

Potassium Tetraphenylimidodiphosphate Complex of 1,4,7,10,13,16-Hexaoxacyclooctadecane An Inorganic (Carbon-Free) Chelate Ring

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Summary. Potassium tetraphenylimidodiphosphate, $[K][Ph_2P(O)NP(O)Ph_2]$, reacts with 18-crown-6 ether to give the monohydrated complex $[K(18\text{-crown-6})][Ph_2P(O)NP(O)Ph_2] \cdot H_2O$. The compound shows an interaction potassium–oxygen, forming an inorganic (carbon free) chelate ring and it is different to the sulphur homolog which has no interaction cation–anion.

Keywords. Alkaline complexes; Crown ether complexes; Imidodiphosphate chelates; Inorganic rings; Phosphazene heterocycles.

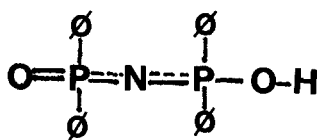
Kaliumtetraphenylimidodiphosphinat-Komplex von 1,4,7,10,13,16-Hexaoxacyclooctadecan. Ein anorganischer (Kohlenstoff-freier) Chelat-Ring

Zusammenfassung. Kaliumtetraphenylimidodiphosphinat, $[K][Ph_2P(O)NP(O)Ph_2]$, reagiert mit 18-Krone-6-ether unter Ausbildung des monohydratisierten Komplexes $[K(18\text{-Krone-6})][Ph_2P(O)NP(O)Ph_2] \cdot H_2O$. Die Verbindung zeigt eine Kalium–Sauerstoff-Wechselwirkung unter Formierung eines anorganischen (Kohlenstoff-freien) Chelat-Ringes. Dies ist im Gegensatz zum Schwefel-Analogen, das keine Kation–Anion-Wechselwirkung zeigt.

Introduction

Bis(diphenylphosphinoyl)amine, [according to IUPAC, N-(P, P-diphenylphosphinoyl)-P, P-diphenylphosphinimidic acid], **1**, and its sulphur analog are powerful β -difunctional ligands, sterically unencumbered about the donor atom, and ideal to study the variations in stereochemistry of metal complexes through the formation of inorganic (carbon free) chelate rings [1].

The alkali salts from **1**, $[M][(Ph_2P(O)NP(O)Ph_2)]$ (M = alkaline ion) have been mainly used to prepare O-bonded complexes with transition and representative ions including: Be [3], Al [4], Ga [5], In [6], Tl [5], Si, Ge [7, 8], Sn [8, 9], Bi [10], Mn [4], Co, Ni [6, 11], Cu [12], Zn [13], Cd, Hg [6], La, Pr, Nd, Eu [14, 15], Mo [16] $[UO_2]$ [4], $[ReO]$ [2]. Recently, there has been an increasing interest in the study of the structures of this kind of complexes and some X-ray determinations have been carried out [2, 8, 15, 16]. The structure of the free ligand has also been determined [17].



1

The alkaline salts of the sulphur homolog of **1**, $[M][Ph_2P(S)NP(S)Ph_2]$, have been subjected to some studies. In this way Schmidpeter reported the lithium dioxan and *THF* adducts, as well as the potassium and ammonium derivatives [18], and McQuillan the IR of the potassium salt [19]. The structure of the free anion in the potassium complex with 1,4,7,10,13,16-Hexaoxacyclo-octadecane, (18-crown-6), $[K(18\text{-crown-6})][Ph_2P(S)NP(S)Ph_2]$ is also known [20].

1 has a very interesting and surprising structure. Previous to its X-ray structure determination [17] it was formulated as a compound with N–H bond [21] or as a molecule with the presence of a non-linear cyclic tautomer [22]. However, the crystal structure determination showed a linear PNP structure, with a symmetric OH–O hydrogen bridge, short PN bonds and long PO distances. It is interesting to note that there are very few examples of compounds with a 180° PNP angle [17].

In spite of the increasing interest in complexes with **1**, almost nothing is known about their alkaline derivatives. Since the sulphur homolog in its 18-crown-6 potassium complex shows a free anion [20] without potassium–sulphur interaction and a PNP angle of $132.8(2)^\circ$ very similar with that of the free ligand [17], $[132.62(11)^\circ]$ and no strong band in the IR which could be attributed to the P_2N vibration, we undertook the present investigation in order to know a) if the $[K(18\text{-crown-6})][Ph_2P(O)NP(O)Ph_2]$ complex also shows the linear PNP arrangement of **1** as a free anion or if it is non-linear; b) if the compound is molecular with the presence of a chelate ring; c) to compare the IR spectrum with the corresponding sulphur derivative, and d) to help in structural and chemical comparisons with recently reported structural determinations.

