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Article

Synthesis and Structure of Nickel-Containing Cuboidal Clusters Derived from $[W_3Se_4(H_2O)_9]^{4+}$. Site-Differentiated Substitution at the Nickel Site in the Series $[W_3NiQ_4(H_2O)_{10}]^{4+}$ (Q = S, Se)

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New Ni-containing heterometallic cuboidal cluster aqua complex $[W_3(NiCl)Se_4(H_2O)_9]^{3+}$, the missing link in the family of the M_3NiQ_4 clusters (M = Mo, W; Q = S, Se), has been prepared by the reaction of $[W_3Se_4(H_2O)_9]^{4+}$ with Ni in 2 M HCl. Single crystals of edge-linked double-cuboidal cluster $[\{W_3NiSe_4(H_2O)_9\}_2](pts)_8\cdot 18H_2O$ (pts = *p*-toluenesulfonate) were grown from the solution of the aqua complex in 3 M Hpts, and their structures were determined. The Ni site in the clusters $[W_3(NiCl)Q_4(H_2O)_9]^{3+}$ selectively coordinates typical π-acceptor ligands such as CO, olefins, acetylenes, phosphines, arsines, or $SnCl_3^-$. This allows stabilization by coordination of such elusive species as $HP(OH)_2$ and $As(OH)_3$. The stability constants for coordination of $HP(OH)_2$, $As(OH)_3$, and $SnCl_3^-$ were determined. The Se for S substitution increases the stability by 1–2 orders of magnitude. Supramolecular adducts with cucurbit[6]uril (Cuc), $[W_3(Ni(HP(OH)_2))Q_4(H_2O)_9]Cl_4\cdot Cuc\cdot 11H_2O$ and $[W_3(NiAs(OH)_3)S_4(H_2O)_8Cl]Cl_3\cdot Cuc\cdot 13H_2O$, were isolated and structurally characterized.

Introduction

The heterometallic chalcogen-bridged clusters with the cuboidal $M_3M'Q_4$ cores have been an area of much research interest in the past decade.[1] Among these, the Ni derivatives have received special attention owing to their potential use as catalysts in important industrial processes such as hydrodesulfurization.[2] Reportedly, the cluster $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ was incorporated into zeolites, giving a heterogeneous catalyst for benzothiophene hydrodesulfurization as well as highly selective catalysts for the synthesis of C_2 species from CO and H_2.[3] The incorporation of Ni into the triangular clusters $[M_3S_4(H_2O)_9]^{4+}$, $[MoW_2S_4(H_2O)_9]^{4+}$, and $[Mo_2WS_4(H_2O)_9]^{4+}$ (M = Mo, W) has been achieved.[4] In HCl solutions, one chloride is attached to the Ni atom, giving single cubes formulated as $[M_3(NiCl)S_4(H_2O)_9]^{3+}$ (M = Mo, W).[5] The compounds $[Mo_3NiS_4(H_2O)_{10}](pts)_4\cdot 7H_2O$,[6] $[Mo_2WNiS_4(H_2O)_{10}](pts)_4\cdot 7H_2O$,[4] $[\{MoW_2NiS_4(H_2O)_9\}_2](pts)_8\cdot 7H_2O$,[4] and $[\{W_3NiS_4(H_2O)_9\}_2](pts)_8\cdot 20H_2O$[4] (pts = *p*-toluenesulfonate) have been structurally characterized. As can be seen, the Mo-rich clusters crystallize as single cubes whereas the W-rich clusters crystallize as edge-linked double cubes. The coordination around Ni is almost regular tetrahedral. Improved syntheses of $[\{W_3NiS_4(H_2O)_9\}_2](pts)_8\cdot 20H_2O$ and $[Mo_3NiS_4(H_2O)_{10}](pts)_4\cdot 7H_2O$ were reported

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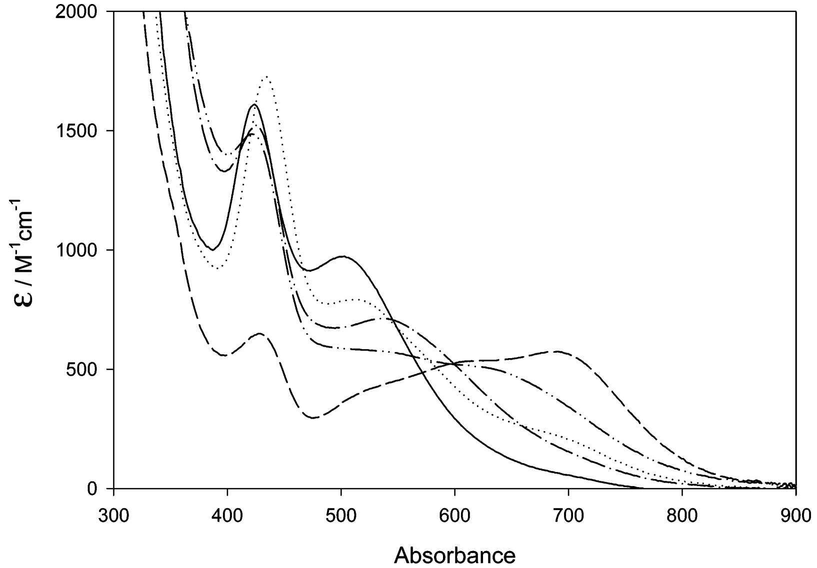

Figure 1. UV−vis spectra for $[W_3(NiL)S_4(H_2O)_9]^{4+}$ in 2 M Hpts: (− −) L = H_2O; (—) L = $HP(OH)_2$; (···) L = $As(OH)_3$; (−·−) L = $OHCH_2CH{=}CHCH_2OH$; (−··−) L = $OHCH_2C{\equiv}CCH_2OH$.

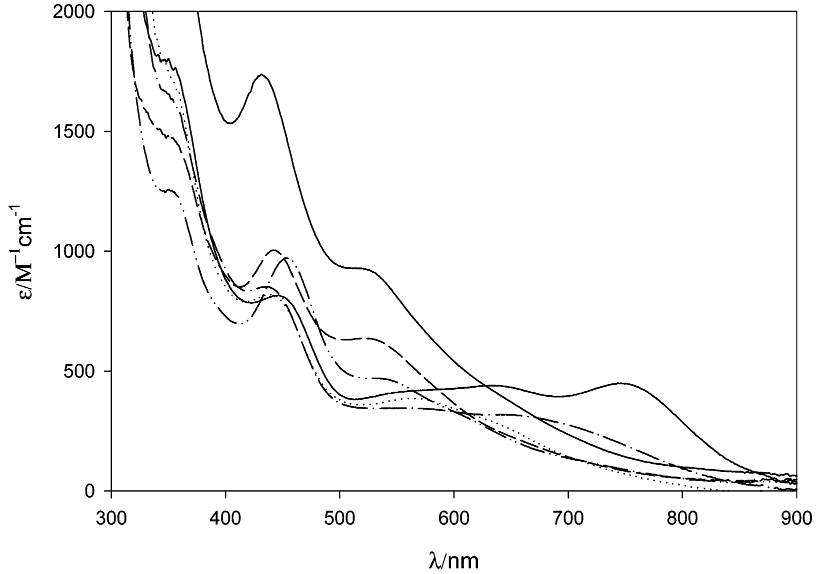

Figure 2. UV−vis spectra of $[W_3(NiL)Se_4(H_2O)_9]^{4+}$ in 2 M Hpts: (—) L = H_2O; (− −) L = $HP(OH)_2$; (···) L = $OHCH_2CH{=}CHCH_2OH$; (−·−) L = $OHCH_2C{\equiv}CCH_2OH$; (−··−) L = $As(OH)_3$; (—, upper line) L = CO.

