1,1-Bis(diphenylphosphinoyl)ethanol. Synthesis and complexes with neodymium and copper nitrates

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A preparative method for the synthesis of 1,1-bis(diphenylphosphinoyl)ethanol (**1**) has been elaborated. In $CHCl_3$ and MeCN solutions compound **1** is associated into H-bonded dimers ($-\Delta H \approx 12$ kcal mol^{-1}). Complexes of compound **1** with Nd^{III}, Cu^{II}, and Cu^{I} nitrates have been studed. The H-bonded dimers are retained upon complexing.

Key words: tetraphenylmethylenediphosphine dioxides; H-bonds; complexing.

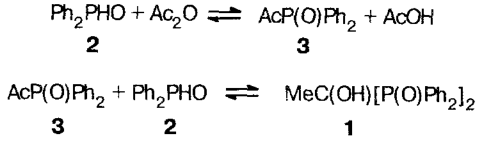
Tetraarylmethylenediphosphine dioxides, specifically their well-known representative, $Ph_2P(O)CH_2P(O)Ph_2$, are attracting the attention of scientists as efficient extractants.[1,2] However, they are not widely used due to the lack of sufficiently simple methods for their synthesis. Therefore, it was interesting to study 1,1-bis(diphenylphosphinoyl)ethanol (**1**), which is easier to synthesize than the unsubstituted analog, as a potential extractant.

The synthesis of compound **1** has been described in a number of papers.[3—7] However, in most cases this compound was not isolated in the pure state, and the presence of compound **1** in the reaction mixture was only judged from NMR spectra. Pure 1,1-bis(diphenylphosphinoyl)ethanol has been isolated by two groups of authors.[3—5] In both cases, the target product was obtained by treatment of $Ph_2P(O)H$ with Ac_2O, but the reaction conditions differed greatly. In one instance,[3] the synthesis was carried out for 6 h at 100 °C, whereas the reaction performed by the other procedure[4,5] was completed in 15 min at 40 °C. It should be noted that, according to later data,[6] heating the same mixture at 80 °C for 7 h results in complete phosphonate-phosphate rearrangement of product **1**. Thus, the second method[4,5] is likely to be the most promising and convenient and provides sufficiently pure compound **1** in high yield.

Results and Discussion

We reproduced the above procedures for the synthesis of compound **1**, and also synthesized it from *O*-methyldiphenylphosphinite by the Arbuzov reaction.[6,8] It was found that the reproduction of these procedures does not provide stable yields of the target product.

It is known that the synthesis of compound **1** from **2** and Ac_2O involves two steps and each of them is reversible.[6]



$$\underset{\mathbf{2}}{Ph_2PHO} + Ac_2O \rightleftharpoons \underset{\mathbf{3}}{AcP(O)Ph_2} + AcOH$$

$$\underset{\mathbf{3}}{AcP(O)Ph_2} + \underset{\mathbf{2}}{Ph_2PHO} \rightleftharpoons \underset{\mathbf{1}}{MeC(OH)[P(O)Ph_2]_2}$$

Compound **3**, $AcP(O)Ph_2$, which is unstable at room temperature and undergoes hydrolysis extremely readily, is formed at the first step. The second step involves the addition of compound **2** to **3** resulting in the target product **1**.

We assumed that the difficulties in reproducing the synthesis of compound **1** arose from the fact that acids and bases catalyze the decomposition of acetylphosphine oxide **3**. In fact, a series of experiments carried out in a NMR tube demonstrated that the ^{31}P NMR signal of compound **1** (δ 32.9) disappears almost completely several minutes after the addition of two or three drops of Et_3N to a solution of compound **1** in dry $CHCl_3$ or after passing dry HCl through the solution at room temperature. Instead, an intense signal of compound **2** appears (δ 21.4, $J_{P,H}$ = 480 Hz). It could be assumed that performing the reaction in a buffer system would hinder the side processes, and precipitation of compound **1**, which is poorly soluble in ether, would shift the equilibrium in the desired direction.

