has been attributed to the greater difficulty in reducing tungsten as compared to molybdenum.[3]

In contrast the corresponding selenido derivatives have received little attention, the only examples structurally characterized being the Sn and Pd derivatives with [$M_3M'Se_4$] single cube structures[4,5] and the Sn and Hg complexes with [$\{M_3Se_4\}M'\{Se_4M_3\}$] corner-shared structures.[6,7] There is no evidence for bonding between the group 6 and the post-transition metals in either the selenido or the sulfido clusters. On the other hand, the extension of this chemistry to non-aqueous media is limited to the preparation of heterobimetallic cubane-like sulfido clusters of molybdenum with a few transition metals, *i.e.* Cu,[8,9] Cr and W[10,11] or Co[12] and to the Cu incorporation into the homologous tungsten clusters.[13] Heterobimetallic sulfido aquo complexes of Pt, Pd and Ni can also be taken into organic solvents by reaction of the aquo species with appropriate ligands such as 1,2-bis(diphenylphosphino)ethane (dppe).[14]

Recently we have centered our investigations in developing synthetic procedures for these heterobimetallic cuboidal clusters in organic solvents through building block strategies using as starting materials various phosphine derivatives of the incomplete [M_3Q_4] (M = Mo, W and Q = S, Se) cuboidal units. We have chosen to start our work by exploring the Cu derivatives because, on the one hand, copper has provided a rich and varied chemistry both in aqueous and organic media and, on the other hand, heterobimetallic chalcogenide clusters of group 6 metals and copper with cubane type structures are known for their capability as optical limiters.[15,16] Here we report the synthesis of the first [Mo_3CuSe_4] selenido clusters. The structures and redox properties of these heterobimetallic cubane complexes are compared with those of their group 6 trinuclear precursors.

Experimental

General procedures

All reactions were performed under a positive pressure of nitrogen. Elemental analyses were carried out with an EA 1108 CHNS-O micro analytical analyzer. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian 300 spectrometer with 85% H_3PO_4 as external reference. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR using KBr pellets. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda-19 spectrophotometer. Electrospray mass spectra were recorded using a Micromass Quattro LC instrument. Isotope patterns were recorded for all cluster cations and compared with theoretical patterns using the MassLynx 3.5 program. In all cases there was good agreement between the experimental and calculated isotopic mass distributions. The polymeric phases $\{Mo_3Se_7Cl_4\}_x$[17] and $\{M_3Se_7Br_4\}_x$[18] were prepared by solid state reactions according to literature methods. [Cu(MeCN)$_4$]PF_6

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† Electronic supplementary information (ESI) available: cyclic voltammograms for compounds **1**–**5**. See http://www.rsc.org/suppdata/dt/b1/b104262a/

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was synthesized from commercial Cu_2O and HPF_6 in acetonitrile.[19] Other reactants were obtained from commercial sources and used as received.

Electrochemical measurements

Cyclic voltammetry experiments were performed with a Echochemie Pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The solvent used in all experiments was MeCN (isocratic grade for liquid chromatography, Merck) dried and degassed by standard methods. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate, synthesized by reaction of tetrabutylammonium bromide and HPF_6, recrystallized from ethanol and dried under vacuum; $E_{1/2}$ values were determined as 1/2 ($E_a + E_c$), where E_a and E_c are the anodic and cathodic peak potentials, respectively. All potentials reported were not corrected for the junction potential.

Syntheses

$[Mo_3Se_4Cl_3(dmpe)_3]PF_6$ 1. To a suspension of $\{Mo_3Se_7Cl_4\}_x$ (0.15 g, 0.15 mmol) in MeCN (20 mL) was added an excess of 1,2-bis(dimethylphosphino)ethane (dmpe) (150 µL, 0.88 mmol) under nitrogen and the reaction mixture was refluxed for 48 h. The color of the solution turned brown immediately. The unreacted solid was separated from the solution by filtration and washed with acetonitrile until it came out colorless. KPF_6 (55 mg, 0.3 mmol) was added to the filtrate and the solvent removed under reduced pressure. The resulting solid was then redissolved in CH_2Cl_2 and filtered in order to eliminate the insoluble KCl or KPF_6 inorganic salts. The solution was taken to dryness, cold MeCN (5 mL) was added and the suspension filtered. This separates a mononuclear impurity identified as $[MoOCl(dmpe)_2]PF_6$ from the solid.[20] Finally the air stable brown solid product was washed with diethyl ether and dried (107 mg, 54%) (Found: C, 16.54; H, 3.72. $C_{18}H_{48}F_6P_7Se_4Cl_3Mo_3$ requires C, 16.56; H, 3.71%). ν_{max}/cm^{-1} (KBr): 1415s(P–CH_2), 1286m(P–CH_3), 1133m, 992w, 947s, 938s, 897s, 840s(P–F), 744m, 708m, 647m, 556s(P–F), 444w, 344w; δ_P(MeCN) −143.9 (1 P, septet, J(P–F) 706 Hz), 25.29 (3 P, d, J(P–P) 19 Hz) and 40.04 (3 P, d, J(P–P) 19 Hz); λ_{max}/nm (MeCN) 271, 371, 461, 704; m/z (MeCN) 1160 (M^+), 1010 (M − dmpe)$^+$ (electrospray-MS 65 V).

