Preparation, Structure, and Reactivity of Heterometallic Sn-Containing Single- and Double-Cube Derivatives of $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$

Rita Hernandez-Molina,† Danil N. Dybtsev,‡ Vladimir P. Fedin,‡ Mark R. J. Elsegood,† William Clegg,† and A. Geoffrey Sykes*,†

Department of Chemistry, The University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK, and
Institute of Inorganic Chemistry, Russian Academy of Sciences, Pr. Lavrentjeva 3,
Novosibirsk 630090, Russia

Received January 16, 1998

The preparation and properties of Sn-containing derivatives of trinuclear $M^{IV}{}_3Se_4{}^{4+}$ incomplete cuboidal clusters $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$ are described. Addition of Sn^{II} to $[Mo_3Se_4(H_2O)_9]^{4+}$ gives the single-cube $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ in 2 M Hpts ($pts^- = p$-toluenesulfonate) and $[Mo_3(SnCl_3)Se_4(H_2O)_9]^{3+}$ in 2 M HCl. The structure has been determined by X-ray crystallography on $(NH_2Me_2)_6\,[Mo_3(SnCl_3)Se_4(NCS)_9]\cdot 0.5H_2O$. The reaction of Sn metal with $[Mo_3Se_4(H_2O)_9]^{4+}$ gives the first example of an Se-containing corner-shared double cube, characterized by X-ray crystallography as $[Mo_6SnSe_8(H_2O)_{18}](pts)_8\cdot 2Hpts\cdot 28H_2O$. The clusters $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ and $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ are also characterized by the ease of elution in Dowex chromatography, ICP elemental analyses, and the stoichiometries of the oxidation with $[Co(dipic)_2]^-$. The preparation of the single-cube $[W_3SnSe_4(H_2O)_{12}]^{6+}$ in 2 M Hpts, $[W_3(SnCl_3)Se_4\,(H_2O)_9]^{3+}$ in 2 M HCl, is also described. Conversion of $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ into corner-shared double-cubes $[Mo_6SnSe_8\,(H_2O)_{18}]^{8+}$, $[Mo_6SnSe_4S_4(H_2O)_{18}]^{8+}$, $[Mo_3W_3SnSe_8(H_2O)_{18}]^{8+}$, and $[Mo_3W_3SnSe_4S_4(H_2O)_{18}]^{8+}$ was achieved by reductive addition of $[Mo_3Se_4(H_2O)_9]^{4+}$, $[Mo_3S_4(H_2O)_9]^{4+}$, $[W_3Se_4(H_2O)_9]^{4+}$, and $[W_3S_4(H_2O)_9]^{4+}$ using $BH_4{}^-$. A similar procedure was used for the conversion of $[W_3Se_4(H_2O)_9]^{4+}$ into $[W_6SnSe_8(H_2O)_{18}]^{8+}$. Transfer of Sn^{II} is observed in the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$, $[W_3SnSe_4(H_2O)_{12}]^{6+}$, and $[W_3SnS_4(H_2O)_{12}]^{6+}$. With the inclusion of similar reactions of $[Mo_3Se_4(H_2O)_9]^{4+}$ etc., the order of affinities for Sn^{II} uptake is $Mo_3S_4{}^{4+} > Mo_3Se_4{}^{4+} > W_3Se_4{}^{4+} > W_3S_4{}^{4+}$. The displacement of In^I from $[W_3InSe_4(H_2O)_{12}]^{5+}$ by Sn^{II} is also consistent with equilibrium processes involving dissociation of the heteroatom.

Introduction

While heteroatom derivatives of trinuclear M^{IV} (M = Mo, W) incomplete cuboidal clusters $[M_3S_4(H_2O)_9]^{4+}$ have been extensively studied,[1,2] and elements from group 6[3] through group 15[4−6] have been incorporated as heteroatoms, the corresponding derivatives of $[M_3Se_4(H_2O)_9]^{4+}$ [7,8] have received little attention. To explore the properties of such clusters we chose to study Sn derivatives, which in the case of $[M_3S_4(H_2O)_9]^{4+}$ have provided a rich and varied chemistry.[9−12] One of the most interesting features in the case of $[Mo_3S_4(H_2O)_9]^{4+}$ is the existence of a single-cube $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ (addition of Sn^{II}) and a corner-shared double-cube $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ (reaction with Sn)[9,12] and the identification of (redox) procedures for interconversion of the two.[9] In the case of $[W_3S_4(H_2O)_9]^{4+}$, the double cube is not formed in the reaction with Sn metal, and an alternative route involving reductive addition of $[W_3S_4(H_2O)_9]^{4+}$ to $[W_3SnS_4(H_2O)_{12}]^{6+}$ is required to prepare $[W_6SnS_8(H_2O)_{18}]^{8+}$.[11] The interconversion of single and double cubes is a theme explored further in this paper, leading to the production of mixed Mo−W and Se−S double cubes. Processes involving transfer of Sn as a heteroatom trinuclear cluster and the displacement of another heteroatom by Sn^{II} are also considered.

Other Mo−Se clusters which have been isolated previously include the $Mo^{IV}{}_3$ incomplete cubes $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$, $x = 1-3$, the single-cubes $[Mo_4Se_4(H_2O)_{12}]^{n+}$, $n = 4-6$, and the double-cube $[Mo_7Se_8(H_2O)_{18}]^{8+}$.[7,13]

Experimental Section

Preparation of $[Mo_3Se_4(H_2O)_9]^{4+}$. Solutions of the yellow-brown $[Mo_3Se_4(H_2O)_9]^{4+}$ were prepared from polymeric $\{Mo_3Se_7Br_4\}_x$. The latter was obtained by heating Mo (4.0 g), Se (7.44 g), and Br_2 (1.44

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S0020-1669(98)00047-0 CCC: $15.00

mL) in a sealed glass ampule to ~350 °C as previously described.[14] The polymeric product and PPh_4Br (2 g per 1 g of polymer) were melted together at 250 °C and heated for ~3 h under N_2 to obtain $(Ph_4P)_2[Mo_3Se_7Br_6]$.[8,13] The solid was powdered and washed with hot EtOH, and the brown solid was left to stand in 4 M Hpts for 10 h under N_2. The filtrate was then treated with PPh_3 in dichloromethane to convert $Se_7 \rightarrow Se_4$ by Se abstraction.[14] The two-phase reaction was stirred for 3−4 h. The organic layer was discarded, and the $[Mo_3Se_4(H_2O)_9]^{4+}$ in the aqueous layer purified by Dowex 50W-X2 cation-exchange chromatography. The column was washed with 0.5 M HCl (200 mL), and the $[Mo_3Se_4(H_2O)_9]^{4+}$ eluted with 2 M HCl. The UV−vis spectrum gave peak λ/nm (ϵ/M^{-1} cm^{-1} per Mo_3) at 433 (5250), 681 (580). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) elemental analyses carried out on a 2 M HCl solution gave a Mo:Se ratio of 3:4.15.

