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Stabilization of tautomeric forms $P(OH)_3$ and $HP(OH)_2$ and their derivatives by coordination to palladium and nickel atoms in heterometallic clusters with the $Mo_3MQ_4{}^{4+}$ core (M = Ni, Pd; Q = S, Se)

M. N. Sokolov, E. V. Chubarova, K. A. Kovalenko, I. V. Mironov,
A. V. Virovets, E. V. Peresypkina, and V. P. Fedin★

A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
3 prosp. Akad. Lavrentieva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 30 9489. E-mail: cluster@che.nsk.su

The cluster aqua complexes $[Mo_3(MCl)Q_4(H_2O)_9]^{3+}$ (M = Pd or Ni) in hydrochloric acid solutions induce isomerization of the hydrophosphoryl compounds $(HO)_2P(O)H$, $(HO)P(O)H_2$, PhP(O)(OH)H, and $Ph_2P(O)H$ into the hydroxo tautomers $P(OH)_3$, $HP(OH)_2$, $PhP(OH)_2$, and $Ph_2P(OH)$, which are stabilized by coordination of the phosphorus atom to the Pd or Ni atoms. The reactions were studied by ^{31}P NMR and UV-Vis spectroscopy. The kinetics of the reactions of phosphorous acid with $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ was investigated by spectrophotometry. The $[Mo_3(Pd(PhP(OH)_2))S_4(H_2O)_2Cl_7]^{3-}$ complex was isolated as a supramolecular adduct with cucurbit[8]uril, and the $[Mo_3(Ni(P(OH)_3))S_4(H_2O)_8Cl]^{3+}$ complex was isolated as an adduct with cucurbit[6]uril. The structures of both compounds were established by X-ray diffraction analysis.

Key words: molybdenum, palladium, chalcogenide clusters, cucurbituril, phosphorus acids.

Earlier,[1—4] we have demonstrated that readily accessible and stable 60-electron cluster aqua complexes with the cuboidal metal chalcogenide core $[M_3(M'Cl)Q_4(H_2O)_9]^{3+}$ (M = Mo, W; M′ = Ni, Pd; Q = S, Se) exhibit unusual reactivity with hydrophosphoryl compounds (*i.e.*, compounds containing the O=P—H group). These complexes induce isomerization of phosphorous acid $(HO)_2P(O)H$, hypophosphorous acid $(HO)P(O)H_2$, and the phenyl-substituted derivatives $Ph_2P(O)H$ and PhP(O)(OH)H to form the corresponding hydroxo tautomers (>P—OH), which are stabilized by coordination to the heterometal atom (palladium or nickel) due to involvement of the lone electron pair of the phosphorus atom that becomes free.[1—4] The formation of the $[Mo_3(Pd(P(OH)_3))S_4(H_2O)_6Cl_3]^+$ and $[W_3(Ni(HP(OH)_2)Se_4(H_2O)_9]^{4+}$ complexes was established by ^{31}P NMR spectroscopy and X-ray diffraction.[1,2] The formation of the $[Mo_3(Pd(PhP(OH)_2))S_4(H_2O)_9]^{4+}$ and $[Mo_3(Pd(Ph_2P(OH))S_4(H_2O)_9]^{4+}$ complexes was proved by ^{31}P NMR spectroscopy.[3] The high affinity of the Ni and Pd atoms (their degree of oxidation can be formally considered as M(0))[5] for soft donors (phosphorus atoms) is, evidently, the driving force for these reactions. It is known[6] that the P—O—H group is readily isomerized into the H—P=O group under standard conditions, which leaves an imprint on the phosphorus chemistry. The fact that the tetrahedral tautomer of phosphorous acid $(HO)_2P(O)H$ is energetically more favorable was confirmed also by quantum-chemical calculations.[7] For the M—P donor-acceptor bond to be formed, it is necessary that this molecule should be isomerized to the three-coordinate form $P(OH)_3$ with a lone electron pair on the phosphorus atom. In spite of the fact that the equilibrium constant of this reaction is very small (~$10^{-10.5}$ in aqueous solution), the formation of $P(OH)_3$ was postulated[6] already in 1920s as the first step in studies of the kinetics of oxidation of phosphorous acid with the Hg^{II}, Ag^I, Cr^{VI}, or V^V ions or halogens. Hydroxyphosphines $RP(OH)_2$ and $R_2P(OH)$ (R = Alk or Ar) exist as the RP(O)(OH)H and $R_2P(O)H$ tautomeric forms, respectively, except for rather bulky substituents (R is 2,2-dimethylbicyclo-[2,2,2]-hept-3-ylmethyl in $RP(OH)_2$)[8] or strong electron-withdrawing substituents (for example, $(CF_3)_2P(OH)$).[9] In the present study, we examined isomerization of a series of phosphorus-containing compounds in the presence of heterometallic molybdenum-palladium and molybdenum-nickel chalcogenide clusters, investigated the kinetics of the reactions of phosphorous acid, and obtained direct structural evidence for the existence of the coordinated $PhP(OH)_2$ molecule.

