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Preparation, Structure, and Reactivity of Ge-Containing Heterometallic Cube Derivatives of $[M_3E_4(H_2O)_9]^{4+}$ (M = Mo, W; E = S, Se)

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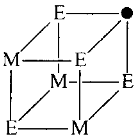
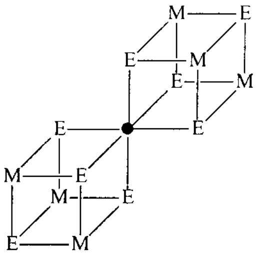
Studies leading to the incorporation of Group 14 germanium into the incomplete cuboidal clusters $[M_3E_4(H_2O)_9]^{4+}$ (M = Mo, W; E = S, Se) have been carried out. From the clusters $[Mo_3E_4(H_2O)_9]^{4+}$, corner-shared double cubes $[Mo_6GeE_8(H_2O)_{18}]$ are obtained with GeO, by heating with Ge powder at 90 °C, or by heating with GeO_2 in the presence of H_3PO_2 as reductant at 90 °C, illustrating the dominance of the double cubes. The yellow−green single cube $[Mo_3GeS_4\ (H_2O)_{12}]^{6+}$ is only obtained by controlled air oxidation of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ over a period of ~4 days followed by Dowex purification. In the case of the trinuclear clusters $[W_3E_4(H_2O)_9]^{4+}$, the single cubes $[W_3GeE_4(H_2O)_{12}]^{6+}$ are dominant and prepared by the reactions with GeO, or GeO_2/H_3PO_2. Conversion of $[W_3GeE_4(H_2O)_{12}]^{6+}$ to the corresponding double cubes is achieved by reductive addition with BH_4^- in the presence of a further equivalent of $[W_3E_4(H_2O)_9]^{4+}$. The crystal structures (pts^- = *p*-toluene-sulfonate) of $[Mo_6GeS_8(H_2O)_{18}](pts)_8{\cdot}28H_2O$, (**1**); $[W_6GeS_8(H_2O)_{18}](pts)_8{\cdot}23H_2O$, (**2**); and $[Mo_6GeSe_8(H_2O)_{18}](pts)_8{\cdot}8H_2O$, (**3**); have been determined, of which (**2**) is the first structure of a W_6 double cube. The M−M bond lengths of ~2.7 Å are consistent with metal−metal bonding, and the M−Ge of ~3.5 Å corresponds to nonbonding separations. Of the Group 13−15 corner-shared double cubes from $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ is the least reactive with $[Co(dipic)_2]^-$ as oxidant (0.077 $M^{-1}\ s^{-1}$), and $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ is next (14.9 $M^{-1}\ s^{-1}$). Both Ge and Sn (Group 14) have an even number of electrons, resulting in greater stability. In contrast, $[W_6GeS_8(H_2O)_{18}]^{8+}$ is much more reactive ($7.3 \times 10^3\ M^{-1}\ s^{-1}$), and also reacts more rapidly with O_2.

Introduction

The metal-depleted incomplete cube $[Mo_3S_4(H_2O)_9]^{4+}$ is noted for its high stability[1] and its ability to incorporate heterometal atoms (M′) to give single and/or double cubes, core structures as illustrated.[2−4]





The incomplete cube $[W_3S_4(H_2O)_9]^{4+}$ has also been studied.[5] Of the ~20 known heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$, those of the Group 13−15 elements, M′ = In,[6,7] Tl,[6,8] Sn,[9−12] Pb,[13−15] As,[16] Sb,[17] and Bi[18] (Ga an exception[6,19]), alongside Hg and Mo,[20,21] are known to form corner-shared double cubes $(Mo_3S_4^{4+})_2M'^{o}$ and, in some cases (M′ = Ga, In, Sn),[6,10] single cubes $(Mo_3S_4^{4+})M'^{n+}$, (*n* = 1, 2 for Groups 13, 14, respectively). The single cubes $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ and $[Mo_3InS_4(H_2O)_{12}]^{5+}$ are converted to the double cubes by reductive addition of $[Mo_3S_4(H_2O)_9]^{4+}$ with BH_4^- (eq 1),[6,11]

$$Mo_3SnS_4^{\ 6+} + Mo_3S_4^{\ 4+} + 2e^- \rightarrow Mo_6SnS_8^{\ 8+} \qquad (1)$$

where this type of conversion is relevant to studies described

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(1) Ooi, B.-L.; Sykes, A. G. *Inorg. Chem.* **1998**, *28*, 3799.

(2) Hernandez-Molina, R.; Sokolov, M. N.; Sykes, A. G. *Acc. Chem. Res.* **2001**, *34*, 223−230.

(3) Saysell, D. M.; Sokolov, M. N. Sykes, A. G. *Sulfur Coordinated Transition Metal Complexes*; Stiefel, E., Matsumoto, K.; American Chemical Society Symposium Series No. 653, Pacifichem Meeting Honolulu, 1996; pp 216−224.

(4) Shibahara, T. *Adv. Inorg. Chem.* **1991**, *37*, 143−173.

(5) Nasreldin, M.; Routledge, C. A.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1994**, 2809.

(6) Hernandez-Molina, R.; Fedin, V. P.; Sokolov, M. N.; Saysell, D. M.; Sykes, A. G. *Inorg. Chem.* **1998**, *37*, 4328.

(7) (a) Sakane, G.; Shibahara, T. *Inorg. Chem.* **1993**, *32*, 777. (b) Sakane, G.; Yao, Y.-G.; Shibahara, T. *Inorg. Chim. Acta* **1994**, *13*, 216.

(8) Varey, J. E.; Sykes, A. G. *Polyhedron* **1996**, *15*, 1887.

(9) Shibahara, T.; Akashi, H. *Inorg. Chem.* **1989**, *28*, 2906.

(10) Varey, J. E.; Lamprecht, G. J.; Fedin, V. P.; Holder, A. A.; Clegg, W.; Elsegood, M. R. J.; Sykes, A. G. *Inorg. Chem.* **1996**, *36*, 5525.

(11) Hernandez-Molina, R.; Dybtsev, D. N.; Fedin, V. P.; Elsegood, M. R. J.; Clegg, W.; Sykes, A. G. *Inorg. Chem.* **1998**, *37*, 2995.

(12) Fedin, V. P.; Sokolov, M. N.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1996**, 4089.

(13) Saysell, D. M.; Huang, Z.-X.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1996**, 2623.

(14) Brorson, M.; Jacobson, C. J. H.; Helgeson, H. K. M.; Schmidt, I. *Inorg. Chem.* **1996**, *35*, 4808.

(15) Saysell, D. M.; Sykes, A. G. *Inorg. Chem.* **1997**, *36*, 2700.

(16) Hernandez-Molina, R.; Edwards, A. J.; Clegg, W.; Sykes, A. G. *Inorg. Chem.* **1998**, *37*, 2989.

(17) Sakane, G.; Hashimoto, K.; Takahashi, M.; Takeda, M.; Shibahara, T. *Inorg. Chem.* **1998**, *37*, 4231.

(18) Saysell, D. M.; Sykes, A. G. *Inorg. Chem.* **1996**, *35*, 5536.

(19) Shibahara, T.; Kobayashi, S.; Tsuji, N.; Sakane, G.; Fukuhara, M. *Inorg. Chem.* **1997**, *36*, 1702.

(20) Sokolov, M. N.; Virovets, A. V.; Dybtsev, D. N.; Gerasko, O. A.; Fedin, V. P.;Hernandez-Molina, R.; Clegg, W.; Sykes, A. G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1659.