later,[7] and $[Mo_3NiSe_4(H_2O)_{10}]^{4+}$ was characterized in solution.[8] The Ni site in these clusters has a tetrahedral environment, being surrounded by three chalcogen atoms of the cluster core and one exchangeable external ligand (H_2O, Cl^-, etc.). This geometry also permits Ni to engage in three Mo(W)−Ni bonds to form an electron-precise tetrahedral M_3-Ni cluster (in terms of 60 e^- magic number formalism), which explains the enhanced stability of these clusters vis-à-vis those with other heterometals. There is some controversy regarding the formal oxidation state attribution because magnetic and X-ray photoelectron spectra speak in favor of $Mo^{IV}Mo^{III}_2Ni^{II}$ formulation and the quantum chemical calculations and the marked preference for the π-acceptor ligands support the $Mo^{IV}{}_3Ni^0$ alternative.[9] The latter can be explained by the availability of Ni d orbitals of the appropriate symmetry in the lowest unoccupied molecular orbital for π backbonding.[10] The tetrahedral geometry is known for both Ni(II) (as in $[Ni(SR)_4]^{2-}$) and Ni(0) (as in $[Ni(CO)_4]$). Whatever the case, this unique NiS_3L site coordinates a wide range of ligands L, with remarkably slow substitution kinetics, much slower than those for the high-spin octahedral Ni^{2+}. The same geometry has been recently recognized for the Ni active site of CO dehydrogenase/acetylCoA synthase.[11] In both cases, coordination of CO takes place under exceptionally mild conditions: at room temperature and

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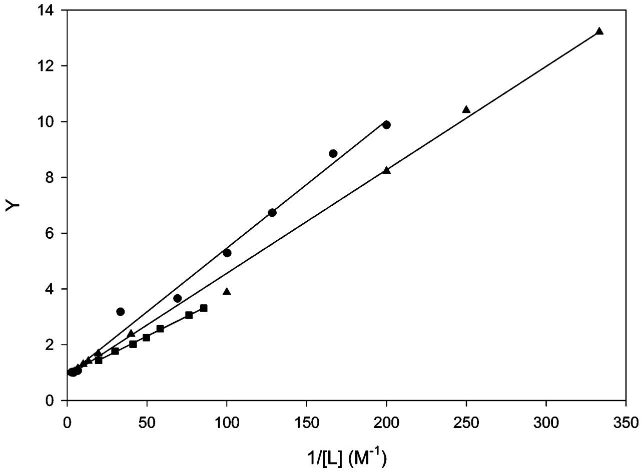

Figure 3. Determination of the formation constants, *K*, for the reaction $[W_3(NiCl)Q_4(H_2O)_9]^{3+} + L \rightleftarrows [W_3(NiL)Q_4(H_2O)_9]^{4+} + Cl^-$; (●) L = $HP(OH)_2$, Q = S; (■) L = $As(OH)_3$, Q = S; (▲) L = $SnCl_3^-$, Q = Se. All solutions were prepared in 2 M HCl and measured at 25 °C. $Y = (\epsilon_\infty - \epsilon_0)/(\epsilon_L - \epsilon_0) = 1/K[L] + 1$.

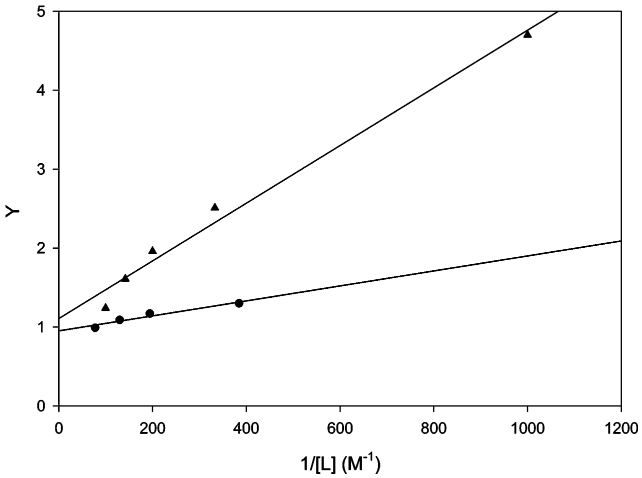

Figure 4. Determination of the formation constants, *K*, for the reaction **1** + L $\rightleftarrows [W_3(NiCl)Se_4(H_2O)_9]^{4+} + Cl^-$: (●) L = $As(OH)_3$; (▲) L = $HP(OH)_2$. All solutions were prepared in 2 M HCl and measured at 25 °C. $Y = (\epsilon_\infty - \epsilon_0)/(\epsilon_L - \epsilon_0) = 1/K[L] + 1$.

Table 1. Formation Constants of the $[W_3(NiL)Q_4(H_2O)_9]^{4+}$ Complexes

complex	K (M^{-1})
$[W_3(NiHP(OH)_2)S_4(H_2O)_9]^{3+}$	21.8(1)[a]
$[W_3(NiHP(OH)_2)Se_4(H_2O)_9]^{3+}$	273.0(5)[a]
$[W_3(NiAs(OH)_3)S_4(H_2O)_9]^{3+}$	35.7(1)[b]
$[W_3(NiAs(OH)_3)Se_4(H_2O)_9]^{3+}$	1054.0(5)[b]
$[W_3(NiSnCl_3)Se_4(H_2O)_9]^{3+}$	27.0(1)

[a] $[L] = [H_3PO_2] + [HP(OH)_2] = [H_3PO_2]_{total}$. [b] $[L] = [As(OH)_3]$, assuming 100% conversion of dissolved As_2O_3 into $As(OH)_3$.

under atmospheric pressure. The crystal structure of the pts salt of $[Mo_3(NiCO)S_4(H_2O)_9]^{4+}$ was determined,[12] and $[Mo_3(NiCO)Se_4(H_2O)_9]^{4+}$ and $[W_3(NiCO)S_4(H_2O)_9]^{4+}$ were detected in solution.[7,8] Ethylene complexes $[Mo_xW_{3-x}(NiC_2H_4)S_4(H_2O)_9]^{4+}$ were reported, with their stability decreasing with increasing x.[4] From the stability constant order $[Mo_3(NiBr)S_4(H_2O)_9]^{3+} > [Mo_3(NiCl)S_4(H_2O)_9]^{3+}$, the Ni site can be classified as soft and, as could be expected, it preferably coordinates the P, As, Sb, or S donors, which, in turn, do not compete with H_2O or Cl^- preferred by the Mo sites.[5] This ability to form strong complexes with phosphines even goes as far as to stabilize energetically less favored tautomers of phosphorous acid H_3PO_3 [$P(OH)_3$] and hypophosphorous acid H_3PO_2 [$HP(OH)_2$].[13] Both $P(OH)_3$ and $HP(OH)_2$ are the simplest water-soluble phosphine ligands and may be of interest as a cheaper alternative to usual water-soluble organic phosphines in two-phase catalytic systems.[14] In the course of our studies to quantify the isomerization of H_3PO_3 and H_3PO_2 by the $[M_3M'Q_4(H_2O)_{10}]^{4+}$ (M′ = Ni, Pd) cluster aqua complexes, we were hindered by the very low reactivity of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ and by the easy oxidation of coordinated $HP(OH)_2$ into $P(OH)_3$.[13] To follow the influence of the constituents of the cluster core (Mo vs W and S vs Se) on the reactivity, we prepared $[W_3NiSe_4(H_2O)_{10}]^{4+}$ for the first time and studied the reactions of $[W_3NiQ_4(H_2O)_{10}]^{4+}$ (Q = S, Se) with various π-acceptor ligands.