Preparation of $[W_3Se_4(H_2O)_9]^{4+}$. A mixture of polymeric $\{W_3Se_7Br_4\}_x$ (5 g), prepared by a similar procedure to the Mo analogue,[8] with concd HCl (20 mL) and H_3PO_2 (5 mL, 1:1 w/w solution in H_2O) as reductant, was heated at 90 °C under N_2 for 12−15 h. The green color of $[W_3Se_4(H_2O)_9]^{4+}$ formed, and H_2Se (absorbed in alkali solution; *use a fumehood*) was released (eq 1). The green solution was diluted

$$W_3Se_7Br_4 + 3H_3PO_2 + 3H_2O \rightarrow W_3Se_4^{\ 4+} + 3H_2Se + 3H_3PO_3 + 4Br^- \quad (2)$$

(×2) and filtered. The $[H^+]$ was then adjusted to ~0.5 M by further dilution and loaded onto a Dowex 50W-X2 cation-exchange column. The column was washed with 0.5 M HCl (200 mL), and $[W_3Se_4(H_2O)_9]^{4+}$ eluted with 2 M HCl. The UV−vis spectrum has peaks λ/nm (ϵ/M^{-1} cm^{-1} per W_3) at 360 (6950) and 625 (500).

Preparation of $[W_3InSe_4(H_2O)_{12}]^{5+}$. A sample of this cluster was prepared by reacting indium wire (6 pieces, each ~1 cm long, 1.6 mm diameter; Johnson Matthey Ltd., Specpure) with $[W_3Se_4(H_2O)_9]^{4+}$ in 2 M HCl (15 mL; 4 mM). The solution (under N_2) was heated at ~70 °C (hot plate) for ~3 h. Purification was by Dowex 50W-X2 chromatography. The blue-green product in 2 M HCl gave UV−vis peak positions λ/nm (ϵ/M^{-1} cm^{-1} per W_3) at 332 (1.2×10^4) and 580 (870).

Other Reagents. The M^{IV}_3 incomplete cubes [UV−vis peak positions λ/nm (ϵ/M^{-1} cm^{-1} per M_3) for $[Mo_3S_4(H_2O)_9]^{4+}$, 370 (4995) and 616 (326) in 2 M HCl, 366 (5550) and 603 (362) in 2 M Hpts,[13,15] and for $[W_3S_4(H_2O)_9]^{4+}$, 317 (6100) and 570 (480) in 2 M HCl, and 315 (6350) and 560 (446) in 2 M Hpts][11,16] were prepared as previously described. The preparation of the cobalt(III) complex $NH_4[Co(dipic)_2]^-$ (dipic = 2,6-dicarboxylatopyridine), 510 (630), and determination of the reduction potential have also been described.[13,17] The strong acid *p*-toluenesulfonic acid (white crystalline solid, Hpts), tin(II) chloride ($SnCl_2 \cdot 2H_2O$), tin metal shot, and triphenylphosphine (PPh_3) were obtained from Aldrich. Dimethylammonium chloride was from BDH-(GP).

Table 1. Crystallographic Data for $(NH_2Me_2)_6[Mo_3SnCl_3Se_4(NCS)_9] \cdot 0.5H_2O$ (**1**) and $[Mo_6SnSe_8(H_2O)_{18}](pts)_8 \cdot 2Hpts \cdot 28H_2O$ (**2**)

	1	**2**
empirical formula	$C_{21}H_{49}Cl_3Mo_3N_{15}O_{0.5}S_9Se_4$	$C_{70}H_{112}Mo_6O_{76}S_{10}Se_8Sn$
fw	1637.0	3816.2
cryst syst	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a, Å	42.602(2)	12.1069(7)
b, Å	11.9783(6)	17.9192(10)
c, Å	21.7785(12)	18.3662(10)
α, deg		63.032(2)
β, deg	95.028(2)	76.024(2)
γ, deg		86.799(2)
V, Å^3	11070.9(10)	3439.4(3)
Z	8	1
ρ_{calc}, g/cm^3	1.964	1.842
μ, cm^{-1}	42.6	30.7
T, °C	−113	−113
R^a	0.0455	0.0495
$R_w{}^b$	0.1303	0.1234

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for "observed" reflections having $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**

Sn−Cl(1)	2.468(2)	Sn−Cl(2)	2.471(3)
Sn−Cl(3)	2.442(3)	Sn−Se(1)	2.7341(7)
Sn−Se(2)	2.7827(7)	Sn−Se(3)	2.8052(7)
Se(1)−Mo(1)	2.4450(7)	Se(1)−Mo(2)	2.4538(7)
Se(2)−Mo(1)	2.4615(7)	Se(2)−Mo(3)	2.4656(7)
Se(3)−Mo(2)	2.4650(6)	Se(3)−Mo(3)	2.4633(7)
Se(4)−Mo(1)	2.4643(7)	Se(4)−Mo(2)	2.4552(6)
Se(4)−Mo(3)	2.4602(6)	Mo(1)−N(1)	2.145(5)
Mo(1)−N(2)	2.170(4)	Mo(1)−N(3)	2.179(5)
Mo(2)−N(4)	2.163(4)	Mo(2)−N(5)	2.150(5)
Mo(2)−N(6)	2.177(5)	Mo(3)−N(7)	2.181(4)
Mo(3)−N(8)	2.135(5)	Mo(3)−N(9)	2.174(4)
Mo(1)−Mo(2)	2.8056(7)	Mo(1)−Mo(3)	2.7774(6)
Mo(2)−Mo(3)	2.7798(6)		
Cl(3)−Sn−Cl(1)	91.63(8)	Cl(3)−Sn−Cl(2)	91.10(15)
Cl(1)−Sn−Cl(2)	89.09(7)	Se(1)−Sn−Se(2)	79.41(2)
Se(1)−Sn−Se(3)	78.361(19)	Se(2)−Sn−Se(3)	76.922(18)
N(1)−Mo(1)−N(2)	82.20(19)	N(1)−Mo(1)−N(3)	80.32(19)
N(2)−Mo(1)−N(3)	80.70(17)	N(5)−Mo(2)−N(4)	85.08(17)
N(5)−Mo(2)−N(6)	81.38(19)	N(4)−Mo(2)−N(6)	81.76(17)
N(8)−Mo(3)−N(9)	79.13(17)	N(8)−Mo(3)−N(7)	83.40(17)
N(9)−Mo(3)−N(7)	80.15(16)	Se(1)−Mo(1)−Se(2)	91.84(2)
Se(1)−Mo(2)−Se(3)	90.72(2)	Se(3)−Mo(3)−Se(2)	89.69(2)
Se(1)−Mo(1)−Se(4)	108.81(3)	Se(2)−Mo(1)−Se(4)	110.28(2)
Se(1)−Mo(2)−Se(4)	108.82(2)	Se(4)−Mo(2)−Se(3)	110.36(2)
Se(4)−Mo(3)−Se(3)	110.25(2)	Se(4)−Mo(3)−Se(2)	110.28(2)

X-ray Crystallography. Crystal data for the complexes $(NH_2Me_2)_6[Mo_3SnCl_3Se_4(NCS)_9] \cdot 0.5H_2O$ (**1**) and $[Mo_6SnSe_8(H_2O)_{18}](pts)_8 \cdot 2Hpts \cdot 28H_2O)$ (**2**) are listed in Table 1, and further details of the structure refinement and calculations are in the Supporting Information. Crystals were examined at 160 K on a Bruker AXS SMART CCD area-detector diffractometer with Mo Kα radiation (λ = 0.710 73 Å). Intensities were integrated from more than a hemisphere of data recorded on 0.3° frames by ω rotation, with unique data essentially complete to 52° in 2θ; cell parameters were refined from the observed rotation angles of all strong reflections in each complete data set. Semiempirical absorption corrections were applied, based on symmetry-equivalent and repeated data.