(21) Sokolov, M. N.; Coichev, N.; Moya, H. D.; Hernandez-Molina, R.; Borman, C. D.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1997**, 1863.

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in this paper. The reverse reaction is brought about by quantitative addition of $[Co(dipic)_2]^-$ or $[Fe(H_2O)_6]^{3+}$ as oxidant, e.g., eq 2,[11]

$$Mo_6SnS_8^{\,8+} - 2e^- \rightarrow Mo_3SnS_4^{\,6+} + Mo_3S_4^{\,4+} \qquad (2)$$

where the further oxidation of $Mo_3SnS_4^{6+}$ to $Mo_3S_4^{4+}$ can occur.[2] The reluctance of $[W_3S_4(H_2O)_9]^{4+}$ to form cubes has been noted in the case of Fe, Pd, Hg, Pb, As, Sb, and Bi, and only six examples are known at present.[2] Germanium is of interest along with tin, since both are from Group 14 and give double cubes having an even number of electrons. The only germanium-containing derivative so far reported is the single cube $[W_3GeS_4(H_2O)_{12}]^{6+}$.[12] In the studies described, comparisons of Mo versus W and S versus Se are of interest.

Experimental Section

Preparation of Trinuclear Reactants. Solutions of trinuclear Mo^{IV}_3 and W^{IV}_3 clusters, $[Mo_3E_4(H_2O)_9]^{4+}$ [1,22] and $[W_3E_4(H_2O)_9]^{4+}$ (E = S, Se),[23] were prepared as previously described and purified by Dowex 50W−X2 cation-exchange chromatography. Procedures for the preparation of all four trinuclear ions $[M_3E_4(H_2O)_9]^{4+}$ (M = Mo, W; E = S, Se) from polymeric $\{M_3E_7Br_4\}_x$ were also used and gave greatly improved yields.[11,12,16] Details of UV−vis spectra in 2 M HCl and 2 M Hpts are included in Table 6 below.

Preparation of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$. In method A, a solution of $[Mo_3S_4(H_2O)_9]^{4+}$ (8.5 mM, 20 mL) in 2 M HCl was added to GeO (0.21 g) under air-free conditions. Fresh, pale yellow GeO (under N_2) was prepared by a modified version of a literature method.[12,24] The color began to change to red−purple almost immediately, eq 3.

$$2Mo_3S_4^{\,4+} + 2GeO + 4H^+ \rightarrow Mo_6GeS_8^{\,8+} + 2H_2O + Ge^{IV} \qquad (3)$$

After completion of the reaction (∼3h), the solution was filtered. Anion metathesis from Cl^- to pts^- was accomplished by loading the product in 0.50 M HCl onto a Dowex 50W−X2 column, which was also under N_2. The column was washed with 0.50 and 1.0 M Hpts (∼100 mL amounts). Unreacted $[Mo_3S_4(H_2O)_9]^{4+}$ was eluted with 1−2 M Hpts (∼4%). The red−purple double cube (∼96%) was eluted with 4.0 M Hpts ([Hpts] increased stepwise). Stock solutions of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ (3−10 mM) in 4.0 M Hpts were stored under N_2 at 4 °C. Little decay was observed over 1 month.

In method B, the same cluster was obtained by reacting a 5−10 mM solution of $[Mo_3S_4(H_2O)_9]^{4+}$ in 1−2 M HCl with Ge powder at 90 °C under N_2. The Ge powder was activated prior to use by treating with H_2O_2/KOH and then washing with H_2O, eq 4.

$$2Mo_3S_4^{\,4+} + Ge \rightarrow Mo_6GeS_8^{\,8+} \qquad (4)$$

Yields from Dowex chromatography were 50−85%. Method C involves the reaction of GeO_2 (0.05 g; Avocado, 99.9%; dissolved in a small volume of concentrated HCl) with $[Mo_3S_4(H_2O)_9]^{4+}$ (6 mM, 20 mL in 2 M HCl) and excess hypophosphorous acid, H_3PO_2, (50:50 w/w H_2O; Aldrich) as reductant, eq 5.

$$2Mo_3S_4^{\,4+} + Ge^{IV} + 4e^- \rightarrow Mo_6GeS_8^{\,8+} \qquad (5)$$

No reaction was observed on addition of $GeCl_4$ (Aldrich; 0.1 mL) to $[Mo_3S_4(H_2O)_9]^{4+}$ (2 mL; 18 mM) in 2 M acid (HCl or Hpts).

In purification procedures, 4 M Hpts was required to elute the product from a Dowex 50W−X2 column, which is consistent with a highly charged double-cube structure. Crystals were obtained from the most concentrated fraction. When a solution in 2 M HCl was exposed to air (with some shaking), 30% decay to $[Mo_3S_4(H_2O)_9]^{4+}$ and Ge^{IV} was observed in 1 day.

Preparation of $[Mo_3GeS_4(H_2O)_{12}]^{6+}$. A solution of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ in 2 M HCl was allowed access to air for ∼4 days, eq 6.

$$2Mo_6GeS_8^{\,8+} + O_2 + 4H^+ \rightarrow 2Mo_3S_4^{\,4+} + 2Mo_3GeS_4^{\,6+} + 2H_2O \qquad (6)$$

The yellow−green single cube $[W_3GeS_4(H_2O)_{12}]^{6+}$ was separated from the incomplete cube $[Mo_3S_4(H_2O)_9]^{4+}$ and double cube by Dowex 50W−X2 chromatography. The single cube is much more stable in air. UV−vis peak positions and absorption coefficients were determined by reaction with a 10:1 excess of $SnCl_2$ in 2 M HCl. Details of the UV−vis spectrum of the $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$ product have been published.[11]

Preparation of $[Mo_6GeSe_8(H_2O)_{18}]^{8+}$. A solution of $[Mo_3Se_4(H_2O)_9]^{4+}$ (4 mM; 16 mL) in 1 M HCl was added to GeO (0.1 g) in 11.3 M HCl (2−3 mL) under rigorous air-free conditions (N_2). An immediate color change to dark green was observed for the reaction, as in eq 3. After 2 h, the reactant solution was diluted to 0.5 M HCl and loaded onto a Dowex column (20 × 1.5 cm). The column was washed with 0.5 M HCl and 1 M HCl (100 mL amounts). No unreacted $[Mo_3Se_4(H_2O)_9]^{4+}$ was eluted; the yield is close to quantitative. The corner-shared double cube was eluted with 2 M HCl or 4 M Hpts. Crystals were obtained from the latter.

Preparation of $[W_3GeS_4(H_2O)_{12}]^{6+}$. Rigorous air-free ($N_2$) conditions were used throughout. To a solution of purple $[W_3S_4(H_2O)_9]^{4+}$ (22.7 mM; 10 mL) in 2 M HCl, GeO (0.05 g) was added and the color changed to orange−brown, eq 7.

$$W_3S_4^{\,4+} + Ge^{II} \rightarrow W_3GeS_4^{\,6+} \qquad (7)$$

Alternatively, a solution of GeO_2 (0.3 g in minimum of 11.3 M HCl) was added followed by the addition of hypophosphorous acid, H_3PO_2, (5 mL, 50:50 w/w H_2O). The solution was heated to ∼80 °C for 2 h. After 30 min, the color began to change to orange−brown. The reaction occurring is described by eq 8.

$$W_3S_4^{\,4+} + Ge^{IV} + 2e^- \rightarrow W_3GeS_4^{\,6+} \qquad (8)$$

The intense purple color of $[W_6GeS_8(H_2O)_{18}]^{8+}$ was never observed in any of these experiments. The product was purified by diluting to 0.5 M HCl and loading the solution onto a Dowex 50W−X2 column. After washing with 0.5 M HCl (150 mL) and then 1 M HCl (100 mL), after which no trinuclear complex were detected, the product was eluted with 2 M HCl. Alternatively, Hpts could be used for elution, when with the assumption that 3 H_2Os are coordinated to the Ge the formula is written as $[W_3GeS_4(H_2O)_{12}]^{6+}$. Upon addition of $[W_3S_4(H_2O)_9]^{4+}$ (5 mM; 10 mL) in 2 M HCl to activated Ge metal powder (0.05 g), no color change was observed in ∼5 h. The mixture was heated at ∼50 °C overnight (∼12 h) with no evidence of any reaction. The same behavior is observed at 90 °C.