Experimental Section

All of the manipulations, including synthesis, column purification, crystallizations, and spectrophotometry, were carried out under N_2. The starting triangular clusters $[W_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se) were prepared according to the published procedures.[15] Ni granules (Aldrich; 5 mm in diameter) were activated before use by immersion into a solution of 4 M HCl. A stock solution of $[W_3(NiCl)S_4(H_2O)_9]^{3+}$ was prepared as reported and kept frozen at −4 °C.[4,16] A 50% (w/w) solution of hypophosphorus acid (Aldrich) was used. All other reagents (As_2O_3, H_3PO_3, 1,4-butene-2-diol, and 1,4-butyne-2-diol) were purchased from Aldrich and used without further purification. Cucurbit[6]uril was prepared according to the published procedure.[17] A crystalline sample of the Co^{III} oxidant $(NH_4)[Co(dipic)_2]$ (dipic = 2,6-pyridinedicarboxylate, peak at 510 nm with $\epsilon = 83$ M^{-1}·cm^{-1}), was prepared as reported (Co^{III}/Co^{II} reduction potential 362 mV vs NHE).[18] CO was generated by the reaction of hot concentrated H_2SO_4 with HCOOH and purified by passing through a column filled with KOH pellets (from CO_2 and SO_2) and then through a solution of sodium pyrogallate (from O_2). A stock solution of $SnCl_3^-$ was prepared by dissolving solid $SnCl_2(s)$ (Merck; pa) in 2 M HCl. The solution was filtered from undissolved solids, and its concentration was determined by redox titration with $I_2(aq)$ (Prolabo). The ion strength was adjusted to 2.0 with LiCl (Merck; pa). The solution was stored under a N_2 atmosphere at 4 °C and used as fast as possible.

For the complexation studies, the equilibrium constant K is defined as follows:

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Table 2. Crystallographic Data for **1a**, **2b**, and **3**

compound	**1a**	**2b**	**3**
chemical formula	$C_{56}H_{128}Ni_2O_{60}S_8Se_8W_6$	$C_{36}H_{77}Cl_4N_{24}NiO_{34}PSe_4W_3$	$C_{36}H_{81}AsCl_4N_{24}NiO_{36}S_4W_3$
M_r	3870.26	2489.09	2381.62
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
T (K)	160	160	160
a (Å)	11.6936(6)	16.5728(5)	12.3438(6)
b (Å)	14.7813(7)	18.5868(6)	12.5011(6)
c (Å)	16.4159(8)	48.7091(16)	24.4502(11)
α (deg)	77.827(2)	90	100.095(2)
β (deg)	84.375(2)	99.391(2)	90.307(2)
γ (deg)	82.585(2)	90	95.425(2)
V (Å^3)	2743.1(2)	14 803.0(8)	3697.0(3)
Z	1	8	2
D_{calcd} (Mg·m^{-3})	2.343	2.234	2.139
μ (mm^{-1})	9.498	7.132	5.688
R [$F^2 > 2\sigma(F^2)$], $wR(F^2)$, S	0.0373, 0.0819, 1.077	0.0667, 0.1496, 1.147	0.0674, 0.1542, 1.259
weighting scheme	calcd $w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 16.1449P]$ where $P = (F_o^2 + 2F_c^2)/3$	calcd $w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 928.1026P]$ where $P = (F_o^2 + 2F_c^2)/3$	calcd $w = 1/[\sigma^2(F_o^2) + (0.0022P)^2 + 145.9019P]$ where $P = (F_o^2 + 2F_c^2)/3$

$$[W_3(NiCl)Q_4(H_2O)_9]^{3+} + L \rightleftarrows [W_3(NiL)Q_4(H_2O)_9]^{4+} + Cl^-$$

The constant was calculated from the following expression:

$$(\epsilon_0 - \epsilon_\infty)/(\epsilon_0 - \epsilon_L) = 1/(K[L]) + 1$$

where ϵ_0 is the absorption coefficient of $[W_3(NiCl)Q_4(H_2O)_9]^{3+}$, ϵ_∞ is the absorption coefficient of $[W_3(NiL)Q_4(H_2O)_9]^{4+}$, and ϵ_L is the absorption coefficient for a mixture of $[W_3(NiCl)Q_4(H_2O)_9]^{3+}$ and $[W_3(NiL)Q_4(H_2O)_9]^{3+}$.

All solutions were prepared in 2.0 M HCl, kept in a N_2 atmosphere to avoid oxidation, and measured at 25 °C after equilibrium was reached. A check for equilibrium was made by repeatedly monitoring the spectral changes, and it was assumed to be reached when no more spectral changes were detected.

UV−vis spectra were obtained on a Shimadzu UV 2101 spectrophotometer. The spectra are shown in Figures 1 (S) and 2 (Se).

$[W_3(NiCl)Se_4(H_2O)_9]^{3+}$ (1) and $[\{W_3NiSe_4(H_2O)_9\}_2](pts)_8\cdot 18H_2O$ (1a). A solution of $[W_3Se_4(H_2O)_9]^{4+}$ (20 mL, 15 mM) in 2 M HCl was heated at 90 °C with Ni granules (1 g) for 12 h. The reaction mixture was purified by cation-exchange chromatography on a Dowex 50W-X2 resin. After dilution to $[H^+] = 0.25$ M and loading, elution with 0.5 M HCl gave a pale-green solution of $[Ni(H_2O)_6]^{2+}$, followed by a dark-green solution of **1** eluted with 1 M HCl. The conversion was quantitative. UV−vis [λ, nm (ϵ, M^{-1}·cm^{-1})]: 457 (817), 633 (454), 753 (572).

1 was converted into $[W_3NiSe_4(H_2O)_{10}]^{4+}$ by reloading the solution of **1** onto a Dowex 50 W-X2 column and eluting with Hpts. Repurification and elution of this solution with 3 M *p*-toluenesulfonic acid on a short Dowex 50 W-X2 column (6 cm × 1 cm) gave a concentrated green solution, from which well-formed rectangular green single crystals of $[\{W_3NiSe_4(H_2O)_9\}_2](pts)_8\cdot 18H_2O$ were grown after 1 day of storage at 4 °C. UV−vis spectrum in 2 M Hpts: (ϵ, M^{-1}·cm^{-1}): 446 (1007), 627 (542), 746 (554). The stoichiometry was determined by X-ray crystallography.

$[W_3(Ni(HP(OH)_2))Q_4(H_2O)_9]Cl_4\cdot C_{36}H_{36}N_{24}O_{12}\cdot 11H_2O$ [Q = S (2a), Se (2b)]. To 1 mL of a 5 mM solution of the corresponding $[W_3(NiCl)Q_4(H_2O)_9]^{3+}$ in 1 M HCl were added 1 mL of a saturated solution of cucurbit[6]uril in 4 M HCl and 1 drop of 50% (w/w) H_3PO_2. The color slowly changed to red-brown within several hours. Dark-red single crystals of X-ray quality were collected on the next day. Yield: quantitative. From the cell parameters, **2a** and **2b** were shown to be isostructural, but the crystal quality of **2a** did not allow data collection.

$[W_3(NiAs(OH)_3)S_4(H_2O)_8Cl]Cl_3\cdot C_{36}H_{36}N_{24}O_{12}\cdot 13H_2O$ (3). To a solution of $[W_3(NiCl)S_4(H_2O)_9]^{3+}$ (3 mM, 3 mL) in 2 M HCl was added As_2O_3 (50 mg, 0.25 mmol), and the color changed rapidly from dark green to orange-red. Then 1 mL of a saturated cucurbit[6]uril solution in 4 M HCl was added, and the solution was left to stand overnight. Brown-red single crystals of X-ray quality were collected. Yield: 60%.

