

## Phosphorous Acid and Arsenious Acid as Ligands

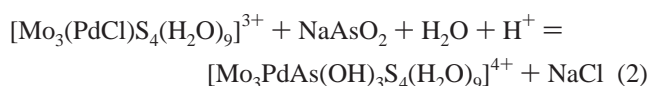
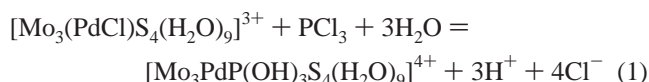
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Phosphorous acid, H<sub>3</sub>PO<sub>3</sub> (systematic name phosphonic acid), has a tetrahedral structure [HP(O)(OH)<sub>2</sub>] with one hydrogen atom attached directly to the phosphorus atom.<sup>1</sup> It is thus only dibasic, and its anions are [HPO<sub>2</sub>(OH)]<sup>-</sup> and [HPO<sub>3</sub>]<sup>2-</sup>. Only in the triesters P(OR)<sub>3</sub> is it possible to encounter phosphorus(III) atoms in an all oxygen environment, and even in such cases, there is a strong tendency to rearrange to the four-connected species [RP(O)(OR)<sub>2</sub>] (Arbuzov reaction with alkyl halides). Arsenic(III) in aqueous solutions gives arsenious acid, which is probably As(OH)<sub>3</sub>, though it has never been isolated or adequately characterized in solutions.<sup>1,2</sup>

The isolation and X-ray crystal structures of complexes of P(OH)<sub>3</sub> and As(OH)<sub>3</sub> are reported for the first time in this work. Coordination is to the Pd site of a heterometal cuboidal cluster cation with the Mo<sub>3</sub>PdS<sub>4</sub><sup>4+</sup> core.<sup>3</sup> The addition of PCl<sub>3</sub> or NaAsO<sub>2</sub> to solutions of [Mo<sub>3</sub>(PdCl)S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup> (the chloride is attached to the Pd, and the nine H<sub>2</sub>O to the 3 × Mo sites, which have less affinity for Cl<sup>-</sup>)<sup>4</sup> in HCl is accompanied by rapid color changes from blue to brown as a result of following reactions:



The formation of [Mo<sub>3</sub>PdP(OH)<sub>3</sub>S<sub>4</sub>Cl<sub>n</sub>(H<sub>2</sub>O)<sub>9-n</sub>]<sup>(4-n)+</sup> complexes in solution was appropriately monitored by <sup>31</sup>P NMR spectroscopy. Addition of 3 equiv of PCl<sub>3</sub> to a 125 mM solution of [Mo<sub>3</sub>(PdCl)S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup> in 4 M HCl at 300K causes the appearance of three unique signals (from three separate species with different *n*; δ = 116.4, 115.9, 115.3 ppm) of low intensity shifted to low field from the free [HP(O)(OH)<sub>2</sub>]. No P–H coupling is observed, confirming the disappearance of the P–H bond. The products of reactions 1 and 2 are stable in solution only in the presence of excess of P(III) and As(III). The formation of the coordinated P(OH)<sub>3</sub> requires isomerization of the [HP(O)(OH)<sub>2</sub>] form (the initial product of hydrolysis of PCl<sub>3</sub>). Though never directly observed, the isomerization to P(OH)<sub>3</sub> has been repeatedly

postulated to be the rate-determining step in numerous kinetic studies of the oxidation of [HP(O)(OH)<sub>2</sub>] with Hg(II), Ag(I), Cr(VI), V(V), and halogens.<sup>5</sup> In the arsenic case, As(OH)<sub>3</sub> is the most likely form in acidic solutions without other complexing ligands.

The crystallization of the new complexes is achieved by adding cucurbituril (C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub>) to the solution. This macrocyclic cavitand forms stable adducts with incomplete cubes [M<sub>3</sub>Q<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> (M = Mo, W; Q = S, Se)<sup>6–8</sup> and with their heterometal cuboidal derivatives, for example, with Mo/Pd cubes [Mo<sub>3</sub>(PdCl)Q<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup>.<sup>9,10</sup> The driving force is the formation of twelve complementary hydrogen bonds between the C=O groups of cucurbituril and the water molecules coordinated to the clusters. The complexes isolated in the present study have the composition {[Mo<sub>3</sub>PdP(OH)<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>(C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub>)}Cl<sub>2</sub>·20H<sub>2</sub>O (**1**) and {[Mo<sub>3</sub>PdAs(OH)<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>(C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub>)}Cl<sub>2</sub>·19H<sub>2</sub>O (**2**).<sup>11</sup>