The structures were determined by direct methods and refined by full-matrix least-squares on F^2 for all data. Anisotropic displacement parameters were refined for non-hydrogen atoms, and isotropic H atoms were included with appropriate riding model constraints. Some disorder was resolved in counterions and solvent molecules. Programs were standard Bruker AXS control (SMART) and integration (SAINT) software, SHELXTL,[18] and local programs. Selected bond lengths and angles are listed in Tables 2 and 3. Complete tables of coordinates, geometry, and displacement parameters can be found in the Supporting Information.

Instruments and Procedures. UV-vis spectra were recorded on Perkin-Elmer Lambda 9 and Shimadzu 2010PC spectrophotometers.

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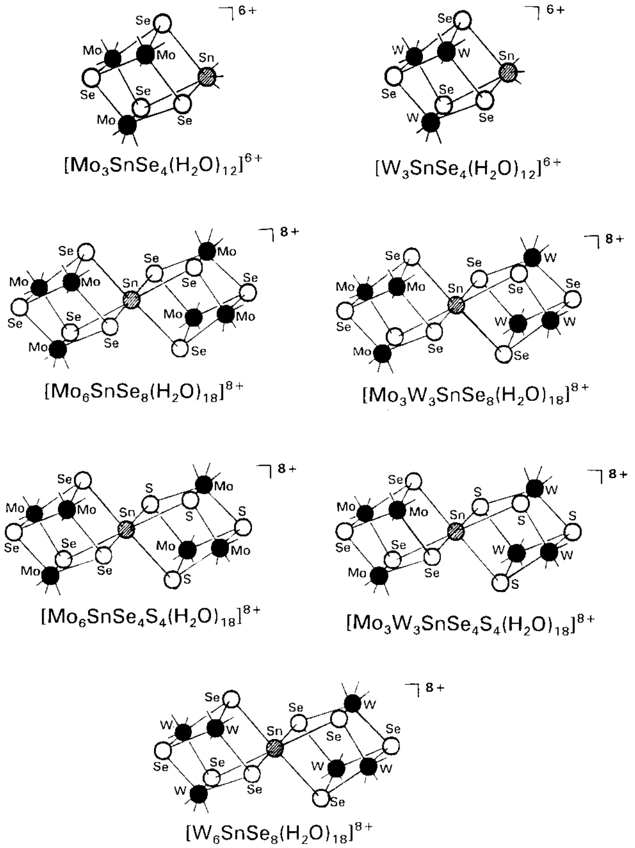
Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **2**

Sn−Se(2)	2.7543(6)	Sn−Se(3)	2.7467(6)
Sn−Se(4)	2.7292(5)	Mo(1)−Se(1)	2.4572(7)
Mo(1)−Se(2)	2.4614(7)	Mo(1)−Se(4)	2.4722(8)
Mo(2)−Se(1)	2.4590(7)	Mo(2)−Se(2)	2.4607(7)
Mo(2)−Se(3)	2.4709(7)	Mo(3)−Se(1)	2.4580(8)
Mo(3)−Se(3)	2.4694(7)	Mo(3)−Se(4)	2.4663(7)
Mo(1)−O(1)	2.206(3)	Mo(1)−O(2)	2.196(4)
Mo(1)−O(3)	2.168(4)	Mo(2)−O(4)	2.217(4)
Mo(2)−O(5)	2.200(4)	Mo(2)−O(6)	2.159(4)
Mo(3)−O(7)	2.186(4)	Mo(3)−O(8)	2.160(4)
Mo(3)−O(9)	2.208(4)	Mo(1)−Mo(2)	2.7128(7)
Mo(1)−Mo(3)	2.7343(7)	Mo(2)−Mo(3)	2.7483(8)
Se(4)−Sn−Se(3)	79.828(16)	Se(4)−Sn−Se(2)	77.879(17)
Se(3)−Sn−Se(2)	78.420(16)	O(3)−Mo(1)−O(2)	78.79(15)
O(3)−Mo(1)−O(1)	77.31(14)	O(2)−Mo(1)−O(1)	78.04(14)
O(6)−Mo(2)−O(5)	81.72(15)	O(6)−Mo(2)−O(4)	77.52(15)
O(5)−Mo(2)−O(4)	75.19(14)	O(8)−Mo(3)−O(7)	82.93(15)
O(8)−Mo(3)−O(9)	79.00(16)	O(7)−Mo(3)−O(9)	78.25(15)
Se(2)−Mo(1)−Se(4)	88.62(2)	Se(2)−Mo(2)−Se(3)	89.68(2)
Se(4)−Mo(3)−Se(3)	90.77(2)	Se(1)−Mo(1)−Se(2)	112.18(3)
Se(1)−Mo(1)−Se(4)	111.24(3)	Se(1)−Mo(2)−Se(2)	112.14(2)
Se(1)−Mo(2)−Se(3)	110.61(3)	Se(1)−Mo(3)−Se(4)	111.42(2)
Se(1)−Mo(3)−Se(3)	110.70(3)		



$[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ $[W_3SnSe_4(H_2O)_{12}]^{6+}$

$[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ $[Mo_3W_3SnSe_8(H_2O)_{18}]^{8+}$

$[Mo_6SnSe_4S_4(H_2O)_{18}]^{8+}$ $[Mo_3W_3SnSe_4S_4(H_2O)_{18}]^{8+}$

$[W_6SnSe_8(H_2O)_{18}]^{8+}$

Figure 1. Schematic structures of Sn heterometallic derivatives obtained in this work from the Se-containing trinuclear clusters $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$.

ICP-AES analyses, using an ATI Unicam model 701 instrument, were on cluster solutions containing 10−100 ppm of the metals in 1−2 M HCl.

Results

Formulae of the single and double cubes synthesized in this work are summarized in Figure 1.

Preparation and Characterization of $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$. A solution of $[Mo_3Se_4(H_2O)_9]^{4+}$ (3 mM; 20 mL) in 2 M HCl was siphoned (via plastic tubing; N_2 pressure) onto $SnCl_2{\cdot}2H_2O$ (0.3 g), both air-free (N_2). The color of the yellow-brown solution became yellow-green instantly. After standing for ~30 min the solution was diluted to 0.4 M HCl and loaded onto a Dowex 50W-X2 cation-exchange column. After it was washed with 0.5 M HCl (200 mL), the product was eluted with 1 M HCl. From the elution behavior, and from previous findings with $[Mo_3SnS_4(H_2O)_{12}]^{6+}$,[9,19] the most likely formula that applies is $[Mo_3(SnCl_3)Se_4(H_2O)_9]^{3+}$. No unreacted trinuclear cluster was observed in the elution procedure, and for the conditions used the conversion is quantitative. The reaction is summarized by eq 2. ICP elemental analysis on the 1 M HCl

$$Mo_3Se_4^{\ 4+} + SnCl_3^{\ -} \rightarrow Mo_3(SnCl_3)Se_4^{\ 3+} \qquad (2)$$

solution gave Mo:Sn:Se of 3.0:1.1:4.1. The single cube was also eluted with 3 M Hpts. Spectra of $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ in 2 M HCl and 2 M Hpts Figure 2, peak positions λ/nm (ϵ/M^{-1} cm^{-1} per Mo_3) 392 (1.49×10^4), 448 (5880), 644 (413) in 2 M HCl; 359 (1.06×10^4), 428 (4320), 615 (186) in 2 M Hpts) provide further evidence for complexing by Cl^-. Whereas $[Mo_3SnSe_4\ (H_2O)_{12}]^{6+}$ in 1 M HCl is quite stable in air with only 0.5% decay in 8 h, the cluster is less stable in Hpts solutions, and a red-brown precipitate forms after 1 day in air. For solutions in 3 M Hpts a similar precipitate builds up on storage for 2−3 weeks at 4 °C under N_2. When the solutions and precipitate are heated for ~1 h, the solid turns gray, consistent with amorphous red selenium.