Preparation of $[W_3GeSe_4(H_2O)_{12}]^{6+}$. The procedure was the same as above, e.g., a solution of $[W_3Se_4(H_2O)_9]^{4+}$ (12 mM; 10 mL) in 2 M HCl was added to GeO (0.05 g) under N_2. The reaction with a solution of GeO_2 and H_3PO_2 could also be used. An immediate color change to orange was observed. Again there was no reaction of $[W_3Se_4(H_2O)_9]^{4+}$ (6 mM; 10 mL) in 2 M HCl with activated Ge metal powder (0.05 g) at 90 °C.

Preparation of $[W_6GeS_8(H_2O)_{18}]^{8+}$. A mixture of $[W_3GeS_4(H_2O)_{12}]^{6+}$ (10 mM; 10 mL) and $[W_3S_4(H_2O)_9]^{4+}$ (7 mM; 15 mL) in 1.0 M HCl was siphoned onto $NaBH_4$ (0.5 g; Aldrich) under rigorous air-free conditions (N_2). An immediate color change to orange−brown was observed. After standing for 30 min, the solution was purified by Dowex 50W−X2 cation-exchange chromatography at 0 °C. The column was washed with 0.5 M HCl (50 mL) and 1 M HCl, which eluted the remaining $[W_3S_4(H_2O)_9]^{4+}$ and $[W_3GeS_4(H_2O)_{12}]^{6+}$. The product [W6-

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(22) Martinez, M.; Ooi, B.-L.; Sykes, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4615.

(23) Fedin, V. P.; Sokolov, M. N.; Mironov, Y. V.; Kolesov, B.; Tkacher, S. V.; Fedorov, V. Y. *Inorg. Chim. Acta* **1990**, *167*, 39.

(24) Brauer, G. *Handbook of Preparative Chemistry*; 2nd ed.; Academic Press: London and New York, 1963; Vol. 1, p 711.

Table 1. Crystallographic Data for $[Mo_6GeS_8(H_2O)_{18}](pts)_8{\cdot}28H_2O$ (**1**), $[W_6GeS_8(H_2O)_{18}](pts)_8{\cdot}23H_2O$ (**2**), and $[Mo_6GeSe_8(H_2O)_{18}](pts)_8{\cdot}8H_2O$ (**3**)

	1	**2**	**3**
empirical formula	$C_{56}H_{148}GeMo_6O_{70}S_{16}$	$C_{56}H_{138}GeW_6O_{65}S_{16}$	$C_{56}H_{108}GeMo_6O_{50}S_8Se_8$
fw	3102.9	3540.3	3118/9
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	13.5499(10)	13.6001(13)	12.3558(5)
b, Å	14.0334(10)	13.9790(14)	34.0069(13)
c, Å	18.4296(13)	18.4290(18)	11.9249(5)
α, deg	92.984(2)	92.715(2)	90
β, deg	104.680(2)	104.859(2)	92.437(2)
γ, deg	118.056(2)	117.882(2)	90
V, Å^3	2930.8(4)	2935.4(5)	5006.1(3)
Z	1	1	2
ρ_{calc}, g cm^{-1}	12.6	64.8	41.9
μ, cm^{-1}	12.6	64.8	41.9
T, °C	−113	−113	−113
R^a	0.0595	0.0816	0.0377
R_w^b	0.1438	0.2097	0.0762
data, parameters	13214, 876	10174, 790	11466, 666

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

$GeS_8(H_2O)_{18}]^{8+}$ was eluted with 2 M HCl or (from a second column) with 4 M Hpts, eq 9.

$$W_3GeS_4^{6+} + W_3S_4^{4+} + 2e^- \rightarrow W_6GeS_8^{8+} \qquad (9)$$

Stock solutions in 2 M HCl were stored at 4 °C under N_2 for ~1 week. Those in 2−4 M Hpts and could be kept for 3 weeks. Crystals were obtained from 4 M Hpts solutions.

Preparation of $[W_6GeSe_8(H_2O)_{18}]^{8+}$. A mixture of $[W_3GeSe_4(H_2O)_{12}]^{6+}$ (11 mM, 10 mL) and $[W_3Se_4(H_2O)_9]^{4+}$ (12 mM, 10 mL) in 1 M HCl was siphoned onto $NaBH_4$ (0.5 g) under N_2. A color change to dark blue was observed immediately. After standing for 30 min, purification was again completed using Dowex 50W−X2 chromatography. The Se-containing double cube is more stable than the S analogue, and no cooling of the column is required. The column was washed with 0.5 M HCl and 1 M HCl to remove unreacted $W_3Se_4^{4+}$ and $W_3GeSe_4^{6+}$ (~9%). Crystals were obtained from 4 M Hpts eluted solutions. Stock solutions in 2 M HCl could be stored at 4 °C under N_2 for ~3 weeks. When a solution in 2 M HCl was exposed to air with some shaking, 10% decay was observed in 1 h.

Attempted Preparation of $[Mo_3W_3GeS_8(H_2O)_{12}]^{8+}$. The conversion of $[W_3GeS_4(H_2O)_{12}]^{6+}$ (0.5 mM; 25 mL) in 2 M HCl to a W_3Mo_3 corner-shared double cube was attempted by adding an equivalent amount of $[Mo_3S_4(H_2O)_9]^{4+}$ (3.5 mM; 5 mL) in 1 M HCl in the presence of excess $NaBH_4$ (0.5 g) under N_2. After Dowex 50W−X2 chromatography at 0 °C, the products were identified by UV−vis spectrophotometry as $[W_3S_4(H_2O)_9]^{4+}$ and $[Mo_6GeS_8(H_2O)_{18}]^{8+}$. The latter gave metal analyses by ICP−AES for Mo:Ge of close to 6:1.

Preparation of Sn^{II} and In^{I} Solutions. Solutions of $SnCl_3^-$ were prepared by dissolving $SnCl_2{\cdot}2H_2O$ (0.4 g, Aldrich) in 2.0 M HCl (50 mL) under air-free conditions. To prepare saturated solutions of InBr, indium wire (3.0 g, Johnson Matthey) was dissolved in HBr (8 mL, 9M; Aldrich) at 50 °C under N_2.[25] A red−brown precipitate was filtered off in air and dried over silica gel in vacuo. Weighed amounts of the solid were used as a source of In^I in experiments described.

Elemental Analyses. A Unicam 701 inductively coupled plasma atomic emission spectrometer (ICP−AES) was used. Solutions in 2 M HCl were analyzed for Mo, W, Ge, and S or Se. For S and Se, the trinuclear clusters $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3Se_4(H_2O)_9]^{4+}$ in 2 M HCl were used as standards.

