Conference paper

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Hydroxylated phosphines as ligands for chalcogenide clusters: self assembly, transformations and stabilization

Abstract: This contribution is a documentation of recent advances in the chemistry of chalcogenide polynuclear transition metal complexes coordinated with mono- and di-phosphines functionalized with hydroxo groups. A survey of complexes containing tris(hydroxymethyl)phosphine (THP) is presented. The influence of the alkyl chain in bidentate phosphines, bearing the $P–(CH_2)_x–OH$ arms, is also analyzed. Finally, isolation and structure elucidation of the complexes with $HP(OH)_2$, $P(OH)_3$, $As(OH)_3$, $PhP(OH)_2$, stabilized by coordination to Ni(0) and Pd(0) centers embedded into chalcogenide clusters, is discussed.

Keyword: ICPC-21.

Introduction

Phosphine ligands are ubiquitous in modern coordination chemistry. Virtually a limitless number of phosphines bearing almost any imaginable functionality have been made accessible by the organophosphorous chemists. Among this very vast family, the hydroxyphosphines are useful precursors for a variety of important phosphorus-containing compounds including aminomethylphosphines, phosphorus heterocycles and polycycles [1–3]. The simplest organic hydroxyphosphine is tris(hydroxymethyl)phosphine (THP), reported in 1958 [4]. It is obtained by addition of PH_3 to CH_2O (Scheme 1) [5, 6].

First complexes with THP were apparently reported in 1973 [7]. In particular, complexes of noble metals with THP catalyze hydrogenation of unsaturated aldehydes [8] and hydration of alkynes [9] in biphasic systems. They also catalyze hydroamidation of CO_2 into DMF, isomerization of allyl alcohols into ketones [10], and hydrogenation of ketones into alcohols [11]. Their solubility in water enables attachment to a

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$$PH_3 \xrightarrow[\text{H}_2\text{O}]{\text{CH}_2\text{O}} [P(CH_2OH)_4]^+ \xrightarrow{OH^-} P(CH_2OH)_3$$
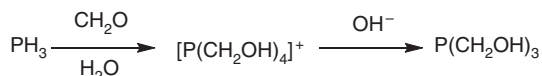
Scheme 1: Preparation of THP.

support surface (such as SiO_2) through the hydroxylic groups of THP [12]. Moreover, hydroxyphosphines and their complexes may be used for development of modern nanoscale and dendrimeric materials. Air oxidation of THP leads to the formation of the corresponding phosphine oxide, THPO, followed by partial loss of CH_2O with the formation of anionic $(HOCH_2)_2PO_2^-$, which can be used for construction of coordination polymers [13].

The significance of phosphines in the cluster chemistry comes from the well-known symbiosis between these ligands and transition metal clusters, in particular, chalcogenide clusters. In fact, many chalcogenide clusters are only known as phosphino complexes: more often than not only phosphines are strongly enough coordinating to prevent uncontrollable transformation of a finite cluster core, formed by self-assembly from a metal cation with a sulfide source, such as H_2S or $(Me_3Si)_2S$, into a bulky metal sulfide [14–16].

The nature of a phosphine exercises enormous influence on the composition and property of the self-assembled clusters [17]. A significant problem is posed by further functionalization of a particular cluster in order to obtain new compounds with any desired set of functional groups. This can be achieved either by use of a phosphine with a specific functionality at the cluster self-assembly step, or by modification of a coordinated phosphine ligand without affecting the cluster core. In this respect the presence of a $P-(CH_2)_x-OH$ sequence in a coordinated phosphine ligand is welcome. The hydroxyl group in THP itself is particularly reactive: it can be acylated, silylated, substituted by amino group, halide etc. [18–21]. Thus, coordination of THP and its analogues not only leads to water soluble sulfide clusters, but can open new ways of cluster functionalization and preparation of dendrimers. This chemistry can be extended to the bidentate phosphines, bearing the $P-(CH_2)_x-OH$ arms, namely, with $x = 1, 3$ and 4.

Another class of hydroxylated phosphines has OH groups directly attached to P(III) centers. In particular, the unstable $P(OH)_3$ and $HP(OH)_2$ molecules 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. However, the R_2P-OH species are not stable towards isomerization into corresponding hydrophosporyl ($R_2HP(=O)$) tautomers. For the isomerization of $P(OH)_3$ into the common dibasic phosphorous acid log $K = 10.3(1.5)$ at 25 °C in aqueous solution [22], and as for $HP(OH)_2$, the estimated ratio $[HP(OH)_2]/[H_2P(O)(OH)] \leq 10^{-12}$ [23]. The organic hydroxyphosphines $RP(OH)_2$ and R_2POH also exist preferentially as the hydrophosphoryl tautomers, except when R is bulky, such as 2,2-dimehtylbicyclo[2,2,2] heptyl-3-methyl [24] or highly electronegative, such as $(CF_3)_2POH$ [25]. There are, nevertheless, examples of stabilization of $P(OH)_3$ by coordination to a d^8 or low-spin d^6 metal center, namely, with Ru(II), Pt(II), Mo(0) and Cr(0). Perhaps the first $P(OH)_3$ complex was reported as early as in 1872 as $PtCl_2·2P(OH)_3$ by Schützenberger [26]. At that time H_3PO_3 was regarded as "normal" tribasic acid, and this formulation corresponded to the expected ability of $P(OH)_3$ to form adducts with metal halides. Much later products formulated as $[Pt(P(OH)_3)_4]Cl_2$ and some polynuclear Rh(III) complexes claimed to contain coordinated $P(OH)_3$ were isolated from reactions of Pt(II) and Rh(III) chloride complexes with H_3PO_3, but at this stage characterization was insufficient and this chemistry has never been resumed [27, 28]. Another product, a dinuclear $K_2[Pt_2(P_2O_5H_2)_4]·2H_2O$, was isolated in the reaction of K_2PtCl_4 with H_3PO_3; it contains four pyrophosphite bridging ligands $P_2O_3(OH)_2^-$ ("pop"), derived from condensation of two molecules of $P(OH)_3$ [29]. Carbonyl complexes $[M(CO)_5(P(OH)_3)]$ were also reported (M = Cr, Mo). The Cr complex and was isolated as a hydrate, $[Cr(CO)_5(P(OH)_3)]·H_2O$ by hydrolysis of $[Cr(CO)_5(PCl_3)]$ in the presence of Et_3N [30]. The synthesis of $[Mo(CO)_6(P(OH)_3)]$, reported in 2004, was achieved by the one-pot reaction of $Mo(CO)_6$ with $HP(O)$ $(OEt)_2$ and water. The structure of the product was confirmed by X-ray analysis [31, 32]. However, the first clear evidence for isomerization of free H_3PO_3 upon coordination was obtained in 1980s, by Franco et al., in the reaction with $[Ru(NH_3)_5(H_2O)]^{2+}$, which produced $[Ru(NH_3)_5(P(OH)_3)]^{2+}$ [33]. This product was characterized only in solution. The first isolated and structurally characterized Ru(II) complex with $P(OH)_3$

was $[CpRu(PPh_3)_2(P(OH)_3)]^+$ [34], prepared by treatment of $[CpRu(PPh_3)_2Cl]$ with H_3PO_3 in the presence of Tl^+ or Ag^+ as chloride scavengers.

