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Preparation, structure and properties of trinuclear $[M_3Se_4(CN)_9]^{5-}$ ($M = Mo$ or W) complexes obtained from M_3Se_7 core compounds and related studies†

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The preparations of $[Mo_3Se_4(CN)_9]^{5-}$ and $[W_3Se_4(CN)_9]^{5-}$ by reacting polymeric $\{M_3Se_7Br_4\}_x$ or the derivative $[M_3Se_7Br_6]^{2-}$ ions (M = Mo or W) with CN^- are described. Both products were isolated as the $Cs_5[M_3Se_4(CN)_9]\cdot CsCl\cdot 4H_2O$ salts. The crystal structures are essentially the same with corresponding cell dimensions within 0.3% of each other, and those for the W compound slightly the larger. The M_3Se_4 cores (approximate symmetry C_{3v}) can be described as distorted incomplete cubes with, in the tungsten case, d_{ave}(W−W) 2.829, d_{ave}(W−μ-Se) 2.449, d_{ave}(W−μ_3-Se) 2.497, d_{ave}(W−C) 2.179 and d_{ave}(C−N) 1.16 Å. A different feature as compared to the sulfide analogues is the weak dimerisation of two trimer units giving short Se · · · Se contacts (≈3.5 Å). The UV/VIS spectra of brown $[Mo_3Se_4(CN)_9]^{5-}$ and green $[W_3Se_4(CN)_9]^{5-}$ indicate a red shift on replacing Mo by W, and a similar shift on exchanging S for Se. In electrochemical studies using cyclic, square-wave and differential pulse voltammetric techniques reduction potentials for the $[M_3Se_4(CN)_9]^{5-/6-}$ couple (*vs.* normal hydrogen electrode) of −0.63 (Mo) and −0.97 V (W) were obtained. Using a Hg–Au electrode two additional reduction steps were observed, and there is evidence for the formation of Hg-containing heterometallic clusters. Properties of the two aqua ions $[M_3Se_7(H_2O)_6]^{4+}$ were also studied, where these are similarly converted to $[M_3Se_4(CN)_9]^{5-}$ by Se-abstraction and substitution of H_2O by CN^-.

Since their first preparation in the mid/late 1980s,[1–4] the trinuclear incomplete cuboidal clusters $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ with a vacant metal subsite have attracted much attention.[5–9] Both M^{IV}_3 ions have high stability in acidic solutions, and are lead-in compounds for a series of heterometallic cuboidal clusters, particularly extensive in the case of Mo.[7–9] More recently the sulfur-rich cluster $[Mo_3S_7(H_2O)_6]^{4+}$ and its selenium analogue $[Mo_3Se_7(H_2O)_6]^{4+}$ have been prepared and their solution chemistry explored.[10,11] These clusters have for example a single μ_3-(S) and three μ-(S_2) bridging ligands, with each disulfido group orientated sideways and $\eta^2:\eta^2$ to the two Mo atoms it bridges. One of the S atoms is equatorial and the other axial to the Mo_3 plane.[12,13] In this paper the aqua ion $[W_3Se_7(H_2O)_6]^{4+}$ has been prepared for the first time from polymeric $\{W_3Se_7Br_4\}_{x'}$ and its properties are considered alongside those of $[Mo_3Se_7(H_2O)_6]^{4+}$.[11] With CN^-, Se abstraction is observed together with CN^- replacement of H_2O ligands yielding $[Mo_3Se_4(CN)_9]^{5-}$ and $[W_3Se_4(CN)_9]^{5-}$. The structure of the tellurium analogue $[Mo_3Te_7(CN)_6]^{2-}$ has been reported, but no Te abstraction is observed with CN^-.[14] Structures of the salts of $[Mo_3Se_4(NCS)_9]^{5-}$ and $[W_3Se_4(NCS)_9]^{5-}$ have contributed to the characterisation of M_3Se_4 cores.[15–17]

Experimental

Preparation of starting materials

The polymeric chain compounds $\{Mo_3Se_7Br_4\}_x$ and $\{W_3Se_7Br_4\}_x$ were first prepared by direct combination of the elements.[11,13] To convert to the tetraphenylphosphonium salt of discrete anions these were heated under N_2 in a melt of PPh_4Br (1.5 g of Mo or W compound) at 280 °C for 3 h. The cold melt was ground, washed free of PPh_4Br using ethanol, and the products $[PPh_4]_2[Mo_3Se_7Br_6]$ and $[PPh_4]_2[W_3Se_7Br_6]$ used without further purification.