In fact, when an ethereal solution of compound **2**, Ac_2O, and pyridine (or α-picoline) in the molar ratio 2 : 4 : 1 is kept at room temperature under argon, compound **1** precipitates. This precipitate (yield ~66 %) has m.p. 158—160 °C after thorough washing with dry ether without recrystallization. According to ^{31}P NMR

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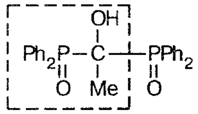
spectral data, the product contains ~5 % of compound **2**. The content of the admixture does not decrease after recrystallization of the precipitate from benzene or ethanol, but the yield of the target product decreases sharply, probably due to the instability of compound **1** when boiled in the solvents used. When a solution of compound **1** in dry $CHCl_3$ is kept in a sealed tube at room temperature for several days, the content of compounds **1** and **2** does not change. However, if air moisture is present, the content of **1** decreases slowly (in several days) and the concentration of compound **2** increases. Furthermore, a weak signal of Ph_2POOH appears in the ^{31}P NMR spectrum (probably, due to the oxidation of compound **2**).

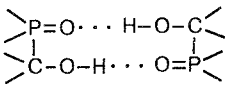
IR spectra and hydrogen bonds of 1,1-bis(diphenylphosphinoyl)ethanol. A molecule of compound **1** contains three functional groups, namely, two P=O groups and one OH group, which can be involved in hydrogen bond formation.



$$\begin{array}{ccccc} & & OH & & \\ & & | & & \\ Ph_2P & - & C & - & PPh_2 \\ \| & & | & & \| \\ O & & Me & & O \end{array}$$

1

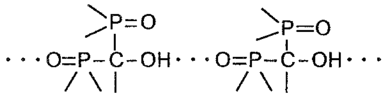
A molecule of compound **1** contains an α-hydroxyphosphoryl moiety (marked with a dashed line), whose H-bonds have been studied in detail.[9] It has been found that these compounds in solution are associated into dimers.



$$\begin{array}{l} >P{=}O\cdots H{-}O{-}C< \\ \;\;| \qquad\qquad\quad | \\ >C{-}O{-}H\cdots O{=}P< \end{array}$$

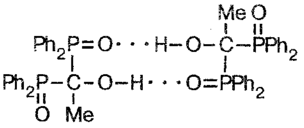
The IR spectra of these dimers are characterized by an intense band corresponding to OH group vibrations (3200—3300 cm^{-1}).

The OH group vibration region in the IR spectrum of solid compound **1** contains an intense broad band at ~3100 cm^{-1} and a less intense band at ~2750 cm^{-1} (an AB structure of the OH-band). Deformation OH vibrations are represented by an intense band at ~1370 cm^{-1}. The PO vibration region in the IR spectrum of compound **1** contains two bands at 1195 and 1180 cm^{-1}; the former band corresponds to the stretching vibrations of free P=O groups while the latter band is associated with the vibrations of P=O groups involved in intramolecular O—H···O=P H-bonds. These data imply association involving only one P=O group, while the other P=O group remains free.



$$\cdots O{=}\underset{/\,\backslash}{P}{-}\underset{|}{\overset{>P=O}{C}}{-}OH\cdots O{=}\underset{/\,\backslash}{P}{-}\underset{|}{\overset{>P=O}{C}}{-}OH\cdots$$

The band related to the intramolecular H-bond (ν(OH) 3100 cm^{-1}) in the IR spectrum of a solution of compound **1** in $CHCl_3$ disappears when the solution is diluted. Instead, a band at 3400 cm^{-1} appears, which is typical of dimeric association.[9] At the same time, the δ(OH) band is shifted towards lower frequencies (1350 cm^{-1}), which indicates the weakening of the H-bonds in the dimer. No bands of free OH group vibrations (~3580 cm^{-1}) were observed in the spectra of solutions of compound **1**. Two bands remained in the region of PO vibrations (1190 and 1170 cm^{-1}). The band at 1190 cm^{-1} corresponds to vibrations of free P=O groups, while the band at 1170 cm^{-1} refers to the P=O groups involved in the H-bonds in the dimer. These spectroscopic data imply that compound **1** in solutions is associated into dimers (**A**), similarly to the association of α-hydroxyphosphoryl compounds.[9]



$$\begin{array}{l} Ph_2P{=}O\cdots H{-}O{-}\overset{Me\;\;O}{\underset{|}{\overset{|}{C}}{-}\overset{\|}{P}Ph_2} \\ Ph_2\underset{\|}{\overset{|}{P}}{-}\underset{|}{C}{-}O{-}H\cdots O{=}PPh_2 \\ \;\;\;O\quad\; Me \end{array}$$