$[Mo_3Se_4Br_3(dmpe)_3]PF_6$ 2. This compound was prepared following the general procedure described for **1** except that the polymeric solid $\{Mo_3Se_7Br_4\}_x$ (0.17 g, 0.15 mmol) was used instead of $\{Mo_3Se_7Cl_4\}_x$ to yield an air stable brown solid (140 mg, 66%) (Found: C, 14.98; H, 3.32. $C_{18}H_{48}F_6P_7Se_4Br_3Mo_3$ requires C, 15.03; H, 3.36%). ν_{max}/cm^{-1} (KBr): 1618m, 1416s(P–CH_2), 1287m, 1135m, 1096m, 949s, 938s, 900s, 834s(P–F), 742m, 711m, 646m, 556s(P–F), 445w, 439w, 343w; δ_P(MeCN) −143.9 (1 P, septet, J(P–F) 706 Hz), 18.41 (3 P, d, J(P–P) 16 Hz) and 39.04 (3 P, d, J(P–P) 16 Hz); λ_{max}/nm (MeCN) 285, 379, 472, 713; m/z (MeCN) 1294 (M^+), 1144 (M − dmpe)$^+$ (electrospray-MS 65 V).

$[W_3Se_4Br_3(dmpe)_3]PF_6$ 3. To a suspension of $\{W_3Se_7Br_4\}_x$ (0.13 g, 0.09 mmol) in MeCN (20 mL) was added an excess of dmpe (100 µL, 0.59 mmol) under nitrogen and the reaction mixture was refluxed for 48 h. The colour of the solution turns green immediately. After filtration, the resulting solution was taken to dryness, redissolved in CH_2Cl_2 and adsorbed in a silica gel column. After washing the column with CH_2Cl_2 and CH_2Cl_2–acetone (9 : 1), elution with a KPF_6 solution in acetone (10 mg mL^{-1}) afforded a very concentrated green solution. This solution was taken to dryness, redissolved in CH_2Cl_2 and filtered in order to eliminate the insoluble KBr or KPF_6 inorganic salts. Slow evaporation in air afforded an air stable green solid (80 mg, 52%) (Found: C, 12.73; H, 2.87. $C_{18}H_{48}F_6P_7Se_4Br_3W_3$ requires C, 12.70; H, 2.84%). ν_{max}/cm^{-1} (KBr): 1618m, 1416s(P–CH_2), 1287m(P–CH_3), 1134m, 1098m, 939s, 900s, 839s(P–F), 739m, 705m, 647m, 557s(P–F), 340w; δ_P(MeCN) −143.9 (1 P, septet, J(P–F) 706 Hz), −2.79 (3 P, s, J(P–W) 172 Hz) and 1.03 (3 P, s, J(P–W) 159 Hz); λ_{max}/nm (CH_3CN) 283, 335, 398, 645. m/z (MeCN) 1557 (M^+), 1407 (M − dmpe)$^+$ (electrospray-MS 65 V).