Results and Discussion

The prepared complex, $[K(18\text{-crown-6})][Ph_2P(O)NP(O)Ph_2] \cdot H_2O$, is an air-stable solid, ready soluble in solvents such as *EtOH*, $CHCl_3$, acetone, but insoluble in H_2O and hexane. The analytical data indicate a 1:1:1 relation potassium tetraphenylimidodiphosphinato- crown ether. The ^{31}P spectrum shows a single resonance, -12.2 ppm, not very far from the corresponding value of the $[K][Ph_2P(O)NP(O)Ph_2]$, -10.5 ppm [10]. The IR spectrum presents a similar pattern to the potassium salt with a strong band appearing at ca. 1210 cm^{-1} . It is known that this band is diagnostic for chelate complexes of the type $M_a[N(XPPh_2)_2]_b$ ($X = O, S$) and is related with the “fosfazene” vibration P_2N . The IR suggests a different structure to that of $[K(18\text{-crown-6})][Ph_2P(S)NP(S)Ph_2]$.

The X-ray structural determination showed the presence of a monohydrated inorganic (carbon free) chelate complex, that is a distinct molecule. The potassium ion is directly coordinated by the six O atoms of the crown ether, the two O atoms of the bidentate anion $[Ph_2P(O)]_2N$ and the O atom of a H_2O molecule (Fig. 1).

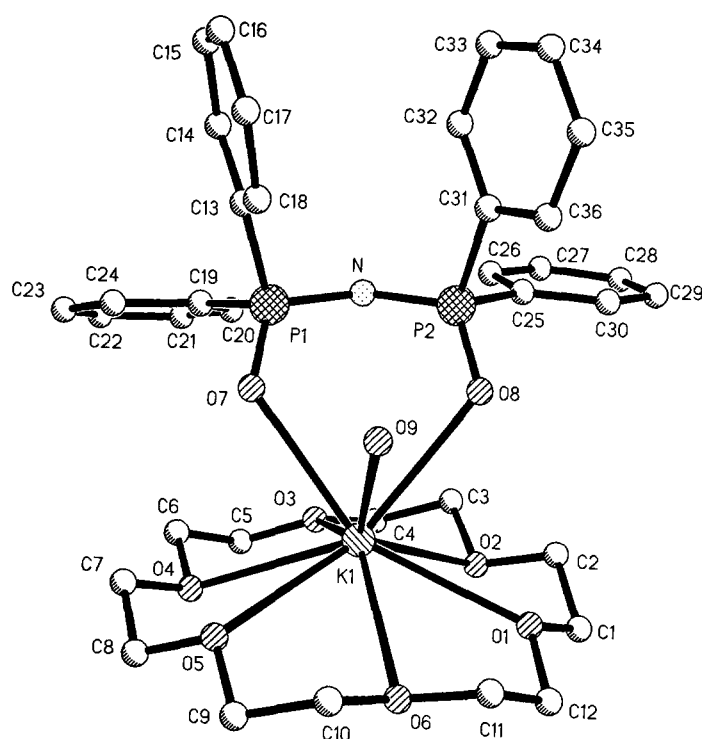


Fig. 1. X-Ray structure of $[K(18\text{-crown-}6)][Ph_2P(O)NP(O)Ph_2] \cdot H_2O$

Table 1. Selected bond lengths [\AA] with estimated standard deviations in parentheses for $[K(18\text{-crown-}6)][Ph_2P(O)NP(O)Ph_2] \cdot H_2O$

K(1)–O(1)	2.905(4)	K(1)–O(2)	3.037(5)
K(1)–O(3)	2.921(4)	K(1)–O(4)	2.991(5)
K(1)–O(5)	2.950(5)	K(1)–O(6)	2.983(5)
K(1)–O(7)	2.832(5)	K(1)–O(8)	2.925(4)
K(1)–O(9)	3.110(5)	P(1)–N	1.592(4)
P(2)–N	1.585(4)	P(1)–O(7)	1.503(3)
P(2)–O(8)	1.496(4)	P(1)–C(13)	1.819(5)
P(1)–C(19)	1.820(5)	P(2)–C(25)	1.819(5)
P(2)–C(31)	1.819(6)		

Table 2. Selected bond angles [$^\circ$] with estimated standard deviations in parentheses for $[K(18\text{-crown-}6)][Ph_2P(O)NP(O)Ph_2] \cdot H_2O$

O(7)–K(1)–O(8)	73.5(1)	P(1)–N–P(2)	129.3(3)
N–P(1)–O(7)	118.8(2)	N–P(2)–O(8)	119.3(2)
K(1)–O(7)–P(1)	117.1(2)	K(1)–O(8)–P(2)	116.8(2)
O(7)–P(1)–C(13)	109.0(2)	O(7)–P(1)–C(19)	109.2(2)
O(8)–P(2)–C(25)	109.5(2)	O(8)–P(2)–C(31)	109.2(2)
C(13)–P(1)–C(19)	106.2(2)	C(25)–P(2)–C(31)	102.1(2)