Oxidation of 1. The stoichiometry of the oxidation of **1** with $[Co(dipic)_2]^-$ was determined by titrating a solution of **1** (0.5 mM) in a spectrophotometric optical cell with aliquots of $[Co(dipic)_2]^-$ (6.51 mM). When the absorbance changes at the peak position 753 nm vs $[Co(dipic)_2^-]$/ $[W_3(NiCl)S_4(H_2O)_9]^{3+}$ ratio are plotted, a sharp change in the gradient is observed at a molar ratio of 2.1:1.0, corresponding to the following oxidation scheme:

$$W_3NiSe_4^{\ 4+} + 2Co^{III} \rightarrow W_3Se_4^{\ 4+} + Ni^{II} + 2Co^{II}$$

Complexation of $[W_3(NiCl)Q_4(H_2O)_9]^{3+}$ with H_3PO_2. The reaction was followed by measurement of the absorption changes at 423 (S) and 448 (Se) nm. A total of 13 solutions with $[W_3NiQ_4]_{tot} = 0.51$ mM (Q = S, Se) and 1 mM < $[H_3PO_2]_{tot}$ < 351 mM (Q = S) and 1 mM < $[H_3PO_2]_{tot}$ < 10 mM (Q = Se) were prepared. The data are plotted in Figures 3 (S) and 4 (Se), and K was found to be 21.8 M^{-1} (Q = S) and 273.0 M^{-1} (Q = Se).

Complexation of $[W_3(NiCl)Q_4(H_2O)_9]^{3+}$ (Q = S, Se) with $As(OH)_3$. The reaction was followed by monitoring of the absorption changes at 436 nm (Q = S) and 448 nm (Q = Se). A total of seven points with $[W_3NiQ_4]_{tot} = 0.51$ mM and $[As(OH)_3]$ in the ranges of 11.7−50.5 mM (S) and 1−50 mM (Se) were taken. The data are plotted in Figures 3 (S) and 4 (Se), and K was found to be 35.7 M^{-1} (Q = S) and 1054.0 M^{-1} (Q = Se).

Complexation of 1 with $SnCl_3^-$. The reaction was followed by monitoring of the absorption changes at 465 nm. A total of 17 readings with $[W_3NiSe_4(aq)]_{tot} = 0.99$ mM and 0.1 mM < $[SnCl_3^-]_{tot}$ < 349 mM were taken. The data are plotted in Figure 3, and K was found to be 28.0 M^{-1}.

Table 1 summarizes the equilibrium constants obtained in these studies.

Complexation Reactions of $[W_3NiS_4(H_2O)_{10}]^{4+}$ in 2 M Hpts. $[W_3NiS_4(H_2O)_{10}]^{4+}$ in Hpts reacts faster with $HP(OH)_2$, $As(OH)_3$, $HOCH_2CH{=}CHCH_2OH$, and $OHCH_2C{\equiv}CCH_2OH$. The reaction (completed in 30 min) of the green $[W_3NiS_4(H_2O)_{10}]^{4+}$ [λ_{max}, nm (ϵ, M^{-1}·cm^{-1}): 428 (657), 600sh (530), 685 (605)] with an excess of H_3PO_2 in 2 M Hpts gives a color change to brown-red, corresponding to $[W_3(NiHP(OH)_2)S_4(H_2O)_9]^{4+}$ [λ_{max}, nm (ϵ,

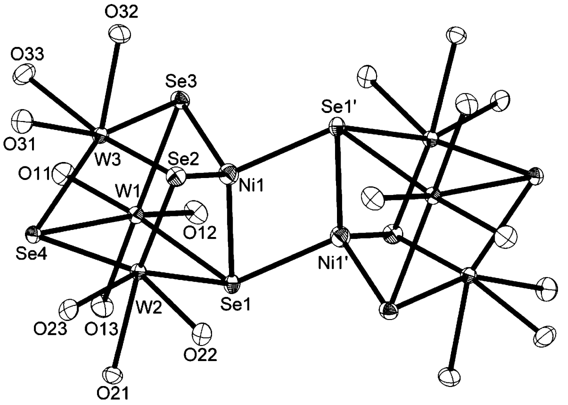

Figure 5. ORTEP representation (50% thermal ellipsoids) of the cluster cation $[W_3NiSe_4(H_2O)_9]_2^{8+}$ in **1**.

$M^{-1}\cdot cm^{-1}$) = 500 (1038), 423 (1682)]. The formation of $[W_3(NiP(OH)_3)S_4(H_2O)_9]^{4+}$ [λ, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 509 (641), 420 (977)] takes several hours to complete. The reaction of $[W_3NiS_4(H_2O)_{10}]^{4+}$ with an excess of As_2O_3 gives a rapid color change to red-brown, corresponding to the formation of $[W_3Ni(As(OH)_3)S_4(H_2O)_9]^{4+}$ [λ_{max}, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 512 (794), 434 (1730)]. A color change from green to brown was observed within 2−3 min when $[W_3NiS_4(H_2O)_{10}]^{4+}$ in 2 M Hpts was reacted with $HOCH_2CH{=}CHCH_2OH$ to give $[W_3Ni(HOCH_2CH{=}CHCH_2OH)S_4(H_2O)_9]^{4+}$ [λ_{max}, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 535 (714), 425 (1527)]. The reaction of $[W_3NiS_4(H_2O)_{10}]^{4+}$ with $HOCH_2C{\equiv}CCH_2OH$ gives a green-brown product corresponding to $[W_3Ni(HOCH_2C{\equiv}CCH_2OH)S_4(H_2O)_9]^{4+}$ [λ_{max}, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 421 (1490)]. The UV−vis spectra of the products are shown in Figure 1.

Complexation Reactions of $[W_3NiSe_4(H_2O)_{10}]^{4+}$ in 2 M Hpts. Similarly, $[W_3NiSe_4(H_2O)_{10}]^{4+}$ gives $[W_3(NiHP(OH)_2)Se_4(H_2O)_9]^{4+}$ [λ, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 442 (1004), 520 (637)], $[W_3(NiAs(OH)_3)Se_4(H_2O)_9]^{4+}$ [λ_{max}, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 453 (972)], $[W_3(Ni(HOCH_2CH{=}CHCH_2OH))Se_4(H_2O)_9]^{4+}$ [λ_{max}, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 566 (385), 439 (818)], $[W_3(Ni(HOCH_2C{\equiv}CCH_2OH))S_4(H_2O)_9]^{4+}$ [λ_{max}, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 438 (417), 563 (345), 645 (318)], $[W_3(NiCO)Se_4(H_2O)_9]^{4+}$ [λ_{max}, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 432 (1736), 516 (908)] (Figure 2).

Crystal Structures. Crystallographic data and details of structure refinement for **1a**, **2b**, and **3** are given in Table 2. The diffraction data were collected on a Bruker SMART 1K CCD diffractometer with Mo Kα radiation (λ = 0.710 73 Å) using ω scans of narrow frames. All structures were solved by direct methods and refined by full-matrix least-squares methods against $|F|^2$ in an anisotropic approximation using the *SHELXTL* program set.[19] Absorption corrections were applied empirically using the *SADABS* program.[20] The crystallographic data have been deposited in the Cambridge Crystallographic Data Center under the deposition codes CCDD 610639 for **1a**, 179026 for **2b**, and 179027 for **3**.

Results and Discussion

1 and $[W_3NiSe_4(H_2O)_{10}]^{4+}$. Two methods were used for the preparation of **1**. One is to react $[W_3Se_4(H_2O)_9]^{4+}$ with metallic Ni in HCl, which is also the general way of making the other three $[M_3(NiCl)Q_4(H_2O)_9]^{3+}$ derivatives.[4,6] This heterogeneous reaction takes several hours for completion.