Oxidants. A sample of the Co^{III} complex $NH_4[Co(dipic)_2]$ was prepared as previously described, peak position 510 nm (630 M^{-1} cm^{-1}).[11] The reduction potential of the Co^{III}/Co^{II} couple is 362 mV. A 0.5 M solution of hydrated iron(III) chloride (BDH, Analar) in 2.0 M Hpts was also used. The reduction potential of the Fe^{III}/Fe^{II} couple is ~770 mV.

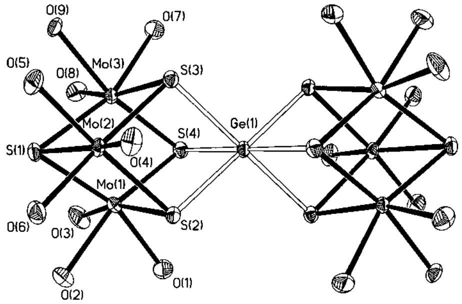

Figure 1. Structure of the centrosymmetric double-cube cation in compound **1**, showing 50% probability displacement ellipsoids and labeling of the unique atoms. Hydrogen atoms are not shown.

X-ray Crystallography. Crystal data for the complexes $[Mo_6GeS_8(H_2O)_{18}](pts)_828H_2O$ (**1**), $[W_6GeS_8(H_2O)_{18}](pts)_8{\cdot}23H_2O$ (**2**), and $[Mo_6GeSe_8(H_2O)_{18}](pts)_8{\cdot}8H_2O$ (**3**), are listed in Table 1, and further details of the structure refinement and calculations are given in the Supporting Information. Crystals were examined on a Bruker AXS SMART CCD area-detector diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å), with methods and programs as previously described.[11] Disorder was resolved in pts anions and in some uncoordinated water molecules for compounds **1** and **2**. The overall water content was estimated from the refinement for compounds **1** and **2**, and appeared to be slightly different for these two compounds, although they are isomorphous. It may well vary between samples and also between individual samples. A minor disorder component was also detected and refined for the three W atoms in compound **2**, but could not be resolved for the other atoms of the cation, since the minor disorder component is only 6.5(3)%. There is no disorder in compound **3**, for which hydrogen atoms were located and refined. This compound is isostructural with the corresponding arsenic-containing double cube.[16]

Results

Crystal Structures. Crystals of salts of the double cubes **1**−**3** were obtained from the most concentrated fractions eluted from Dowex columns with 4 M Hpts solutions. Figure 1 shows the structure of the cation of compound **1**.

Figure 2 shows the cation of compound **3** together with its immediately surrounding anions and water molecules. Selected bond lengths and angles are listed in Table 2. Complete tables of coordinates, geometry, and displacement parameters can be found in the Supporting Information (CIF). The geometry of the double cubes is comparable with those previously reported for other shared heteroatoms,[16] with short Mo−Mo and W−W

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(25) Dronskowski, R. *Inorg. Chem.* **1994**, *33*, 5927.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**−**3**

	compound **1**	compound **2**	compound **3**
Ge−S/Se	2.4457(13)	2.532(5)	2.5816(5)
	2.4929(13)	2.473(4)	2.5712(5)
	2.4270(13)	2.451(4)	2.6493(6)
Mo/W−S/Se	2.3358(14)	2.344(4)	2.4577(7)
	2.3304(14)	2.356(5)	2.4491(7)
	2.3393(14)	2.354(4)	2.4592(7)
	2.3393(14)	2.336(4)	2.4687(7)
	2.3349(14)	2.347(5)	2.4590(7)
	2.3373(14)	2.366(4)	2.4625(7)
	2.3419(14)	2.337(4)	2.4637(7)
	2.3394(14)	2.339(5)	2.4581(7)
	2.3404(14)	2.346(5)	2.4532(7)
Mo/W−O	2.180(4)	2.170(12)	2.201(4)
	2.173(4)	2.179(13)	2.163(4)
	2.152(4)	2.133(12)	2.143(3)
	2.192(4)	2.135(12)	2.172(4)
	2.164(4)	2.140(12)	2.152(4)
	2.149(4)	2.183(12)	2.206(4)
	2.177(4)	2.157(12)	2.155(4)
	2.181(4)	2.150(15)	2.197(3)
	2.150(4)	2.176(13)	2.182(4)
Mo/W−Mo/W	2.6856(7)	2.6622(12)	2.7322(6)
	2.7004(7)	2.6757(12)	2.7445(6)
	2.6797(6)	2.6753(13)	2.7293(6)
S/Se−Ge−S/Se	80.02(4)−83.09(4)	78.98(14)−82.02(14)	80.24(2)−83.52(2)
S/Se−Mo/W−S/Se	85.63(5)−87.58(5)	85.66(16)−87.40(15)	86.46(2)−88.72(2)
	108.55(5)−109.78(5)	109.22(17)−110.61(16)	110.73(2)−112.17(2)
O−Mo/W−O	76.08(15)−83.27(16)	76.4(5)−81.7(5)	74.41(14)−80.28(14)
Mo/W−S/Se−Mo/W	69.84(4)−70.52(4)	68.68(11)−69.67(12)	67.19(2)−67.85(2)
Mo/W−S/Se−Ge	94.42(5)−97.31(5)	94.91(16)−97.86(16)	93.63(2)−96.76(2)

distances indicative of metal−metal bonding interactions and long nonbonding Mo−Ge and W−Ge distances. The Ge atom lies on a crystallographic inversion center in each case, and it is octahedrally coordinated by six sulfides in **1**−**2** and six selenides in **3**. Each Mo or W atom is also octahedrally coordinated by three sulfides or selenides and three aqua ligands in a fac- arrangement, ignoring the metal−metal interactions. Other details of the double-cube geometry have been discussed previously.[16] Attempts to obtain crystals of salts of $[W_3GeS_4(H_2O)_{12}]^{6+}$ and $[W_3GeSe_4(H_2O)_{12}]^{6+}$ or related single cubes were unsuccessful.

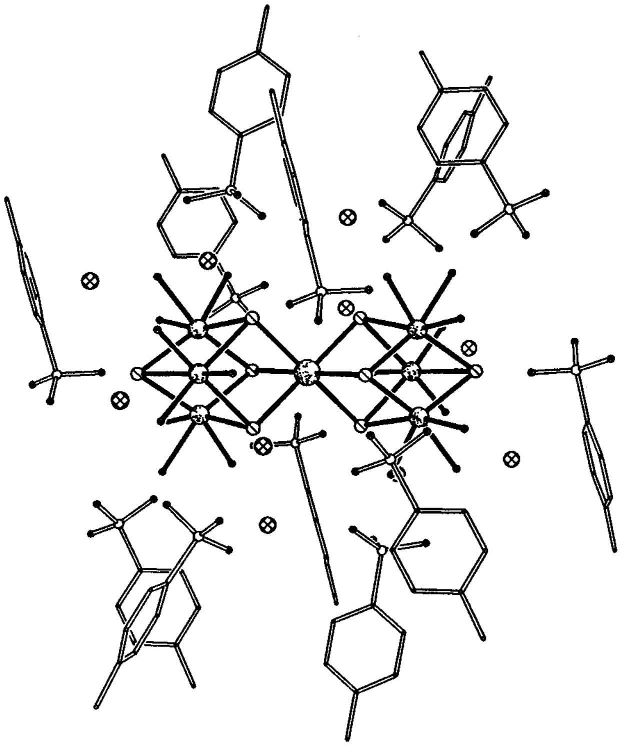

Figure 2. The double-cube cation in compound **3** (filled bonds), together with all the anions (hollow bonds) and water molecules (crosshatched circles) that engage in direct hydrogen bonds with it, forming a surrounding sheath.