$[Mo_3Se_4CuCl_4(dmpe)_3]PF_6$ 4. To a brown solution of $[Mo_3Se_4Cl_3(dmpe)_3](PF_6)$ **1** (65 mg, 0.05 mmol) and tetrabutylammonium chloride (TBACl) (20 mg, 0.072 mmol) in 20 mL of THF was added an excess of $[Cu(MeCN)_4]PF_6$ (85 mg, 0.22 mmol) under nitrogen. After refluxing the reaction mixture for 24 h, a colloidal dark red suspension was formed and complete precipitation was achieved by addition of 20 mL of diethyl ether. The precipitated product was filtered off, redissolved in CH_2Cl_2 and adsorbed in a silica gel column. After washing the column with CH_2Cl_2, elution with a KPF_6 solution in acetone (10 mg mL^{-1}) afforded a very concentrated red solution. This solution was taken to dryness, redissolved in 15 mL of CH_2Cl_2 and filtered in order to eliminate the insoluble KBr or KPF_6 inorganic salts. The $Bu^n{}_4NCl$ salt was separated from the solution by four consecutive water extractions (4 × 15 mL). After drying the organic solution with anhydrous $MgSO_4$, the resulting solution was taken to dryness to yield an air stable red solid (33 mg, 47%) (Found: C, 15.43; H, 3.42. $C_{18}H_{48}F_6P_7Se_4Cl_4CuMo_3$ requires C, 15.39; H, 3.45%). ν_{max}/cm^{-1} (KBr): 1414s(P–CH_2), 1286m(P–CH_3), 1133m, 941s, 904s, 841s(P–F), 744m, 712m, 651m, 557s(P–F), 446w, 412w, 391w, 366w; δ_P(MeCN) −143.9 (1 P, septet, J(P–F) 706 Hz), 27.41 (3 P, d, J(P–P) 18 Hz) and 37.32 (3 P, d, J(P–P) 18 Hz); λ_{max}/nm (MeCN) 326, 380, 511; m/z (MeCN) 1259 (M^+), 1010 (M − CuCl − dmpe)$^+$ (electrospray-MS, 90 V).

$[Mo_3Se_4CuBr_4(dmpe)_3]PF_6$ 5. This compound was prepared following the general procedure described for **4** except that the corresponding bromide derivatives, $[Mo_3Se_4Br_3(dmpe)_3](PF_6)$ (70 mg, 0.049 mmol) and tetrabutylammonium bromide (TBABr) (20 mg, 0.062 mmol) were used. The dark red precipitate obtained upon diethyl ether addition was dissolved in 10 mL of CH_2Cl_2, the solution filtered and a microcrystalline red solid was obtained by slow diffusion of Et_2O into the filtrate (35 mg, 46%) (Found: C, 13.82; H, 3.04. $C_{18}H_{48}F_6P_7Se_4Br_4CuMo_3\cdot CH_2Cl_2$ requires C, 13.69; H, 3.02%). ν_{max}/cm^{-1} (KBr): 1416s(P–CH_2), 1287m (P–CH_3) 1137m, 939s, 903s, 839s(P–F), 741m, 712m, 650m, 557s(P–F), 446w, 342w, 318w, 304w; δ_P(MeCN) −143.9 (1 P, septet, J(P–F) 706 Hz), 15.75 (3 P, d, J(P–P) 18 Hz) and 30.37 (3 P, d, J(P–P) 18 Hz); λ_{max}/nm (MeCN) 329, 391, 517; m/z (MeCN) 1438 (M^+), 1144 (M − CuBr − dmpe)$^+$ (electrospray-MS, 90 V).

X-Ray crystallography

Suitable crystals for X-ray studies for **1** and **3** were grown from sample solutions in acetonitrile by slow evaporation at room temperature. Single crystals for **4** and **5** were obtained by slow diffusion of Et_2O into sample solutions in CH_2Cl_2. The crystals are air stable and were mounted on the tip of a glass fiber with the use of epoxy cement. X-Ray diffraction experiments were carried out on a Bruker SMART CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The data were collected with a frame width of 0.3° in ω and a counting time of 30 and 40 s per frame for compounds **1** and **3**, respectively, and 35 s per frame for compounds **4** and **5**, at a crystal to detector distance of 4 cm. The software SAINT[21] was used for integration of intensity reflections and scaling and SADABS[22] for absorption correction. Final cell parameters

Table 1 Crystallographic data for $[Mo_3Se_4Cl_3(dmpe)_3]PF_6$ **1**, $[W_3Se_4Br_3(dmpe)_3]PF_6$ **3**, $[Mo_3CuSe_4Cl_4(dmpe)_3]PF_6$ **4** and $[Mo_3CuSe_4Br_4(dmpe)_3]PF_6$ **5**