Table 3. Bond Lengths (Å) and Angles (deg) in **1**[a]

W1−O11	2.154(5)	W3−O33	2.159(5)
W1−O13	2.160(5)	W3−O32	2.174(5)
W1−O12	2.194(6)	W3−O31	2.189(5)
W1−Se3	2.454(3)	W3−Se3	2.468(2)
W1−Se4	2.483(2)	W3−Se2	2.475(3)
W1−Se1	2.493(3)	W3−Se4	2.477(3)
W1−Ni1	2.741(3)	W3−Ni1	2.652(2)
W1−W3	2.749(2)	Ni1−Se3	2.306(3)
W1−W2	2.773(3)	Ni1−Se2	2.307(2)
W2−O23	2.161(5)	Ni1−Se1	2.375(3)
W2−O22	2.176(5)	Ni1−Se1^i	2.386(2)
W2−O21	2.183(5)	Ni1−Ni1^i	2.570(3)
W2−Se2	2.455(3)	Se1−Ni1^i	2.386(2)
W2−Se4	2.475(3)	W3−O33	2.159(5)
W2−Se1	2.481(2)	W3−O32	2.174(5)
W2−Ni1	2.699(2)	W3−O31	2.189(5)
W2−W3	2.815(1)		
O11−W1−O13	78.97(18)	Se3−Ni1−Se2	114.42(4)
O11−W1−O12	78.70(18)	Se3−Ni1−Se1	108.44(4)
O13−W1−O12	78.24(18)	Se2−Ni1−Se1	111.29(4)
O11−W1−Se3	89.15(13)	Se3−Ni1−Se1^i	105.12(4)
O13−W1−Se3	161.05(13)	Se2−Ni1−Se1^i	102.83(3)
O12−W1−Se3	85.02(12)	Se1−Ni1−Se1^i	114.67(4)
O11−W1−Se4	83.06(12)	W2−Se4−W1	68.00(2)
O13−W1−Se4	83.11(12)	W3−Se4−W1	67.31(1)
O12−W1−Se4	156.02(12)		
Se3−W1−Se4	110.29(2)	O33−W3−Se4	85.96(12)
O11−W1−Se1	160.18(12)	O32−W3−Se4	157.78(13)
O13−W1−Se1	87.10(12)	O31−W3−Se4	86.30(12)
O12−W1−Se1	84.74(12)	Se3−W3−Se4	110.00(2)
Se3−W1−Se1	100.27(2)	Se2−W3−Se4	106.44(2)
Se4−W1−Se1	109.39(2)	O33−W3−Se4	85.96(12)
W3−W1−W2	61.31(1)	Ni1−Se1−Ni1^i	65.33(3)
O23−W2−O22	76.19(15)	Ni1−Se1−W2	67.48(2)
O23−W2−O21	73.56(15)	Ni1^i−Se1−W2	119.33(3)
O22−W2−O21	76.66(14)	Ni1−Se1−W1	68.48(2)
O23−W2−Se2	93.61(11)	Ni1^i−Se1−W1	122.86(3)
O22−W2−Se2	85.23(12)	W2−Se1−W1	67.75(2)
O21−W2−Se2	159.78(11)	Ni1−Se2−W2	68.96(3)
O23−W2−Se4	83.84(12)	Ni1−Se2−W3	67.25(3)
O22−W2−Se4	157.23(11)	W2−Se2−W3	69.65(2)
O21−W2−Se4	87.37(11)	Ni1−Se3−W1	70.24(3)
Se2−W2−Se4	107.11(2)	Ni1−Se3−W3	67.39(3)
O23−W2−Se1	153.49(12)	W1−Se3−W3	67.90(2)
O22−W2−Se1	84.74(12)	W2−Se4−W3	69.28(2)
O21−W2−Se1	84.34(12)	Se3−W3−Se2	103.34(2)
Se2−W2−Se1	103.09(2)	W3−W1−W2	61.31(1)
Se4−W2−Se1	110.04(2)	O32−W3−Se3	83.64(12)
Ni1−W2−W3	57.44(2)	O31−W3−Se3	156.32(12)
W1−W2−W3	58.93(1)	O33−W3−Se2	158.74(12)
O33−W3−O32	76.86(18)	O32−W3−Se2	86.39(12)
O33−W3−O31	75.90(17)	O31−W3−Se2	87.51(12)
O33−W3−Se3	87.89(12)	O32−W3−O31	76.01(18)

[a] Symmetry codes: (i) 1 − *x*, 1 − *y*, 1 − *z*.

Alternatively, Ni^{2+} salts in combination with a reducing agent, H_3PO_2, can be used, as in the case of $[Mo_3(NiCl)S_4(H_2O)_9]^{3+}$, in what is a much faster procedure.[21] However, in the present study, the main product of this reaction turned out to be red $[W_3(NiHP(OH)_2)Se_4(H_2O)_9]^{4+}$, which is sufficiently stable to be purified by cation-exchange chromatography. This product is formed, obviously, by isomerization of H_3PO_2. Moreover, stock solutions of $[W_3Se_4(H_2O)_9]^{4+}$ often contain some amount of H_3PO_2, which is used for its preparation from $W_3Se_7Br_4$ and which is not so easy to remove, and in this case the reaction of $[W_3Se_4(H_2O)_9]^{4+}$

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(19) Sheldrick, G. M. *SHELXTL User's Manual*; Bruker AXS Inc.: Madison, WI, 1994.

(20) Sheldrick, G. M. *SADABS Empirical Absorption Program*; University of Goettingen: Goettingen, Germany, 1996.

(21) Sokolov, M. N.; Hernández-Molina, R.; Dybtsev, D. N.; Chubarova, E. V.; Solodovnikov, S. F.; Pervukhina, N. V.; Vicent, C.; Llusar, R.; Fedin, V. P. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2335.

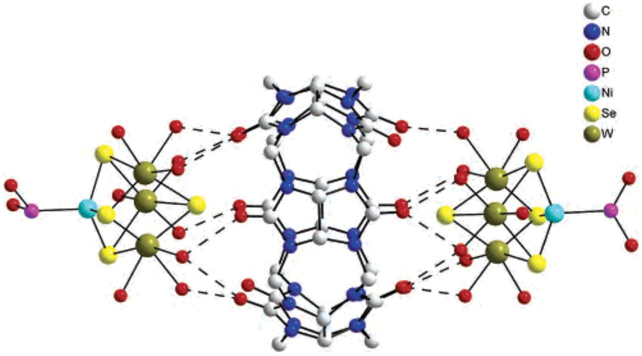

Figure 6. View of the supramolecular associate $\{[W_3(NiHP(OH)_2)Se_4(H_2O)_9]_2(C_{36}H_{36}N_{24}O_{12})\}^{4+}$ in **2a**.

with Ni also can give a mixture of dark-green **1** and red $[W_3(NiHP(OH)_2)Se_4(H_2O)_9]^{4+}$. The difference in charge makes their chromatographic separation quite easy. Strong coordination to Cl^- in HCl solutions is a general feature of heterometallic cuboidal clusters, which is evidenced both in solution studies and in the compounds, isolated in the solid state. Thus, at C_{HCl} of around 1 M, the $[M_3(M'Cl)Q_4(H_2O)_9]^{3+}$ species predominate.[5,22] The equilibrium can be shifted toward aquation by removing Cl^- after loading onto a cation exchanger, washing with 0.5 M Hpts, which is noncomplexing, and eluting the higher-charged aqua complex with 1−3 M Hpts.