$HP(OH)_2$ was even more elusive. Prior to our work there were only indirect indications that $HP(OH)_2$ might be involved in some catalytic cycles. Thus, Pd-catalyzed formation of $HP(O)(OR)(OH)$ from NaH_2PO_2 and ROH (with H_2 as by-product) is believed to proceed via $HP(OH)_2$ [35], and cross-coupling of $H_2PO_2^-$ with ArX with the formation of $ArP(H)(O)(OH)$ is catalyzed by $[Pd(PPh_3)_4]$, presumably via $\{Ar-Pd-PH(OH)_2\}$ intermediates [36]. More recently, $[CpRu(PPh_3)_2(HP(OH)_2)]^+$ was obtained by treatment of $[CpRu(PPh_3)_2Cl]$ with H_3PO_2 in the presence of Tl^+ or Ag^+ as chloride scavengers and structurally characterized [34]. It is worth mentioning that elusive phosphine oxide (H_3PO) was first obtained in solution by electrochemical methods starting from white phosphorus and trapped as a ligand in half-sandwich CpRu(II) complexes following tautomerization to phosphinous acid, $H_2P(OH)$ [37].

Stabilization of Ph_2POH by coordination was reported for $[Au(Ph_2POH)Cl]$, $[Pt(Ph_2POH)_2Cl_2]$, $[Au(Ph_2POH)GeCl_3]$, $[Au(Ph_2POH)_2]^+$ [38], obtainable either directly from diphenylphosphine oxide or by hydrolysis of coordinated Ph_2PCl molecule. Mono and dinuclear complexes of $PdCl_2$ with $^tBu_2POH$ were prepared from $[(COD)PdCl_2]$ and $^tBu_2P(O)H$. These structures were confirmed by X-ray analysis, and the complexes were successfully used in cross-coupling reactions [39]. Pt(II) complexes with Me_2POH and Ph_2POH efficiently catalyze nitrile hydrolysis under neutral conditions [40]. Complex $[(^tBuPhP(OH))_2Pd_2Cl_4]$, prepared from $[(COD)PdCl_2]$ and enantiopure $^tBuPhP(O)H$, catalyzes asymmetric allylic substitution [41]. Oxydation of Ph_2PH in the coordination sphere of Rh(III) also gives complexes with Ph_2POH and μ-Ph_2PO^- without breaking the Rh–P bond [42].

We have found that Ni(0) and Pd(0) centers, incorporated into cuboidal $\{M_3Q_4\}$-based chalcogenide clusters (M = Mo, W; Q = S, Se), revert the tautomerization and stabilize the R_2P-OH tautomers by direct coordination. This property seems to be general and has allowed isolation and structure elucidation of the complexes with $HP(OH)_2$, $P(OH)_3$, $PhP(OH)_2$. Elusive $As(OH)_3$ has also been pinned down in this way.

Assessment of coordination properties of THP

It is well known that the coordination ability of the phosphines depends on the nature of the substituent groups at the P atom: electron-accepting groups increase, and electron-donating groups decrease this property. Allen and collaborators have suggested use of the $^1J_{P-Se}$ coupling constants from the selenides (R_3PSe) as a probe for the electronic effects of the substituents and thus the donor properties of the phosphines: electron-acceptor groups will increase this parameter [43]. For this purpose, we have prepared THPSe by reactions of THP with KSeCN and Ph_3PSe (reaction of $[P(CH_2OH)_4]Cl$ with Se or KSeCN also produces THPSe). THPSe has following NMR characteristics (in CD_3OH): δ ^{31}P 37.2, δ ^{13}C 58.4, δ ^1H 4.22, δ ^{77}Se – 508.5 ppm, $^1J_{C-H}$ 147.5, $^1J_{P-Se}$ 678.0 Hz. The latter value is close to the value reported for Me_3PSe (684 Hz) [44]. This closeness means that introduction of the hydroxylic substituents (i.e. transformation of $-CH_3$ groups into $-CH_2OH$) does not significantly alter inherently strong basicity of the aliphatic phosphines, and THP can be regarded as strong donor, *au pair* with PMe_3, and much stronger that PPh_3 ($^1J_{P-Se}$ 732 Hz). Experimental confirmation of the strong donating ability of THP is our observation of its complexing with Cd^{2+} in 1 : 3 M:L stoichiometry: with other phosphines the number of coordinated PR_3 ligands does not exceed two [13]. Consequently, THP must be fully suitable for efficient coordination of the cluster core in a nascent chalcogenide cluster to prevent its incontrollable growth into binary metal sulfides, if the strategy of cluster formation by metal cation sulfidation in the presence of a phosphine, put forward by the Cecconi and Fenske groups, is followed. Indeed, this strategy proved successful with transition metals from 8 to 10 groups, as discussed below.

Self-assembly of the transition metal sulfide clusters in the presence of THP

Reaction of $FeCl_2 \cdot 4H_2O$ and $P(CH_2OH)_3$ with H_2S in methanol produces $[Fe_6S_8(P(CH_2OH)_3)_6]^{2+}$ (Fig. 1) as the only product according to ^{31}P NMR [45]. UV-Vis and ESR spectra (Fig. 2) of $[Fe_6S_8(P(CH_2OH)_3)_6]Cl_2$ contain three
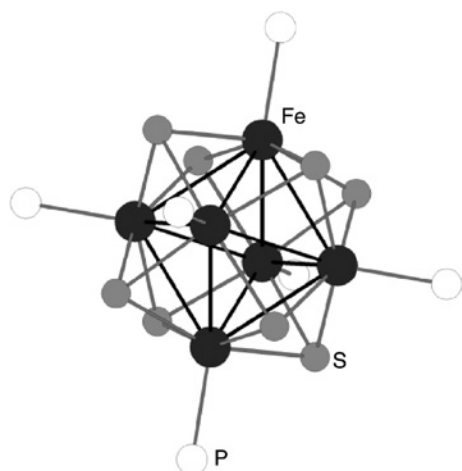
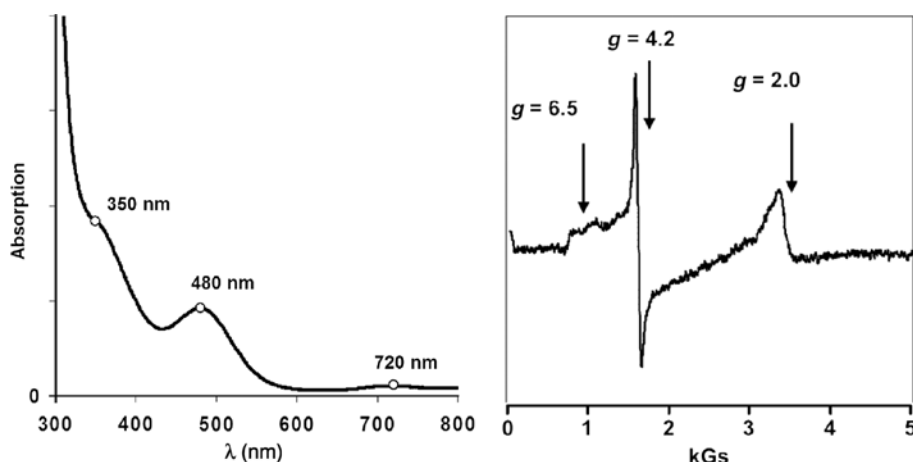**Fig. 1:** View of the $\{Fe_6S_8\}^{2+}$ cluster core with coordinated THP (only P atoms are shown).