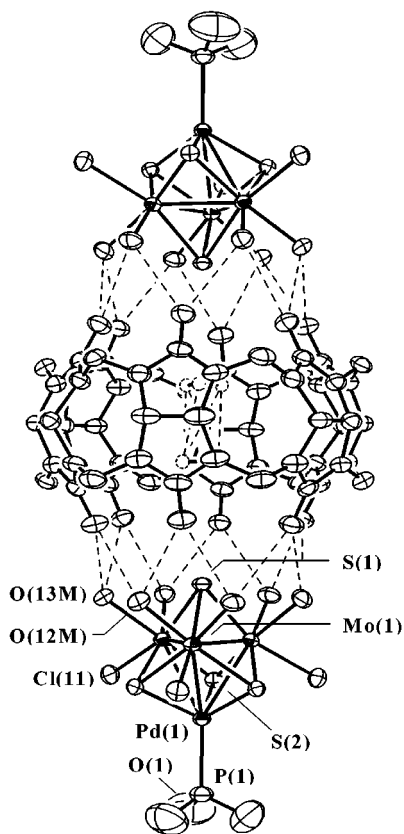
The compounds **1** and **2** appear to be isostructural.<sup>12,13</sup> The only difference is the number of water molecules inside the cucurbituril cavity: two in **1** and one in **2**. Supramolecular adduct {[Mo<sub>3</sub>PdE(OH)<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>(C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub>)}<sup>2+</sup> (where E = P (**1**) or As (**2**)) is shown in Figure 1, with important bond distances given in the figure caption. The centrosymmetric supramolecular adduct lies on the special position of space group *Pa* $\bar{3}$ , with site symmetry  $\bar{3}$ , resulting in ideal three-fold symmetry of the cluster with equivalent Mo–Mo, Mo–Pd, Pd–S, and E–O bonds. Each

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- (11) {[Mo<sub>3</sub>PdP(OH)<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>(C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub>)}Cl<sub>2</sub>·20H<sub>2</sub>O (**1**). 17 mg of PCl<sub>3</sub> was added to 5 mL of 12 mM [Mo<sub>3</sub>(PdCl)S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup> solution in 4 M HCl. Immediate color change took place from dark blue to dark brown, which was followed by the addition of 1.5 mL of 20 mM cucurbituril solution in 4 M HCl. The reaction mixture was stirred and left for 6 days at room temperature. Dark brown crystals of **1** were obtained (yield 28%). Anal. Calcd for {[Mo<sub>3</sub>PdP(OH)<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>(C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub>)}Cl<sub>2</sub>·20H<sub>2</sub>O (%): C 14.10; H 3.48; N 10.96; Cl 9.25. Found: C 14.39; H 3.05; N 11.24; Cl 9.40. {[Mo<sub>3</sub>PdAs(OH)<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>(C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub>)}Cl<sub>2</sub>·19H<sub>2</sub>O (**2**). 30 mg of NaAsO<sub>2</sub> was added to 5 mL of 47 mM [Mo<sub>3</sub>(PdCl)S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>3+</sup> solution in 4 M HCl. Immediate color change took place from dark blue to dark brown, followed by addition of 1.5 mL of 20 mM cucurbituril solution in 4M HCl. The reaction mixture was stirred and left for 3 days at room temperature. Dark brown crystals of **2** were obtained (yield 92%). Anal. Calcd for {[Mo<sub>3</sub>PdAs(OH)<sub>3</sub>S<sub>4</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>(C<sub>36</sub>H<sub>36</sub>N<sub>24</sub>O<sub>12</sub>)}Cl<sub>2</sub>·19H<sub>2</sub>O (%): C 13.79; H 3.34; N 10.72; Cl 9.04; S 8.18. Found: C 13.64; H 3.25; N 10.40; Cl 9.06; S 8.10.