Other reagents

The strong acid *p*-toluenesulfonic acid (Hpts, Aldrich), potassium cyanide (BDH), triphenylphosphine, PPh_3 (Aldrich, 5% solution in toluene) and the water soluble sodium tris(3-sulfonatophenyl)phosphine tetrahydrate, $Na_3(3\text{-}SO_3C_6H_4)_3P\cdot 4H_2O$ (Strem) referred to as PR_3^{3-} were used. Samples of the latter were shown to contain 10.3% phosphine oxide impurity using ^{31}P NMR spectroscopy. All other reagents were of analytical grade purity.

X-Ray crystallography

Crystal data for $Cs_5[W_3Se_4(CN)_9]\cdot CsCl\cdot 4H_2O$: $C_9H_8ClCs_6N_9O_4Se_4W_3$, $M = 2006.5$, triclinic, space group $P1$, $a = 11.842(10)$, $b = 12.219(9)$, $c = 14.671(12)$ Å, $\alpha = 90.50(4)$, $\beta = 112.40(4)$, $\gamma = 115.27(3)°$, $U = 1737(2)$ Å^3, $Z = 2$, $D_c = 3.836$ g cm^{-3}, $\mu = 20.40$ mm^{-1} (Mo-Kα, λ = 0.710 73 Å), $F(000) = 1724$, $T = 160$ K. A crystal of size 0.38 × 0.29 × 0.29 mm was examined on a Stoe-Siemens four-circle diffractometer. Cell parameters were refined from 2θ values (30–40°) of 30 reflections measured at ±ω to minimise systematic errors. Intensities were measured with ω–θ scans and on-line profile fitting.[18] 6716 measured reflections ($2\theta \leqslant 50°$), corrected semiempirically for absorption (transmission 0.077–0.109), yielded 6081 unique data ($R_{int} = 0.0730$) for structure solution (direct methods) and refinement (least-squares on F^2 values with weighting $w^{-1} = \sigma^2(F_o^2) + (0.0862P)^2 + 42.0712P$, where $P = (F_o^2 + 2F_c^2)/3$). One Cs^+ ion is disordered over two sites. Hydrogen atoms were not located, C and N atoms were refined with isotropic, other atoms with anisotropic displacement parameters. An isotropic extinction parameter x was refined to 0.00160(15), whereby $F'_c = F_c/(1 + 0.001x\lambda^3F_c^2/\sin 2\theta)^{\frac{1}{4}}$. Final $R' = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.1459$ for all data, conventional $R = 0.0514$ on F values of 5708 reflections having $F_o^2 > 2\sigma(F_o^2)$, goodness of fit = 1.116 on all F^2 values with 246 refined parameters. Some difference electron density peaks of up to 4 e Å^{-3} lay close to heavy atoms. Programs: SHELXTL[19] and local

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† *Non-SI unit employed*: M = mol dm^{-3}.

Table 1 Selected bond lengths (Å) and angles (°) for $Cs_5[W_3Se_4(CN)_9]\cdot CsCl\cdot 4H_2O$

W(1)–W(2)	2.840(3)	W(1)–Se(1)	2.498(2)
W(1)–W(3)	2.822(2)	W(2)–Se(1)	2.494(3)
W(2)–W(3)	2.826(2)	W(3)–Se(1)	2.498(2)
W(1)–Se(2)	2.446(2)	W(1)–Se(4)	2.441(2)
W(2)–Se(2)	2.445(2)	W(2)–Se(3)	2.454(2)
W(3)–Se(3)	2.460(3)	W(3)–Se(4)	2.447(2)
W(1)–C(1)	2.157(15)	W(1)–C(2)	2.190(14)
W(1)–C(3)	2.178(13)	W(2)–C(4)	2.193(13)
W(2)–C(5)	2.153(13)	W(2)–C(6)	2.173(14)
W(3)–C(7)	2.178(14)	W(3)–C(8)	2.180(14)
W(3)–C(9)	2.201(13)	C(1)–N(1)	1.15(2)
C(2)–N(2)	1.161(19)	C(3)–N(3)	1.178(18)
C(4)–N(4)	1.162(19)	C(5)–N(5)	1.173(19)
C(6)–N(6)	1.14(2)	C(7)–N(7)	1.167(19)
C(8)–N(8)	1.16(2)	C(9)–N(9)	1.151(19)
W(3)–W(1)–W(2)	59.87(4)	W(3)–W(2)–W(1)	59.76(5)
W(1)–W(3)–W(2)	60.37(6)	Se(4)–W(1)–Se(2)	100.80(7)
Se(4)–W(1)–Se(1)	108.23(6)	Se(2)–W(1)–Se(1)	107.23(8)
Se(2)–W(2)–Se(3)	99.75(6)	Se(2)–W(2)–Se(1)	107.39(8)
Se(3)–W(2)–Se(1)	108.62(7)	Se(4)–W(3)–Se(3)	99.19(9)
Se(4)–W(3)–Se(1)	108.05(6)	Se(3)–W(3)–Se(1)	108.30(7)
W(2)–Se(1)–W(3)	68.95(6)	W(2)–Se(1)–W(1)	69.35(8)
W(3)–Se(1)–W(1)	68.80(5)	W(2)–Se(2)–W(1)	70.98(8)
W(2)–Se(3)–W(3)	70.19(6)	W(1)–Se(4)–W(3)	70.53(5)