Fig. 2: Absorption (left, r.t.) and ESR (right, 77 K) spectra of $[Fe_6S_8(P(CH_2OH)_3)_6]$ in MeOH solution.

signals ($g_{eff} = 6.5$, 4.2 и 2.0) in agreement with the values reported for structurally characterized $[Fe_6S_8(PEt_3)_6]$ $(BPh_4)_2$ ($g_{eff} = 7.0$, 4.9 и 2.0) [46]. Intercalation of $[Fe_6S_8(P(CH_2OH)_3)_6]Cl_2$ into MoS_2 [47, 48] gives $MoS_2([Fe_6S_8(P(CH_2OH)_3)_6]Cl_2)_{0.06}$. This composition is typical for incorporation of hexanuclear clusters of such type [49, 50]. Magnetic susceptibility for $MoS_2([Fe_6S_8(P(CH_2OH)_3)_6]Cl_2)_{0.06}$ estimated in the range 80–300 K (9 kOe) yielded, for six Fe atoms, $\mu_{eff} = 11.8(1)\,\mu_B$ and $S = 5.42(4)$ (i.e. $\mu_{eff} = 4.83(5)\,\mu_B$, $S = 1.97(3)$ per Fe atom). This means that low-spin: high-spin Fe^{3+} ions ratio is 4 : 2. Thus the effective magnetic moment for $[Fe_6S_8(P(CH_2OH)_3)_6]Cl_2$ cluster is higher than for other reported $\{Fe_6S_8P_6\}^{2+}$ clusters (five low-spin and one high-spin Fe^{3+}) [51–53]. The coordination with $P(CH_2OH)_3$ unexpectedly increases the paramagnetism of the cluster core.

No Ru analogues of $[Fe_6S_8(P(CH_2OH)_3)_6]^{2+}$ could be obtained. Instead, reaction of $[Ru(PPh_3)_3Cl_2]$ with THP in ethanol leads to $[Ru_2(\mu\text{-}Cl)_3(P(CH_2OH)_3)_6]Cl$ as single detectable product, according to ^{31}P NMR. The same complex was obtained from $RuCl_3$ and THP in poor yield (9 %). Crystal structure of $[Ru_2(\mu\text{-}Cl)_3(P(CH_2OH)_3)_6]$ Cl contains binuclear cations $[Ru_2(\mu\text{-}Cl)_3(P(CH_2OH)_3)_6]^+$ and Cl^- anions. The binuclear complex has $\{P_3Ru(\mu\text{-}Cl)_3RuP_3\}^+$ core built of two confacial octahedra with non-bonding Ru…Ru distance of 3.350 Å. Attempts at sulfidation did not give identifiable products [54].

Reaction of $CoCl_2 \cdot 6H_2O$ and $P(CH_2OH)_3$ with H_2S in ethanol gives $[Co_6S_8(P(CH_2OH)_3)_6]$ as the only product (^{31}P NMR: $\delta = 28.6$ ppm) [55]. This can be isolated only as a dark-brown oil of the composition $[Co_6S_8(P(CH_2OH)_3)_6] \cdot 5H_2O$. Acylation of $[Co_6S_8(P(CH_2OH)_3)_6]$ with excess of $(CH_3CO)_2O$ or $(C_2H_5CO)_2O$ gives

acylated products $[Co_6S_8(P(CH_2OC(O)CH_3)_3)_6] \cdot H_2O$ and $[Co_6S_8(P(CH_2OC(O)CH_2CH_3)_3)_6]$ in moderate yields; it is known that direct acylation of free $P(CH_2OH)_3$ produces $P(CH_2OC(O)CH_3)_3$ [21]. The crystal structure of $[Co_6S_8(P(CH_2OC(O)CH_3)_3)_6] \cdot H_2O$ contains hexanuclear clusters $[Co_6S_8(P(CH_2OC(O)CH_3)_3)_6]$ (Fig. 3) with nearly regular octahedral $\{Co_6(\mu_3\text{-}S)_8\}$ cores with short Co…Co distances (2.78–2.82 Å), typical for all known Co_6S_8 clusters with alkyl phosphines. The Co–P distances in $[Co_6S_8(P(CH_2OC(O)CH_3)_3)_6] \cdot H_2O$ is 2.105 Å, being somewhat shorter than in $[Co_6S_8(PEt_3)_6](BPh_4)$ [56]) and $[Co_6S_8(PPh_3)_6]$ (ca. 2.16 Å) [57]). The shortening might be due to the increase in π-acceptor properties of the phosphines ligands on going from alkyl and aryl phosphines to $P(CH_2OC(O)CH_3)_3$ with electronegative acetate substituent in the alkyl radical. High-resolution ^{31}P, ^{1}H and ^{13}C NMR spectra and corresponding J_{P-X} values show that $[Co_6S_8(THP)_6]$ and $[Co_6S_8(P(CH_2OOCCH_2CH_3)_3)_6]$ possess similar geometry. Cyclic voltammetry shows reversible redox process with E_a and E_c at 0.16 and −0.05 V, and an irreversible anodic wave at + 0.52 V (vs. Ag/AgCl couple) [55].

Rhodium behaves differently. Interaction of $RhCl_3 \cdot 3H_2O$ with $P(CH_2OH)_3$ in methanol gives a mononuclear complex (^{31}P: δ 34.5 ppm). Bubbling H_2S through this solution gives a dark-red solution and a complicated pattern in ^{31}P NMR spectrum (doublet of triplets and triplet of doublets in 1 : 2 ration, Fig. 4, $^{1}J_{P-Rh} = 122.7$ Hz, $^{2}J_{P-P} = 14.3$ Hz for 12.0 ppm signal, $^{1}J_{P-Rh} = 81.9$ Hz, $^{2}J_{P-P} = 15.8$ Hz for 40.4 ppm signal). This pattern closely resembles that reported for $[Rh_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)(\mu_2\text{-}Cl)_2(PEt_3)_6](PF_6)$, obtained by Cecconi et al. in 3 % yield [58], and thus corresponds to the formation of $[Rh_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)(\mu_2\text{-}Cl)_2(THP)_6]^+$ (Fig. 5). According to ^{31}P NMR data, this cluster is the only product. In the crystal structure of $[Rh_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)(\mu_2\text{-}Cl)_2(THP)_6]Cl$ the cluster cation has Rh…Rh distances of 3.26 Å, indicating no metal-metal bonding. The Rh–P and Rh–(μ_2-S,Cl) bonds are 2.32 Å and 2.42 Å, respectively. The Rh-(μ_3-S) bond distance is 2.41 Å.