The Mo derivatives were found to be more robust to air oxidation, and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ can be handled in air, although for storage for longer periods,[4,5] it is necessary to keep the solutions under N_2. The Se analogue $[Mo_3NiSe_4(H_2O)_{10}]^{4+}$ is more readily oxidized.[8] The W derivatives are by far much more unstable, and air-free conditions are required for their manipulation and storage. Even with such precautions, dilute solutions of $[W_3NiQ_4(H_2O)_{10}]^{4+}$ cubes are oxidized (probably by a trace amount of O_2) in 1−2 weeks.

$$2W_3NiQ_4^{4+} + O_2 + 4H^+ \rightarrow 2W_3Q_4^{4+} + 2Ni^{II} + 2H_2O$$

The qualitative order of stability toward air oxidation can thus be given as

$$[Mo_3NiS_4(H_2O)_{10}]^{4+} > [Mo_3NiSe_4(H_2O)_{10}]^{4+} > [W_3NiSe_4(H_2O)_{10}]^{4+} > [W_3NiS_4(H_2O)_{10}]^{4+}$$

Table 4. Bond Lengths (Å) and Angles (deg) in **2a**

W1−O11	2.215(8)	W2−Se4	2.485(1)
W1−O12	2.307(7)	W3−O31	2.182(7)
W1−O13	2.184(8)	W3−O32	2.210(7)
W1−W2	2.745(2)	W3−O33	2.210(7)
W1−W3	2.774(1)	W3−Ni	2.694(2)
W1−Ni	2.711(2)	W3−Se2	2.475(1)
W1−Se1	2.476(1)	W3−Se3	2.478(1)
W1−Se3	2.473(1)	W3−Se4	2.481(2)
W1−Se4	2.482(2)	Ni−Se1	2.308(2)
W2−O21	2.149(7)	Ni−Se2	2.308(2)
W2−O22	2.196(9)	Ni−Se3	2.307(2)
W2−O23	2.157(9)	Ni−P	2.128(4)
W2−W3	2.746(2)	P−O41	1.586(11)
W2−Ni	2.714(2)	P−O42	1.619(13)
W2−Se1	2.481(1)		
W2−Se2	2.476(2)		
O11−W1−O12	76.60(26)	O31−W3−O32	77.28(27)
O11−W1−O13	75.47(28)	O31−W3−O33	75.82(27)
O11−W1−Se1	156.18(20)	O31−W3−Se2	90.22(19)
O11−W1−Se3	89.48(18)	O31−W3−Se3	157.87(19)
O11−W1−Se4	85.84(18)	O31−W3−Se4	84.11(18)
O12−W1−O13	79.52(27)	O32−W3−O33	76.11(26)
O12−W1−Se1	82.81(19)	O32−W3−Se2	84.37(19)
O12−W1−Se3	85.08(17)	O32−W3−Se3	85.13(18)
O12−W1−Se4	157.55(18)	O32−W3−Se4	156.48(19)
O13−W1−Se1	89.23(21)	O33−W3−Se2	158.01(19)
O13−W1−Se3	160.53(21)	O33−W3−Se3	87.08(18)
O13−W1−Se4	82.64(22)	O33−W3−Se4	85.55(18)
W2−W1−W3	59.68(1)	Se2−W3−Se3	101.42(4)
W2−W1−Ni	59.67(3)	Se2−W3−Se4	110.21(4)
W3−W1−Ni	58.83(3)	Se3−W3−Se4	108.82(4)
Se1−W1−Se3	100.66(4)	Se1−Ni−Se2	110.89(7)
Se1−W1−Se4	110.57(4)	Se1−Ni−Se3	111.30(7)
Se3−W1−Se4	108.93(4)	Se1−Ni−P	108.50(11)
W1−W2−W3	60.69(1)	Se2−Ni−Se3	112.34(7)
W1−W2−Ni	59.53(3)	Se2−Ni−P	107.07(11)
O21−W2−O22	77.01(31)	Se3−Ni−P	106.49(11)
O21−W2−O23	79.51(29)	W1−Se1−W2	67.25(3)
O21−W2−Se1	88.70(19)	W1−Se1−Ni	68.93(5)
O21−W2−Se2	158.58(19)	W2−Se1−Ni	68.95(5)
O21−W2−Se4	84.59(21)	W2−Se2−W3	67.37(3)
O22−W2−O23	78.24(33)	W2−Se2−Ni	69.03(5)
O22−W2−Se1	84.64(25)	W3−Se2−Ni	68.47(5)
O22−W2−Se2	84.37(25)	W1−Se3−W3	68.16(3)
O22−W2−Se4	156.13(22)	W1−Se3−Ni	69.00(4)
O23−W2−Se1	160.98(24)	W3−Se3−Ni	68.44(4)
O23−W2−Se2	86.46(24)	W1−Se4−W2	67.11(3)
O23−W2−Se4	83.61(23)	W1−Se4−W3	67.99(3)
W3−W2−Ni	59.13(3)	W2−Se4−W3	67.16(3)
Se1−W2−Se2	100.13(4)	W1−Ni−W2	60.80(3)
Se1−W2−Se4	110.29(4)	W1−Ni−W3	61.76(3)
Se2−W2−Se4	110.01(4)	W2−Ni−W3	61.03(3)
W1−W3−W2	59.63(1)	Ni−P−O41	116.42(41)
W1−W3−Ni	59.41(3)	Ni−P−O42	116.49(45)
W2−W3−Ni	59.85(3)	O41−P−O42	105.09(66)

[a] Symmetry codes: (i) 1 − *x*, *y*, 1.5 − *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*.

Ligand-Exchange Reactions. No reactions of $[Mo_3(NiCl)S_4(H_2O)_9]^{3+}$ with H_3PO_2, As_2O_3, $SnCl_2$, and $OHCH_2CH{=}CHCH_2OH$ in 2 M HCl were detected because the competing coordination of the chloride prevents the coordination of other ligands. Some color changes from green to dark green and brown were observed when the reactions were run in Hpts, but they were slow and incomplete even after 3 days because the peaks corresponding to $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ were still present in the electronic spectra. Only with As_2O_3 was a color change from green to purple detected, and the spectrum indicated complete formation of $[Mo_3(NiAs(OH)_3)S_4(H_2O)_9]^{4+}$ [λ, nm (ϵ, $M^{-1}\cdot cm^{-1}$): 569 (280), 483 (370)], while for H_3PO_2, H_3PO_3, and the olefin, the electronic spectra showed the presence of much unreacted $[Mo_3NiS_4(H_2O)_{10}]^{4+}$. With H_3PO_3, the final spectrum shows a new peak at 502 nm, which corresponds to the formation of $[Mo_3(NiP(OH)_3)S_4(H_2O)_9]^{4+}$, together with a peak of almost equal intensity at 653 nm from the starting $[Mo_3NiS_4(H_2O)_{10}]^{4+}$. Adding HCl to $[Cl^-]$ of about 1 M to these solutions leads to the formation of $[Mo_3(NiCl)S_4(H_2O)_9]^{3+}$ in all cases. However, it was recently shown that, even in HCl under drastic conditions (excess of H_3PO_2 and prolonged heating), $[Mo_3(NiHP(OH)_2)S_4(H_2O)_9]^{4+}$ and $[Mo_3(NiP(OH)_3)S_4(H_2O)_9]^{4+}$ can be obtained.[13d] The W derivatives were found to be more reactive, and the coordination of $HP(OH)_2$,

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(22) Fedin, V. P.; Gramlich, V.; Wörle, M.; Weber, T. *Inorg. Chem.* **2001**, *40*, 1074.

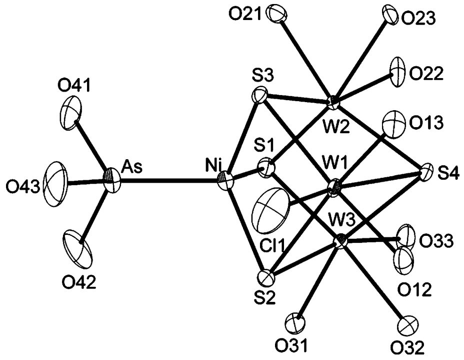

Figure 7. ORTEP representation (50% thermal ellipsoids) of the cluster cation $[W_3(NiAs(OH)_3)S_4(H_2O)_8Cl]^{3+}$ in **3**.