programs. Selected bond lengths and angles are given in Table 1.

Crystal data for $Cs_5[Mo_3Se_4(CN)_9]\cdot CsCl\cdot 4H_2O$: $C_9H_8ClCs_6Mo_3N_9O_4Se_4$, $M = 1742.8$, triclinic, space group $P1$, $a = 11.818(10)$, $b = 12.191(8)$, $c = 14.635(8)$ Å, $\alpha = 90.94(5)$, $\beta = 112.23(6)$, $\gamma = 115.16(5)^\circ$, $U = 1727(2)$, $Z = 2$, $D_c = 3.352$ g cm^{-3}, $\mu = 11.6$ mm^{-1}, $F(000) = 1532$, $T = 160$ K. Intensity data were not measured.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/467.

Electrochemical measurements

These were carried out using a computer-interfaced PAR Model 173 potentiostat. Prior to each experiment, the glassy carbon electrode was polished with 0.3 mm alumina, sonicated for 1 min, and rinsed thoroughly with distilled water. A mercury–gold electrode was prepared by coating a freshly polished gold electrode surface with triply-distilled mercury, and can be considered as equivalent to a hanging mercury-drop electrode. The working compartment was made air-free by passing N_2 through the electrochemical cell. The reference electrode was Ag–AgCl, and a platinum wire counter electrode was used. Potassium chloride (0.10 M) was the supporting electrolyte in all cases.

Results and Discussion

Preparation of $[M_3Se_4(CN)_9]^{5-}$ clusters (M = Mo or W)

The most direct method was by treating the polymeric material $\{M_3Se_7Br_4\}_x$ with CN^-, and is the same for both M = Mo and W. A suspension of $\{M_3Se_7Br_4\}_x$ (1 g) in an aqueous solution of KCN (1 g in 10 cm^3) was stirred for ≈60 min [equation (1)].

$$M_3Se_7Br_4 + 12CN^- \longrightarrow [M_3Se_4(CN)_9]^{5-} + 3SeCN^- + 4Br^- \quad (1)$$

After filtering, CsCl (1 g) was added. The solutions, brown for $[Mo_3Se_4(CN)_9]^{5-}$ and green for $[W_3Se_4(CN)_9]^{5-}$, were kept at ambient temperatures for 5–7 d (volume 2–3 cm^3). Dark brown (Mo) or green (W) crystals of $Cs_5[M_3Se_4(CN)_9]\cdot CsCl\cdot 4H_2O$ separated, were filtered off and washed with diethyl ether. Yield 0.65 g (43% for Mo) and 0.54 g (38% for W). Alternatively the reactions of $[PPh_4]_2[M_3Se_7Br_6]$ with CN^- [equation (2)] could be used.

$$[M_3Se_7Br_6]^{2-} + 12CN^- \longrightarrow [M_3Se_4(CN)_9]^{5-} + 3SeCN^- + 6Br^- \quad (2)$$

Preparation of solutions of $[M_3Se_7(H_2O)_6]^{4+}$ (M = Mo or W)

The procedure in the case of $[Mo_3Se_7(H_2O)_6]^{4+}$ has been described in an earlier study.[11] The tungsten analogue was prepared by a similar method [equation (3)]. Thus a solution of

$$[W_3Se_7Br_6]^{2-} + 6H_2O \longrightarrow [W_3Se_7(H_2O)_6]^{4+} + 6Br^- \quad (3)$$