Reaction of $NiCl_2$ with two equivalents of THP in ethanol gives dark-orange solution of $[Ni(THP)_2Cl_2]$ (^{31}P NMR: − 6.2 ppm). Passing H_2S through this solution gives a dark-red solution (λ_{max} 347 nm; reported [16] for $[Ni_3S_2(PEt_3)_6]^{2+}$ 360 nm), with the ^{31}P NMR signal shifted to + 14.0 ppm, corresponding to the formation of $[Ni_3S_2(P(CH_2OH)_3)_6]^{2+}$ [59]. This cluster undergoes further evolution: in 3 days the signal of $[P(CH_2OH)_4]^+$ at + 24.0 ppm appears, together with two other signals of equal intensity at + 14.5 and at + 42.3 ppm, attributable to the $\{P,P\text{-}\boldsymbol{P}CH_2OP\}$ and $\{P,P\text{-}PCH_2O\boldsymbol{P}\}$ atoms in the bidentate ligand $(HOCH_2)_2PCH_2OP(CH_2OH)_2$, corresponding to the formation of $[Ni_3S_2((HOCH_2)_2PCH_2OP(CH_2OH)_2)_3]^{2+}$. Formation of $[P(CH_2OH)_4]^+$ can be explained by disproportionation $2P(CH_2OH)_3 + H^+ = [P(CH_2OH)_4]^+ + HP(CH_2OH)_2$, which simultaneously furnishes the secondary phosphine necessary for condensation. Oxidation of $HP(CH_2OH)_2$ into $HOP(CH_2OH)_2$, followed by condensation with remaining THP, produces $(HOCH_2)_2PCH_2OP(CH_2OH)_2$ – an interesting analogue of $(HOCH_2)_2PCH_2CH_2P(CH_2OH)_2$ (dhmpe). This condensation was reported for monomeric Pt, Pd [5]
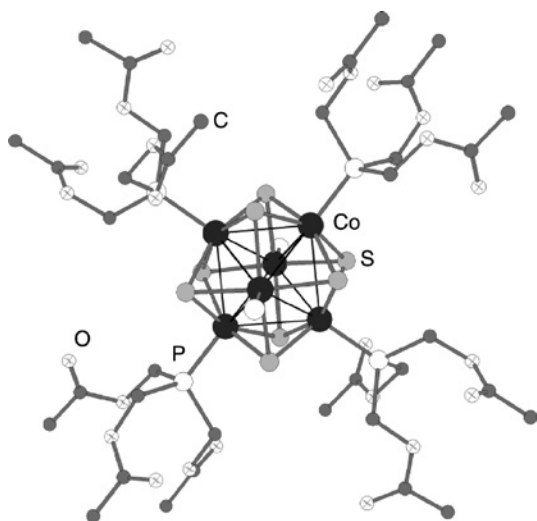
Fig. 3: View of $[Co_6S_8(P(CH_2O(O)CCH_3)_3)_6]$ in $[Co_6S_8(P(CH_2OC(O)CH_3)_3)_6] \cdot H_2O$. The hydrogen atoms and two phosphine ligands are omitted for clarity.
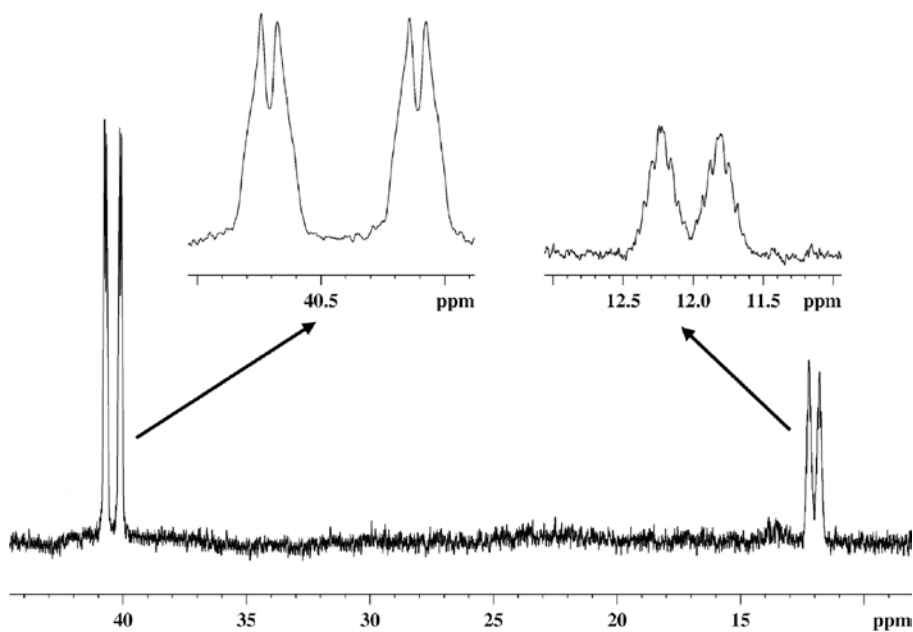
Fig. 4: ^{31}P NMR spectrum of [Rh$_3$(μ_3-S)$_2$(μ_2-S)(μ_2-Cl)$_2$(P(CH$_2$OH)$_3$)$_6$]Cl solution in methanol.

and Rh [60] complexes. Reaction of [MCl$_2$(P(CH$_2$OH)$_3$)$_2$] (M = Pd, Pt) with P(CH$_2$OH)$_3$ in excess produced [M((CH$_2$OH)$_2$PCH$_2$OP(CH$_2$OH)$_2$)$_2$]$^{2+}$, but attempts to isolate free {P,P-PCH$_2$OP} ligand failed because of its rapid decomposition into P(CH$_2$OH)$_3$ and HP(O)(CH$_2$OH)$_2$ [6].

It must be born in mind that the presence of large amounts of OH-groups around the cluster core makes these complexes highly hydrophilic and their crystallization is often a formidable task. Our attempts to isolate [Ni$_3$S$_2$((HOCH$_2$)$_2$PCH$_2$OP(CH$_2$OH)$_2$)$_3$]$^{2+}$ with PF$_6$$^-$, BF$_4$$^-$ or BPh$_4$$^-$ ions, commonly used for such purpose, failed, but with [Mo$_6$Cl$_{14}$]$^{2-}$, which can be regarded as a larger equivalent of PF$_6$$^-$, we succeeded in growing single crystals of [Ni$_3$S$_2${(CH$_2$OH)$_2$PCH$_2$OP(CH$_2$OH)$_2$}$_3$][Mo$_6$Cl$_{14}$]·0.8H$_2$O. The crystal structure contains trinuclear cations [Ni$_3$S$_2$({P,P-PCH$_2$OP})$_3$]$^{2+}$ (Fig. 6, (HOCH$_2$)$_2$PCH$_2$OP(CH$_2$OH)$_2$ = {P,P-PCH$_2$OP}, cluster anions [Mo$_6$Cl$_{14}$]$^{2-}$ and solvent water molecules which form hydrogen bonds with OH groups of the {P,P-PCH$_2$OP} ligands. Each Ni atom has square planar environment and is coordinated with two sulfur atoms and two phosphorus atoms of the THP with the following geometry: Ni…Ni 2.784(1), Ni-S 2.205(1), Ni−P 2.115(2) Å [59].

Reaction of [Pt{P(CH$_2$OH)$_3$}$_2$Cl$_2$] [6] with H$_2$S gives [Pt$_3$S$_2${P(CH$_2$OH)$_3$}$_6$]Cl$_2$ as single product [61]. This water soluble colorless chloride salt is stable in solutions for at least 1 year, and crystallizes from concentrated solutions. In the presence of NH$_4$PF$_6$ [Pt$_3$S$_2$(P(CH$_2$OH)$_3$)$_6$](PF$_6$)(OH)·H$_2$O was obtained [62]. The crystals of
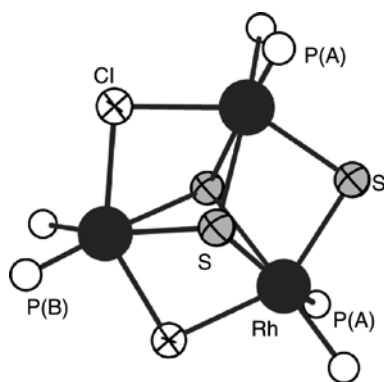
Fig. 5: Structure of the [Rh$_3$(μ_3-S)$_2$(μ_2-S)(μ_2-Cl)$_2$(THP)$_6$]$^+$ cation.
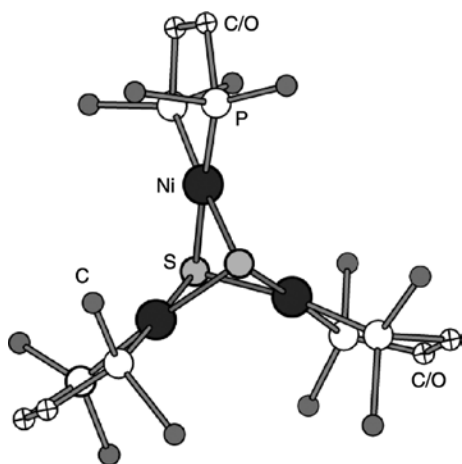
Fig. 6: View of $[Ni_3S_2\{(HOCH_2)_2PCH_2OP(CH_2OH)_2\}_3]^{2+}$. Hydrogen atoms and OH groups of the ligand are omitted for clarity.
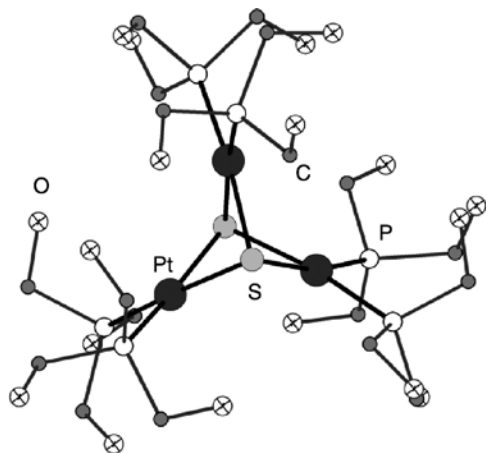