Table 1 presents selected bond lengths and Table 2 selected bond angles. The $Ph_2P(O)NP(O)Ph_2$ moiety has a fosfazene angle PNP of $129.3(3)^\circ$ similar with that found in other chelate complexes with the title ligand [2, 8, 15, 16]. The two distances P–N are identical and the two P–O are slightly different. The angles around the phosphorous indicate a tetrahedral arrangement. The P–C distances are consistently larger than those found in other complexes [2] and in the free ligand, and correspond with the value of 1.82 \AA present in PPh_3 . The structural situation of the moiety K(18-crown-6) shows the six macrocyclic O atoms in a situation roughly coplanar, forming a least-squares plane (l.s.p.) with an average deviation of 0.20 \AA and maximum deviation 0.27 \AA for O(5). The K ion lies 1.05 \AA above the plane of the ether O atoms, and the O(7), O(8), O(9) plane is practically parallel to the l.s.p. of the crown ether (dihedral angle of 2°).

There is a similar chelate complex to the one described here: potassium-(18-crown-6)-ethylacetoacetate enolate [24]. In this compound the potassium is also bound to both oxygens of the enolate atoms and to the six O atoms of the crown. The K–O(chelate) bond lengths in $[K(18\text{-crown-6})][Ph_2(O)NP(O)Ph_2] \cdot H_2O$, are slightly longer [$2.832(3)$ and $2.925(4) \text{ \AA}$] than those present in the ethylacetoacetate derivative [2.651 and 2.733 \AA] [24].

$[K(18\text{-crown-6})][Ph_2P(O)NP(O)Ph_2] \cdot H_2O$ presents a totally different structure to the sulphur derivative, it shows an interaction $Ph_2P(O)NP(O)Ph_2$ -metal and a *cis* situation. The six bonds K–O(crown ether) are not equivalent [$2.905(4)$ – $3.037(5) \text{ \AA}$]. This fact and the 1.05 \AA separation of the potassium above the plane of the oxygens of the crown ether prove the existence of a strong interaction anion–cation. The different behaviour of the crown ether metal complexes with sulphur and oxygen anions is known from other systems: KNCS is charge separated through effective complexation with 18-crown-6 [25], while K_2MoO_4 only partially so [26]. The stronger K–O bond, as well as the chelate effect, are responsible for the different behaviour of the $[K(18\text{-crown-ether})][(Ph_2P(X)NP(X)Ph_2)]$ ($X = O, S$).

Experimental Part

All chemicals were of reagent grade and were used without further purification. Bis(diphenylphosphinoyl)amine was synthesized via methods already reported in the Ref. [23], its potassium salt, $K[Ph_2P(O)NP(O)Ph_2]$, was synthesized following Ref. [14].

Monohydrated Potassium (1,4,7,10,13,16-Hexaoxacyclooctadecane)-N-(P,P-diphenylphosphinoyl)-P,P-diphenyl phosphinimidate, $[K(18\text{-crown-6})][Ph_2P(O)NP(O)Ph_2] \cdot H_2O$

$[K][Ph_2P(O)NP(O)Ph_2]$ (0.455 g, 1 mmol) was dissolved in 25 ml methanol and was added to a solution of 18-crown-6 ether (0.264 g, 1 mmol) in 10 ml methanol. After stirring for one hour, the volume of the solution was reduced in vacuum at room temperature, until a solid began to precipitate. The reaction mixture was cooled in ice, the white solid was filtered and dried in air. Yield: 0.6 g (85%). Analysis for $C_{36}H_{46}K_1P_2N_1O_9$ (737.81): calcd. C 58.61, H 6.28, N 1.90; found C 58.55, H 6.25, N 1.85.

X-Ray Structure Determination

Crystal data: $C_{36}H_{46}K_1P_2N_1O_9$, mol. wt. 737.81, orthorhombic, $P2_12_12_1$, $a = 10.130(3)$, $b = 15.492(5)$, $c = 24.092(7) \text{ \AA}$, $v = 3781(1) \text{ \AA}^3$, $z = 4$, $D_x = 1.296 \text{ g cm}^{-3}$, $MoK\alpha$, $\lambda = 0.71069$, $\mu = 2.7 \text{ cm}^{-1}$, $F(000) = 1560.0$, $T = 295 \text{ K}$, $R = 0.030$ for 2111 unique observed reflections.