Compound	**1**	**3**	**4**	**5**
Empirical formula	$Mo_3Se_4Cl_3C_{18}H_{48}P_7F_6$	$W_3Se_4Br_3C_{18}H_{48}P_7F_6$	$Mo_3Se_4CuCl_4C_{18}H_{48}P_7F_6$	$Mo_3Se_4CuBr_4C_{19}H_{48}P_7F_6Cl_2$
Formula weight	1305.36	1702.47	1404.35	1665.10
Crystal system	Cubic	Cubic	Monoclinic	Monoclinic
a/Å	20.9212(10)	21.0599(5)	12.607(6)	12.7990(5)
b/Å			15.879(8)	23.8115(9)
c/Å			21.314(11)	16.5128(6)
β/°			90.180(14)	90.7810(10)
V/Å^3	9157.1(8)	9340.5(4)	4267(4)	5032.0(3)
Space group (Z)	$I23$ (8)	$I23$ (8)	$P2_1/n$ (4)	$P2_1/n$ (4)
μ(Mo-Kα)/mm^{-1}	4.446	13.332	5.320	7.584
θ range/°	1.38–23.20	1.38–23.22	1.60–22.01	1.50–26.37
Reflections collected	22579	22949	18013	31879
Unique reflections/R_{int}	2199/0.0891	2251/0.0672	5215/0.1368	10286/0.0651
$R1^a/wR2^b$ ($I > 2\sigma$)	0.0503/0.1427	0.0297/0.0919	0.0615/0.1181	0.0489/0.1261
$R1^a/wR2^b$ (all data)	0.0521/0.1436	0.0363/0.0955	0.1237/0.1299	0.0994/0.1450
Max. shift/esd	0.008	0.044	0.002	0.004
Residual ρ/e Å^{-3}	1.650/−0.926	1.441/−0.936	1.883/−0.691	1.497/−1.161

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma F_o$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

were obtained by global refinement of reflections obtained from integration of all the frames data. The resolution, maximum θ, has been established based on the merging R-factor ($R_{shell} < 0.25$) computed from the integrated intensity of the reflection and that of its symmetry equivalents for successive thin shells with increasing resolution. The crystal parameters and basic information relating to data collection and structure refinement for compounds **1**, **3**, **4** and **5** are summarized in Table 1.

The structures were solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXTL software package.[23] Compounds **1** and **3** crystallize in the cubic space group $I23$ and are isostructural with $[W_3S_4Br_3(dmpe)_3]PF_6$.[24] The structure of **1** was successfully refined taking into account a merohedral racemic twinning, with a two-fold axis along the face diagonal and inversion twin law: (0 1 0, 1 0 0, 0 0 −1) (−1 0 0, 0 −1 0, 0 0 −1) which interchanges and reverses h and k without modifying l. The final refinement yields the following BASF (batch scale factor) values: 0.190(26), 0.059(29), 0.215(26). Other feasible merohedral twin laws were also considered with worse results.[25]

Compounds **4** and **5** are isostructural with $[Mo_3CuS_4Cl_4(dmpe)_3]PF_6$ and $[W_3CuS_4Br_4(dmpe)_3]PF_6$ respectively.[16] Structure **4** was successfully refined in the monoclinic space group $P2_1/n$ in spite of having all angles close to 90°. All attempts made to refine this structure in an orthorhombic space group as a single or pseudo-merohedral twin crystal have failed.[25] The non-hydrogen cation atoms of structures **1**–**5** were refined anisotropically; the positions of all hydrogen atoms were generated geometrically, assigned isotropic thermal parameters and allowed to ride on their respective parent carbon atoms.

Two independent PF_6^- anions were found in structures **1** and **3**, both in special positions. One of the PF_6^- anions was refined anisotropically, and the phosphorus atom of the other highly disordered PF_6^- was placed on the highest electronic density peak; the fluorine atoms were geometrically generated, assigned isotropic thermal parameters and allowed to ride on their parent phosphorus atom. The site occupancies of the highly disordered PF_6^- anion were assigned to assure the ratio cluster/PF_6^- equals unity to be compatible with the observed cluster charge. On the other hand, the PF_6^- anion in structure **5** was refined anisotropically while only the phosphorus atom of this anion in structure **4** was refined anisotropically. In this latter case the fluorine atoms were treated as disordered in an equatorial plane and refined isotropically. Structure **5** shows one molecule of CH_2Cl_2 disordered in two positions which was refined with one half site occupancies.

CCDC reference numbers 164458–164461.

See http://www.rsc.org/suppdata/dt/b1/b104262a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis

Our recent investigations on cubane-type sulfido compounds have shown that preassembled $[M_3S_4]$, M = Mo or W, molecular units with terminal phosphine ligands can easily capture Cu(I) in organic solvents to yield a series of cationic clusters with general formula $[M_3CuS_4X_4(dmpe)_3]^+$ (X = Cl, Br) in moderate (50–75%) yields. The extension of this chemistry to the selenido clusters requires that the corresponding trinuclear synthons, namely the $[M_3Se_4X_3(dmpe)_3]^+$ complexes, were available in acceptable yields.