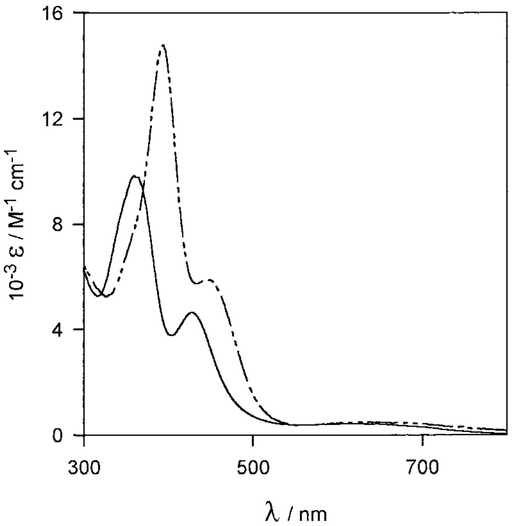


Figure 2. UV−vis spectra of $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ in 2 M HCl (··−··) and 2 M Hpts (—), ϵ's per Mo_3. In 2 M HCl the cluster is present as the chloro complex $[Mo_3(SnCl_3)Se_4(H_2O)_9]^{3+}$.

Crystals were obtained by the addition of a 1 M HCl solution of $[Mo_3Se_4(H_2O)_9]^{4+}$ (5 mM, 20 mL) to $SnCl_2{\cdot}2H_2O$ (0.20 g). The resultant yellow-green solution was stirred for 5 min, when sodium thiocyanate (2.0 g) and excess dymethylammonium chloride were added. The brown-orange solution was further stirred for 1−2 min and allowed to stand at room temperature. After 1 day dark brown crystals of $(NH_2Me_2)_6[Mo_3(SnCl_3)Se_4(NCS)_9]{\cdot}0.5H_2O$ were filtered off and dried in air. Yield: 0.13 g (81%). Anal. Calcd for $C_{21}H_{50}N_{15}Cl_3Mo_3O_{0.5}Se_4S_9Sn$: C,

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(19) In the case of $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$ a formation constant $K > 10^2$ M^{-3} is deduced from the extent of reaction at $[Cl^-] \leq 0.05$ M.[9] The 1:1 complexing of Cl^- to $[Mo_4S_4(H_2O)_{12}]^{5+}$ ($K = 1.98\ M^{-1}$)[20] and to $[Mo_3S_4(H_2O)_9]^{4+}$ ($K = 3.0\ M^{-1}$)[21] is much less extensive at 25 °C, I = 2.00 M ($LiClO_4$).

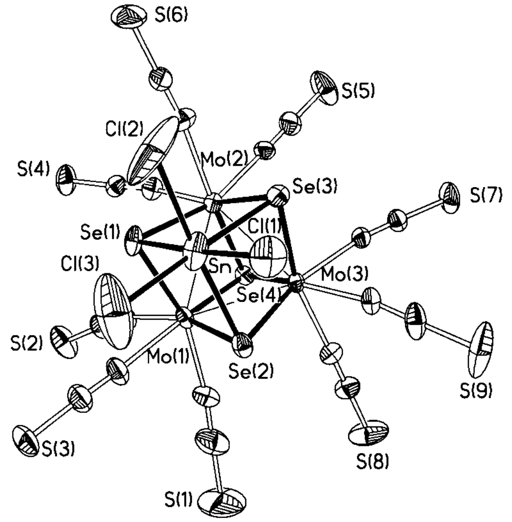

Figure 3. View of the anion single-cube $[Mo_3(SnCl_3)Se_4(NCS)_9]^{6-}$ with 50% probability ellipsoids and atomic labeling. Thiocyanate N and C atoms are numbered as the corresponding S atoms.

15.32; N, 12.70; H, 3.04. Found: C, 15.50; N, 12.99; H, 2.80. The structure of the anion is shown in Figure 3.

Preparation and Characterization of $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$. All procedures were carried out under N_2. Tin shot was added to a solution of $[Mo_3Se_4(H_2O)_9]^4$ (6 mM, 20 mL) in 2 M HCl, and the solution was deoxygenated by bubbling N_2 through for 30 min. After standing overnight the solution was diluted to 0.5 M HCl and loaded onto a Dowex 50W-X2 cation-exchange column. The column was washed with 0.5 M HCl (100 mL) followed by 1 M HCl. No yellow-green band corresponding to $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ was observed. The dark green $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ product eq 3 was eluted with 2 M HCl. On

$$2Mo_3Se_4{}^{4+} + Sn \rightarrow Mo_6SnSe_8{}^{8+} \qquad (3)$$

recolumning $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ (particularly after storage), small amounts of $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ followed by $[Mo_3Se_4(H_2O)_9]^{4+}$ were eluted at the 1 M HCl stage. Coordination of Cl^- to the Mo's results in elution of the 8+ double cube with 2 M HCl.[19−21]

ICP elemental analyses on the product eluted with 2 M HCl gave a Mo:Sn:Se ratio of 6.0:1.04:8.18, consistent with an Mo_6SnSe_8 core structure. Elution of the green cube was also possible with 4 M Hpts, but not with 2 M Hpts, indicating a high charge and double-cube structure. UV−vis spectra in 2 M HCl and 2 M Hpts are very similar, Figure 4, with no evidence for extensive coordination of Cl^- as in the case of the single-cube $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$. Peak positions for $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ λ/nm (ϵ/M^{-1} cm^{-1} per Mo_6) are 443 (2.56×10^4) and 599 (1.33×10^4) in 2 M HCl and 432 (2.52×10^4) and 585 (1.29×10^4) in 2 M Hpts, Figure 4.

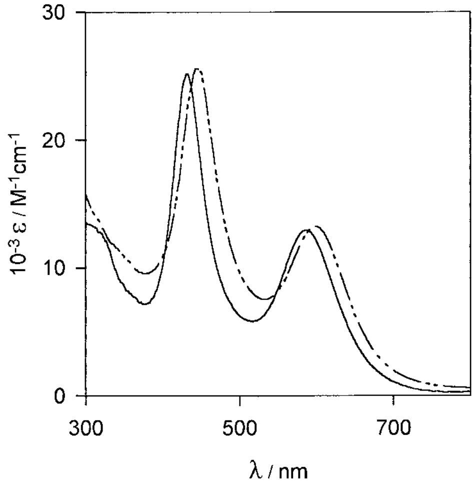

Figure 4. UV−vis spectra of $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$, ϵ's per Mo_6, in 2 M HCl (••−••) and 2 M Hpts (−). In 2 M HCl, some Cl^- complexing to the Mo's occurs.