Results and Discussion

The addition of the hydrophosphoryl compounds $(HO)_2P(O)H$, $(HO)P(O)H_2$, PhP(O)(OH)H, or $Ph_2P(O)H$ to hydrochloric acid solutions of the

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heterometallic cluster aqua complexes $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ (Q = S or Se) changes the color of the solution from blue to brown, which is characteristic of coordination of phosphorus-containing ligands to the palladium atom in these clusters. This fact suggests that the reaction involves isomerization of the reagents to tautomeric forms with the lone electron pair on the phosphorus atom, and this electron pair is donated to the palladium atom. It is known[10] that the palladium atom in the $Mo_3PdQ_4{}^{4+}$ clusters is not virtually coordinated by oxygen-containing donors in the presence of other donor ligands. Meanwhile, coordination of oxygen-containing ligands to oxophilic molybdenum atoms is not accompanied by such radical changes in the UV-Vis absorption spectra of the cluster. Under analogous conditions, the $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ complex produces the $[Mo_3(PdPPh_3)S_4Cl_4(H_2O)_5]$ complex even in the presence of an excess of triphenylphosphine. Coordination of triphenylphosphine to palladium in the latter complex was established by X-ray diffraction.[3] The maxima in the UV-Vis absorption spectra of the complexes with the PPh_3, PPh_2OH, and $PhP(OH)_2$ ligands are observed at virtually the same positions and are independent of the number of Ph groups in the ligand, whereas the presence of the coordinated $P(OH)_3$ and $HP(OH)_2$ molecules leads to additional shifts of these maxima to lower frequencies by 20—30 nm (Table 1). Therefore, the similarity of the UV-Vis spectra of all the complexes under study indicates that the phosphorus-containing ligands are coordinated to the palladium atoms. The ^{31}P NMR spectra provide unambiguous evidence that coordination causes isomerization of the ligands. The isomerization is accompanied by the migration of the hydrogen atom from phosphorus to oxygen. The P—H bond cleavage results in the disappearance of the doublet in the case of H_3PO_3 and $Ph_2P(O)H$ (P—H bonds are absent from $P(OH)_3$ and $PhP(OH)_2$) or the transformation of the triplet into the doublet (one P—H bond remains in $HP(OH)_2$). The P—H bond is characterized by the large constant $^1J_{P-H}$ (see Table 1) and can easily be revealed by measuring proton-decoupled spectra. The coordination causes a strong (>100 ppm) downfield shift of the signal. The real spectral pattern is complicated by the fact that several mixed chloro aqua complexes $[Mo_3Pd(PR_3)Q_4(H_2O)_{9-x}Cl_x]^{(4-x)+}$ are formed in hydrochloric acid solutions, resulting in the appearance of three—four closely-spaced signals. The reactivity decreases in the series $Ph_2P(O)H >$ $> PhHP(O)OH > H_3PO_2 \gg H_3PO_3$. The formation of the complex with the coordinated $PhP(OH)_2$ ligand was confirmed by X-ray diffraction study of a supramolecular adduct with the macrocyclic cavitand, *viz.*, cucurbit[8]uril, $(H_3O)_3[Mo_3(Pd(PhP(OH)_2)S_4(H_2O)_2Cl_7][2PhP(O)(OH)_2 \subset CB[8]] \cdot nH_2O$. Due to disorder of the cluster component observed in studies of three single crystals, we failed to completely solve the structure (see the Experimental section). However, the presence of the $[Mo_3(Pd\{PhP(OH)_2\})S_4(H_2O)_2Cl_7]^{3-}$ ions (Fig. 1) and the cucurbit[8]uril molecules containing two inclusion molecules of phenylphosphinic acid $PhP(O)(OH)_2$ (oxidation product of PhHP(O)OH) as the major components of the crystal lattice is beyond doubt. These two structural components are linked to each other by a hydrogen bond network involving also water molecules of crystallization.

Several complexes with the ligands under study, have been described in the literature. However, all these complexes, except for $[Ru(NH_3)_5(P(OH)_3)]^{2+}$ [11] and the gold complexes $[(Ph_2POH)AuCl]$ and $[(Ph_2POH)AuGeCl_3][(Ph_2POH)_2Au]^+$,[12] were synthesized by hydrolysis of the $[Cr(CO)_5(PCl_3)]$ and $[PtCl_2(Ph_2PCl)_2]$ complexes[13—16] or oxidation of coordinated phosphorus hydrides (Rh^{III} complexes with

Table 1. Chemical shifts in the ^{31}P NMR spectra (δ, *J*/Hz) and UV-Vis absorption spectra (λ_{max}/nm (ε/L mol^{-1} cm^{-1})) of the $[Mo_3(M'L)Q_4(H_2O)_9]^{4+}$ complexes (M´ = Pd or Ni; Q = S or Se) in 4 *M* HCl

M´	Q	$P(OH)_2H$		$P(OH)_3$		$PhP(OH)_2$		$Ph_2P(OH)$		PPh_3	
		δ	λ_{max}	δ	λ_{max} (ε)	δ	λ_{max} (ε)	δ	λ_{max} (ε)	δ	λ_{max} (ε)
Pd	S	122.7, 123.2, 123.9 ($^1J_{P-H}$ = 405)	235, 295, 454	116.4, 115.9, 115.3, 114.6	296 435 (3680)	130.9, 131.6, 132.3	255, 323, 475 (1000)	113.7, 113.8, 114.0	255, 323, 477 (1110)	31.6, 32.5, 33.4	256, 323, 477 (1722)
	Se	121.6, 119.0, 116.5 ($^1J_{P-H}$ = 405)	—	112.9, 112.2, 111.6, 110.8	310 444 (2250)	131.7, 132.7, 133.7	258, 314, 463	111.9	260, 317, 467	31.3, 32.2, 33.3	257, 325, 477
Ni	S	141.6 ($^1J_{P-H}$ = 411)	—	133.6, 134.4, 135.3	—	147.8	—	—	—	39.7, 40.7, 41.9	316, 488, 574 (940)