A colourless crystal of $0.28 \times 0.31 \times 0.34$ mm was used for measurements with a Enraf–Nonius CAD-4 diffractometer; graphite-monochromate MoK α radiation, ω/Θ scan technique, $2\Theta_{\max}$ 60°. Cell parameters were determined from a least-squares fitting of 24 reflections, $24 < 2\Theta < 28^\circ$. Crystal and instrument stability were monitored by remeasurement of two check reflections every 2 h: $2\ 9\ 2$ and $0\ \bar{2}\ 15$. Range in hkl : h 0 to 14, k 0 to 21, l 0 to 33. 5834 reflections measured, 2111 independent reflections with $I > 2\sigma(I)$ used for refinement. No absorption correction applied because of the small value of the μ .

Positions of K and two P-atoms were revealed by the Patterson method, positions of other non-H atoms were determined in three subsequent difference maps. The H atoms were positioned according to the idealized geometry with $d(C-H) = 0.96 \text{ \AA}$ and isotropic $U = 0.10 \text{ \AA}^2$. All non-H atoms were refined anisotropically using the block-diagonal least squares method with a total of 442 variables; $R = 0.030$ (with unit weight), $S = 1.21$. The H-atoms for the H₂O molecule were not localized. Atomic scattering factors from International Tables for X-ray Crystallography (1974). Structure solution using SHELXTL PC.

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References

- [1] Haiduc I., Silaghi-Dumitrescu I. (1986) *Coord. Chem. Rev.* **74**: 127
- [2] Rossi R., Marchi A., Magon L., Casellato U., Tamburini S., Graziani R. (1991) *J. Chem. Soc. Dalton Trans* 263
- [3] Paciorek K. L., Kratzer R. H. (1966) *Inorg. Chem.* **5**: 189
- [4] Haiduc I., Botha V. P., Ziegler A. (000) 1er Symposium International de Chimie Hétérocyclique Minérale. Besançon 1975. Cited in Ref. 1
- [5] Cea-Olivares R. and Zimbrón A. unpublished results
- [6] Cea-Olivares R., Toscano R. A., Carreón G., Valdés-Martínez J. (1992) *Monatsh. Chem.* **123**: 391
- [7] Schmidpeter A., Stoll K. (1968) *Angew. Chem.* **80**: 558. *Intern. Ed. Engl.* (1968) **7**: 549
- [8] Schmidpeter A., Stoll K. (1967) *Angew. Chem.* **79**: 242. (1967) *Intern. Ed. Engl.* **7**: 252
- [9] Day R. O., Holmes R. R., Schmidpeter A., Stoll K., Howe L. (1991) *Chem. Ber.* **124**: 2443
- [10] Williams D. J. (1980) *Inorg. Nucl. Chem. Lett.* **16**: 189
- [11] Davison A., Switkes E. S. (1971) *Inorg. Chem.* **10**: 837
- [12] Keller H. J., Schmidpeter A. (1967) *Z. Naturforsch.* **22B**: 231
- [13] Schmidpeter A., Böhm R., Groeger H. (1964) *Angew. Chem.* **76**: 860. (1964) *Intern. Ed. Engl.* **3**: 704
- [14] Rodríguez I., Alvarez C., Gómez-Lara J., Cea-Olivares R. (1985–1986) *Lanthanide Actinide Res.* **1**: 253
- [15] Rodríguez I., Alvarez C., Gómez-Lara J., Toscano R. A., Platzer N., Mulheim C., Rudler H., Cea-Olivares R. (1987) *J. Chem. Soc., Chem. Commun.* 1502
- [16] Rietzel M., Roesky H. W., Katti K. V., Schmidt H. G., Herbst-Irmer R., Noltemeyer M., Sheldrick M., Symons M. C. R., Abu-Raqabah A. (1991) *J. Chem. Soc., Dalton Trans.* 263
- [17] Nöth H. (1982) *Z. Naturforsch.* **37B**: 1491
- [18] Schmidpeter A., Groeger H. (1966) *Z. Anorg. Allg. Chem.* **345**: 106
- [19] McQuillan G. P., Oxtton I. A. (1982) *Inorg. Chim. Acta.* **29**: 69
- [20] Cea-Olivares R., Nöth H. (1987) *Z. Naturforsch.* **42B**: 1507
- [21] Korshak V. V., Gribova I. A., Artamanova T. V., Bushmarina A. N. (1960) *Vysokomol. Soed.* **2**: 377. Cited in Schmulbach C. D. (1962) *Progr. Inorg. Chem.* **4**: 1975

- [22] Fluck E., Goldmann F. L. (1963) *Chem. Ber.* **96**: 3091
- [23] Wang F. T. Najdzionek J., Leneker K. L., Wasserman H., Braitsch D. M. (1987) *Synth. React. Inorg. Met.-Org. Chem.* **8**: 119
- [24] Riche C., Pascard-Billy C., Cambillau C., Bram G. (1977) *J. Chem. Soc., Chem. Comm.* 183
- [25] Seiler P., Dobler M., Dunitz J. D. (1974) *Acta Cryst.* **30B**: 2744
- [26] Nagano O. (1979) *Acta Cryst.* **35B**: 464

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