Table 3. ICP−AES Analyses and Stoichiometry Determinations with the Co^{III} Complex $[Co(dipic)_2]^-$ as Oxidant for the Ge-Containing Single and Double Cube Derivatives of Incomplete Cubes $[M_3E_4(H_2O)_9]^{4+}$ (M = Mo, W; E = S, Se) in 2.0 M HCl

cube	ratios	moles of Co^{III} per cube
$Mo_6GeS_8^{8+}$	6.0:1.0:8.6 (Mo:Ge:S)	3.71[a]
$W_6GeS_8^{8+}$	6.0:1.1:8.5 (W:Ge:S)	4.00
$Mo_6GeSe_8^{8+}$	6.0:1.08[b] (Mo:Ge)	4.00
$W_6GeSe_8^{8+}$	6.0:1.12:8.2 (W:Ge:Se)	1.90[c]
$W_3GeS_4^{6+}$	3.0:1.0:3.96 (W:Ge:S)	1.96
$W_3GeSe_4^{6+}$	3.0:0.97:4.10 (W:Ge:Se)	2.16

[a] With $[Fe(H_2O)_6]^{3+}$ as oxidant, 3.85 mol per cube. [b] Se not determined. [c] Value for first stage of oxidation to single cube.

Analyses of Products. Metal and chalcogenide analyses for single and double cubes were determined by ICP−AES analyses on 2 M HCl solutions, Table 3. Second column purifications were carried out, and values listed were an average of two determinations.

UV−vis Spectra of Products. Peak positions for the trinuclear incomplete cubes and Ge-containing cubes in 2 M HCl and 2 M Hpts are given in Table 4. To calculate ϵ values for the single and double cube derivatives, these were air oxidized to the trinuclear forms, eqs 10 and 11,

$$M_6GeE_8^{\ 8+} + O_2 + 4H^+ \rightarrow 2M_3E_4^{\ 4+} + Ge^{IV} + 2H_2O \quad (10)$$

$$2W_3GeE_4^{\ 6+} + O_2 + 4H^+ \rightarrow 2W_3E_4^{\ 4+} + 2Ge^{IV} + 2H_2O \quad (11)$$

or in the case of $[Mo_3GeS_4(H_2O)_{12}]^{6+}$, quantitative conversion to $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$ was achieved by reaction with $SnCl_3^-$.[11] UV−vis spectra of the trinuclear products are known accurately, Table 4. The visible range absorbance is greater for

Table 4. UV−vis Absorbance Peak Positions for Trinuclear M_3^{IV} Incomplete Cubes $[M_3E_4(H_2O)_9]^{4+}$ (M = Mo, W; E = S, Se) and for Ge-Containing Single and Double Cube Derivatives as Aqua Ions in 2.0 M HCl and 2.0 M Hpts

cluster	color	acid	λ/nm (ϵ/M^{-1} cm^{-1})
$[Mo_3S_4(H_2O)_9]^{4+}$	green	2.0 M HCl	370(4995); 616(326)
		2.0 M Hpts	366(5550); 603(362)
$[Mo_3Se_4(H_2O)_9]^{4+}$	yellow−brown	2.0 M HCl	433(5250); 681(580)
		2.0 M Hpts	427(5820); 646(595)
$[W_3S_4(H_2O)_9]^{4+}$	purple	2.0 M HCl	317(6100); 570(480)
		2.0 M Hpts	315(6350); 560(446)
$[W_3Se_4(H_2O)_9]^{4+}$	green	2.0 M HCl	360(6950): 625(500)
		2.0 M Hpts	359(6660); 618(547)
$[Mo_6GeS_8(H_2O)_{18}]^{8+}$	red−purple	2.0 M HCl	389(14000); 528(5900); ~900(?)
		2.0 M Hpts	380(12900); 522 (5600); 900(310)
$[W_6GeS_8(H_2O)_{18}]^{8+}$	purple	2.0 M HCl	308(8940); 388(5570); 578(1530); ~700(?)
		2.0 M Hpts	310(7610); 516(4380); 720(400)
$[Mo_6GeSe_8(H_2O)_{18}]^{8+}$	dark green	2.0 M HCl	452(21690); 596(11680)
		2.0 M Hpts	438(21690); 596(11680)
$[W_6GeSe_8(H_2O)_{18}]^{8+}$	dark−blue	2.0 M HCl	336(7000); 368(7660); 590(6390)
$[Mo_3GeS_4(H_2O)_{12}]^{6+}$	yellow−green	2.0 M HCl	328(8760); 390(3490); 650sh(380)
$[W_3GeS_4(H_2O)_{12}]^{6+}$	orange−brown	2.0 M HCl	303(16300); 386(12600); ~500(?)
		2.0 M Hpts	290sh; 305sh(~5000); 343(00);495(380)
		2.0 M $HClO_4$	290 (900); 305sh(~500); 345 (4700); 500(500)
$[W_3GeSe_4(H_2O)_{12}]^{6+}$	orange	2.0 M HCl	333(12100); 360sh(~7500); 399(6000)
		2.0 M Hpts	320(9140); 352(5300)

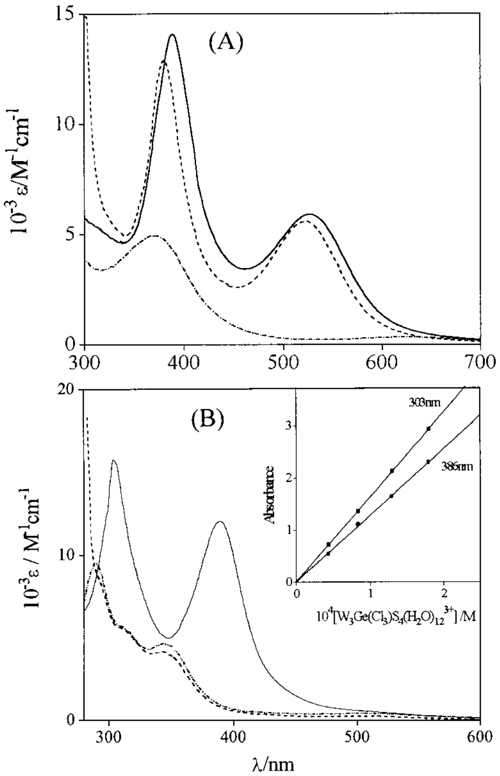

Figure 3. (A) UV−vis spectra of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ in 2.0 M HCl (—) and 2.0 M Hpts (- -), ϵ values per Mo_6. The spectrum of $[Mo_3S_4(H_2O)_9]^{4+}$ is also given (-•-). (B) UV−vis spectra of $[W_3GeS_4(H_2O)_{12}]^{6+}$ in 2.0 M HCl (—), 2.0 M Hpts (- - -), and 2.0 M $HClO_4$ (-•-). Inset shows application of Beer's Law at two wavelengths in 2.0 M HCl.

the double cubes. Small shifts in absorbance are observed for $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ in 2.0 M Hpts and 2.0 M HCl, Figure 3A, most likely due to some Cl^- complexing at the Mo's. Major shifts are observed for the single cubes $[W_3GeE_4(H_2O)_{12}]^{6+}$ in 2.0 M HCl as compared to 2.0 M Hpts (and in one case 2.0 M $HClO_4$). These effects are attributable to Cl^- coordination of the Ge, Figure 3B. Both of the $[W_3GeE_4(H_2O)_{12}]^{6+}$ cubes obey Beer's Law, e.g., inset to Figure 3B.