The excision of polymeric $\{M_3Q_7X_4\}_x$ (Q = S, Se) phases has proved to be the most efficient synthetic entry to trinuclear clusters with $[M_3Q_7]$ and $[M_3Q_4]$ units. In 1990 Saito *et al.* described the interaction of $\{Mo_3Se_7Cl_4\}_x$ with PEt_3 which probably gives a mixture of several phosphine complexes of $[Mo_3Se_4]^{4+}$ based on its reactivity.[26] One year later Fedin *et al.* reported the synthesis of the $[Mo_3Se_4Cl_3(dppe)_3]^+$ complex by direct excision of the solid $\{Mo_3Se_7Cl_4\}_x$ phase in acetonitrile under reflux conditions in 29% yield[17] and the preparation of the $[W_3Se_4Br_3(dppe)_3]^+$ complex from the corresponding polymeric phase by excision with Et_4NBr under mild vibrational conditions using a ball mill followed by extraction of the $[W_3Se_7Br_6]^{2-}$ complex with acetonitrile and further reaction of this complex with the diphosphine.[18] In this latter case the overall yield obtained was around 13%.

In the course of our investigations we have found that the solvent plays a crucial role in the excision of polymeric $\{M_3S_7X_4\}_x$ phases with diphosphines, dmpe or dppe, and that the reaction in boiling acetonitrile with reaction times close to 48 h is a general route for the preparation of complexes with formula $[M_3S_4X_3(diphosphine)_3]^+$.[27] When we apply in this work these synthetic conditions to the selenium systems with dmpe we have found that the yields obtained improve considerably with regard to those obtained by Fedin *et al.* for the dppe derivatives, namely 54% for $[Mo_3Se_4Cl_3(dmpe)_3]PF_6$ (**1**), 66% for $[Mo_3Se_4Br_3(dmpe)_3]PF_6$ (**2**) and 52% for $[W_3Se_4Br_3(dmpe)_3]PF_6$ (**3**). The corresponding yields for the sulfido clusters are all close to 95%.

Reactivity studies of $[M_3Se_4]$ units towards a second transition metal are limited to some preliminary results regarding the incorporation of Mo into $[W_3Se_4(H_2O)_9]^{4+}$ and the Ni and Pd

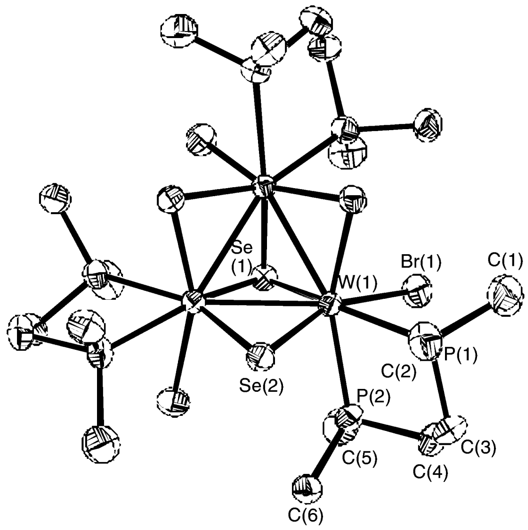

Fig. 1 ORTEP plot (50% thermal probability ellipsoids) of the cation of **3** $[W_3Se_4Br_3(dmpe)_3]^+$. Only the atoms of the asymmetric unit are labeled.

insertion into the $[Mo_3Se_4]^{4+}$ aquo ion.[5,28,29] In this work we have investigated the reactivity of the incomplete cuboidal trinuclear selenido clusters of general formula $[M_3Se_4X_3(dmpe)_3]^+$ in organic solvents with the mononuclear copper complex $[Cu(MeCN)_4]^+$ according to eqn. (1).

$$[M_3Se_4X_3(dmpe)_3]^+ + [Cu(MeCN)_4]^+ \longrightarrow [M_3CuSe_4X_4(dmpe)_3]^+ \quad (1)$$

Unlike the sulfido system, the reaction only takes place for molybdenum and the final products have been characterized as the heterobimetallic cubane type clusters $[Mo_3CuSe_4Cl_4(dmpe)_3]PF_6$ (**4**) and $[Mo_3CuSe_4Br_4(dmpe)_3]PF_6$ (**5**). The yields obtained are close to 50%. The global charge of the cluster core $[Mo_3CuSe_4]$ is 5+ *cf.* the 4+ charge of its trinuclear precursor. The lack of affinity of the $[W_3Se_4]^{4+}$ core for Cu(I) differs from the reactivity reported for Sn(II) where the affinity of the $[W_3Se_4]^{4+}$ core for Sn uptake is higher than that of the $[W_3S_4]^{4+}$ unit.[6]