Fig. 7: Crystal structure of cation $[Pt_3S_2(P(CH_2OH)_3)_6]^{2+}$.

both salts contain trinuclear cations $[Pt_3S_2\{P(CH_2OH)_3\}_6]^{2+}$ (Fig. 7) with central $\{Pt_3(\mu_3\text{-}S)_2\}^{2+}$ core featuring non-bonding Pt…Pt distances (3.15–3.20 Å). Each Pt atom has square planar environment from two capping sulfides and two phosphorous atoms of the $P(CH_2OH)_3$ ligands. The Pt–S and Pt–P bond lengths are 2.36 и 2.26, respectively. This geometry is very close to that observed in $[Pt_3S_2(PMe_2Ph)_6](BEt_4)_2$ [63] In cyclic voltammogramm single reversible one-electron redox couple appears at − 0.63 V, followed by irreversible reduction at − 1.59 V. The irreversibility of the second step may be related to the change of coordination geometry on going from square planar Pt(II) in $[Pt_3S_2\{P(CH_2OH)_3\}_6]^{2+}$ to tetrahedral Pt(0) in the product of two-electron reduction. A closely related complex, $[Pt_3S_2(dppe)_3]^{2+}$, exhibits a single reduction peak at − 2.10 V. Presumably in this case reduction proceeds in single two-electron step.

Our attempts to obtain the Pd analogue failed. Reaction of $K_2[PdCl_4]$ with $P(CH_2OH)_3$, generated *in situ* from $[P(CH_2OH)_4]Cl$ and KOH, gave orange needles of $K[Pd(P(CH_2OH)_3)Cl_3]$ in 40 % yield [64].

Coordination of hydroxyalkyldiphosphines to the $M_3S_4^{4+}$ unit

The $M_3S_4^{4+}$ (M = Mo, W) cluster core is a robust entity, offering unique possibilities of cluster modification from which valuable properties result. Coordination of diphosphine ligands such as in $[M_3S_4Y_3(diphosphine)_3]^+$ (Y = halogen, hydrogen) enhances the cluster stability, and proper functionalization of the ligand with

hydroxo group leads to water-soluble clusters that are stable within a wide pH range. These water-soluble complexes are excellent candidates as catalysts under biphasic conditions or as a co-catalyst to be immobilized in solid surfaces. Small ligand variations can have significant effects on the solubility, reactivity, and aqueous speciation of the resulting molecular clusters. We have studied coordination of hydroxyalkyldiphosphines $(HO(CH_2)_xPC_2H_4P(CH_2)_xOH)_2$ with $x = 1$ (dhmpe), $x = 3$ (dhprpe) and $x = 4$ (dhbupe).

The cluster complex with hydroxydiphosphine $[Mo_3S_4Cl_3(dhmpe)_3]Cl$ [65] was prepared by reaction of dhmpe in methanol and $(Bu_4N)_2[Mo_3S_7Cl_6]$ in acetonitrile, in the presence of 0.1 M aqueous HCl, in order to suppress ligand deprotonation. Solutions of $[Mo_3S_4Cl_3(dhmpe)_3]Cl$ in aqueous HCl are green, while water solutions are brown. This difference has been interpreted as the result of partial substitution of Cl with a deprotonated hydroxylic group of dhmpe at one or two of the metal centers, Fig. 8. Accordingly, ESI-mass-spectra contain signals of $[Mo_3S_4L(L-H)_2(H_2O)]^{2+}$ and $[Mo_3S_4L(L-H)_2]^{2+}$ as major species in aquous solutions (Fig. 8), resulting from the ability of a hydroxyl group of one or two dhmpe (L) to coordinate to the cluster $\{Mo_3S_4\}$ core as tridentate P,P,O ligand (L–H). Acidification of the solutions of $[Mo_3S_4L(L−H)_2(H_2O)]^{2+}$ in the presence of X^- (X = Cl, NCS) yields $[Mo_3S_4X_3L_3]^+$, while with KOH $[Mo_3S_4L_3(OH)_3]^+$ is the product.

The complex with dhprpe $(dhprpe = (HOCH_2CH_2CH_2)_2PC_2H_4P(CH_2CH_2CH_2OH)_2)$ $[Mo_3S_4Cl_3(dhprpe)_3]Cl$ was prepared from $[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2]$ and dhprpe in acetonitrile. Upon increasing the length of the hydroxyalkyldiphosphine alkyl chain from methyl to propyl, water solubility increases by a factor of one hundred, and the product becomes highly hygroscopic and difficult to crystallize. Crystal structure was determined for $[Mo_3S_4Cl_3(dhprpe)_3]_2[Mo_6Cl_{14}] \cdot 3H_2O$ [66], which was obtained from acidified solutions after addition of $[Mo_6Cl_{14}]^{2-}$. From basic solutions crystals of $[Mo_3S_4(dhprpe-H)_3]PF_6 \cdot 5H_2O$ with tridentate deprotonated dhprpe-H (P,P,O) ligand were obtained (Fig. 9). Kinetics of acid-base equilibrium between $[Mo_3S_4Cl_3L_3]^+$ and $[Mo_3S_4(L−H)_3]^+$ (Fig. 9) was investigated by $^{31}P\{^1H\}$ NMR, ESI-MS and stop-flow techniques.
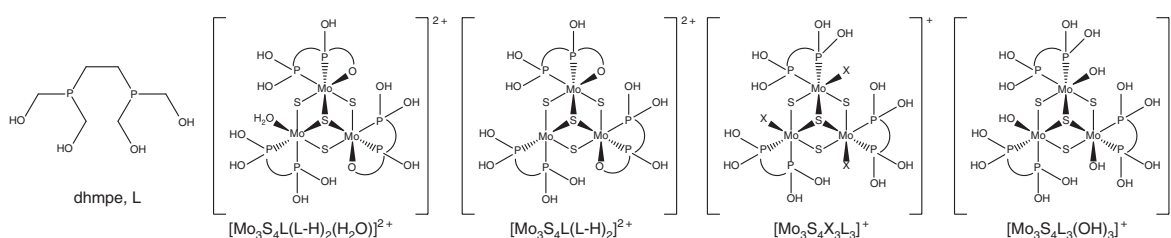
Fig. 8: From left to write structures of dhmpe, $[Mo_3S_4L(L−H)_2(H_2O)]^{2+}$, $[Mo_3S_4L(L−H)_2]^{2+}$, $[Mo_3S_4X_3L_3]^+$, and $[Mo_3S_4X_3L_3]^+$ (X = Cl, SCN, OH) are shown (L = bidentate P-coordinated dhmpe, L−H = tridentate P− and O-coordinated deprotonated dhmpe).
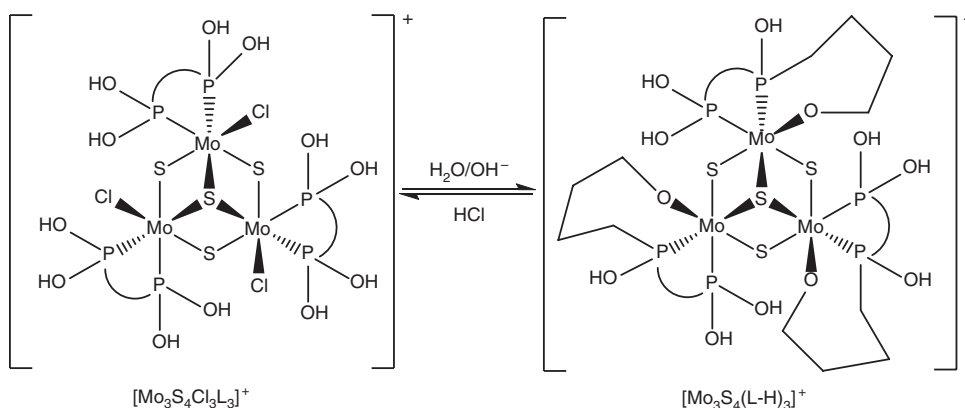
Fig. 9: Equilibrium between $[Mo_3S_4Cl_3L_3]^+$ and $[Mo_3S_4(L−H)_3]^+$ (L = bidentate P-coordinated dhprpe, L−H = tridentate P− and O-coordinated deprotonated dhprpe).