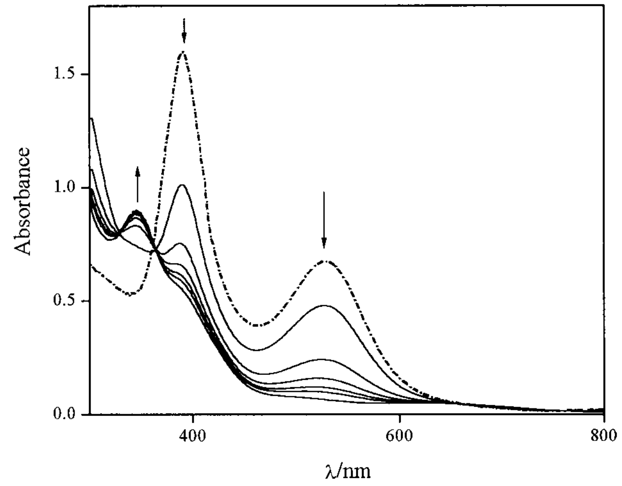

Figure 4. Scan spectra at 6 min intervals in 1 cm light path optical cell for the reaction (25 °C) of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ (0.10 mM) with $[Co(dipic)_2]^-$ (0.2 mM) in 2.0 M HCl.

Redox Stoichiometries. UV−vis scan spectra for $[Co(dipic)_2]^-$ (2:1 mole ratio) oxidation of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ are shown in Figure 4. Stoichiometries were determined by addition of aliquots of $[Co(dipic)_2]^-$ from a Hamilton microsyringe to the cluster in 2 M Hpts or 2 M HCl, with monitoring UV−Vis absorbance changes at cluster peak positions. Average values from at least two determinations are reported (moles of Co^{III} per cluster), Table 3. The titration with $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ is slow and requires ~1 h for complete reaction. The stoichiometry for the $[Fe(H_2O)_6]^{3+}$ oxidation of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$, monitored at 522 nm, was carried out as a check. With $[W_6GeS_8(H_2O)_{18}]^{8+}$ the stoichiometry of the reaction to $[W_3GeS_4(H_2O)_{12}]^{6+}$ was determined. In separate experiments the stoichiometries for the single cubes $[W_3GeS_4(H_2O)_{12}]^{6+}$ and $[W_3GeSe_4(H_2O)_{12}]^{6+}$ were obtained. From these studies, overall equations for the double and single cube reactions can be written as in eqs 12 and 13.

$$M_6GeE_8{}^{8+} + 4Co^{III} \rightarrow 2M_3E_4{}^{4+} + Ge^{IV} + 4Co^{II} \tag{12}$$

$$M_3GeE_4{}^{6+} + 2Co^{III} \rightarrow M_3E_4{}^{4+} + Ge^{IV} + 2Co^{II} \tag{13}$$

Kinetics of $[Co(dipic)_2]^-$ Oxidations. First-order rate constants k_{obs} (25 °C) were determined for six single and double cubes, with concentrations in the range (1−6) × 10^{-5} M,

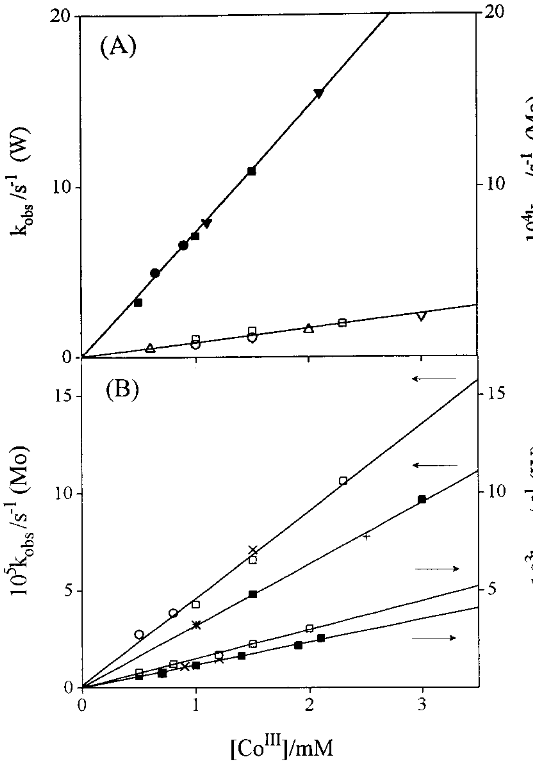

Figure 5. Dependence of first-order rate constants k_{obs} (25 °C) for the $[Co(dipic)_2]^-$ (reactant in >20-fold excess) oxidation of (A) $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ (open symbols) and $[W_6GeS_8(H_2O)_{18}]^{8+}$ (solid), $[H^+] = 2.0$ (□, ■); 1.5 (▽, ▼); 1.0 (○, ●); 0.50 (△), $I = 2.0$ M (Lipts); and (B) of $[W_3GeS_4(H_2O)_{12}]^{6+}$ and $[W_3GeSe_4(H_2O)_{12}]^{6+}$, $[H^+] = 2.0$ (■, □); 1.5 (+); 1.0 (×); 0.5 (●, ○), solid symbols $I = 2.0$ M (LiCl); open $I = 2.0$ M (Lipts).

Table 5. Rate Constants k_{Co} (25 °C) for the Oxidation of Germanium-Containing Single and Double Cubes in Aqueous Solutions, (1−6) × 10^{-5} M, with $[Co(dipic)_2]^-$ in Large Excess and $I = 2.0$ M (LiCl) and 2.0 M (Lipts), as Indicated

	k_{Co}/M^{-1}s^{-1} (2.0 M Cl$^-$)	k_{Co}/M^{-1}s^{-1} (2.0 M pts$^-$)	ratio[a]
$[Mo_6GeS_8(H_2O)_{18}]^{8+}$	12.8(1)	7.7(1) × 10^{-2}	166
$[W_6GeS_8(H_2O)_{18}]^{8+}$	2.8(1) × 10^4	7.3(3) × 10^3	3.8
$[Mo_6GeSe_8(H_2O)_{18}]^{8+}$	>145	6.9(4)	>21
$[Mo_3GeS_4(H_2O)_{12}]^{6+}$	3.2(2) × 10^{-2}	4.6(3) × 10^{-2}	0.70
$[W_3GeS_4(H_2O)_{12}]^{6+}$	1.17(5)	1.49(6)	0.79
$[W_3GeSe_4(H_2O)_{12}]^{6+}$	1.04(6)		
$[Mo_6SnS_8(H_2O)_{18}]^{8+}$	2.32(8) × 10^3 [b]	14.9[c]	156

[a] k_{Co} in 2.0 M Cl$^-$ and k_{Co} in 2.0 M pts$^-$. [b] Seo M.-S. and Sykes A. G., unpublished work. [c] Reference 11.

$[Co(dipic)_2]^-$ in >20-fold excess, and ionic strengths 2.00 M LiCl or Lipts (Supporting Information, Tables S1−S6). Linear dependencies are observed for k_{obs} versus $[Co(dipic)_2^-]$, e.g., Figure 5, from which second-order rate constants k_{Co}, Table 5, are obtained. Only one $[Co(dipic)_2]^-$ is involved in the rate determining step, and 9+ (double) and 7+ (single) transient intermediates react rapidly with further $[Co(dipic)_2]^-$. The reactions are independent of $[H^+]$ in the range 0.5−2.0 M and have been assigned as outer sphere. Rate constants for $[W_6GeS_8(H_2O)_{18}]^{8+}$ are ≥10^5 times faster than those for $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ and $[W_3GeS_4(H_2O)_{12}]^{6+}$. For the double cubes $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ and $[Mo_6SnS_8(H_2O)_{18}]^{8+}$, the ratio of rate constants in 2.0 M Cl$^-$ and 2.0 M pts$^-$ exhibit large 160-fold differences.