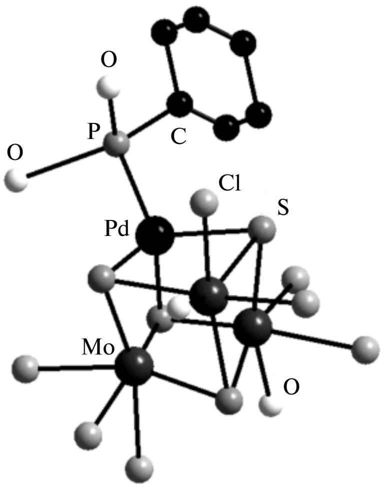

Fig. 1. Structure of the $[Mo_3(Pd(PhP(OH)_2))S_4(H_2O)_2Cl_7]^{3-}$ cluster complex.

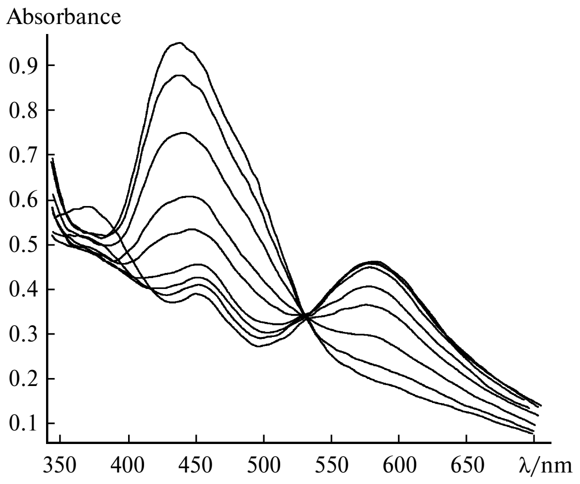

Fig. 2. Absorbance change with time for the reaction of H_3PO_3 with $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ in 4 *M* HCl.

Ph_2POH and μ-PPh_2O^-) rather than by isomerization of the corresponding compounds containing the H—P=O fragment in the presence of metal as a complexing agent. Oxidation affords initially the $[RhCl_2(Ph_2PH)_4]^+$ complex, which is gradually oxidized in solution.[17]

We found that bis(hydroxy)phosphine is also readily oxidized in the palladium coordination sphere to give tris(hydroxy)phosphine $P(OH)_3$. This reaction was studied by ^{31}P NMR spectroscopy. Isomerization of H_3PO_2 and coordination of $HP(OH)_2$ (which proceed much faster than those for H_3PO_3) in hydrochloric acid afford the chloro aqua complexes $[Mo_3Pd\{HP(OH)_2\}Q_4(H_2O)_{9-x}Cl_x]^{(4-x)+}$, which are readily identified based on a series of characteristic doublets in the NMR spectra. However, these lines lose intensity already after one day, and signals of the $[Mo_3Pd\{P(OH)_3\}Q_4(H_2O)_{9-x}Cl_x]^{(4-x)+}$ complex, free H_3PO_3, and H_3PO_4 appear. After several days, only the complex with $P(OH)_3$ is present in solution. These observations can be explained as follows. The first step produces the complex with $HP(OH)_2$. In the second step, $HP(OH)_2$ is oxidized to $P(OH)_3$ and, in the presence of an excess of H_3PO_2, is displaced from the coordination sphere to form phosphorous acid. The ease of oxidation of the $HP(OH)_2$ molecule coordinated to the palladium atom did not allow us to isolate the corresponding complex as the solid phase; instead, the $[Mo_3(Pd(P(OH)_3))S_4(H_2O)_6Cl_3]^+$ complex crystallized as a supramolecular adduct with cucurbit[6]uril.[1] The ability of palladium black to catalyze H_3PO_2 oxidation by protons in acidic solution has long been known.[6] Hence, it can be hypothesized that this heterogeneous process involves chemosorption of $HP(OH)_2$ on the particle surface of palladium black followed by oxidation.

The reactions of H_3PO_3 with $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ (Q = S or Se) appeared to be rather slow, which allowed us to study the kinetics by spectrophotometry. The absorbance change in one of experiments is shown in Fig. 2.

During the first two—three minutes, a rather rapid change is observed in the 350—420 nm region of the spectrum, after which the changes become slower. An isobestic point is observed at $\lambda = 533$ nm for Q = S and at 545 nm for Q = Se, which is indicative of the presence of only two forms of the cluster. The positions of these isobestic points and the average extinction coefficients ($\bar{\varepsilon}$) in the spectra

$$\bar{\varepsilon} = A/(C_M \cdot l),$$

where C_M is the concentration of the cluster, are independent of $C_{H_3PO_3}$. Therefore, the reaction involves two clearly distinguishable steps. The first rapid step is, apparently, associated with the coordination of the $(HO)_2P(O)(H)$ molecules (in essence, of phosphine oxide) to the oxophilic molybdenum atom in the cluster (reaction is promoted by the statistical factor; three molybdenum atoms in the cluster have nine coordination sites). The second step involves the isomerization and coordination of phosphorous acid to the palladium atom in the cluster and the replacement of the Cl^- ion. The first (fast) step produces the $[Mo_3(PdCl)Q_4(H_3PO_3)_n(H_2O)_m]^{3+}$ complex. Taking into account the large stability constants of the complexes with such ligands, a high H_3PO_3 concentration used in the experiments, and the fact that the characteristics of the isobestic points are independent of $C_{H_3PO_3}$, it can be concluded that *n* remains constant and is close to the limiting value upon coordination of H_3PO_3 to molybdenum in all experiments. Otherwise, one would assume that a change in *n* (number of H_3PO_3 molecules coordinated to molybdenum) has no effect on the spectra of the clusters.