$As(OH)_3$, $SnCl_3^-$, $HOCH_2CH{=}CHCH_2OH$, and $OHCH_2C{\equiv}C{-}CH_2OH$ takes place even in 2 M HCl (see Figures 1 and 2). On the contrary, no reaction was observed with H_3PO_3 under these conditions even after 1 day at room temperature. The reaction with H_3PO_2 is faster than that with H_3PO_3 but is still slower than that with $As(OH)_3$, where the color change is almost immediate. This reflects a very low proportion of the free species $HP(OH)_2$ and $P(OH)_3$ in the tautomeric equilibria. The stability of the $HP(OH)_2$ complexes is exceptional, and red $[W_3(NiHP(OH)_2)Se_4(H_2O)_9]^{4+}$ can be eluted from the cation-exchange column with up to 4 M HCl without any sign of decomposition. In our previous works, the formation of the $HP(OH)_2$ complexes for the Mo-containing clusters $[Mo_3(NiHP(OH)_2)S_4(H_2O)_9]^{4+}$ and $[Mo_3(PdHP(OH)_2)Q_4(H_2O)_9]^{4+}$ ($Q = S$, Se) could only be detected by ^{31}P NMR, but rapid oxidation of the coordinated $HP(OH)_2$ ligand into $P(OH)_3$ prevented their isolation.[13] Substituting W for Mo must increase the electron density on Ni in the cluster, thus modifying the reactivity of the ligands attached to it.[4] The effect of the "softer" Se atoms on the stability of the complexes with P and As donor atoms is also evident: the complexes of the selenide clusters are stronger by at least 1 order of magnitude. The apparent greater stability of the $As(OH)_3$ complexes (contrary to the well-known sequence P > As > Sb >> Bi) is explained by the unfavorable value of the equilibrium constant for the reaction $H_2P(O)(OH) \leftrightarrow HP(OH)_2$, the exact value of which is not known but is estimated to be as low as 10^{-12}.[23] The formation of the $SnCl_3^-$ complex $[W_3(NiSnCl_3)Se_4(H_2O)_9]^{3+}$ deserves special attention as the first example of coordination of the $SnCl_3^-$ ligand to a Ni center in an aqueous solution. Even though we have not succeeded in crystallizing the complex, the overall spectral pattern and lack of reactivity of the pure cuboidal cluster $[M_4S_4(H_2O)_{12}]^{5+}$[23c] toward $SnCl_3^-$ support our formulation.[23c] Though the Pd complexes $[Mo_3(PdSnCl_3)Q_4(H_2O)_9]^{3+}$ ($Q = S$, Se)[23c] are stronger by 2 orders of magnitude, the complex may have interesting catalytic properties in view of the ability of a $Ni{-}SnCl_3$ complex, $[(PPh_3)_3NiSnCl_3]$, to isomerize olefins.[24] The Ni−Sn-bonded species are not numerous and are less studied than the Pd−Sn and Pt−Sn ones.[25]

Table 5. Bond Lengths (Å) and Angles (deg) in **3**[a]

W1−O12	2.158(11)	W2−Ni	2.649(4)
W1−O13	2.191(12)	W2−W3	2.718(3)
W1−S3	2.339(4)	W3−O33	2.142(11)
W1−S2	2.342(4)	W3−O32	2.146(10)
W1−S4	2.361(4)	W3−O31	2.17(1)
W1−Cl1	2.469(6)	W3−S1	2.343(4)
W1−Ni	2.674(3)	W3−S2	2.352(4)
W1−W3	2.714(3)	W3−S4	2.356(4)
W1−W2	2.739(3)	W3−Ni	2.684(4)
W2−O22	2.13(1)	Ni−S1	2.204(4)
W2−O23	2.195(10)	Ni−S3	2.210(4)
W2−O21	2.194(10)	Ni−S2	2.215(4)
W2−S1	2.342(4)	Ni−As	2.225(4)
W2−S3	2.348(4)	As−O43	1.718(14)
W2−S4	2.353(4)	As−O42	1.739(13)
		As−O41	1.741(13)
O12−W1−O13	76.29(39)	W1−W3−W2	60.57(2)
O12−W1−S3	162.07(31)	S1−Ni−S3	110.30(16)
O13−W1−S3	89.21(30)	S1−Ni−S2	108.27(16)
O12−W1−S2	90.57(27)	S3−Ni−S2	108.56(16)
O13−W1−S2	159.57(33)	S1−Ni−As	104.64(13)
S3−W1−S2	100.21(13)	S3−Ni−As	111.40(13)
O12−W1−S4	83.57(31)	S2−Ni−As	113.57(13)
O13−W1−S4	86.40(31)	W2−Ni−W1	61.94(4)
S3−W1−S4	106.29(13)	W2−Ni−W3	61.27(4)
S2−W1−S4	107.91(13)	W1−Ni−W3	60.85(4)
O12−W1−Cl1	80.34(33)	O43−As−O42	96.34(80)
O13−W1−Cl1	80.06(34)	O43−As−O41	95.83(71)
S3−W1−Cl1	86.90(17)	O42−As−O41	99.25(71)
S2−W1−Cl1	82.38(19)	O43−As−Ni	123.35(51)
S4−W1−Cl1	161.01(18)	O42−As−Ni	115.89(43)
Ni−W1−W3	59.76(4)	O41−As−Ni	120.85(44)
Ni−W1−W2	58.58(4)	Ni−S1−W2	71.20(12)
W3−W1−W2	59.79(2)	Ni−S1−W3	72.28(12)
O22−W2−O23	76.20(37)	W2−S1−W3	70.91(10)
O22−W2−O21	78.89(40)	Ni−S2−W1	71.80(12)
O23−W2−O21	76.83(36)	Ni−S2−W3	71.93(12)
O22−W2−S1	90.02(28)	W1−S2−W3	70.63(11)
O23−W2−S1	159.26(27)	Ni−S3−W1	71.94(12)
O21−W2−S1	85.44(27)	Ni−S3−W2	71.00(12)
O22−W2−S3	160.10(29)	W1−S3−W2	71.53(11)
O23−W2−S3	88.27(28)	W2−S4−W3	70.51(10)
O21−W2−S3	85.57(28)	W2−S4−W1	71.06(11)
S1−W2−S3	101.15(13)	W3−S4−W1	70.26(10)
O22−W2−S4	85.64(31)	Ni−W2−W1	59.48(4)
O23−W2−S4	87.32(27)	W3−W2−W1	59.64(2)
O21−W2−S4	160.02(28)	S1−W3−S2	99.39(13)
S1−W2−S4	107.30(12)	O33−W3−S4	84.54(33)
S3−W2−S4	106.29(13)	O32−W3−S4	85.33(33)
Ni−W2−W3	60.01(4)	O31−W3−S4	159.15(27)
S1−W3−S4	107.16(12)	Ni−W3−W1	59.38(4)
S2−W3−S4	107.74(13)	Ni−W3−W2	58.72(4)

[a] Symmetry codes: (i) $1 - x$, $2 - y$, $1 - z$; (ii) $1 - x$, $2 - y$, $-z$.

Structure Descriptions. X-ray analysis of **1a** reveals the presence of a double cubane-type cluster aqua complex $[\{W_3NiSe_4(H_2O)_9\}_2]^{8+}$, as shown in Figure 5. These cations are surrounded by the pts⁻ anions, to which they are bound via H bonds (2.6−2.7 Å). The two cuboidal subunits $W_3NiSe_4^{4+}$ are related by a center of symmetry on the midpoint of the Ni−Ni bond [Ni−Ni 2.570(3) Å]. In the S analogues [{W₃-

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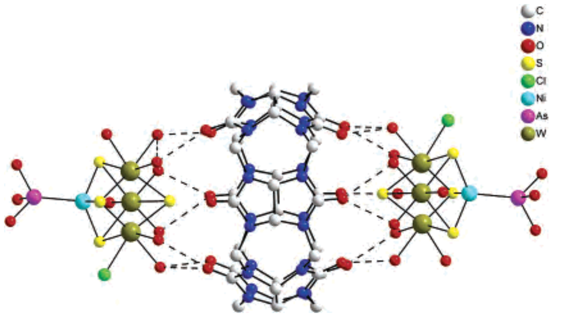

Figure 8. View of the supramolecular associate $\{[W_3(NiAs(OH)_3)S_4(H_2O)_8Cl]_2(C_{36}H_{36}N_{24}O_{12})\}^{6+}$ in **3**.