Compounds **4** and **5** are the first compounds reported with an $[Mo_3CuSe_4]$ central unit. These clusters, **4** and **5**, are air stable while most of the homologous heterobimetallic single and double cube complexes reported up to date are oxygen sensitive and rigorous air-free techniques are required.[3] In our opinion, the presence of phosphines as ligands provides both the trinuclear precursors and the heterobimetallic cubane clusters with enhanced stability in comparison with the aquo species. This assumption is supported by the electrospray mass spectrometry (ESI-MS) results. As already found for the analogous sulfido clusters, the main feature of the ESI spectra in compounds **1**–**5** is the presence of an abundant molecular peak. When the ionization energy for the cubane compounds **4** and **5** is increased, peaks due to the simultaneous loss of CuX plus one diphosphine, followed by the loss of a second diphosphine, are observed. This is indicative of a very robust central $[Mo_3CuSe_4]$ unit, particularly when compared with the fragmentation pathway of the very stable trinuclear precursors for which successive loss of diphosphine ligands is also observed.

Structures

Trinuclear clusters. Clusters **1**–**3** have an $\{M_3Se_4\}$ incomplete cuboidal unit as shown in Fig. 1 for compound **3**. The three metal atoms in **1** and **3** define an equilateral triangle with one capping and three asymmetrically coordinated selenium ligands according to the crystallographic C_3 symmetry. Table 2 summarizes the most relevant bond distances for these complexes together with those reported for the analogous cyano and thiocyanato clusters.

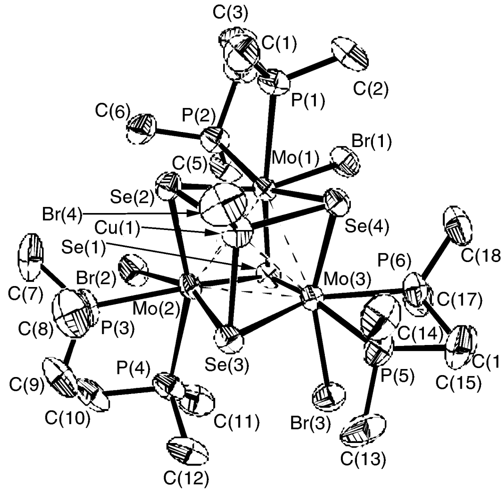

Fig. 2 ORTEP plot (50% thermal probability ellipsoids) of the cation of **5** $[Mo_3Se_4CuBr_4(dmpe)_3]^+$.

The metal–metal bond distances in **1** and **3** are identical and slightly longer than those in the $[M_3Se_4(SCN)_9]^{5-}$ complexes. The shorter M–Se bond lengths (*trans* to the halide atoms) in **1** and **3** are similar to those measured for the $[M_3Se_4(SCN)_9]^{5-}$ anion while the longer M–Se bond lengths (*trans* to the phosphorus atom) are closer to those observed for the $[W_3Se_4(CN)_9]^{5-}$ ion. The overall geometry of the $[M_3Se_4]$ core is basically the same as for the $[M_3S_4]$ units. The M–M bond lengths in **1** and **3** are 0.07 Å longer than the corresponding distances in the sulfur derivatives.[27] The metal–ligand distances follow the tendencies observed for the analogous sulfur complexes except that the larger selenium atoms lead to longer M–Se bonds. The present structures (**1** and **3**) do not present the weak dimerization through Se–Se interactions observed for the previously reported $\{M_3Se_4\}$ cyano and thiocyanato cluster complexes.[30]

Cubane clusters. The cationic cluster cation of **5** is depicted in Fig. 2 from which the essential cubane-type geometry, also present in compound **4**, is immediately evident. Compounds **4** and **5** are isostructural with $[Mo_3CuS_4Cl_3(dmpe)_3]PF_6$ and $[W_3CuS_4Br_3(dmpe)_3]PF_6$, respectively.[16]

With a precise structure of the sulfide derivatives already determined, the most significant structural objective remaining in the $[Mo_3CuQ_4X_3(dmpe)_3]^+$ series is stereochemical definition of the $[Mo_3CuSe_4]$ core and the structural changes observed in proceeding from the trinuclear $[Mo_3Se_4]$ unit to the $[Mo_3CuSe_4]$ cubane core. Table 3 lists an average of the most important bond distances for **4**, **5** and the corresponding sulfido clusters using the atom numbering scheme defined in Fig. 2.