The kinetic data processing for the second (slower) step showed the absence of the second pathway of replacement of Cl^- by $P(OH)_3$. It was also found that the absorbance of the solution measured after a rather long period of time depends substantially on $C_{H_3PO_3}$. Hence, the reactions of the $[Mo_3(PdCl)Q_4(H_3PO_3)_n(H_2O)_m]^{3+}$ clusters with H_3PO_3 are apparently reversible.[18] Then the kinetic equation takes the form

$$(e^{-k^*\tau}\cdot\beta_1{}^*C_XC_M + C_M)/(1 + \beta_1{}^*C_X) = [M] = \Delta D/(\Delta\varepsilon\cdot l),$$

$$k^* = k_2[X] + k^*{}_{-1}, \qquad \beta_1{}^* = k_2/k^*{}_{-1},$$

where k_2 is the rate constant of the forward reaction, $k^*{}_{-1}$ is the apparent rate constant of the backward reaction ($k^*{}_{-1} = k_{-2}\cdot[Cl^-]$ and it remains constant under the experimental conditions at C_{HCl} = 4 mol L^{-1} = const), C_X is the initial H_3PO_3 concentration, C_M is the initial concentration of the $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ cluster (Q = S or Se), [M] is the equilibrium concentration of the cluster, $\Delta D = D - \varepsilon_{MX}\cdot C_M$ is the difference between the current absorbance and the expected absorbance when the degree of conversion in the reaction is 100%, $\Delta\varepsilon = \varepsilon_M - \varepsilon_{MX}$ is the difference between the extinction coefficients of the clusters and the corresponding complexes, and l is the cell path length. The processing of the experimental data was carried out using the weighted nonlinear least-squares method.[19] The statistical weights were determined based on the errors in the measurement of the absorbance. The rate constants are given in Table 2.

Earlier,[10,20] the rate constants of the reactions of the $Mo_3PdS_{4aq}{}^{4+}$ complex with phosphines (X), *viz.*, 1,3,5-triaza-7-phosphaadamantane (PTA) and tris(3-sulfonatophenyl)phosphine ($TPPTS^{3-}$), have been determined. The reactions were carried out in 2 *M* *p*-toluenesulfonic acid (Hpts), in which the palladium complex exists as the double cuboidal cluster $\{[Mo_3PdS_4(H_2O)_9]_2\}^{8+}$. The very fast reactions afford the cuboidal $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$ complexes. The rate constants of the forward reactions are $2.78\cdot10^6$ L mol^{-1} s^{-1} for X = PTA and $9.6\cdot10^5$ L mol^{-1} s^{-1} for X = $TPPTS^{3-}$. These constants are substantially larger than the rate constants for the reactions of $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ (Q = S or Se) with H_3PO_3 in 4 *M* HCl determined in the present study (see Table 2). This is attributable to several factors. First, the reactivity of the cluster increases in Hpts solution, in which chloride is not coordinated to the Pd atom in the cluster, and, consequently, there is no need to replace this ion in the presence of a large molar excess. Second, the PTA and $TPPTS^{3-}$ ligands are coordinated without additional tautomerization.

Table 2. Rate constants of the forward reaction (k_2) and the apparent rate constants of the backward reaction ($k^*{}_{-1}$) $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+} + H_3PO_3 = [Mo_3(PdP(OH)_3)Q_4(H_2O)_9]^{4+} + Cl^-$

Q	k_2/L mol^{-1} s^{-1}	$k^*{}_{-1}$/s^{-1}
S	$(1.18\pm0.05)\cdot10^{-4}$	$(2.3\pm0.2)\cdot10^{-5}$
Se	$(3.0\pm0.1)\cdot10^{-3}$	$(4.5\pm0.2)\cdot10^{-3}$

The nickel-containing $[Mo_3(NiCl)S_4(H_2O)_9]^{3+}$ cluster is less reactive than the palladium-containing cluster and it does not react with hydrophosphoryl compounds in hydrochloric acid solutions at room temperature. A rise in the temperature accelerates the reaction. Heating in a 1 *M* HCl solution over a long period of time afforded the complexes with $HP(OH)_2$, $P(OH)_3$, $Ph_2P(OH)$, and $PhP(OH)_2$, which was proved by ^{31}P NMR spectroscopy. The reactions are accompanied by a change in the color of the solutions from green to different tints of red. The chemical shifts in the NMR spectra are observed at lower field than those in the spectra of analogous palladium clusters. The same situation was also observed for the $[Mo_3(M'PPh_3)S_4(MeCp)_3]^+$ [21] and $[Mo_3(M'PPh_3)S_4Cl_4(H_2O)_5]$ complexes.[22] We failed to prepare the complex with $HP(OH)_2$ in pure form (as well as in the case of palladium clusters). Studies by NMR spectroscopy demonstrated that the reactions always produce mixtures of complexes containing the $HP(OH)_2$ and $P(OH)_3$ ligands. In Hpts solutions, the reactivity of the nickel cluster, like that of the palladium cluster, is higher.