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**Figure 1.** Supramolecular adduct  $\{[\text{Mo}_3\text{PdP}(\text{OH})_3\text{S}_4\text{Cl}_3(\text{H}_2\text{O})_6]_2 \cdot [(\text{H}_2\text{O})_2\text{C}_{36}\text{H}_{36}\text{N}_{24}\text{O}_{12}]\}^{2+}$  (probability ellipsoids at 50% level) with partial numeration scheme. The enumeration in **2** is similar. Main bond distances in **1** (Å): Pd(1)–Mo(1), 2.8276(12); Pd(1)–S(2), 2.356(2); Pd(1)–P(1), 2.259(4); Mo(1)–Mo(1)', 2.7599(13); Mo(1)–S(1), 2.347(2); Mo(1)–S(2), 2.323(2); Mo(1)–S(2)', 2.328(2); Mo(1)–Cl(11), 2.489(2); Mo(1)–O(12M), 2.203(6); Mo(1)–O(13M), 2.228(6); P(1)–O(1), 1.561(12). Main bond distances in **2** (Å): Pd(1)–Mo(1), 2.7995(14); Pd(1)–S(2), 2.360(3); Pd(1)–As(1), 2.368(3); Mo(1)–Mo(1)', 2.7616(18); Mo(1)–S(1), 2.333(4); Mo(1)–S(2), 2.324(3); Mo(1)–S(2)', 2.330(3); Mo(1)–Cl(11), 2.492(3); Mo(1)–O(12M), 2.217(7); Mo(1)–O(13M), 2.224(8); As(1)–O(1), 1.765(16).

Mo atom is coordinated by two  $\text{H}_2\text{O}$  molecules and one  $\text{Cl}^-$  ligand, the latter occupying position trans to the unique  $\mu_3\text{-S}$ , which caps the Mo atoms only. Six coordinated water molecules form complementary hydrogen bonds with portal oxygen atoms of cucurbituril, the  $\text{O}\cdots\text{O}$  distances being 2.809–2.953 Å in **1** and 2.754–2.873 Å in **2**.

The P–O distance in **1** (1.561(12) Å) is close to that found in crystalline  $[\text{HP}(\text{O})(\text{OH})_2]$  (1.538–1.553 Å)<sup>1</sup> and significantly

shorter than that observed in  $\text{P}(\text{OR})_3$  ethers (1.604–1.654 Å according to Cambridge Structural Database, CSD).<sup>14</sup> Our attempts to find structural information on  $\text{H}_3\text{AsO}_3$  were unsuccessful. Nevertheless, a search in the CSD revealed the structure of  $(\text{C}_3\text{H}_{12}\text{N}_2)_2[\text{H}_2\text{As}_6\text{Mo}_4\text{O}_{22}] \cdot 2\text{H}_2\text{O}$ ,<sup>15</sup> in which the  $\text{AsO}_2\text{OH}$  fragment is present, with an As–O distance of 1.801 Å. The latter is slightly longer than found in **2** (1.765(16) Å). The As–O distances in  $\text{As}(\text{OR})_3$  ethers (1.783–1.855 Å according to CSD) are also longer than in **2**. All three OH groups of the  $\text{E}(\text{OH})_3$  ligands make relatively strong hydrogen bonds with solvent water molecules, with  $\text{O}\cdots\text{O}$  distances of 2.75 Å in **1** and 2.66 Å in **2**. Though the hydrogen atoms were not directly located in both structures, it is unlikely that  $[\text{EO}_3(\text{OH})_{3-x}]^{x-}$  are present instead of  $\text{E}(\text{OH})_3$ .  $\text{As}(\text{OH})_3$  is known to be very weak acid ( $\text{p}K_1 = 9.22$ ),<sup>1a</sup> and  $\text{P}(\text{OH})_3$  is expected to be about as weak, and though some increase in acidity can take place on coordination, the acid dissociation will be suppressed in 4 M HCl.

A notable feature of both **1** and **2** is a considerable shortening of the Mo–Mo bonds in the tetrahedral unit  $\text{Mo}_3\text{Pd}$  (by 0.05–0.06 Å) compared to what is usually observed in the derivatives of  $\text{Mo}_3\text{PdS}_4^{4+}$ , where Pd is bonded to Cl, CO, alkene, or to a sulfur atom of another  $\text{Mo}_3\text{PdS}_4$  unit.<sup>2,10</sup> The Pd–P and Pd–As bonds are unexceptional, though they are on the shorter end of the Pd– $\text{E}(\text{OR})_3$  (E = P, As) bond length statistics.<sup>14</sup>