$[PPh_4]_2[W_3Se_7Br_6]$ (0.5 g) in 4 M Hpts (50 cm^3) was kept at 50–60 °C for 6 h. The yellow-orange solution obtained after filtration was diluted seven-fold with H_2O and loaded onto a Dowex 50W-X2 cation-exchange resin column. A well defined tight band at the top of the column was eluted with strong acid, *e.g.* 2–4 M Hpts. Inductively coupled plasma analyses gave a Mo to Se ratio of 3 : 7.2 for $[Mo_3Se_7(H_2O)_6]^{4+}$, and 3 : 7.1 for $[W_3Se_7(H_2O)_6]^{4+}$. Solution yields were $[Mo_3Se_7(H_2O)_6]^{4+}$ (44%) and $[W_3Se_7(H_2O)_6]^{4+}$ (35%). Increasing absorbance is observed towards the UV with shoulders only at ≈370 ($\varepsilon = 1150$) and ≈480 (200) for $[Mo_3Se_7(H_2O)_6]^{4+}$, and ≈375 (1014) and ≈500 nm (330 M^{-1} cm^{-1} per M_3) for $[W_3Se_7(H_2O)_6]^{4+}$. More definitive are the $[M_3Se_4(H_2O)_9]^{4+}$ UV/VIS spectra obtained on reacting $[M_3Se_7(H_2O)_6]^{4+}$ in 2–3 M Hpts (50 cm^3) with 5% triphenylphosphine in toluene (5 cm^3) (solutions were stirred for ≈20 min), or with a ≈ten-fold excess of the water-soluble phosphine $PR_3{}^{3-}$, when faster conversions were observed. Peak positions are at 425 ($\varepsilon = 2460$) and 648 (263) for $[Mo_3Se_4(H_2O)_9]^{4+}$,[15] and 359 (≈6660) and 618 nm (≈547 M^{-1} cm^{-1}) for $[W_3Se_4(H_2O)_9]^{4+}$. In both phosphine reactions the μ-diselenide bonds are cleaved and Se abstraction occurs, equation (4).

$$[M_3Se_7(H_2O)_6]^{4+} + 3PR_3 + 3H_2O \longrightarrow [M_3Se_4(H_2O)_9]^{4+} + 3SePR_3 \quad (4)$$

Conversion of $[M_3Se_7(H_2O)_6]^{4+}$ into $[M_3Se_4(CN)_9]^{5-}$ (M = Mo or W)

Solutions of $[M_3Se_7(H_2O)_6]^{4+}$ in 2 M Hpts were diluted to $[H^+] = 0.5$ M and loaded onto a Dowex 50W-X2 column. After washing with water elution was with 0.1 M KCN. Abstraction of Se by CN^-, and CN^- replacement of H_2O occurs, equation (5).

$$[M_3Se_7(H_2O)_6]^{4+} + 12CN^- \longrightarrow [M_3Se_4(CN)_9]^{5-} + 3SeCN^- + 6H_2O \quad (5)$$

Conversion of $[M_3Se_4(H_2O)_9]^{4+}$ into $[M_3Se_4(CN)_9]^{5-}$ (M = Mo or W)

A solution of $[M_3Se_4(H_2O)_9]^{4+}$ in 2 M HCl was taken to dryness on a vacuum line and a solution of 0.1 M KCN added. Alternatively $[M_3Se_4(H_2O)_9]^{4+}$ was eluted from a cation-exchange column with 0.1 M CN^-. Substitution of H_2O by CN^- gives $[M_3Se_4(CN)_9]^{5-}$. In none of these reactions are M–Se–M bridges cleaved by the concentrations of CN^- used. A similar situation applies for the sulfido-bridged cluster $[Mo_3S_4(H_2O)_9]^{4+}$.[20]

Structures

The structure of the $[W_3Se_4(CN)_9]^{5-}$ anion is shown in Fig. 1. It has essentially C_{3v} symmetry with one μ_3-Se and three μ_2-Se. Mean bond lengths are W–W 2.829, W–μ_2-Se 2.449, W–μ_3-Se 2.497, W–C 2.179 and C–N 1.16 Å. Crystals of the corresponding