The rate constants of the reactions of the nickel cluster with the PTA and $TPPTS^{3-}$ ligands in a 2 *M* Hpts solution were determined.[20] The rate constants of these reactions are 119 L mol^{-1} s^{-1} for X = PTA and 58 L mol^{-1} s^{-1} for X = $TPPTS^{3-}$, which are substantially smaller that those for the palladium clusters. Therefore, our data on the reactions of nickel and palladium clusters with hydrophosphoryl compounds agree well with the data[20] on the reactions of these clusters with phosphines.

The complex with $P(OH)_3$ was prepared in good yield by the reaction of a hydrochloric acid solution of $[Mo_3S_4(H_2O)_9]^{4+}$ with Ni^{2+} and H_3PO_2. Careful heating (to 40 °C) affords the green $[M_3(NiCl)S_4(H_2O)_9]^{3+}$ complex.[23] At higher temperature, the reaction produces a red-colored solution, which can be purified and concentrated by ion-exchange chromatography. This solution is stable in air for several months. The $\{[Mo_3(NiP(OH)_3)S_4(H_2O)_8Cl]CB[6]\}Cl_3\cdot13H_2O$ complex (**1**) was isolated from this solution as a supramolecular adduct with cucurbit[6]uril (CB[6]), and this complex was structurally characterized (Fig. 3). The principal geometric parameters of the cluster cation are given in Table 3. The $P(OH)_3$ molecule, in which the hydrogen atoms were localized for the first time, is coordinated to the nickel atom through the phosphorus atom (Ni—P, 2.165(2) Å). The geometry of this coordinated molecule deviates substantially from tetrahedral geometry toward pyramidal geometry; the O—P—O angles are in the range of 99—105°, whereas the O—P—Ni angles vary from 113 to 120°. The coordination polyhedron of the nickel atom (without consideration of the Ni—Mo bonds) is a slightly distorted

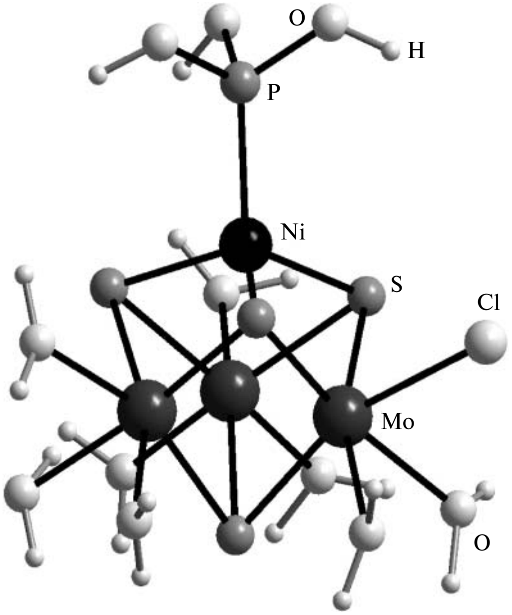

Fig. 3. Structure of the $[Mo_3(Ni(P(OH)_3)S_4(H_2O)_8Cl]^{3+}$ cluster complex.

Table 3. Selected bond lengths (*d*) in the structure of **1**

Bond	*d*/Å	Bond	*d*/Å
Mo(1)—Mo(2)	2.7379(8)	Mo(2)—O(23M)	2.213(4)
Mo(1)—Mo(3)	2.7446(7)	Mo(3)—Ni(1)	2.6625(9)
Mo(1)—Ni(1)	2.6818(10)	Mo(3)—S(2)	2.3448(16)
Mo(1)—S(1)	2.3512(16)	Mo(3)—S(3)	2.3526(15)
Mo(1)—S(2)	2.3481(16)	Mo(3)—S(4)	2.3438(16)
Mo(1)—S(4)	2.3432(17)	Mo(3)—O(31M)	2.191(4)
Mo(1)—O(11M)	2.160(4)	Mo(3)—O(32M)	2.224(4)
Mo(1)—O(12M)	2.173(5)	Mo(3)—O(33M)	2.207(4)
Mo(1)—O(13M)	2.183(4)	Ni(1)—S(1)	2.2019(18)
Mo(2)—Mo(3)	2.7650(7)	Ni(1)—S(3)	2.1952(17)
Mo(2)—Ni(1)	2.6853(10)	Ni(1)—S(4)	2.1940(17)
Mo(2)—S(1)	2.3449(16)	Ni(1)—P(1)	2.165(2)
Mo(2)—S(2)	2.3532(15)	P(1)—O(1P)	1.589(6)
Mo(2)—S(3)	2.3366(16)	P(1)—O(2P)	1.595(6)
Mo(2)—Cl(21)	2.508(2)	P(1)—O(3P)	1.571(6)
Mo(2)—O(22M)	2.186(4)		

tetrahedron, and the $P(OH)_3$ molecule is oriented so that the P—O and Ni—S bonds are in an eclipsed conformation. The coordinated $P(OH)_3$ molecule, like other ligands (H_2O,[24] Cl^-,[25] and $PhSO_2^-$ [23]), has no effect on the bond lengths and bond angles in the $Mo_3NiS_4^{4+}$ cluster core (Table 4).