The Mo–Mo bond lengths are 0.05 Å for **4** and 0.07 Å for **5**, longer than the corresponding distances in the sulfur derivatives. The six intermetallic distances within the cuboidal $[Mo_3Cu]$ unit in **4** are about the same. The Mo–Cu distance in **5** is 0.02 Å longer than the Mo–Mo bond lengths. This distortion of the tetrametallic unit can be regarded as an elongation along the C_3 axis, going through Cu and Se(1), and is less pronounced that that observed for the analogous sulfido complexes. The shortening of the Mo–Cu distance in **4** as compared with **5** of 0.04 Å is accompanied by a lengthening of 0.02 Å in the Mo-μ_3-Se(1) bond length. While a cubane core is now an unexceptional unit in inorganic chemistry, only $[Mo_3PdSe_4Cl_3(H_2O)_7]^+$ has been shown by X-ray diffraction to contain an $[Mo_3M'Se_4]$ core with M′ being a transition metal.[5]

As for the sulfur clusters, there is no significant structural rearrangement in proceeding from $[Mo_3Se_4X_3(dmpe)_3]^+$ to $[Mo_3CuSe_4X_4(dmpe)_3]^+$. The addition of a Cu atom to the

Table 2 Selected averaged bond distances (Å) for compounds **1** and **3** and other relevant trinuclear clusters reported with $[M_3Se_4]$ cores[a]

Distance/Å	$[Mo_3Se_4Cl_3$-$(dmpe)_3]PF_6$ **1**	$[W_3Se_4Br_3$-$(dmpe)_3]PF_6$ **3**	$(Me_4N)_5$-$[Mo_3Se_4(NCS)_9]$ (ref. 34)	$(Me_3NH)_5$-$[W_3Se_4(NCS)_9]$ (ref. 30)	$Cs_5[W_3Se_4(CN)_9]CsCl\cdot 4H_2O$ (ref. 32)
M–M	2.836(2)	2.8365(8)	2.817[6]	2.795[3]	2.829[9]
M–μ_3-Se(1)	2.478(3)	2.4871(17)	2.452[8]	2.458[5]	2.497[2]
M–μ-Se(2)[b]	2.404(2)	2.4157(14)			
M–μ-Se(2)[c]	2.450(2)	2.4539(14)			
M–μ-$Se(2)_{av}$	2.43[3]	2.44[3]	2.409[9]	2.388[5]	2.449[7]
M–X	2.491(5)	2.6453(16)			
M–P(1)	2.512(5)	2.523(4)			
M–P(2)	2.601(5)	2.597(4)			

[a] Standard deviations for averaged values are given in square brackets. [b] Mo–μ-Se distance *trans* to Mo–X bond. [c] Mo–μ-Se distance *trans* to Mo–P(2) bond.

Table 3 Selected averaged bond distances (Å) for compounds **4** and **5** and their sulfur analogs[a]

Distance/Å	$[Mo_3Se_4CuCl_4(dmpe)_3]PF_6$ **4**	$[Mo_3Se_4CuBr_4(dmpe)_3]PF_6$ **5**	$[Mo_3S_4CuCl_4(dmpe)_3]PF_6$ (ref. 16)	$[Mo_3S_4CuBr_4(dmpe)_3]PF_6$ (ref. 16)
M–M	2.839[4]	2.8606[9]	2.782[1]	2.7936(9)
M–Cu	2.839[4]	2.878[6]	2.823[3]	2.8233(13)
M–μ_3-Se(1)	2.492[1]	2.4726[23]	2.368[1]	2.354(2)
M–μ_3-Se(2)[b]	2.436[9]	2.4447[19]	2.320[2]	2.3245(17)
M–μ_3-Se(2)[c]	2.493[7]	2.483[2]	2.360[1]	2.3607(17)
Cu–μ_3-Se(2)	2.394[1]	2.402[4]	2.304[1]	2.3037(18)
M–X	2.481[4]	2.645[11]	2.473[12]	2.6205(9)
M–P(1)	2.526[9]	2.541[5]	2.536[4]	2.5499(19)
M–P(2)	2.587[12]	2.592[2]	2.589[5]	2.606(2)

[a] Standard deviations for averaged values are given in square brackets. [b] Mo–μ-Se distance *trans* to Mo–X bond. [c] Mo–μ-Se distance *trans* to Mo–P(2) bond.

$[Mo_3Se_4]$ core is coupled with an elongation of the Mo–μ_3-Se(2) bond while the Mo–Mo bond remains practically unchanged. In contrast, the Mo–Mo distance in the corresponding sulfido complexes shows a 0.02 Å increase upon addition of the Cu atom.