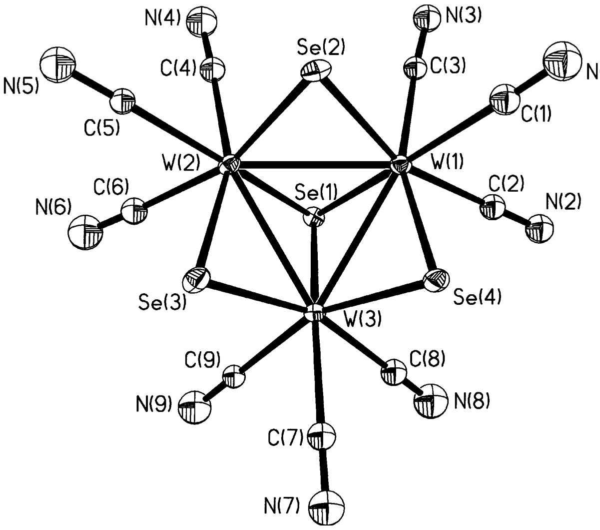

Fig. 1 Structure of the $[W_3Se_4(CN)_9]^{5-}$ anion showing the atom labelling scheme and 50% probability displacement ellipsoids

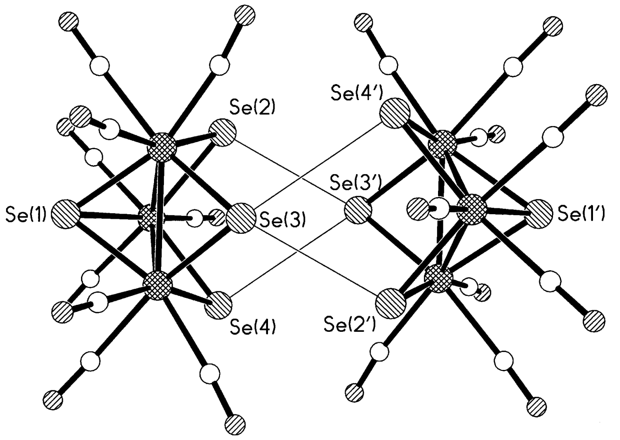

Fig. 2 Structure of the $[W_3Se_4(CN)_9]^{5-}$ anions showing Se···Se interactions between two adjacent clusters

molybdenum complex are isomorphous, with cell axes differing by less than 0.3%, so the structure is probably insignificantly different. The W–Se bonds are slightly longer than those in the $[W_3Se_4(NCS)_9]^{5-}$ anion (mean W–μ_2-Se 2.393, W–μ_3-Se 2.458 Å),[17] and the Mo–Se bonds in $[Mo_3Se_4(NCS)_9]^{5-}$ (mean Mo–μ_2-Se 2.409, Mo–μ_3-Se 2.452 Å).[15] These are the only previously reported structures with incomplete cuboidal M_3Se_4 cores (M = Mo or W). The same type of structure is well known for the M_3S_4 core; the most recent release of the Cambridge Structural Database[21] contains 16 structures of W complexes and 31 structures of Mo complexes. The overall geometry of these M_3S_4 cores is essentially the same as for the M_3Se_4 cores, except that the smaller sulfur atoms lead to shorter M–S bonds, ranging from 2.237 to 2.353 Å for W–μ_2-S_2, from 2.331 to 2.404 Å for W–μ_3-S, from 2.238 to 2.393 Å for Mo–μ_2-S, and from 2.317 to 2.421 Å for Mo–μ_3-S.

As found previously for the $[W_3Se_4(NCS)_9]^{5-}$ anion,[17] the $[W_3Se_4(CN)_9]^{5-}$ anion in the present structure is weakly dimerised through Se···Se interactions, Fig. 2. The observed distances are 3.415 for Se(2)···Se(3′) and 3.686 Å for Se(4)···Se(3′), comparable to the distances of 3.361–3.585 Å in the $[W_3Se_4(NCS)_9]^{5-}$ weak dimer,[17] and shorter than the intramolecular distances of 3.737–3.746 Å between pairs of μ_2-Se atoms in the present structure.