Given the ease of formation and stability of  $\text{P}(\text{OH})_3$  and  $\text{As}(\text{OH})_3$  complexes, it may be asked why it took so long to prepare and structurally characterize them. At least in the case of phosphorus, the reason may be two-fold: the stability of the  $[\text{HP}(\text{O})(\text{OH})_2]$  tautomer (which itself coordinates through its oxygens to harder metal ions, such as  $\text{Cu}(\text{H}_2\text{PO}_3)_2$ )<sup>16</sup> and possible ox-red instability of solutions with softer metals (like noble metals), whose preference to phosphorus might be expected to stabilize the  $\text{P}(\text{OH})_3$  tautomer. In one case, heating  $\text{K}_2\text{PtCl}_4$  and  $\text{H}_3\text{PO}_3$  gives  $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_2]^{2-}$ , where a new P,P' binding ligand  $[(\text{O})\text{P}(\text{OH})-\text{O}-\text{P}(\text{O})(\text{OH})]^{2-}$  results from a condensation reaction.<sup>17</sup> The present study implies that certain soft metal sites in clusters may lend themselves as better partners for coordinated  $\text{P}(\text{OH})_3$ . Indeed, solution studies show a high affinity of the palladium atom of  $\text{Mo}_3\text{PdS}_4$  clusters to phosphines.<sup>18</sup> In its coordinated form,  $\text{P}(\text{OH})_3$  may be the simplest “water-soluble” phosphine with possible applications in “water friendly” catalytic cycles.<sup>19</sup> The ability of other heterometal centers ( $\text{M}' = \text{Ni}, \text{Fe}, \text{Cu}$ ) of cuboidal clusters  $\text{M}_3\text{MQ}_4^{4+}$  (M = Mo, W; Q = S, Se) to coordinate to  $\text{E}(\text{OH})_3$  (E = P, As) is currently under study.

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**Supporting Information Available:** Tables of X-ray crystallographic data in CIF format for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) Crystal data for **1**:  $\text{C}_{36}\text{H}_{106}\text{Cl}_3\text{Mo}_6\text{N}_{24}\text{O}_{50}\text{P}_2\text{Pd}_2\text{S}_8$ , F. W. 3065.91, crystal dimensions  $0.36 \times 0.34 \times 0.32 \text{ mm}^3$ , cubic, space group  $P\bar{a}3$ ,  $a = 21.669(6)$ ,  $V = 10175(5) \text{ \AA}^3$ ,  $\rho_{\text{calcd}} = 2.001 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.7107 \text{ \AA}$ ,  $T = 212(1) \text{ K}$ . Absorption corrections were made by integration from crystal shape. A total of 3953 reflections (unique only) were collected with a STOE STADI4 diffractometer. Final refinement converged with  $R_1 = 0.0599$  and  $wR_2 = 0.1462$  against 2832 reflections with  $F_0 \geq 4\sigma(F_0)$ .
- (13) Crystal data for **2**:  $\text{C}_{36}\text{H}_{104}\text{As}_2\text{Cl}_3\text{Mo}_6\text{N}_{24}\text{O}_{49}\text{Pd}_2\text{S}_8$ , F. W. 3135.79, crystal dimensions  $0.40 \times 0.38 \times 0.35 \text{ mm}^3$ , cubic, space group  $P\bar{a}3$ ,  $a = 21.7016(12)$ ,  $V = 10220.6(10) \text{ \AA}^3$ ,  $\rho_{\text{calcd}} = 2.038 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.7107 \text{ \AA}$ ,  $T = 300(1) \text{ K}$ . Absorption corrections were made by measuring of  $\psi$ -scan curves. Crystal appeared to be a merohedry twin with twinning matrix of (0 1 0, 1 0 0, 0 0 1) and relative weights of components equal to 0.431(2):0.569(2). Total/unique 9820/3145 reflections were collected ( $R_{\text{int}} = 0.0770$ ) with a Bruker P4 diffractometer. Final refinement converged with  $R_1 = 0.0587$  and  $wR_2 = 0.1512$  against 2347 reflections with  $F_0 \geq 4\sigma(F_0)$ . The atomic displacement ellipsoids of oxygen atoms of  $\text{E}(\text{OH})_3$  groups both in **1** and **2** are relatively large and elongated in the direction perpendicular to the E–O bond, which indicates possible oscillations of these groups around the Pd–E bonds.

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