The crystal structure of compound **1** consists of alternating layers containing free cucurbit[6]uril molecules and supramolecular adducts of the composition cluster : cucurbit[6]uril = 2 : 1. The structure of the supramolecular adduct of the $[Mo_3(Ni(P(OH)_3)S_4(H_2O)_8Cl]^{3+}$ cluster complex with cucurbit[6]uril is shown in Fig. 4. The water molecules in the *cis* positions with respect to the μ_3-S atom, which links three molybdenum atoms, form hydrogen bonds with the oxygen atoms of the portals of cucurbit[6]uril. The O...O distances are in the range of 2.647(7)—2.797(6) Å.

The geometry of the free $P(OH)_3$ molecule was calculated by *ab initio* methods.[7] The P—O bond lengths (1.64—1.67 Å) are larger than the experimental bond lengths in the $\{[Mo_3(Ni(P(OH)_3)S_4(H_2O)_8Cl]CB[6]\}Cl_3 \cdot 14H_2O$ (1.571(6)—1.595(6) Å) and $\{[Mo_3(Pd(P(OH)_3)S_4(H_2O)_6Cl_3]_2CB[6]\}Cl_2 \cdot 20H_2O$ (1.56 Å) complexes. An analogous shortening of the P—O bond was observed upon coordination of phosphites $P(OR)_3$.[27,28] The arrangement of the hydrogen atoms in the coordinated $P(OH)_3$ molecule (all atoms point toward the Ni—P bond) differs from that calculated for the free molecule, where only one hydrogen atom points to-

Table 4. Comparison of the bond lengths (Å) in the $Mo_3NiS_4^{4+}$ cluster core in complexes containing the $P(OH)_3$, CO, H_2O, $PhSO_2^-$, and Cl^- ligands coordinated to the nickel atom

Compound	d_{av}, d_{min}/d_{max}		
	Mo—Ni	Mo—S	Ni—S
$\{[Mo_3(Ni(P(OH)_3)S_4(H_2O)_8Cl]CB[6]\}Cl_3 \cdot 14H_2O$ (**1**)	2.67 2.663(1)/2.685(1)	2.34 2.337(2)/2.353(1)	2.20 2.194(2)/2.202(2)
$[Mo_3Ni(CO)S_4(H_2O)_9](pts)_4 \cdot 7H_2O$[26]	2.68 2.671(25)/2.684(24)	2.33 2.318(18)/2.343(20)	2.20 2.193(20)/2.209(28)
$[Mo_3(Ni(H_2O))S_4(H_2O)_9](pts)_4 \cdot 7H_2O$[24]	2.64 2.630(28)/2.647(22)	2.33 2.318(51)/2.352(32)	2.20 2.203(60)/2.210(51)
$\{[Mo_3(Z))S_4Cl_{1.17}(H_2O)_{7.83}][Mo_3(Z))S_4Cl_{2.22}(H_2O)_{6.78}]$—$(C_{36}H_{36}N_{24}O_{12})\}$ $Cl_{2.61} \cdot 15H_2O$[23] (Z = $Ni(PhSO_2)$)	2.67 2.668(2)/2.680(7)	2.33 2.320(4)/2.348(3)	2.19 2.182(3)/2.198(3)
$\{[Mo_3(NiCl)S_4Cl(H_2O)_8](PyH{\subset}C_{36}H_{36}N_{24}O_{12})\}Cl_3 \cdot 14.5H_2O$[25]	2.64 2.636(9)/2.651(16)	2.32 2.305(50)/2.326(50)	2.18 2.174(10)/2.195(60)
$\{[Mo_3(NiCl)S_4Cl_2(H_2O)_7](C_{36}H_{36}N_{24}O_{12})\}Cl \cdot 13H_2O$[25]	2.65 2.645(42)/2.651(2)	2.33 2.313(18)/2.349(14)	2.20 2.200(9)/2.194(8)

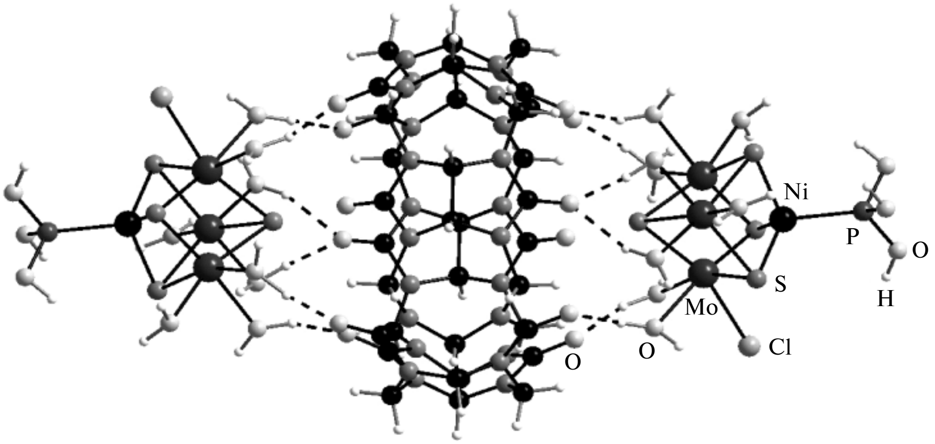

Fig. 4. Structure of the supramolecular adduct of the $[Mo_3(Ni(P(OH)_3)S_4(H_2O)_8Cl]^{3+}$ cluster complex with cucurbit[6]uril. The O—H...O hydrogen bonds are indicated by dashed lines.