UV/VIS spectra

Peak positions λ/nm (ε/M^{-1} cm^{-1} per trimer) were obtained for both $[M_3Se_4(CN)_9]^{5-}$ clusters (Fig. 3) and are 350 (5070), 443 (5460), 677 (730) (M = Mo); and 322 (8700), 387 (6200), 622 (860) (M = W). The spectrum of $[Mo_3S_4(CN)_9]^{5-}$, 342 (4500), 377 (5500), 610 (500) has been reported previously.[20] The relative peak positions Mo > W indicate higher energy ligand-to-metal charge transfer (LMCT) transitions for the W cluster, and Se > S with the higher energy transitions for the S clusters. Both effects correlate with known redox properties of the elements. Thus in the $[IrCl_6]^{2-}$ oxidations of $[M^V{}_2O_4(H_2O)_6]^{2+}$ and $[M^{IV}{}_3O_4(H_2O)_9]^{4+}$ the M = W reactions are 10^5–10^6 times faster than those with M = Mo.[22] Also the electronegativity of sulfur is greater than that of selenium. Müller *et al.*[20] have reported molecular orbital calculations relating to the electronic structures of $[Mo_3S_4(CN)_9]^{5-}$ and other Mo–S complexes. These show that the bonding within a central Mo_xS_y moiety is rather localised (70–80% Mo 4d and S 3p). Li *et al.*[23] on the other hand have reported calculations consistent with delocalisation and multiple bonding in the quasi-aromatic $Mo_3(\mu_2\text{-}S)_3$ fragment of the $Mo_3S_4{}^{4+}$ core. An additional band for $[Mo_3Se_4(CN)_9]^{5-}$ at 247 nm (ε = 17 000 M^{-1} cm^{-1} per Mo_3) is observed also for $[Mo_3S_4(CN)_9]^{5-}$, and is assigned to CN→Mo charge transfer. Data for the lower energy peaks in the visible region for $[M_3Y_4(H_2O)_9]^{4+}$ (M = Mo or W; Y = S or Se) in 2 M Hpts and 1 M HCl, and for $[M_3Y_4(CN)_9]^{5-}$ and $[M_3Y_4(NCS)_9]^{5-}$ (N bonded) are given in Table 2. Trends observed for the thiocyanato complexes are an interesting feature indicating a greater 'mixing in' with this terminal ligand.

Table 2 A comparison of the lowest energy transition in the UV/VIS electronic spectra λ/nm (ε/M^{-1} cm^{-1} per M_3) for M_3Y_4 clusters (M = Mo or W, Y = S or Se)

Cluster	Mo/S	W/S	Mo/Se	W/Se
$[M_3Y_4(H_2O)_9]^{4+}$ in 2 M Hpts	602 (251)[a]	560 (490)[a]	648 (263)[b]	618
$[M_3Y_4(H_2O)_9]^{4+}$ in 1 M HCl	620 (315)[a]	570 (480)[a]	677[c]	623[d]
$[M_3Y_4(CN)_9]^{5-}$ in H_2O	610 (500)[e]	579 (370)[f]	677 (730)	611 (860)
$[M_3Y_4(NCS)_9]^{5-}$ in 1 M NCS		640 (730)[a]		680

[a] Refs. 5 and 6. [b] Ref. 15. [c] Absorbance ratio $A_{431}:A_{677}$ = 11.2. [d] Absorbance ratio $A_{358}:A_{623}$ = 13.6. [e] Ref. 18. [f] Ref. 24.

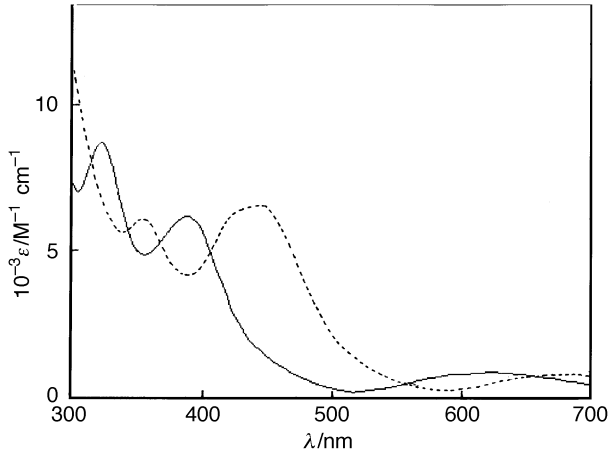

Fig. 3 The UV/VIS spectra of $[Mo_3Se_4(CN)_9]^{5-}$ (---) and $[W_3Se_4(CN)_9]^{5-}$ (——) in H_2O

Electrochemical studies

The $Mo^{IV}{}_3$ cluster $[Mo_3Se_4(CN)_9]^{5-}$ gives an irreversible cyclic voltammogram, Fig. 4, but a quasi-reversible response at −0.86 (average) *vs.* Ag–AgCl electrode (−0.63 *vs.* NHE), Table 3, by SWV corresponding to the $Mo^{IV}{}_3 + e^- \rightleftharpoons Mo^{III}M^{IV}{}_2$ change, Fig. 5. Cyclopentadienyl analogues $[Mo_3S_4Cp_3]^+$ and $[Mo_3S_4Cp_3]$ (Cp = η^5-C_5H_5) having the same core oxidation states have been studied previously.[25,26] In the case of $[Mo_3S_4(CN)_9]^{5-}$, the reduction potential for the same one-