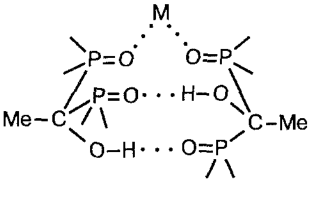
A

We have previously established a relationship between the shift of P=O vibration frequency and the enthalpy of the H-bonds in H-complexes of phosphoryl compounds.[10]

$$-\Delta H = (-0.41 \pm 0.71) + (57.2 \pm 2.87)\,\frac{\nu_1^2 - \nu^2}{\nu_1^2 - \nu_2^2}$$

Here ν_1 and ν are the vibration frequencies of a free P=O group and that in an H-complex, respectively; the value ν_2 = 987 cm^{-1} has been accepted for a protonated phosphoryl group. Using this equation and the vibration frequencies for the P=O groups (ν_1 = 1190 cm^{-1}, ν = 1170 cm^{-1}), we estimated the enthalpy of one H-bond in the dimer **A** (~6 kcal mol^{-1}). The value of Δν(PO) in the spectrum of a solution of compound **1** equals to 20 cm^{-1}. The same value of Δν(PO) has been found for H-complexes of triphenylphosphine oxide with phenol.[10] It thus follows that the acidity of the OH group in compound **1** is similar to p*K* of phenol.

IR spectra and structure of complexes in solutions. The following complexes of compound **1** (L) with neodymium and copper nitrates were obtained: $L_2Nd(NO_3)_3 \cdot 2H_2O$ (**4**), $L \cdot Cu(NO_3)_2$ (**5**), $L \cdot CuNO_3 \cdot H_2O$ (**6**), and $L_2 \cdot Cu(NO_3)_2$ (**7**). The IR spectra of these complexes in MeCN and $CHCl_3$ contain intense bands ν(OH) 3300 cm^{-1}, δ(OH) 1350 cm^{-1}, and ν(P=O) 1160—1170 cm^{-1}, which are similar to those in the spectrum of dimer **A**. Therefore, it is believed that the dimeric structure of the ligand is also retained in the solutions of the complexes. An analysis of molecular models allows us to suggest the general structure (**B**) for the complexes with a specific boat-like conformation of the cycle.

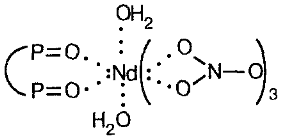


B

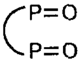
Each molecule of compound **1** in the structure of complex **B** is monodentate.

The IR spectrum of complex **4** contains intense bands of NO_3^- group vibrations* (ν_5 = 1490 cm^{-1}, ν_1 = 1300 cm^{-1}); the bands are separated by 190 cm^{-1}, which is known to imply the bidentate chelate coordination of NO_3^- groups.[11] The region of P=O vibrations in the spectrum contains two intense bands. One band is at 1175 cm^{-1}, which almost coincides with the P=O band of dimer **B** (P=O···HO, 1170 cm^{-1}). The other band corresponding to vibrations of free P=O groups is displaced upon coordination with Nd^{3+} from 1190 to 1165 cm^{-1}. The spectrum of complex **4** also contains absorption bands of the coordinated water molecule ($H_2O\cdots Nd^{3+}$): $\nu(H_2O)$ ~3450 cm^{-1} and $\delta(H_2O)$ 1650 cm^{-1}.

An X-ray diffraction analysis[12] of an analogous nitrate complex of Nd^{3+} showed that the coordination polyhedron of the metal consists of ten oxygen atoms and that the NO_3^- groups behave as if they were bidentate. Taking these results and the spectroscopic analysis data into account, structure **C** can be suggested for complex **4**.