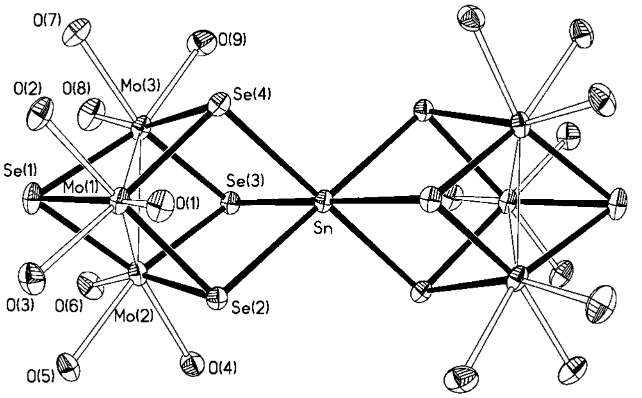

Figure 5. View of the cation corner-shared double-cube $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ with 50% probability ellipsoids and atomic labeling for the unique atoms.

A 2 M HCl solution of $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ in air undergoes ∼25% decay in 1 h, as monitored at 595 nm. Successive scan spectra for the full decay process gave isosbestic points at 360 and 420 nm with evidence for formation of $[Mo_3(SnCl_3)Se_4(H_2O)_9]^{3+}$ and $[Mo_3Se_4(H_2O)_9]^{4+}$ eq 4. Only 0.5% decay

$$Mo_6SnSe_8{}^{8+} - 2e^- \rightarrow Mo_3SnSe_4{}^{6+} + Mo_3Se_4{}^{4+} \qquad (4)$$

of $Mo_3SnSe_4{}^{6+}$ occurs in air over 8 h. A 2 M Hpts solution of the double cube gives an appreciably faster ∼66% decay in air within 1 h, and subsequent decay of $Mo_3SnSe_4{}^{6+}$ in 2 M Hpts is also faster.

Crystals suitable for X-ray crystallography were prepared by loading $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ (∼0.8 mM) in 0.5 M HCl onto a short Dowex column, washing with 0.5 M Hpts (100 mL) to remove Cl^-, and then eluting with 4 M Hpts. The solution was kept at ∼4 °C for ∼10 days to obtain crystals of $[Mo_6SnSe_8(H_2O)_{18}](pts)_8 \cdot 2Hpts \cdot 28H_2O$. The structure of the cation is shown in Figure 5.

In view of the 10 pts^- anions per $Mo_6SnSe_8{}^{8+}$ core, and the difficulty in crystallographic studies of distinguishing between Hpts and pts^-, further experiments were required to determine the charge on the double cube. This was done by air-free titrations with $[Co(dipic)_2]^-$. Aliquots of $[Co(dipic)_2]^-$ (1.47 mM) were added from a 0.25 mL Hamilton microsyringe to the double cube (1×10^{-4} M) in an optical cell (1×1 cm cross-section; ∼3 mL volume), both solutions in 2 M Hpts. From graphs of absorbance at 595 nm against $[Co(dipic)_2{}^-]$ added (two titrations) Co^{III}, double-cube ratios of 2:1 and 1.8:1 were

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(20) Li, Y.-J.; Nasreldin, M.; Humanes, M.; Sykes, A. G. *Inorg. Chem.* **1992**, *31*, 3011.

(21) Richens, D. T.; Pittet, P.-A.; Merbach, A. E.; Humanes, M.; Lamprecht, G. J.; Ooi, B.-L.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, 2305.

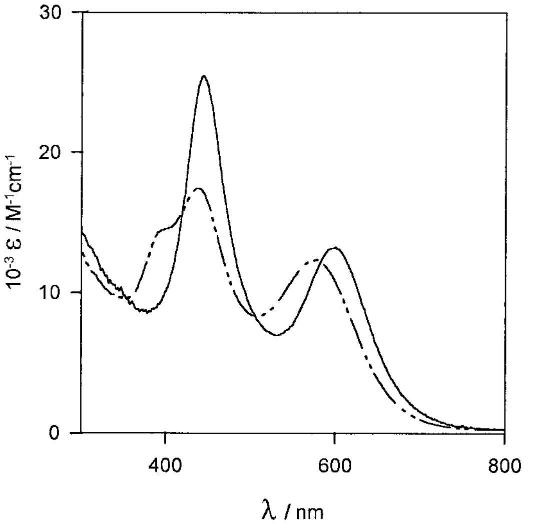


Figure 6. Comparison of UV−vis spectra of $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ (—), and $[Mo_6SnSe_4S_4(H_2O)_{18}]^{8+}$ (••—••) both in 2 M HCl, ε's per Mo_6.

obtained. The final product is $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$, and eq 5

$$Mo_6SnSe_8^{\ 8+} + 2Co^{III} \rightarrow Mo_3SnSe_4^{\ 6+} + Mo_3Se_4^{\ 4+} + 2Co^{II} \qquad (5)$$

confirms the 8+ charge on the double cube.

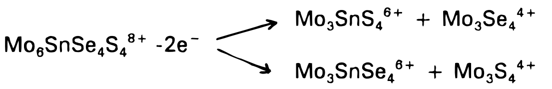
Conversion of $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ to $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$. Under rigorous air-free conditions an equimolar mixture of $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ (2 mM; 10 mL) and $[Mo_3Se_4(H_2O)_9]^{4+}$ (5 mM; 4 mL) was siphoned (via plastic tubing; N_2 pressure) onto $NaBH_4$ (0.4 g). An immediate color change to dark green was observed, and the spectrum of $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ was obtained (eq 6). The two redox-controlled reactions 6 and 5

$$Mo_3SnSe_4^{\ 6+} + Mo_3Se_4^{\ 4+} + 2e^- \rightarrow Mo_6SnSe_8^{\ 8+} \qquad (6)$$

summarize the interconversion of single- and double-cubes $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ and $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$. From UV−vis spectrophotometric changes, yields approach quantitative conversion.

Preparation of $[Mo_6SnSe_4S_4(H_2O)_{18}]^{8+}$. An equimolar mixture of $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ (1.65 mM, 20 mL) and $[Mo_3S_4(H_2O)_9]^{4+}$ (1.50 mM; 22.5 mL), both in 1 M HCl and under N_2, were siphoned into a conical flask containing $NaBH_4$ (0.4 g) under N_2. An immediate color change from yellow-green to brown was observed. After the solution had been standing for 30 min, Dowex 50W-X2 column purification was carried out as before, yielding some unreacted cluster followed by the brown-purple double-cube product eluted with 2 M HCl. ICP analysis on a recolumned sample gave an Mo:Sn:S:Se ratio of 6.0:1.05:4.2:4.8 (S/Se less sensitive), consistent with a core formula $Mo_6SnSe_4S_4$. The reaction can be summarized by eq 7. The UV−vis spectrum in 2 M HCl gives peaks λ/nm (ε/M^{-1} cm^{-1} per Mo_6) at 439 (1.75 × 10^4) and 575 (1.23 × 10^4), see Figure 6. Some 30% air oxidation is observed in 1 h. A sample of $[Mo_6SnSe_4S_4(H_2O)_{18}]^{8+}$ (1 mM; 15 mL) was allowed to air oxidize for ∼18 h. The product solution was loaded onto a Dowex 50W-X2 column (10 × 1.5 cm diameter) and washed with 0.5 M HCl (80 mL) and then with 1 M HCl. The products were characterized from UV−vis spectra. The first yellow-green band eluted was a mixture of the chloro complexes $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$ and $[Mo_3(SnCl_3)Se_4(H_2O)_9]^{3+}$, followed by a small amount of green $[Mo_3S_4(H_2O)_9]^{4+}$ and then by more substantial amounts of yellow-brown $[Mo_3Se_4(H_2O)_9]^{4+}$. The reaction can therefore be represented as in eq 8:

$$Mo_3SnSe_4^{\ 6+} + Mo_3S_4^{\ 4+} + 2e^- \rightarrow Mo_6SnSe_4S_4^{\ 8+} \qquad (7)$$



$$Mo_6SnSe_4S_4^{\ 8+} \ -2e^- \begin{cases} \rightarrow Mo_3SnS_4^{\ 6+} + Mo_3Se_4^{\ 4+} \\ \rightarrow Mo_3SnSe_4^{\ 6+} + Mo_3S_4^{\ 4+} \end{cases} \qquad (8)$$

with $Mo_3S_4^{\ 4+}$ having a greater affinity for Sn than $Mo_3Se_4^{\ 4+}$. The stoichiometry was confirmed as 2 equiv of oxidant to one of double cube (2.08:1) by spectrophotometric titration of the Co^{III} oxidant $[Co(dipic)_2]^-$ (2.41 mM) against the double cube (2.07 × 10^{-4} M) in 2.0 M HCl.

Preparation of $[Mo_3W_3SnSe_8(H_2O)_{18}]^{8+}$. The reactants in this case were $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ (0.6 mM, 30 mL) in 1 M HCl and $[W_3Se_4(H_2O)_9]^{4+}$ (2.8 mM, 6.4 mL) in 2 M HCl, both air-free (N_2). The mixture was siphoned onto $NaBH_4$ (0.4 g) under N_2, when the color change was to dark green. After 30 min the product was purified by cation-exchange chromatography at 0 °C. With 1 M HCl, elution of unreacted $[Mo_3(SnCl_3)Se_4(H_2O)_9]^{3+}$ was followed by $[W_3Se_4(H_2O)_9]^{4+}$. The double-cube product was eluted with 2 M HCl (eq 9). The UV−vis spectrum gave peak positions λ/nm (ε/M^{-1} cm^{-1} per Mo_3W_3) at 338 (1.24 × 10^4), 447 (1.35 × 10^4), and 591 (1.22 × 10^4). In air 30% decay was observed in 5 min, and incorporation of W_3 into the double cube increases the sensitivity to air (cf. 25% decay in 1 h for Mo_6).

$$Mo_3SnSe_4^{\ 6+} + W_3Se_4^{\ 4+} + 2e^- \rightarrow Mo_3W_3SnSe_8^{\ 8+} \qquad (9)$$

Preparation of $[Mo_3W_3SnSe_4S_4(H_2O)_{18}]^{8+}$. The procedure required a mixture of $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ (3.7 mM, 10 mL) and $[W_3S_4(H_2O)_9]^{4+}$ (1.6 mM, 22.7 mL) in 1 M HCl which was siphoned onto $NaBH_4$ (0.5 g), as described above. The color turned to brown-purple, and chromatographic separation of the product was carried out (eq 10). In air 25% decay was observed in 5 min. The UV−vis spectrum has peaks λ/nm at 396, 461, and 578.

$$Mo_3SnSe_4^{\ 6+} + W_3S_4^{\ 4+} + 2e^- \rightarrow Mo_3W_3SnSe_4S_4^{\ 8+} \qquad (10)$$

Preparation and Properties of $[W_3SnSe_4(H_2O)_{12}]^{6+}$. A 2 M HCl solution of green $[W_3Se_4(H_2O)_9]^{4+}$ (5 mM, 20 mL) under N_2 was siphoned onto $SnCl_2{\cdot}2H_2O$ (0.20 g) in an air-free conical flask. The color began to change to yellow-orange almost immediately. After it was washed with 0.5 M HCl (200 mL), the single band was eluted with 1 M HCl. Assuming a 3+ product, the reaction is summarized by eq 11. The same product was obtained by reacting 1−2 M HCl solutions of $[W_3Se_4(H_2O)_9]^{4+}$ (5−10 mM) with Sn powder at 60 °C under N_2 (85% yield). The Sn powder was activated by treatment with 6 M HCl prior to use. Stock solutions of the $[W_3(SnCl_3)Se_4(H_2O)_9]^{3+}$ product (3−30 mM) in 1−2 M HCl were stored under N_2 at 4 °C. Under these conditions, negligible oxidation occurs within 1 month. With slow bubbling of air through solutions there is 5% decay in 1 h. Heating of the solutions leads to decomposition and formation of $[W_3Se_4(H_2O)_9]^{4+}$ in a few minutes. Column chromatography of the fully oxidized solutions gave a green product, characterized by its UV−vis spectrum as $[W_3Se_4(H_2O)_9]^{4+}$ (95−100% yields). The relevant equation is eq 12.

$$W_3Se_4^{\ 4+} + SnCl_3^{\ -} \rightarrow W_3(SnCl_3)Se_4^{\ 3+} \qquad (11)$$

$$W_3SnSe_4^{6+} + {}^1/_2O_2 + 2H^+ \rightarrow 2W_3Se_4^{4+} + Sn^{IV} + H_2O \qquad (12)$$

Elemental ICP analyses on a solution of $[W_3SnSe_4(H_2O)_{12}]^{6+}$ in 2 M HCl gave a W:Sn:Se ratio of 3.1:1.0:4.2, consistent with the formula proposed. In 2 M HCl solution the UV−vis absorption spectrum of $[W_3(SnCl_3)Se_4(H_2O)_9]^{3+}$ gives peak positions λ/nm (ϵ/M^{-1} cm^{-1} per W_3) at 335 (1.23×10^4) and 414 (11 300). Solutions of $[W_3SnSe_4(H_2O)_{12}]^{6+}$ eluted in 3 M Hpts were also prepared. The UV−vis spectrum gives significant shifts compared to those observed for $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$. The X-ray crystal structure of $(NH_2Me_2)_6[W_3(SnCl_3)Se_4(NCS)_9]\cdot0.5H_2O$ has been reported,[22] and is also supportive of chloride complexing to the Sn.

No reaction of $SnCl_4$ (0.1 mL) with $[W_3Se_4(H_2O)_9]^{4+}$ (5 mL; 5 mM) in 2 M HCl was observed.

Preparation of $[W_6SnSe_8(H_2O)_{18}]^{8+}$. A mixture of $[W_3SnSe_4(H_2O)_{12}]^{6+}$ (1.8 mM; 10 mL) and $[W_3Se_4(H_2O)_9]^{4+}$ (3.6 mM; 5 mL) in 1 M HCl was siphoned onto $NaBH_4$ (0.5 g) under rigorous air-free conditions. There was an instant color change to blue. After standing for 15 min the solution was diluted to 0.5 M HCl, loaded onto a Dowex 50W-X2 column, and washed with 0.5 M HCl and then 2 M HCl. Elution of $[W_3SnSe_4(H_2O)_{12}]^{6+}$ took place with 2 M HCl. The next band eluted was blue 8+ product. This was collected in ice and stored air-free at 4 °C. Under these conditions 10% decay was observed in 1 day. With slow bubbling of air through solutions 100% decay was observed in 2 min. The products were a 1:1 mixture of $[W_3SnSe_4(H_2O)_{12}]^{6+}$ and $[W_3Se_4(H_2O)_9]^{4+}$. Three bands were observed in the UV−vis spectrum in 2 M HCl at 360, 407 (sh), and 590 nm (ϵ values not determined).