Redox properties

Electrochemical properties of the cubane type clusters **4** and **5**, and their trinuclear precursors **1**–**3** have been investigated by cyclic voltammetry. Two different types of electrochemical behavior have been found when reducing the $[M_3Se_4]$ complexes. The molybdenum compound **1** presents a quasi-reversible reduction wave at $E_{1/2} = -0.60$ V ($\Delta E = 78$ mV) followed by an irreversible reduction process at $E_c = -1.21$ V. This behavior compares with that observed for the $[Mo_3S_4X_3(dmpe)_3]^+$ (X = Cl, Br) sulfido cluster cations[27] and by analogy we have tentatively assigned these two reduction waves to the processes $Mo_3^{IV} \leftrightarrow Mo_2^{III}Mo^{IV} \leftrightarrow Mo_3^{III}$, that is a bi-electron process followed by a monoelectronic one. In contrast the molybdenum and tungsten bromide trimers **2** and **3** show three irreversible reduction waves at −0.54, −0.87 and −1.20 V for **2** and −0.91, −1.12 and −1.41 V for **3**. Substitution of molybdenum by tungsten causes a cathodic shift on the reduction potential values. The cyclic voltammogram of complexes **2** and **3** resembles those reported for some $[Mo_3S_4]$ clusters for which three monoelectronic electron transfers have been proposed.[31] As a consequence we postulate a similar reduction mechanism, that is $M_3^{IV} \leftrightarrow M^{III}M_2^{IV} \leftrightarrow M_2^{III}$-$M^{IV} \leftrightarrow M_3^{III}$. The cluster $[Mo_3Se_4(CN)_9]^{5-}$ gives an irreversible reduction process with a cathodic peak potential *vs.* Ag–AgCl electrode of −0.96 V ($E_a = -0.86$ V) attributed to the process $M_3^{IV} \leftrightarrow M^{III}M_2^{IV}$ in agreement with the proposed mechanism for the first reduction wave.[32] The high negative charge of this cyano cluster explains the more negative potential values observed for the first reduction process as compared with those obtained for our trinuclear cluster cations in **1**–**3**. These selenium clusters are more easily reduced than their homologous sulfides with positive potential shifts for the first reduction potential of 20–90 mV. Prior redox potential data reflecting the effect of S/Se substitution are consistent with the present results.[32,33]

Compounds **4** and **5**, in contrast with **1** and **2**, present an analogous redox behavior with a quasi-reversible reduction wave at $E_{1/2} = -0.35$ V ($\Delta E = 66$ mV) for **4** and $E_{1/2} = -0.29$ V ($\Delta E = 58$ mV) for **5**, followed by two irreversible reduction waves at −0.97 and −1.22 V for **4** and −0.87 and −1.12 V for **5**. The Cu insertion into complexes **1** and **2** to give **4** and **5** results in an anodic shift of the first reduction potential of 0.25 V in both cases. This was previously observed for the homologous sulfur complexes where the first quasi-reversible reduction process observed at half wave potentials of −0.32 V for $[Mo_3CuS_4Cl_4(dmpe)_3]^+$ and −0.23 V for $[Mo_3CuS_4Br_4(dmpe)_3]^+$ has been tentatively assigned to the process $Mo_3^{IV}Cu^I \leftrightarrow Mo^{III}$-$Mo_2^{IV}Cu^I$.[16] This assignment can be extended by analogy to the first reduction process observed for **4** and **5**. The peak potentials values for the second and third reduction waves for compound **5** are similar to those observed for **2**. These similarities are also observed when comparing the reduction potential between **1** and **4**. Based on this we have assigned these reduction waves to the following two monoelectronic processes $Mo^{III}Mo_2^{IV}Cu^I \leftrightarrow Mo_2^{III}Mo^{IV}Cu^I \leftrightarrow Mo_3^{III}Cu^I$. Further experiments are needed to confirm the proposed reduction mechanism.

Conclusions

The incorporation of Cu(I) into incomplete cuboidal $[Mo_3Se_4X_3(dmpe)_3]^+$ (X = Cl or Br), complexes gives heterobimetallic clusters $[Mo_3CuSe_4X_4(dmpe)_3]^+$ with single cube type structures. No equivalent reaction with the analogous tungsten trimer has been observed. The outer phosphine ligands in $[W_3Se_4]$ and $[Mo_3Se_4Cu]$ provide these systems with a high stability *vs.* air oxidation in contrast with their homologous aquo species making these heterobimetallic clusters more accesible for further studies. The $[Mo_3CuSe_4X_4(dmpe)_3]^+$ complex cations are easier to reduce than their trinuclear precursors.

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