The cluster complexes with dhbupe were prepared for both Mo and W clusters [67]. Highly hygroscopic samples [Mo$_3$S$_4$Cl$_3$(dhbupe)$_3$]Cl and [W$_3$S$_4$Br$_3$(dhbupe)$_3$]Br were obtained by reacting [M$_3$S$_4$X$_4$(PPh$_3$)(H$_2$O)$_2$] (M = Mo, X = Cl or M = W, X = Br) with the ligand in acetonitrile, and crystal structure was determined for (H$_3$O)$_4$[Mo$_3$S$_4$Cl$_3$(dhbupe)$_3$]$_2$[Mo$_6$Cl$_{14}$]$_3$ [66]. In the basic pH range the halide ligands are substituted by hydroxo groups to afford the corresponding [Mo$_3$S$_4$(OH)$_3$(dhbupe)$_3$]$^+$ and [W$_3$S$_4$(OH)$_3$(dhbupe)$_3$]$^+$ complexes. Unlike dhmpe and dhprpe, dhbupe is not able to form complexes in the (P,P,O) tridentate mode due to unfavorable chelate effect (a seven-membered ring would be expected).

Thus, reactivity, water solubility, and speciation of the cluster complexes with hydroxyalkyldiphosphines (HO(CH$_2$)$_x$PC$_2$H$_4$P(CH$_2$)$_x$OH)$_2$ are strongly affected by the length of the alkyl chain between P atom and OH group. Acidic solutions containing coordinating X$^-$ anions, i.e. Cl$^-$, in all cases contain the complex with X$^-$ coordinated to each metal center and the hydroxyalkyldiphosphine acting as a P,P-bidentate ligand. However, diverging behavior patterns that strongly depend on the value of x are observed under neutral and basic conditions. In all cases the phosphorus atoms remain coordinated but the third coordination site at each metal center, i.e. that occupied by X$^-$ in acid media, can be occupied by water, OH$^-$ or a deprotonated hydroxyalkyl phosphine group. When x = 4, the tris(hydroxo) complex is formed in basic solutions, and kinetic studies suggest a mechanism with two parallel reaction pathways involving water and OH$^-$ attacks resulting in the formal substitution of X$^-$ by hydroxo ligands. The reverse reaction of the hydroxo clusters with HX acids occurs with protonation of the OH$^-$ ligands followed by substitution of coordinated water by X$^-$. In contrast, when x = 2 or 3, the chemistry in solution is mainly determined by the formation of species with coordinated deprotonated hydroxyalkyl groups. Detailed mechanistic studies reveal that the opening of the chelate ring to form the complexes with coordinated X$^-$ occurs through two parallel attacks by H$^+$ and X$^-$ with close rates. The reverse reaction involves chloride substitution and chelate ring closure, and also occurs through two parallel paths, in this case involving attacks by H$_2$O and OH$^-$. An additional observation that illustrates the subtle factors affecting the reactivity of these species is that when x = 3, the interconversion between the complexes containing X$^-$ and deprotonated hydroxyalkyl groups occurs in a single kinetic step, thus showing that the reactions proceed at the three metal centers with statistically controlled kinetics. In contrast, when x = 1, separate kinetic steps are observed at the three metal centers, showing significant deviations from the statistical predictions.

Heterometallic Mo$_3$M′Q$_4$ clusters and the problem of stabilization of P^{III}-OH species

The incomplete cuboidal clusters {M$_3$Q$_4$L$_9$} (M = Mo, W; Q = S, Se) can incorporate more than 20 chalcophilic transition and post-transition metals in low oxidation states (Fig. 10). For group 10, heteroatoms in

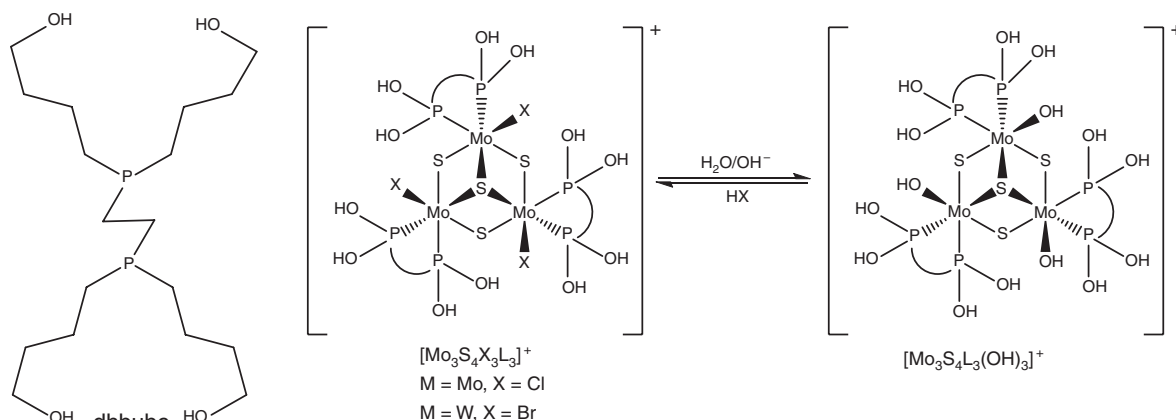

$[Mo_3S_4X_3L_3]^+$
M = Mo, X = Cl
M = W, X = Br

$[Mo_3S_4L_3(OH)_3]^+$

Fig. 10: Structure of dhbupe and equilibrium between [M$_3$S$_4$X$_3$L$_3$]$^+$ and of [M$_3$S$_4$(OH)$_3$L$_3$]$^+$ are shown (L = bidentate P-coordinated dhprpe).

zero oxidation states can be used as the source of M', including bulk Ni sheets and Pd black, *in situ* generated Pd(0) and Ni(0), or Pd(dba)$_2$/Pd$_2$(dba)$_3$ (dba is dibenzylideneacetone) [68]. These clusters offer unique possibility to study chemistry at the Ni(0) and Pd(0) centers in a sulfide (or selenide) environment. The most intriguing aspect of the reactivity of [M$_3$M'Q$_4$(H$_2$O)$_{10}$]$^{4+}$ aqua complexes is their high affinity towards the hydrophosphoryl compounds R$_2$P(O)H (R=OH, Ph, H). The clusters induce their isomerization into the R$_2$P−OH species, and the P atom uses the lone pair released after isomerization for coordination at Ni or Pd. In this way phosphorous and hypophosphorous acids H$_3$PO$_3$, H$_3$PO$_2$, and their phenyl-substituted derivatives Ph$_2$P(O)H and Ph(OH)P(O)(H) isomerize into P(OH)$_3$, HP(OH)$_2$, PhP(OH)$_2$, and Ph$_2$POH. The high affinity of the Ni and Pd sites in the clusters for P-donors constitutes main driving force for these reactions. The ^{31}P NMR spectra provide unambiguous evidence for isomerization of the ligands. The P−H bond cleavage results in the disappearance of the ^{1}J$_{P−H}$ doublet in the case of H$_3$PO$_3$ and Ph(OH)P(O)(H) (formation of P(OH)$_3$ and PhP(OH)$_2$), or in the transformation of the triplet into the doublet (only one P−H bond remains in HP(OH)$_2$). The coordination of HP(OH)$_2$ was detected with ^{31}P NMR, by appearance of the characteristic ^{1}J$_{P−H}$ double pattern, for the following complexes listed in Table 1.