Tin Transfer Reactions. An equimolar amount of $[Mo_3S_4(H_2O)_9]^{4+}$ (3.75 mM, 2.8 mL) was added to $[W_3SnSe_4(H_2O)_{12}]^{6+}$ (2.1 mM, 5.0 mL), both in 2 M HCl under N_2. Immediate reaction is observed. Dowex chromatography gives $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$ and $[W_3Se_4(H_2O)_9]^{4+}$ as products (eq 13). Sn transfer from $[W_3SnS_4(H_2O)_{12}]^{6+}$ to $[Mo_3S_4(H_2O)_9]^{4+}$

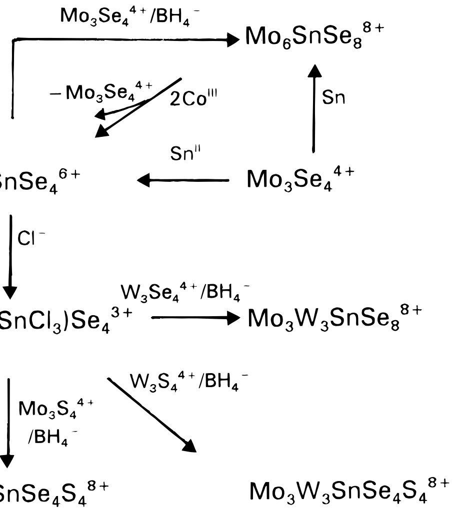
$$Mo_3S_4^{4+} + W_3SnSe_4^{6+} \rightarrow Mo_3SnS_4^{6+} + W_3Se_4^{4+} \qquad (13)$$

was demonstrated previously.[11] No corresponding reactions of $[W_3S_4(H_2O)_9]^{4+}$ with $[W_3SnSe_4(H_2O)_{12}]^{6+}$ or of $[W_3S_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$ with $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ are observed. However, the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ gives an equilibrium mix. A solution of $SnCl_2\cdot2H_2O$ (1 mM; 3.04 mL) in 2 M HCl was added to a mixture of $[Mo_3S_4(H_2O)_9]^{4+}$ (0.34 mM; 10 mL) and $[Mo_3Se_4(H_2O)_9]^{4+}$ (2.55 mM; 1.19 mL) in 2 M HCl. The products were separated by Dowex chromatography. On elution with 1 M HCl three bands were obtained. The first one, green-yellow in color, turned out to be a mixture of $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ and $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$. The second was green $[Mo_3S_4(H_2O)_9]^{4+}$ and the third was $[Mo_3Se_4(H_2O)_9]^{4+}$, relative amounts of which were determined from UV−vis spectra. These enabled the equilibrium constant K for eq 14,

$$Mo_3SnSe_4^{6+} + Mo_3S_4^{4+} \rightleftharpoons Mo_3Se_4^{4+} + Mo_3SnS_4^{6+} \qquad (14)$$

to be determined as $K = 4.0(9)$, the average of two determinations. Relative affinities of the different cores for Sn are $Mo_3S_4^{4+} > Mo_3Se_4^{4+} > W_3Se_4^{4+} > W_3S_4^{4+}$.

Scheme 1



Displacement of Heteroatom In by Sn. A solution of blue-green $[W_3InSe_4(H_2O)_{12}]^{5+}$ in 2 M HCl (2.1 mM, 5 mL) under N_2 was added to $SnCl_2\cdot2H_2O$ (0.03 g), also air-free. The color began to change to yellow-orange almost immediately. After completion of the reaction 3 min the solution was loaded onto a Dowex 50W-X2 column (5 × 2 cm), also under N_2. The column was washed with 0.5 M HCl, and elution with 1 M HCl gave the product $[W_3(SnCl_3)Se_4(H_2O)_9]^{3+}$ as a single band (eq 15).

$$W_3InSe_4^{5+} + Sn^{II} \rightarrow W_3SnSe_4^{6+} + In^{I} \qquad (15)$$

Discussion

Reactions of $[Mo_3Se_4(H_2O)_9]^{4+}$ are summarized in Scheme 1. X-ray crystal structures of $(NH_2Me_2)_6[Mo_3(SnCl_3)Se_4(NCS)_9]\cdot0.5H_2O$ and $[Mo_6SnSe_8(H_2O)_{18}](pts)_8\cdot2Hpts\cdot28H_2O$ have been determined. Important features are the short Mo−Mo distances (mean 2.788 Å), indicative of metal−metal bonding and long Mo−Sn separations (mean 3.870 Å), nonbonding for the single cube; and corresponding Mo−Mo (mean 2.732 Å) bonding and Mo−Sn (mean 3.858 Å) nonbonding separations in the double cube. These features are consistent with the formalism $Mo_3Se_4^{4+}Sn^{2+}$ and $(Mo_3Se_4^{4+})_2Sn^0$ previously referred to.[6] The NCS^- ligands are coordinated through the nitrogen atoms, with N and S atoms clearly distinguished by their different X-ray scattering powers, and by N−C and C−S bond lengths. In the case of $[Mo_6SnSe_8(H_2O)_{18}]^{8+}$ the 8+ charge is not deduced directly from the X-ray structure, which indicates 10 pts^- anions per double cube. The stoichiometry determined with $[Co(dipic)_2]^-$ as oxidant confirms the 8+ charge (eq 5). It is concluded that two molecules of Hpts are incorporated in the crystal lattice per double cube. Incorporation of Hpts in crystals of cubes has been observed previously, but is difficult to confirm because of the extensive H-bonding (H_2O with pts^-) in the vicinity of the cluster.[23] In other respects, the crystal structures are similar to those for the $Mo_3S_4^{4+}$ derivatives $(NH_2Me_2)[Mo_3(SnCl_3)S_4(NCS)_9]\cdot0.5H_2O$ and $[Mo_6SnS_8(H_2O)_{18}](pts)_8\cdot26H_2O$ previously reported.[9,12]

Peak positions from UV−vis spectra of Se clusters are compared with the corresponding S for Se clusters in Table 4. In the case of the Sn-containing single cubes, the spectra are particularly sensitive to use of 2 M Hpts or 2 M HCl. From

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[22] Fedin, V. P.; Sokolov, M. N.; Virovets, A. V.; Podberezskaya, N. V.; Fedorov, V. E. *Inorg. Chim. Acta* **1998**, *269*, 292.

[23] Shibahara, T.; Sakane, G.; Maeyama, M.; Kobashi, H.; Yamamoto, T.; Watase, T. *Inorg. Chim. Acta* **1996**, *251*, 207.