Table 3 Summary of electrochemical data (25 °C) for $[Mo_3Se_4(CN)_9]^{5-}$ and $[W_3Se_4(CN)_9]^{5-}$ in aqueous solution, N_2 atmosphere, I = 0.10 M (KCl) *

Complex	Method	Ep_c/V	Ep_a/V	$E_{\frac{1}{2}}$/V	$E°'$/V	Reversibility	Electrode
$[Mo_3Se_4(CN)_9]^{5-}$	CV	−0.96	−0.62			irrev	GC
	SWV				−0.87		
	DPV				−0.86		
	CV	−0.86	−0.79	−0.83		q-rev	Hg–Au
	CV	−1.17	−1.11	−1.14		q-rev	
	CV	−1.39				irrev	
	SWV				−0.82		
	SWV				−1.13		
	SWV				−1.29		
	DPV				−0.83		
	DPV				−1.13		
	DPV				−1.28		
$[W_3Se_4(CN)_9]^{5-}$	CV	−1.28	−1.08	−1.18		q-rev	GC
	SWV				−1.20		
	CV	−1.19	−1.09	−1.14		q-rev	Hg–Au
	CV	−1.33				irrev	
	CV	−1.67				irrev	
	SWV				−1.15		
	SWV				−1.30		
	SWV				−1.62		

* Abbreviations used: CV = cyclic voltammetry, SWV = square wave voltammetry, DPV = differential pulse voltammetry, GC = glassy carbon electrode, Hg–Au is Hg coated Au electrode, CV peak to peak separation (Δ*E*p) gives $E_{\frac{1}{2}}$ if quasi-reversible (q-rev); potentials are given *vs.* Ag–AgCl electrode, add 0.22 V to convert to values *vs.* NHE.

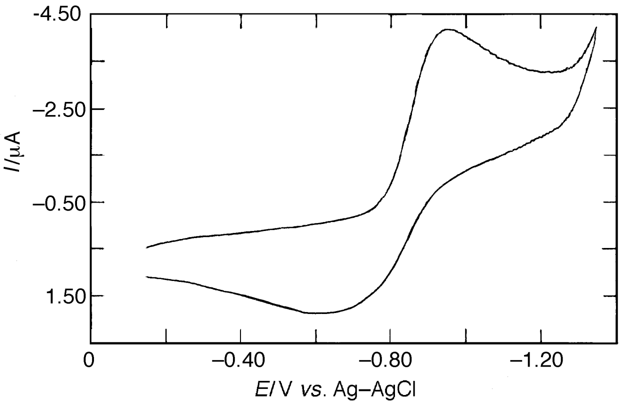

Fig. 4 Cyclic voltammogram for $[Mo_3Se_4(CN)_9]^{5-}$ at a glassy carbon electrode in 0.10 M KCl, cathodic potential −0.96 V and anodic potential −0.62 V *vs.* Ag–AgCl electrode, irreversible behaviour indicated

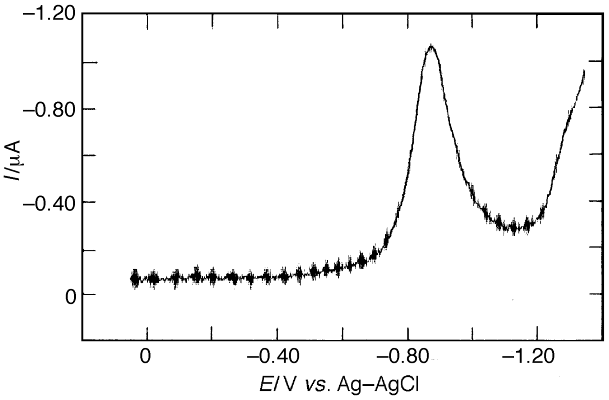

Fig. 5 Square-wave voltammogram for the $[Mo_3Se_4(CN)_9]^{5-/6-}$ couple giving a reduction potential $E°'$ = −0.87 V *vs.* Ag–AgCl (−0.65 V *vs.* NHE) in 0.10 M KCl