Complexing of $W_3GeS_4^{6+}$ with Chloride. From UV−vis spectra, Figure 3, the shift in absorbance for 2 M HCl, as compared to 2 M Hpts (or 2 M $HClO_4$), is more extensive for the single cubes (complexing to the Ge) than the double cubes. On loading a mixture of $[W_3S_4(H_2O)_9]^{4+}$ and $[W_3GeS_4\,(H_2O)_{12}]^{6+}$ onto a Dowex 50W−X2 column and eluting with 1 M HCl, $[W_3GeS_4(H_2O)_{12}]^{6+}$ elutes prior to $[W_3S_4(H_2O)_9]^{4+}$, indicating extensive Cl$^-$ complexing of the latter and $[W_3(GeCl_3)S_4(H_2O)_9]^{3+}$ as a dominant form. From UV−vis changes at 386 nm, considering interaction of a single chloride only, eq 14,

$$W_3GeS_4^{\;6+} + Cl^- \rightleftharpoons W_3(GeCl)S_4^{\;5+} \tag{14}$$

equation 15 is obtained,

$$\frac{\epsilon_o - \epsilon_\infty}{\epsilon_o - \epsilon_{Cl}} = \frac{1}{K[Cl^-]} + 1 \tag{15}$$

where ϵ_o, ϵ_∞, and ϵ_{Cl} are absorption coefficients for $W_3GeS_4^{6+}$, $W_3(GeCl)S_4^{5+}$, and experimental mixes at different [Cl$^-$], respectively. A nonlinear plot of the left-hand side of (15) against $[Cl^-]^{-1}$ is obtained.

Stopped-flow studies with [Cl$^-$] varied over the range up to 2.0 M provide further evidence for the coordination of three chlorides to the Ge. Thus, at 386 nm, a rapid first stage is followed by two further steps, giving biphasic kinetics. The first stage is too fast to monitor. The complexing of Cl$^-$ to Ge is close to completion at 2.0 M levels, with much less affinity for Cl$^-$ than in the case of $[Mo_3SnS_4(H_2O)_{12}]^{6+}$. From studies on the reaction of $[W_3GeS_4(H_2O)_{12}]^{6+}$ with $[Cl^-] = 1.0$ M, a biphasic treatment gives equilibration rate constants (25 °C) of 69 and 5 s^{-1}. These experiments provide further evidence for octahedral Ge and the formula $[W_3GeS_4(H_2O)_{12}]^{6+}$.

Heterometal Exchange. A solution of $W_3GeS_4^{6+}$ and Sn^{II} (0.25 mL Hamilton microsyringe), both in 2.0 M HCl, were mixed under air-free conditions to give equal 0.05 mM concentrations. UV−vis absorbance changes were instant and corresponded to >98% exchange of Sn^{II} for Ge^{II}, eq 16.

$$W_3GeS_4^{\;6+} + Sn^{II} \rightarrow W_3SnS_4^{\;6+} + Ge^{II} \tag{16}$$

The UV−vis spectrum of $W_3SnS_4^{6+}$ is given in ref 12. Similar experiments involving addition of a 15-fold excess of InBr to $[W_3GeS_4(H_2O)_{12}]^{6+}$ (0.13 mM) gave >99% exchange of In^I for Ge^{II}, eq 17.

$$W_3GeS_4^{\;6+} + In^{I} \rightarrow W_3InS_4^{\;5+} + Ge^{II} \tag{17}$$

No reverse reaction was observed on addition of a 20-fold excess of Ge^{II} to $[W_3InS_4(H_2O)_{12}]^{5+}$ (0.05 mM). The UV−vis spectrum of $W_3InS_4^{5+}$, and the ability of Sn^{II} to displace In^I, has been reported previously.[6] Relative affinities for $[W_3S_4(H_2O)_9]^{4+}$ are therefore Sn^{II} > In^I > Ge^{II}. Similar behavior is observed with $[W_3Se_4(H_2O)_9]^{4+}$.

Discussion

In this work, different germanium heterometallic derivatives of $[M_3E_4(H_2O)_9]^{4+}$ (M = Mo, W; E = S, Se) have been prepared. Whereas three procedures involving respectively GeO, GeO_2, and Ge metal powder give the double cube $[Mo_6GeS_8(H_2O)_{18}]^{8+}$, the single cube $[Mo_3GeS_4(H_2O)_{12}]^{6+}$ is more difficult to obtain, and a procedure involving slow air oxidation of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ is required. The Se analogue $[Mo_3Se_4(H_2O)_9]^{4+}$ exhibits similar behavior, but the route to $[Mo_3GeSe_4(H_2O)_{12}]^{6+}$ is more difficult because of the competing oxidation of μSe^{2-} to give a precipitate of red Se. In sharp contrast with $[W_3S_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$, the GeO and GeO_2

procedures give the 6+ single cubes $[W_3GeS_4(H_2O)_{12}]^{6+}$ and $[W_3GeSe_4(H_2O)_{12}]^{6+}$. Such behavior has not been observed previously in studies with other Group 13−15 heteroatoms. For example, Sn^{II} and Sn are known to react with $[Mo_3S_4(H_2O)_9]^{4+}$ to give the single and double cubes, respectively.[10,11] The single cubes $[W_3GeE_4(H_2O)_9]^{4+}$ are converted to double cubes $[W_6GeE_8(H_2O)_{18}]^{8+}$ by reductive addition, which involves the addition of $[W_3E_4(H_2O)_9]^{4+}$ in the presence of BH_4^-. Attempts to use this same procedure to obtain the double cube $[Mo_3W_3GeS_8(H_2O)_{18}]^{8+}$ gives $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ as the only detectable product, again illustrating the special stability of the Mo_6 cube. Octahedral coordination is observed for Group 13−15 heteroatoms, and in cases where single and double cubes have been prepared, e.g., Ge, Sn, and In, both are octahedral. In contrast, single cubes with tetrahedral heteroatoms (Fe, Co, Ni, Pd) give edge-linked double cubes in which the heteroatom remains tetrahedral.[2]

In common with all other corner-shared double cubes with Group 13−15 heteroatoms and two d block elements (Hg, Mo),[20,21,26] those with germanium have 8+ charges. The exclusive nature of the 8+ charge irrespective of group in the Periodic Table, is consistent with the formalism $(Mo_3S_4^{4+})_2M'^{o}$.[16] It is also consistent with the widely used preparative route involving reaction of the metal with $[Mo_3S_4(H_2O)_9]^{4+}$ [16] and provides a model of intercalation on a molecular scale.[20] The X-ray crystal structure of the $[W_6GeS_8(H_2O)_{18}]^{8+}$ cation is the first W_6 structure to be determined. The double cubes $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ and $[W_6Ge\ S_8(H_2O)_{18}]^{8+}$ have short Mo−Mo (2.689 Å) and W−W (2.671 Å), consistent with metal−metal bonding, and nonbonding M−Ge separations of ∼3.5 Å. No crystal structures of the Ge single cubes have been possible, but the structures $[Mo_3(SnCl_3)S_4(NCS)_9]^{6-}$ and $[W_3(SnCl_3)S_4(NCS)_9]^{6-}$ have been reported previously,[10,27] and feature similar M−M (bonding) and M−M′ (nonbonding) effects. In the case of $[Mo_3S_4(H_2O)_9]^{4+}$, the formation of single as opposed to double cubes with the Group 13−15 heteroatoms is not as common, but those with M′ = Ga, In, Sn, and now Ge have been prepared. Two other examples have been reported with M′ = Sb, Bi,[28] using dithia-phosphate instead of H_2O as ligands (see also ref 29). In the case of $[W_3S_4(H_2O)_9]^{4+}$, heterometal derivatives are less common, and cubes are obtained only with Ge, In, and Sn.