These values are in excellent agreement with the value reported for [CpRu(PPh$_3$)$_2$(HP(OH)$_2$)]$^+$ (406 Hz) . All these complexes are stable under Ar in 2–4 M HCl, except for [Mo$_3$Pd(HP(OH)$_2$)S$_4$(H$_2$O)$_9$]$^{4+}$, which in 1 h quantitatively gives the P(OH)$_3$ complex [Mo$_3$Pd(P(OH)$_3$)S$_4$(H$_2$O)$_9$]$^{4+}$. According to X-ray data, in {[W$_3$Ni(HP(OH)$_2$)Q$_4$(H$_2$O)$_9$]Cl$_4$(cuc)}·11H$_2$O coordinated HP(OH)$_2$ has the folowing geometry: Ni−P 2.128(3), P−O 1.588(11) – 1.612(12) Å.

The coordination of Ph$_2$POH and PhP(OH)$_2$ was detected for {Mo$_3$PdQ$_4$} (X=S, Se), {W$_3$PdS$_4$} and {Mo$_3$NiS$_4$} clusters.

Typical order of reactivity is Mo<W; Ni<Pd, S≈Se, which correlates with the relative stability of the M(0) oxidation state in the clusters, and Ph$_2$P(O)H>Ph(OH)P(O)H >> H$_3$PO$_3$ [68]. The nickel cluster [Mo$_3$(NiCl)S$_4$(H$_2$O)$_9$]$^{3+}$ is the least reactive and only prolonged heating afforded the complexes with HP(OH)$_2$, P(OH)$_3$, Ph$_2$P(OH), and PhP(OH)$_2$ [69]. The {W$_3$Ni} and {W$_3$Pd} clusters give much more stable complexes with the hydroxophosphines, which can be purified with cation-exchange chromatography [70]. Titration of [W$_3$NiS$_4$(H$_2$O)$_{10}$]$^{4+}$, [W$_3$NiSe$_4$(H$_2$O)$_{10}$]$^{4+}$, [W$_3$PdS$_4$(H$_2$O)$_{10}$]$^{4+}$ and [W$_3$PdSe$_4$(H$_2$O)$_{10}$]$^{4+}$ with H$_3$PO$_2$, H$_3$PO$_3$, and As(OH)$_3$ allowed spectrophotometric determination of the stability constants, listed in Table 2 [71, 72].

Kinetic studies of the reaction between [Mo$_3$PdS$_4$(H$_2$O)$_{10}$]$^{4+}$ and H$_3$PO$_2$ indicate that this reaction occurs with biphasic kinetics. The first step corresponds to the formation of a Pd−O coordinated intermediate, with *tet*-H$_3$PO$_2$ (e.g. the hydrophosphoryl tautomer) acting as the ligand. The second step corresponds to the isomerization into *pyr*-HP(OH)$_2$. The rate constants for both steps show first order dependence on C$_{H_3PO_2}$,

Table 1: Chemical shifts and constants of spin-spin interaction for [M'M$_3$(HP(OH)$_2$Q$_4$(H$_2$O)$_9$]$^{3+}$ (M=Mo, W; M'=Ni, Pd).

Cluster	δ (ppm)	^{1}J$_{P−H}$
[W$_3$Pd(HP(OH)$_2$)S$_4$(H$_2$O)$_9$]$^{4+}$	121	355
[W$_3$Ni(HP(OH)$_2$)Se$_4$(H$_2$O)$_9$]$^{4+}$	129	393
[Mo$_3$Pd(HP(OH)$_2$)S$_4$(H$_2$O)$_9$]$^{4+}$	123	405
[Mo$_3$Pd(HP(OH)$_2$)Se$_4$(H$_2$O)$_8$]$^{4+}$	119	405
[Mo$_3$Ni(HP(OH)$_2$)S$_4$(H$_2$O)$_9$]$^{4+}$	142	411

indicating the participation of another H$_3$PO$_2$ molecule in each kinetic step. The second order rate constants derived for both steps are k$_1$=(12.5 ± 0.3)×10^{-2} M^{-1}s^{-1} and k$_2$=(2.6 ± 0.1)×10^{-2} M^{-1}s^{-1}. For a better understanding of the mechanism DFT calculations were carried out and they indicate a mechanism for tautomerization of the H$_3$PO$_2$ molecule coordinated in the first step, that involves an 1,2 H-shift catalyzed by the second H$_3$PO$_2$ molecule, which is made possible by its capability for accepting a proton from a P−H bond [73].

Table 2: Formation constants for the reaction of $[M_3(PdCl)S_4(H_2O)_9]^{3+}$ (M = Mo, W) with $HP(OH)_2$, $P(OH)_3$, and $As(OH)_3$.

Cluster	Ligand (medium)	K (mol^{-1})
$[W_3(PdCl)S_4(H_2O)_9]^{3+}$	$HP(OH)_2$ (2 M HCl)	2900
$[W_3(PdCl)S_4(H_2O)_9]^{3+}$	$As(OH)_3$ (2 M HCl)	3300
$[W_3(PdCl)S_4(H_2O)_9]^{3+}$	$HP(OH)_2$ (2 M HCl)	43
$[W_3(PdCl)S_4(H_2O)_9]^{3+}$	$As(OH)_3$ (2 M HCl)	183
$[W_3(PdCl)S_4(H_2O)_9]^{3+}$	$P(OH)_3$ (4 M HCl)	20
$[W_3(PdCl)Se_4(H_2O)_9]^{3+}$	$P(OH)_3$ (4 M HCl)	3
$[W_3(NiCl)S_4(H_2O)_9]^{3+}$	$HP(OH)_2$ (2 M HCl)	22
$[W_3(NiCl)Se_4(H_2O)_9]^{3+}$	$HP(OH)_2$ (2 M HCl)	273
$[W_3(NiCl)S_4(H_2O)_9]^{3+}$	$As(OH)_3$ (2 M HCl)	36
$[W_3(NiCl)Se_4(H_2O)_9]^{3+}$	$As(OH)_3$ (2 M HCl)	1054

Coordination of H_3PO_3 to $[Mo_3(PdCl)Q_4(H_2O)_9]^{3+}$ (Q = S, Se) is also biphasic. The first, very rapid, step corresponds to coordination of the *tet*-$HP(O)(OH)_2$ through oxygen (Scheme 2), and the second step, which is slow and reversible, corresponds to isomerization into *pyr*-$P(OH)_3$ complex with the following parameters: $k_f (1.18 \pm 0.05) \cdot 10^{-4}$ M^{-1}s^{-1}, $k_b (2.3 \pm 0.25) \cdot 10^{-5}$ s^{-1} (Q = S); $k_f (3.0 \pm 0.1) \cdot 10^{-3}$ M^{-1}s^{-1}, $k_b (4.5 \pm 0.2) \cdot 10^{-3}$ s^{-1} (Q = Se) [69]. A significant difference with respect to H_3PO_2 is that the rate of the second resolved kinetic step in the tautomerization of H_3PO_3 does not depend on the H_3PO_3 concentration but on the concentration of the Hpts acid used for the control of the ionic strength. Nevertheless, a mechanism quite similar to that previously discussed for H_3PO_2 has been proposed, in which the tautomerization process involves initial protonation of the intermediate with the *tet*-H_3PO_3 with an external proton, i.e. the H-shift does not take place through the deprotonation–protonation of the O-coordinated intermediate but through its protonation–deprotonation, the initial attack being carried out by H_3O^+.