Table 4. Summary of UV−vis Spectra of Single- and Double-Cube Sn Derivatives of $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$ and a Comparison with Spectra of S (for Se) Clusters

cluster	solution	λ/nm (ϵ/M^{-1} cm^{-1})	reference
$[Mo_3Se_4(H_2O)_9]^{4+}$	2 M Hpts	427 (5820); 646 (595)	this work[a]
	2 M HCl	433 (5250); 681 (580)	
$[Mo_3SnSe_4(H_2O)_{12}]^{6+}$	2 M Hpts	359 (1.06×10^4); 428 (4320); 615 (186)	this work
	2 M HCl	392 (1.49×10^4); 448 (5880); 644 (413)	
$[Mo_3S_4(H_2O)_9]^{4+}$	2 M Hpts	366 (5550); 603 (362)	6
	2 M HCl	370 (4995); 616 (326)	
$[Mo_3SnS_4(H_2O)_{12}]^{6+}$	2 M Hpts	331 (6330); 375 (2817)	9
	2 M HCl	356 (1.40×10^4); 424 (8260)	
$[W_3Se_4(H_2O)_9]^{4+}$	2 M Hpts	359 (6660); 618 (547)	22
	2 M HCl	360 (6950); 625 (500)	8
$[W_3SnSe_4(H_2O)_{12}]^{6+}$	2 M HCl	335 (1.23×10^4); 414 (1.13×10^4)	this work
$[W_3S_4(H_2O)_9]^{4+}$	2 M Hpts	315 (6350); 560 (446)	16
	2 M HCl	317 (6100); 570 (480)	11
$[W_3SnS_4(H_2O)_{12}]^{6+}$	2 M HCl	303 (1.28×10^4); 396 (2.12×10^4)	11
$[Mo_6SnSe_8(H_2O)_{18}]^{8+}$	2 M Hpts	320 (sh); 432 (2.52×10^4); 585 (1.29×10^4)	this work
	2 M HCl	443 (2.56×10^4); 599 (1.33×10^4	
$[Mo_6SnS_8(H_2O)_{18}]^{8+}$	2 M Hpts	310 ($\sim 10^4$); 379 (2.21×10^4); 544 (1.55×10^4)	9
$[Mo_6SnSe_4S_4(H_2O)_{18}]^{8+}$	2 M HCl	400 (sh); 439 (1.75×10^4); 575 (1.23×10^4)	this work
$[Mo_3W_3SnSe_8(H_2O)_{18}]^{8+}$	2 M HCl	338 (1.24×10^4); 447 (1.35×10^4); 591 (1.22×10^4)	this work
$[Mo_3W_3SnSe_4S_4(H_2O)_{18}]^{8+}$	2 M HCl	396; 461; 578	this work[b]
$[Mo_3W_3SnS_8(H_2O)_{18}]^{8+}$	2 M HCl	355 (1.04×10^4); 389 (1.06×10^4); 548 (7400)	11
$[W_6SnS_8(H_2O)_{18}]^{8+}$	2 M HCl	311 (1.66×10^4); 393 (9800); 548 (13 500)	11
$[W_6SnSe_8(H_2O)_{18}]^{8+}$	2 M HCl	360; 407 (sh); 590	this work[b]

[a] Revised values cf. refs 7 and 8. [b] ϵ values not determined.

previous studies on $[Mo_3SnS_4(H_2O)_{12}]^{6+}$, the Sn has high affinity for Cl^-, and the complexing to give $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$ is essentially complete at $[Cl^-] = 0.05$ M. An estimate of K for the coordination of three Cl^- to the Sn is $>10^2$ M^{-3}.[9] Similar observations are expected to hold also for $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ and $[W_3SnSe_4(H_2O)_{12}]^{6+}$. The complexing of Cl^- to the Mo and W atoms as components of the clusters is much weaker, see ref 19.

Redox-controlled interconversions of single and double cubes have been carried out with near-quantitative yields, better than those observed in the case of the $[Mo_3S_4(H_2O)_9]^{4+}$ derivatives.[9] The Sn-containing cubes from $[W_3Se_4(H_2O)_9]^{4+}$ were not studied as extensively as those from $[Mo_3Se_4(H_2O)_9]^{4+}$ but show similar properties. An important difference is that the double-cube $[W_6SnSe_8(H_2O)_{18}]^{8+}$ is not obtained by reaction of $[W_3Se_4(H_2O)_9]^{4+}$ with Sn. Instead, the latter gives the same single-cube derivative as does Sn^{II}, and the double cube is obtained by reductive addition of $[W_3SnSe_4(H_2O)_{12}]^{6+}$ and $[W_3Se_4(H_2O)_9]^{4+}$ in the presence of BH_4^-. The same method is required in the case of $[W_6SnS_8(H_2O)_{18}]^{8+}$ and finds general use in the preparation of mixed Mo-W- and Se-S-containing double cubes with core clusters $Mo_6SnSe_4S_4^{8+}$, $Mo_3W_3SnSe_8^{8+}$, and $Mo_3W_3SnSe_4S_4^{8+}$. Preparation of an isomeric form of the latter incorporating $Mo_3S_4^{4+}$ and $W_3Se_4^{4+}$ is possible using a similar procedure.

Reactions in which there is transfer of Sn from an Sn-containing single cube to a trinuclear cluster have been studied and are consistent with equilibria of the kind (eq 16)

$$Mo_3Se_4^{4+} + W_3SnSe_4^{6+} \rightleftarrows Mo_3SnSe_4^{6+} + W_3Se_4^{4+} \quad (16)$$

which can proceed by direct bimolecular exchange or by dissociation and reequilibration as in (eq 17)

$$Mo_3Se_4^{4+} + Sn^{II} \rightleftarrows Mo_3SnSe_4^{6+} \quad (17)$$

Experiments reported indicate relative affinities in the order $Mo_3S_4^{4+} > Mo_3Se_4^{4+} > W_3Se_4^{4+} > W_3S_4^{4+}$. The affinities in the case of the two Mo_3 clusters are very similar with the equilibrium constant $K = 4.0$ for eq 14, the only measured value, favoring the $Mo_3SnS_4^{6+}$ derivative. The order has been accounted for by considering covalent index terms.[24]

Displacement of In^I by Sn^{II} is a further demonstration of equilibria of the kind referred to in eq 17. It has already been demonstrated that there is no reaction between aqua Ni^{2+} and $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ (with displacement of Fe^{2+}) or between Fe^{2+} and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (with displacement of Ni^{2+}).[25] We have previously suggested that the ability of Cu^{2+} to displace heteroatoms in $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ may be due to redox changes.[26] Whether Sn^{II} is able to displace transition metals from single cubes is an interesting point to be tested. An important difference in the case of the Mo_3FeS_4 and Mo_3NiS_4 cubes is the evidence for short Mo−Fe and Mo−Ni distances and metal−metal bonding.[6] No metal−metal bonding is apparent with the electron-rich main group elements Sn and In as heteroatoms, a point that has been well established in the case of the $[Mo_3S_4(H_2O)_9]^{4+}$ derivatives.[6] The same conclusion is arrived at from X-ray crystallography on the Sn derivatives of $[Mo_3Se_4(H_2O)_9]^{4+}$ described in this paper.

Acknowledgment. We thank the European Union HCMP for their support under Network Grant ERBCHRX-CT94-0632, and the University of La Laguna in Tenerife for a leave of absence (R.H.-M). We are also grateful for an EU INTAS collaboration (Research Grant No. 96-1256) with Novosibirsk. We thank the UK Engineering and Physical Sciences Research Council for an equipment grant (to W.C.).

Supporting Information Available: Listings of crystallographic data, atomic coordinates, and bond lengths are available (16 pages). Two crystallographic files, in CIF format, are also available. Access and ordering information is given on any current masthead page.

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