Table 5 summarizes second-order rate constants k_{Co} (25 °C) for the oxidations of Ge-containing cubes with $[Co(dipic)_2]^-$. The double cube $[W_6GeS_8(H_2O)_{18}]^{6+}$ reacts $\sim 10^5$ times faster than $[Mo_6GeS_8(H_2O)_{18}]^{8+}$, and 5×10^5 times faster with $[W_3GeS_4(H_2O)_{12}]^{6+}$ in 2.0 M pts^-. The greater redox reactivity of $[W_6GeS_8(H_2O)_{18}]^{8+}$ is attributed to the stronger reducing properties of $W^{IV}{}_3$ as compared to $Mo^{IV}{}_3$. Thus, in terms of the formalism $(Mo_3S_4^{4+})_2Ge^{o}$ and $(W_3S_4^{4+})_2Ge^{o}$,[16] insufficient transfer of electron density from $W_3S_4^{4+}$ to Ge^{o} occurs, and $(W_3S_4^{4+})Ge^{2+}$ is the more stable.

Rate constants for the $[Co(dipic)_2]^-$ oxidation of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$, Table 5, are ∼160 times greater in 2.0 M Cl^- than 2.0 M pts^-, an effect not previously observed. A possible explanation is that pts^- and solvent H_2O form some sort of protective hydrogen-bonded sheath around the 8+ ion, as in the crystal structure, Figure 2. Complexing of Cl^- to Mo/W may also contribute. A similar effect is observed with $[Mo_6SnS_8(H_2O)_{18}]^{8+}$, but with $[W_6GeS_8(H_2O)_{18}]^{8+}$, when rate constants are close to the fast stopped-flow limit, a smaller effect is observed. The structuring is less with the single cubes.

Table 6. Summary of Rate Constants k_{Co} (25 °C) for the $[Co(dipic)_2]^-$ Oxidation of Heterometal (M′) Corner-Shared Derivatives, $[Mo_6M'S_8(H_2O)_{18}]^{8+}$, of $[Mo_3S_4(H_2O)_9]^{4+}$ at $[H^+] = 0.5{-}2.0$ M, $I = 2.0$ M (pts^-)

M′	$k_{Co}/M^{-1}s^{-1}$	reference
Ge	0.077	this work
Sn	14.9	10
Pb	2.76×10^5	13, 15
In	3.09×10^4	6
Tl	very fast	6
As	2.10×10^4	16
Bi	3.6×10^4	18
Mo	0.31	21

Heterometal exchange reactions with $[W_3GeS_4(H_2O)_{12}]^{6+}$ indicate an order of reactivity $Sn^{II} > In^{I} > Ge^{II}$. A possible mechanism is dissociation eq 18,

$$W_3GeS_4^{\ 6+} \rightarrow W_3S_4^{\ 4+} + Ge^{II} \tag{18}$$

followed by addition of, e.g., Sn^{II}, eq 19.

$$W_3S_4^{\ 4+} + Sn^{II} \rightarrow W_3SnS_4^{\ 6+} \tag{19}$$

However, Beer's Law applies for $[W_3GeE_4(H_2O)_{12}]^{6+}$ (E = S, Se), e.g., Figure 3B, and there is no evidence for dissociation to the extent implied in (18). Instead, reaction paths in which one or two bonds cleave and Sn^{II} then begins to coordinate may be relevant, as in the case of $[Zn(H_2O)_6]^{2+}$ with $[Ni(edta)]^-$ (edta = ethylenediaminetetraacetate) when $[Zn(edta)]^-$ and $[Ni(H_2O)_6]^{2+}$ are formed.[30]

A comparison of rate constants for the oxidation of $[Mo_6M'S_8(H_2O)_{18}]^{8+}$ in 2 M pts^-, Table 6, shows that the Ge cube is the least reactive, with Sn next. Both are Group 14 and have an even number of electrons. The example with M′ = Mo is an exception as already discussed.[16] A molecular orbital treatment has been considered for $[Mo_6SnS_8(H_2O)_{18}]^{8+}$.[31] This shows that four electrons from the Sn are located in two molecular orbitals (HOMO and SHOMO, the second highest OMO), symmetry a_{1u} and a_{1g}. Because these orbitals are nondegenerate, the Group 14 double cubes must be diamagnetic (2 + 2 electron populations). Group 13 containing double cubes have one electron less, and the Group 15 cubes one electron more in the LUMO, both giving decreased stability.

In conclusion, although Ge metal is quite inert, it reacts with $[Mo_3S_4(H_2O)_9]^{4+}$ to give $[Mo_6GeS_8(H_2O)_{18}]^{8+}$, which is the most stable Group 13−15 double cube. The next most stable double cube is with Sn (also Group 14), where both have an even number of electrons. The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Ge^{II} (from GeO or Ge^{IV}/H_3PO_2) also gives the double cube, whereas in the case of Sn^{II} (and In^{I}, Ga^{I}) the single cubes are obtained. Similar observations apply with Se for S. Understandably, procedures involving a reductant favor formation of the double cubes. In sharp contrast with $[W_3E_4(H_2O)_9]^{4+}$ (E = S, Se), the single cubes are obtained, and the double cube is only accessed by reductive addition with BH_4^- and $[W_3S_4(H_2O)_9]^{4+}$.

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(26) Shibahara, T.; Yamamoto, T.; Kanadani, H.; Kuroya, H. *J. Am. Chem. Soc.* **1987**, *109*, 3495.

(27) Müller, A.; Fedin, V. P.; Diemann, E.; Bögge, H.; Krickemeyer, E.; Sölter, D.; Giuliana, A. M.; Barbieri, R.; Adler, P. *Inorg. Chem.* **1994**, *33*, 2243.

(28) Lu, S. F.; Huang, J.-Q.; Wu, Q.-J.; Huang, X.-Y.; Yu, R.-M.; Zheng, Y.; Wu, D.-X. *Inorg. Chim. Acta* **1997**, *261*, 201.

(29) Hernandez-Molina, R.; Elsegood, M. R. J.; Clegg, W.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **2001**, 2173.

(30) Wilkins, R. G. *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, 2nd ed; VCH: Weinheim, Germany, 1991.

(31) Bahn, C. C.; Tan, A.; Harris, S. *Inorg. Chem.* **1998**, *37*, 2770.

The formation of single $(W_3E_4^{4+})Ge^{2+}$ rather than double $(W_3E_4^{4+})_2Ge^{o}$ cubes relates to the preference W has for higher oxidation states. Formation of $[W_3S_4(H_2O)_9]^{4+}$ derivatives is much less extensive than in the case of $[Mo_3S_4(H_2O)_9]^{4+}$, and so far only Ge, Sn, In, along with Mo, Ni, and Cu (6 from 13 attempted) give heteroatom derivatives.[31] Rate constants with $[Co(dipic)_2]^-$ as an oxidant have been used as a measure of redox reactivity, and it has been demonstrated that $[W_6GeS_8(H_2O)_{18}]^{8+}$ is $\geq 10^5$ times more reactive than $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ and $[W_3GeS_4(H_2O)_{12}]^{6+}$.

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Supporting Information Available: Three X-ray crystallographic files in CIF format; listing of rate constants (six pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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