ward the lone electron pair.[7] In the structure of compound **1**, the arrangement of the hydrogen atoms (in spite of the difficulties of their determination against the background of strongly scattering heavy atoms) was additionally confirmed by hydrogen bonding. Two hydrogen atoms of the coordinated $P(OH)_3$ groups are involved in hydrogen bonds with the oxygen atoms of two water solvate molecules (H...O, 1.746 and 1.756 Å; the O—H...O angles are 156.6° and 150.9°, respectively), and one hydrogen atom forms a hydrogen bond with the chloride anion (H...Cl, 2.224 Å; the O—H...Cl angle is 142.6°).

To summarize, we studied the influence of the heterometal (Ni and Pd) and chalcogen (S and Se) atoms on the ability of heterometallic cuboidal clusters with the $Mo_3M'Q_4^{4+}$ core to coordinate phosphine tautomeric forms of hydrophosphoryl molecules. We found that the palladium clusters are even more reactive in these reactions than the corresponding nickel clusters, and the selenide clusters are more reactive than the sulfide clusters. The complex with the $PhP(OH)_2$ ligand was isolated for the first time, and the coordinated $P(OH)_3$ molecule was completely (including the positions of the hydrogen atoms) structurally characterized.

Experimental

The starting solutions of the $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ cluster in 1 *M* HCl and the $[Mo_3Q_4(H_2O)_9]^{4+}$ cluster in 2 *M* HCl (Q = S or Se) were prepared according to standard procedures[29—31] and were brought to the desired concentration $[H^+]$ by adding 12 *M* HCl. Cucurbit[8]uril (CB[8])[32] and cucurbit[6]uril (CB[6])[33] were synthesized according to procedures described earlier.

The $NiCl_2 \cdot 6H_2O$ (Reachim), $NH_4H_2PO_2$ (Reachim), PhPH(O)(OH) (Aldrich), and $Ph_2P(O)H$ (Aldrich) compounds were used without additional purification.

Trihydroxophosphinenickeloctaaquachlorotetrasulfidotrimolybdenum trichloride cucurbit[6]uril tridecahydrate, $\{[Mo_3(Ni(P(OH)_3)S_4(H_2O)_8Cl]CB[6]\}Cl_3 \cdot 13H_2O$ (1). Nickel chloride hexahydrate, $NiCl_2 \cdot 6H_2O$ (790 mg, 10-fold excess) and $NH_4H_2PO_2$ (270 mg, 10-fold excess) were added to a 10 *mM* $[Mo_3S_4(H_2O)_9]^{4+}$ solution ($3 \cdot 10^{-4}$ mol, 30 mL) in 2 *M* HCl. The solution was magnetically stirred under argon at 60 °C for 24 h to afford a red solution containing $[Mo_3(NiP(OH)_3)S_4(H_2O)_9]^{4+}$. The solution was purified and concentrated on a DOWEX 50 WX-2 cation-exchange resin using 1 *M* hydrochloric acid as the eluent. A 20 *mM* solution of cucurbit[6]uril ($1 \cdot 10^{-4}$ mol, 5 mL) in 4 *M* HCl and 10 drops of glycerol (1—2 mL) were added to a 5 *mM* $[Mo_3(NiP(OH)_3)S_4(H_2O)_9]^{3+}$ solution ($2.5 \cdot 10^{-5}$ mol, 5 mL) in 1 *M* HCl. The solution was kept in an open beaker at room temperature for one week, during which single crystals precipitated. These crystals were used for X-ray diffraction study. The yield was 37.4 mg (72%). Found (%): C, 20.71; H, 3.92; Cl, 6.76; N, 15.98. $C_{36}H_{81}Cl_4Mo_3N_{24}NiO_{36}PS_4$. Calculated (%): C, 20.85; H, 3.94; Cl, 6.84; N, 16.21.

Synthesis of the supramolecular adduct of $[Mo_3Pd(PhP(OH)_2)S_4(H_2O)_9]^{4+}$ with cucurbit[8]uril. A 10 *mM* PhP(O)(H)(OH) solution ($2 \cdot 10^{-6}$ mol, 0.2 mL) in methanol was added to a 12 *mM* $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ solution ($2.5 \cdot 10^{-5}$ mol, 2 mL) in 4 *M* HCl. After one day, the color of the solution changed from dark-blue to red-brown. Then a 5 *mM* cucurbit[8]uril solution ($5 \cdot 10^{-6}$ mol, 1 mL) in 6 *M* HCl was added to the reaction mixture. After one day, the fine precipitate that formed was filtered off. The solution was kept in an open beaker for three weeks, during which red-brown crystals precipitated. These crystals were studied by X-ray diffraction (space group *C*2/*c*, *a* = 36.176(2) Å, *b* = 12.5786(7) Å, *c* = 23.6621(12) Å, β = 101.1549(17)°).