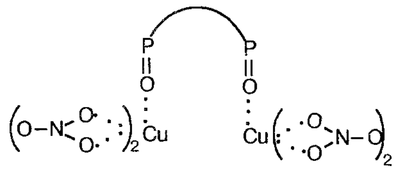
C

Here  denotes free P=O groups in dimer **A**.

The ^{31}P NMR spectrum of complex **4** in MeCN at room temperature contains a broadened signal at δ 86.4 shifted downfield in comparison with the signal of free ligand **1** (δ 32.9), probably due to a decrease in the electron density at the phosphorus atoms of the ligand involved in coordination.[13]

The IR spectrum of complex **5** contains intense vibration bands of the NO_3^- groups (ν_5 = 1490 cm^{-1}, ν_1 = 1295 cm^{-1}); the band separation (195 cm^{-1}) is typical of bidentate coordination[11] of NO_3^- groups. The region of PO-vibrations contains two bands at 1160 and 1140 cm^{-1}. The former band relates to P=O groups involved in the H-bonds in dimer **B**, while the latter one corresponds to vibrations of P=O groups coordinated to copper (P=O···Cu^{2+}).

The visible region of the spectra of copper complexes contains bands of d—d transitions.[14] The spectrum of a solution of complex **5** in $CHCl_3$ displays a d—d transition band at ~820 nm corresponding to a tetragonal complex with a rather strong axial bond. It is known that the shortest-wave transition (~500 nm) is observed in the case of planar-square complexes, while an increase in axial interaction results in a regular increase in wavelength corresponding to the d—d transition.[14,15] Taking into account the parameters of the IR and electron spectra, structure **D** can be suggested for complex **5**.

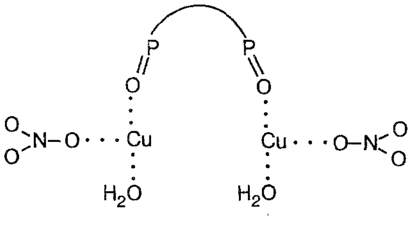


D

Dissolution of compound **5** in ethanol immediately results in a white voluminous precipitate of complex **6**. Its ^{31}P NMR spectrum (in DMF) contains one narrow signal at 76.6 ppm which, as in the spectrum of complex **4**, is shifted downfield compared to the signal of the original ligand. This reflects the participation of the P=O groups in complexing.[13]

The IR spectrum of complex **6** (KBr pellets) contains intense bands corresponding to vibrations of NO_3^- groups (ν_5 = 1415 cm^{-1}, ν_1 = 1300 cm^{-1}). The band separation is 115 cm^{-1}, which is typical of monodentate coordination[11] of NO_3^- groups. The presence of two bands of P=O group vibrations (1162 and 1135 cm^{-1}) is due to their coordination with the OH group of ligand **1** and with Cu^+, respectively. The spectrum of complex **6** also contains absorption bands typical of coordinated water ($H_2O\cdots Cu^+$): $\nu(H_2O)$ ~3420 cm^{-1}, $\delta(H_2O)$ 1650 cm^{-1}.

According to the IR spectroscopic data, structure **E** can be suggested for complex **6**.



E

According to the IR spectrum (KBr pellets), complex **7** contains NO_3^- groups of two types: monodentate groups (ν_5 = 1415 cm^{-1}, ν_1 = 1300 cm^{-1}) and bidentate groups (ν_5 = 1470 cm^{-1}, ν_1 = 1300 cm^{-1}). Two bands of P=O group vibrations (1160 and

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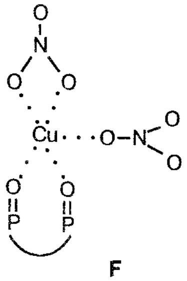
* For notations see Ref. 11.

1135 cm^{-1}) characterize their coordination with the OH group and with Cu^+, respectively.

Probably, complex **7** can be represented as structure **F**.



F

Dissolution of complex **7** in ethanol is accompanied by its decomposition to give cupric diphenylphosphinate, $(Ph_2PO_2)_2Cu$. The IR spectrum of the salt contains two intense bands of PO group vibrations, ν_{as} 1130 cm^{-1} and ν_s 1060 cm^{-1}, typical of salts of phosphorus-based acids.[16] This salt was also obtained from diphenylphosphinic acid and copper(II) nitrate. The spectra of both samples turned out to be identical.