The kinetics of the reaction of $[W_3PdSe_4(H_2O)_{10}]^{4+}$ with H_3PO_2 similarly involves two steps, the first one corresponding to the substitution at Pd to form an intermediate with O-coordinated tetrahedral H_3PO_2, and the second step to the isomerization of the coordinated H_3PO_2. However, in this case both rate constants are independent on $C_{H_3PO_2}$, $k_{1obs} = (6.8 \pm 0.8) \times 10^{-2}$ s^{-1} and $k_{2obs} = (1.3 \pm 0.3) \times 10^{-3}$ s^{-1} [72]. Nevertheless, these results can be interpreted within the mechanism discussed above. In the first resolved kinetic step the substitution occurs with saturation kinetics with respect to the H_3PO_2 concentration, and tautomerization in the second resolved step occurs with a mechanism similar to that previously commented, but with the rate-determining step displaced from protonation of the O-coordinated intermediate to isomerization of the O-coordinated deprotonated intermediate with pyramidal $H_2PO_2^-$ into the more stable P-coordinated form.

The formation of the complexes was confirmed by X-ray analysis of supramolecular adducts with macrocyclic cavitand cucurbit[6]uril (($C_{36}H_{36}N_{24}O_{12}$), CUC[6]). The adducts with cucurbit[6]uril were purposefully used to crystallize the complexes out of dilute solutions by the formation of complementary hydrogen bonds between water molecules, coordinated to the cluster, and the carbonyl groups of the cavitand portals. Crystal structures were determined for $\{[Mo_3PdP(OH)_3S_4Cl_3(H_2O)_6]_2 \cdot CUC[6]\}Cl_2 \cdot nH_2O$ (Pd-P 2.26 Å) (Fig. 11), $[Mo_3Ni(P(OH)_3)S_4(H_2O)_8Cl]Cl_3 \cdot CUC[6] \cdot 14H_2O$ $[W_3Pd(P(OH)_3)S_4(H_2O)_8Cl]Cl_3 \cdot CUC[6] \cdot 12.5H_2O$, $\{[W_3Pd(PhP(OH)_2)S_4(H_2O)_7Cl_2]Cl_2\}_2 \cdot CUC[6] \cdot 9.5H_2O$ (Pd–P 2.247(5) Å), $[W_3(Ni(HP(OH)_2))Q_4(H_2O)_9]Cl_4 \cdot CUC[6] \cdot 11H_2O$ (Q = S, Se) [70–77].

The bond lengths and angles in coordinated $P(OH)_3$ can be compared with the values calculated for free $P(OH)_3$ [78]. The P–O bonds become shorter upon coordination (1.57–1.59 Å in the (Mo_3NiS_4), 1.56 Å in $\{Mo_3PdS_4\}$, and 1.54–1.60 Å in the $\{W_3PdS_4\}$ complex, instead of 1.64–1.67 Å in free $P(OH)_3$. The O–H bonds
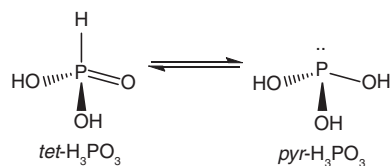
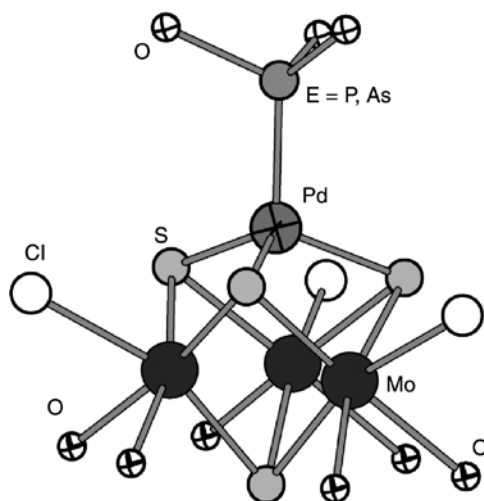**Scheme 2:** Tautomeric forms of phosphorous acid.

Fig. 11: View of $[Mo_3(PdE(OH)_3)S_4Cl_3(H_2O)_6]^+$ cluster complex.

hardly change, but there is also a tendency towards less distorted tetrahedral geometry in coordinated $P(OH)_3$ (the OPO angles are 99–105, 100–105, 100–105, and 94–105°, respectively).

It is known that free $As(OH)_3$ is present in solutions of As_2O_3 in water, but cannot be isolated. However, coordination to the Ni or Pd site allowed us to isolate first complexes with $As(OH)_3$ as As-donor ligand. The reaction of $[W_3NiSe_4(H_2O)_{10}]^{4+}$ with $As(OH)_3$ is very fast, and even $[Mo_3(NiCl)S_4(H_2O)_9]^{3+}$, despite being the least reactive of all the series, quantitatively goes into $[Mo_3(NiAs(OH)_3)S_4(H_2O)_9]^{4+}$, while for H_3PO_2 and H_3PO_3 the electronic spectra showed the presence of much unreacted $[Mo_3NiS_4(H_2O)_{10}]^{4+}$. X-ray structures were determined for $\{[Mo_3PdAs(OH)_3S_4Cl_3(H_2O)_6]_2\}\cdot CUC[6]\}Cl_2\cdot nH_2O$ (Pd–As 2.368(3) Å, As–OH 1.765(16) Å) and for $[W_3(NiAs(OH)_3)S_4(H_2O)_9]Cl_4\cdot CUC[6]\cdot 13H_2O$ (Ni–As 2.25(4) Å, As–OH 1.72–1.74 Å) [72, 75]. The apparent ease of formation and the greater stability of the $As(OH)_3$ complexes (contrary to the well-known sequence P > As > Sb >> Bi) is explained by the contribution from the highly unfavorable values of the equilibrium constants of the reactions $H_2P(O)(OH) \rightarrow HP(OH)_2$ and $HP(O)(OH)_2 \rightarrow P(OH)_3$ [71, 72, 74].

The geometry of the $PhP(OH)_2$ ligand was determined for the first time. The P–O bonds are 1.59–1.60 Å, P–C 1.760(21) Å, the two O–P–C angles are 98.1 and 102.2°, the O–P–O angle – 105.3°. Both P–O and P–C distances are considerably (by 0.05–0.07 Å) shorter than in free, non-coordinated $PhP(OR)_2$ molecules [33]. The Pd–P bond is 2.256(5) Å, that is, virtually the same as in the complex with $P(OH)_3$. The S–Pd–P angles are 114–120°. The phenyl ring plane is almost orthogonal to the Mo_3 plane in the cluster. Another example of an $RP(OH)_2$ ligand [34] is $P(OMe)(OH)_2$ found in $[Ru(P(OMe)(OH)_2)(dppe)_2]^{2+}$.

Conclusions

The symbiosis between the chalcogenide polynuclear transition metal complexes and phosphines functionalized with hydroxo groups turned out not only possible but rather fruitful. Apart from the obvious utilitarian goal (making clusters water soluble and amenable to further functionalization), this combination has allowed to reveal unexpected reactivity patterns, such as condensation of the phosphine ligands promoted by the cluster formation; pH-dependent change in the coordination mode of phosphines; and, perhaps most exciting, stabilization of such elusive species as $HP(OH)_2$, $P(OH)_3$, $As(OH)_3$ by direct coordination to cluster core. However, we feel strongly that synthetic potential of this chemistry is far from exhausted. For example, the clusters discussed in this review, are, topologically speaking, excellent platforms for making dendrimers by easy functionalization of the appended OH groups. From the point of view of fundamental chemistry, nothing is known about the reactivity of coordinated $P(OH)_3$, $HP(OH)_2$ and its analogues. Last, but not the least, catalytic activity of these clusters is waiting to be tested.

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