Kinetics of the formation of $[Mo_3(PdP(OH)_3)Q_4(H_2O)_9]^{4+}$ (Q = S, Se). Different amounts of an H_3PO_3 solution (C = 10 mol L^{-1}) were added to a solution containing $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ ($C = (1—10) \cdot 10^{-4}$ mol L^{-1}) and hydrochloric acid. The resulting solution was rapidly stirred (τ < 10 s), and its absorbance was recorded as a function of time in a temperature-controlled cell (25.0±0.2 °C, l = 0.1 and 1 cm) on a Specord UV—Vis spectrophotometer. The HCl concentration (4.0 mol L^{-1}) was kept constant, whereas the concentration of phosphorous acid was varied from 1 to 8 mol L^{-1}.

Study of the formation of $[Mo_3(PdL)Q_4(H_2O)_9]^{4+}$ (L = $P(OH)_3$, $HP(OH)_2$, $PhP(OH)_2$, $Ph_2P(OH)$; Q = S, Se) by ^{31}P NMR spectroscopy. In a standard experiment, a 75 *mM* solution (1 mL) of the corresponding phosphorus-containing compound (molar ratio cluster : P = 1 : 3) was added to a 25 *mM* solution (1 mL) of the heterometallic cuboidal cluster $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ in 4 *M* HCl; H_3PO_3 and H_3PO_2 were dissolved in water; and PhP(OH)(O)(H) and $Ph_2P(O)(H)$ were dissolved in methanol. The NMR spectra were recorded after 1—2 h (after 12 h or a longer period of time for L = H_3PO_3). The NMR spectroscopic data are given in Table 1.

X-ray diffraction analysis. The structure of the supramolecular complex $\{[Mo_3(Ni(P(OH)_3)S_4(H_2O)_8Cl]CB[6]\}Cl_3 \cdot 13HCl$ (**1**) was established by X-ray diffraction. The X-ray diffraction data were collected on an automated four-circle Bruker X8APEX diffractometer equipped with a CCD area detector using Mo-Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The crystallographic data and details of X-ray diffraction study are given in Table 5. The semiempirical absorption correction was applied based on the intensities of equivalent reflections using the SADABS program.[34] The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for all nonhydrogen atoms (except for some disordered water solvate molecules) using the SHELXTL program package.[35] The hydrogen atoms were revealed from difference electron density maps and refined with geometric restraints. The occupancies of the positions of the oxygen atoms of the water solvate molecules were refined from crystal-chemical considerations and taking into account the thermal parameters. The hydrogen atoms of the water solvate molecules were not localized. The main bond lengths are given in Table 3. The structure of the $(H_3O)_3[Mo_3(Pd(PhP(OH)_2)S_4(H_2O)_2Cl_7][2PhP(O)(OH)_2{\subset}CB[8]] \cdot nH_2O$ complex was established by X-ray diffraction. For one single crystal, the unit cell parameters were measured on an automated four-circle Nonius CAD4 diffractometer at room temperature. Three single crystals prepared in different syntheses were studied at 150 K on an automated four-circle Bruker Nonius X8APEX diffractometer. The results of all measurements are in good agreement with each other. The crystal structure is monoclinic, *a* = 36.1763(7) Å, *b* = 12.5786(12) Å, *c* = 23.6621(12) Å, β = 101.1549(17)°, *V* = 10564(2) Å^3. The structure solution (space group *C*2/*c*) revealed a complicated and rare type of disorder: the cluster complex is disordered over two positions relative to a twofold axis, whereas the center of the Ph ring of the $PhP(OH)_2$ ligand coordinated to the nickel atom lies on an inversion center. Due to the first effect, the cluster cores in two positions superimpose with each other, which substantially hinders the identification of the terminal ligands. Due to the second effect, the structure contains cluster—ligand—cluster—ligand... pseudochains. Analysis of the profiles of the diffraction maxima demonstrated that the crystals are nonmerohedral twins. At the same time, the metrics of the unit cell argues against merohedral twinning. An error in the unit cell parameters ("omission of twinning") is also excluded, because one and the same unit cell was found in the experiments performed with the use of four different crystals and on two diffractometers. In addition, we examined rocking frames about the {100}, (010}, and {001} directions and also did not reveal a multiple increase in the unit cell parameters. The structure refinement converged to $R_1 \approx 0.19$. X-ray diffraction analysis allowed us to determine the structure of the cluster core and reveal the $PhP(OH)_2$ molecule included in the cavity of Q[8]. However, the accuracy of the interatomic distances is low and the complete composition of the compound was not determined.

Table 5. Crystallographic data and details of X-ray diffraction study for complex **1**

Parameter	**1**
Molecular formula	$C_{36}H_{81}Cl_4Mo_3N_{24}NiO_{36}PS_4$
Molecular weight	2073.79
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.3329(7)
b/Å	12.4821(8)
c/Å	24.4975(17)
α/deg	100.403(3)
β/deg	90.725(3)
γ/deg	95.405(3)
V/Å^3	3691.0(4)
Z	2
ρ_{calc}/g cm^{-3}	1.866
μ/cm^{-3}	1.134
$2\theta_{max}$/deg	56.6
Temperature/K	150
Number of measured/ independent/observed	37968/17000/11125
($I > 2\sigma(I)$) reflections, R_{int}	0.0415
Number of parameters in refinement	1056
R_1 ($I > 2\sigma(I)$)	0.0604
wR_2 (for all reflections)	0.1841

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