$NiS_4(H_2O)_9\}_2](pts)_8{\cdot}20H_2O$ and $[\{W_2MoNiS_4(H_2O)_9\}_2](pts)_8{\cdot}20H_2O$, the Ni−Ni bond is predictably shorter, 2.561(5) Å in the W_3Ni cluster and 2.549(5) Å in the W_2MoNi cluster.[4] Thus, **1a** adds to the still small family of edge-linked double-cuboidal clusters, which also includes the Pd derivatives $[\{Mo_3PdQ_4(H_2O)_9\}_2]^{8+}$ (Q = S, Se) and $[\{W_3PdS_4(H_2O)_9\}_2]^{8+}$ as well as $[\{Mo_3CuS_4(H_2O)_9\}_2]^{8+}$ and $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$.[1a] Coordination around Ni (without Ni−Ni and Ni−W bonds) can be described as distorted tetrahedral, with two sets of Ni−Se distances: Ni−μ_3-Se of about 2.31 Å and longer Ni−μ_4-Se of 2.38−2.39 Å. The central Ni_2Se_2 unit can be described as a rhombus with angles of 65.3° (∠NiSeNi) and 114.6° (∠SeNiSe). Similar structural features were found for the sulfide analogues. The main distances are given in Table 3.

In the structure of **2b**, the cluster cations $[W_3(NiHP(OH)_2)Se_4(H_2O)_9]^{4+}$ form 2:1 adducts (Figure 6) with macrocyclic cavitand cucurbit[6]uril via H bonds between the six complementary water molecules and six carbonyl groups of the cavitand portal (2.610−2.845 Å; Table 4). This complementarity greatly facilitates crystallization of cuboidal cluster aqua complexes, as was demonstrated in our previous works.[26] The bis(hydroxyphosphine) ligand $HP(OH)_2$ is bound to the Ni atom through a short bond of 2.128(4) Å. In $[Mo_3(Ni(P(OH)_3))S_4(H_2O)_8Cl]^{3+}$, the Ni−P bond is 2.165(2) Å.[13d] In the complexes with PPh_3, the Ni−P bond is 2.197(9) Å in $[Mo_3(NiPPh_3)S_4(H_2O)_5Cl_4]$[27a] and 2.160(2) Å in $[Cp'_3Mo_3(NiPPh_3)S_4]^+$.[27b] The P−O bond lengths [1.586(11) and 1.619(13) Å] are close to those observed in $[Mo_3(NiP(OH)_3)S_4(H_2O)_8Cl]^{3+}$ [1.571(6)−1.595(6) Å][13d] and in the recently prepared $[CpRu(PPh_3)_2(HP(OH)_2)]^+$ [1.579(3)−1.556(3) Å].[28] The geometry of the coordinated $HP(OH)_2$ ligand in **2b** deviates significantly from tetrahedral toward pyramidalization: the OPNi angles (116°) are larger and the OPO angles are smaller (105°) than the ideal tetrahedral value. This pyramidalization does not occur in $[CpRu(PPh_3)_2(HP(OH)_2)]^+$ (∠OPO 110°),[28] but the coordinated $P(OH)_3$ in $[Mo_3(NiP(OH)_3)S_4(H_2O)_8Cl]^{3+}$ also displays the same tendency toward pyramidalization.[13d] The coordinated $HP(OH)_2$ molecule is oriented in a way that the P−O and Ni−Se bonds adopt a staggered conformation. The $NiPSe_3$ tetrahedron is slightly flattened in the direction toward the three Se atoms (∠SeNiSe 111−112°). One of the O atoms of the coordinated $HP(OH)_2$ and one from a coordinated water molecule are involved into H bonding with one solvent water molecule [O···O(P) 2.72(2) Å, O···O(W) 2.68(1) Å], defining a bridging "chelate" ring POOO at one of the Ni−W bonds. In **1a**, the NiW_3 tetrahedron is more distorted than that in **2b** (Ni−W 2.65−2.74 Å, W−W 2.75−2.82 Å in the former and Ni−W 2.69−2.71 Å, W−W 2.75−2.77 Å in the latter). By way of contrast, the Ni−Se and W−Se bonds are hardly affected on going from **1a** to **2b**. In $[W_3Se_4(H_2O)_9](pts)_4{\cdot}12H_2O$, the W−W distances are 2.75−2.77 Å.[29]

The $As(OH)_3$ complex **3** is isostructural with $[Mo_3(NiP(OH)_3)S_4(H_2O)_8Cl]Cl_3{\cdot}C_{36}H_{36}N_{24}O_{12}{\cdot}13H_2O$. The cluster cation $[W_3(NiAs(OH)_3)S_4(H_2O)_8Cl]^{3+}$ (Figure 7 and Table 5) forms a 2:1 adduct with cucurbit[6]uril through complementary H bonds (2.6−2.9 Å; Figure 8). The $As(OH)_3$ molecule [As−O 1.72(1)−1.74(1) Å] is coordinated to Ni through As [Ni−As 2.225(4) Å], which can be compared with 2.272(2) Å in $[Mo_3(NiAsPh_3)S_4(H_2O)_5Cl_4]$ and with 2.255(1) Å in $[Cp'_3Mo_3(NiAsPh_3)S_4]^+$.[27] The coordinated $As(OH)_3$ ligand is pyramidalized to a larger degree than coordinated $HP(OH)_2$ and $P(OH)_3$: ∠OAsO 96−99°; ∠OAsNi 116−123°. In the only other structurally characterized $As(OH)_3$ complex $[Mo_3(PdAs(OH)_3)S_4(H_2O)_6Cl_3]_2Cl_2{\cdot}C_{36}H_{36}N_{24}O_{12}{\cdot}19H_2O$, the geometry around As is much closer to tetrahedral (∠OAsPd 113.8°; ∠OAsO 104.7°).[13a] The coordination polyhedron of the Ni atom is close to a tetrahedron with no significant distortions. The orientation of the coordinated $As(OH)_3$ molecule leads to staggered conformations of the As−O and Ni−S bonds (dihedral angles OAsNiS around 52−65°). In contrast, the orientation of $As(OH)_3$ in $[Mo_3(PdAs(OH)_3)S_4(H_2O)_6Cl_3]_2Cl_2{\cdot}C_{36}H_{36}N_{24}O_{12}{\cdot}19H_2O$ is closer to the eclipsed conformation (dihedral angles OAsPdS only 25°). It is interesting to compare the geometries of the W_3NiS_4 cluster cores in **3** and in the complex $[W_3(Ni(C_2H_4))S_4(H_2O)_9]^{4+}$: a change from n-donor $As(OH)_3$ to π-acceptor C_2H_4 does not affect the Ni−S and W−S bonds and affects only slightly the W−W bonds [average 2.723(3) Å in **3**; 2.7137(9) Å in the C_2H_4 complex] and significantly lengthens the Ni−W bonds [average 2.669(3) Å in **3**; 2.701(2) Å in the C_2H_4 complex].[4] A similar lengthening of the M−M bonds is observed when Cp (instead of H_2O or Cl) is coordinated to the Mo (or W) sites in $[Cp'_3M_3(NiEPh_3))S_4]^+$. These effects may be due to the competition between the ligand-based π orbitals and metal-centered d orbitals, which participate in the M−M bonding. In an extreme case ($[Mo_3(CuCl)S_4(H_2O)_9]^{4+}$), coordination of a strong π acceptor (CO) to Cu even leads to cluster destruction with liberation of $Cu(CO)(aq)^+$.[8]

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of complexes **1a**, **2b**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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