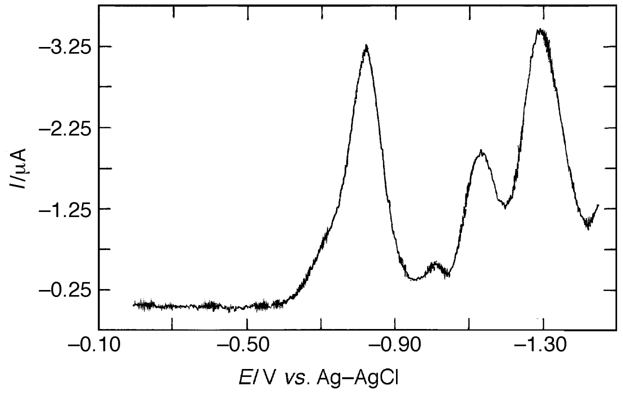

Fig. 6 Square-wave voltammogram for $[Mo_3Se_4(CN)_9]^{5-}$ at a Hg–Au electrode in 0.10 M KCl, giving an $E°'$ value of −0.82 V *vs.* Ag–AgCl (−0.60 V *vs.* NHE) for the $[Mo_3Se_4(CN)_9]^{5-/6-}$ couple and two additional peaks at −1.13 and −1.29 assigned to a Hg-adduct (see text)

electron process has been reported as −1.49 V *vs.* NHE.[20,27] It is concluded that the Se core ligands stabilize the lower 6− oxidation state. In the case of the tungsten analogue $[W_3Se_4(CN)_9]^{5-}$ the reduction potential of −1.19 V *vs.* Ag–AgCl (−0.97 V *vs.* NHE), Table 3, confirms that the W^{IV}_3 cluster is more difficult to reduce than the Mo^{IV}_3. Using a glassy carbon electrode both clusters give only one redox stage for the potential range explored. Reduction potentials (*vs.* NHE) for the same redox change $M^{IV}_3 + e^- \rightleftharpoons M^{III}M^{IV}_2$ and other couples are for $[Mo_3S_4(Hnta)_3]^{2-/3-}$ (−0.42), $[W_3S_4(Hnta)_3]^{2-/3-}$ (−0.90), $[Mo_3S_4Cl_3(dmpe)_3]^{+/0}$ (−0.42) and $[W_3S_4(Hnta)_3]^{2-/3-}$ (−0.89 V),[28,29] where Hnta is singly-protonated nitrilotriacetate (aqueous solutions), and dmpe = 1,2-bis(dimethylphosphino)ethane (organic solvent). Again the Mo clusters are more readily reduced. The differences observed for the Mo and W analogues of 0.48 and 0.47 V are similar to the 0.34 V value observed in the present studies.

Using a Hg–Au electrode additional redox steps are observed, *e.g.* Fig. 6. The first peak remains initially unchanged and is assigned to the $[Mo_3Se_4(CN)_9]^{5-/6-}$ couple. The two additional peaks are assigned to Hg heterometallic adducts $[Mo_3HgSe_4(CN)_9]^{5-}$ or a related cluster, in which case couples such as $[Mo_3HgSe_4(CN)_9]^{6-/7-}$ and $[Mo_3HgSe_4(CN)_9]^{7-/8-}$ may be relevant. No colour changes were observed using the Hg–Au electrode. The tungsten complex gives similar behaviour with reduction potentials as listed in Table 3. A hanging mercury-drop electrode was used in the studies by Shibahara *et al.*[28] on the Hnta complexes, when three stages were also observed.

Conclusions

Studies on $[Mo_3Se_4(CN)_9]^{5-}$ and $[W_3Se_4(CN)_9]^{5-}$ have further established the chemistry of M_3Se_4 clusters. The structures have virtually identical geometries and short M–M distances observed are consistent with metal–metal bonding. Unlike aqua M_3Se_4 (and M_3S_4) complexes, electrochemical reduction is possible with the cyano products. Reduction potentials (*vs.* NHE) associated with the $M^{IV}{}_3 + e^- \rightleftharpoons M^{III}M^{IV}{}_2$ couple −0.63 (Mo) and −0.97 V (W) illustrate a more readily accessed redox chemistry, with Mo the more easily reduced. Previously the reduction potential for the $[Mo_3S_4(CN)_9]^{5-/6-}$ couple has been reported as −1.49 V (*vs.* NHE),[20,26] and from the differences in reduction potentials observed a value in the range −1.80 to −1.90 is estimated for the $[W_3S_4(CN)_9]^{5-/6-}$ couple. Red shifts in the UV/VIS spectra are observed on replacing Mo with W and Se with S, consistent with LMCT transitions.

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