It should be noted that complex **5**, unlike **7**, does not decompose in ethanol, but transforms into complex **6**; this is accompanied by reduction of Cu^{2+} into Cu^+. Possibly, this difference is due to the lower stability of complex **7**, which contains a monodentate NO_3^- group (structure **F**) that dissociates more readily in ethanol, thus decreasing the stability of complex **7** (in comparison to **5**).

Thus, a specific feature of the complexes studied is the simultaneous coordination of P=O with the metal and with OH groups of the ligand. Furthermore, complexing does not destroy the H-bonds of the ligand dimeric structure.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer (KBr pellets, solutions in $CHCl_3$ and in MeCN). ^{31}P NMR spectra were recorded on a Bruker HX-90 spectrometer (85 % H_3PO_4 as the external standard). Spectra in the visible region were recorded on a Specord UV-VIS M-40 spectrophotometer.

1,1-Bis(diphenylphosphinoyl)ethanol (1). Dry ether (60 mL) was added in an argon atmosphere to an overcooled (~35 °C) melt of diphenylphosphine oxide (3.0 g, 15 mmol), and the mixture was stirred for 2—3 min until complete dissolution occurred, then Ac_2O (3.1 g, 30 mmol) and pyridine (0.6 g, 7.5 mmol) were added at 25 °C with stirring. After 4 days the precipitate that formed was filtered off under argon, washed with dry ether (3×15 mL), and dried *in vacuo* over P_2O_5 to give 2.2 g of compound **1** (yield 67.5 %), m.p. 158—160 °C (*cf.* Refs. 3, 5: 159—160 °C, 159 °C). Found (%): C, 69.96; H, 5.30; P, 13.78. $C_{26}H_{24}O_3P_2$. Calculated (%): C, 69.95; H, 5.42; P, 13.88.

$L_2 \cdot Nd(NO_3)_3 \cdot 2H_2O$ complex (4). A solution of compound **1** (0.2 g, 0.45 mmol) in $CHCl_3$ was mixed with a solution of $Nd(NO_3)_3 \cdot 6H_2O$ (0.0959 g, 0.45 mmol) in acetone. A small amount of dry ether was added. The precipitate of complex **4** that formed after some time was filtered off, washed with ether, and dried *in vacuo* over P_2O_5. Found (%): N, 3.25; P, 9.45. $C_{52}H_{52}N_3NdO_{17}P_4$. Calculated (%): N, 3.34; P, 9.83.

The complexes with $Cu(NO_3)_2 \cdot 3H_2O$ were obtained in a similar way.

$L \cdot Cu(NO_3)_2$ complex (5). Found (%): C, 50.29; H, 3.73; N, 4.43; P, 9.86. $C_{26}H_{24}CuN_2O_9P_2$. Calculated (%): C, 50.54; H, 3.91; N, 4.53; P, 10.28.

$L_2 \cdot Cu(NO_3)_2$ complex (7). Found (%): C, 57.42; H, 4.66; P, 11.26. $C_{52}H_{48}CuN_2O_{12}P_4$. Calculated (%): C, 57.80; H, 4.48; P, 11.46.

$L \cdot CuNO_3 \cdot H_2O$ complex (6). Dissolution of complex **5** in ethanol immediately resulted in a voluminous precipitate, which was filtered off and dried *in vacuo* over P_2O_5. Found (%): N, 2.35; P, 10.98. $C_{26}H_{26}CuNO_6P_2$. Calculated (%): N, 2.34; P, 10.36.

Cupric diphenylphosphinate. A solution of diphenylphosphinic acid (0.2005 g, 0.92 mmol) in ethanol was mixed with a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.1108 g, 0.46 mmol) in ethanol, and a small amount of dry ether was added. The precipitate that formed after some time was filtered off, washed with ether, and dried *in vacuo* over P_2O_5. Found (%): C, 57.92; H, 3.97; P, 12.44. $C_{24}H_{20}CuO_4P_2$. Calculated (%): C, 57.89; H, 4.05; P, 12.44.

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