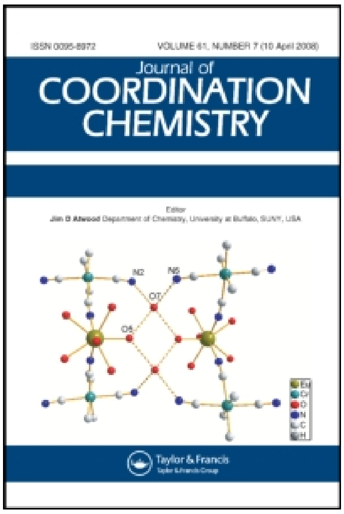

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Synthesis, Crystal and Molecular Structure of Tetrapyrrolidinyl PNP-lariat Ether Complex with Ki(H_2O)$_2$ Monohydrate

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SYNTHESIS, CRYSTAL AND MOLECULAR STRUCTURE OF TETRAPYRROLIDINYL PNP-LARIAT ETHER COMPLEX WITH $KI(H_2O)_2$ MONOHYDRATE

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The crystal and molecular structure of the title compound, $C_{24}H_{50}N_7O_8IKP_3$ crystallizing in $P2_1/c$ space group has been determined. The oxygen atoms of the crown ether exist in an almost ideal envelope conformation. The inorganic cyclophosphazene ring P_3N_3 is slightly deviated from planarity. All endocyclic P–N bond lengths are equal within experimental error with the mean value 1.585(5) Å. The K^+ ion is coordinated by oxygen atoms from the crown ether and two water molecules but not by the cyclophosphazene nitrogen atom.

Keywords: Cyclophosphazene; Lariat ether; Phosphazene bond

INTRODUCTION

One of the most rapidly developing aspects of supramolecular chemistry is the design and synthesis of lariat ethers, which arouse great interest in the pharmaceutical, agrochemical and food industries, and in materials science, owing to the diverse applications of these complexes. Cyclophosphazenes substituted by ethers create supramolecular compounds of predicted wide uses and interesting properties. In these compounds both the nitrogen and the oxygen atoms have lone-pair electrons, which may create a three dimensional cave for coordinating cations. Preliminary complexation studies by means of a simple chromatographic test have indicated the tetrapyrrolidinyl cyclophosphazene PNP-crown derivative (L) as the most promising PNP-lariat ether ligand exhibiting a wide spectrum of complexation abilities [1]. In this case there are three possible structural units capable of binding metal cations: (a) polyether oxygen donors of the macrocyclic PNP-crown skeleton, (b) exocyclic nitrogen atoms of pyrrolidinyl substituents (side arms) and (c) endocyclic nitrogen atoms of the

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cyclophosphazene ring [1]. K^+ is a hard cation, which can interact electrostatically with the oxygen and nitrogen donor atoms.

The aim of our study was to determine the X-ray crystal structure of the complex of potassium iodide with L. Solid state studies, if not directly applicable to the solution phase are very important in this area, as they involve the key molecules (host and guest), and can confirm directly the participation of a side arm in the cation binding [2].

SYNTHESIS

Equimolar amounts (0.1 mmol) of the crystalline ligand and KI have been dissolved in 5 mL of methanol. The vessel was covered. After 3 months solvent almost completely evaporated and left colorless crystals (**II**, thereinafter).

EXPERIMENTAL

A roughly spherical crystal of (**II**), was mounted on a KM-4 automatic four-circle diffractometer. Three-dimensional X-ray intensity data were collected with graphite monochromated CuK_α radiation at room temperature using the ω–2θ scan technique. A half of Ewald sphere was collected. The unit cell parameters were determined from least-squares refinement of the setting angles of 99 reflections in the θ range 5–60°. Details concerning crystal data and refinement are given in Table I.

Examination of two standard reflections monitored after each 100 reflections measured, showed the final coefficient for decay correction equal to 0.931, what

TABLE I Crystal data and structure refinement for **II**

Empirical formula	$C_{24}H_{50}IKN_7O_8P_3$
Formula weight	823.62
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 17.755(2)$ Å
	$b = 10.8570(10)$ Å
	$c = 20.434(2)$ Å
	$\beta = 107.860(10)^\circ$
Volume	3749.2(7) Å^3
Z, Calculated density	4, 1.459 Mg/m^3
Absorption coefficient	9.343 mm^{-1}
$F(000)$	1696
Crystal size	0.25 × 0.25 × 0.25 mm
θ range for data collection	2.61° to 60.11°
Index ranges	$-19 \leq h \leq 18$, $0 \leq k \leq 12$, $0 \leq l \leq 22$
Reflections collected/unique	5348/5348 [R(int) = 0.0000]
Completeness to $2\theta = 60.11$	90.2%
Max. and min. transmission	0.204 and 0.029
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5348/0/399
Goodness-of-fit on F^2	0.900
Final R indices ($I > 2\sigma(I)$]	$R1 = 0.0540$, w$R2 = 0.1370$
R indices (all data)	$R1 = 0.1189$, w$R2 = 0.1567$
Largest diff. peak and hole	0.677 and -0.728 e. Å^{-3}

corresponds to 7.36% increase of the intensities. During the data reduction the decay correction coefficient was taken into account. A colorless, transparent crystal of (**II**) used for data collection became brownish. Lorentz-polarization correction was applied to the intensity data.

An empirical absorption correction based on the ψ-scan technique [3] was used and the program X-RED was applied [4]. The maximum and minimum transmission factors were 0.204 and 0.029. The structure of (**II**) was solved by direct methods. All the non-hydrogen atoms were refined anisotropically using a full-matrix, least-squares techniques on F^2. The hydrogen atoms were set in calculated positions and were treated as "riding" on the adjacent carbon atom [d(C–H = 0.97 Å] and refined with individual isotropic temperature factors equal to 1.2 times the value of an equivalent temperature factor of the parent carbon atom. At the end of refinement, a maximum of approximate height $4\,e \cdot Å^{-3}$ appeared in a difference Fourier synthesis and was interpreted as an oxygen atom O(12), probably from the water molecule. We could not localize all hydrogen atoms belonging to water molecules. The solution and refinements were performed with SHELXS97 [5] and SHELXL97 [6]. The graphical manipulations were performed using the XP routine of the SHELXTL [7] and ORTEP [8]. Atomic scattering factors were those incorporated in the computer programs. Selected interatomic bond distances and angles are listed in Table II.

Full crystallographic details have been deposited with CCDC, UK [9].

RESULTS AND DISCUSSION

The crystals and molecular structures of ligand, tetrapyrrolidinyl PNP-lariat ether (L), and its complex with potassium iodide (**I** hereafter) were previously determined [1]. One OH^- (or H_2O) group coordinating to K^+ ion in addition to oxygen atoms belonging to the crown ether was discovered in (**I**). Since the crystal structure of (**I**) was not of very good quality (final $R1$ $[I > 2\sigma(I)] = 7.4\%$) [1], we decided to recrystallize it to obtain better crystals to redetermine its crystal and molecular structure. The measurement of unit cell dimensions revealed a monoclinic unit cell (**II**), which could not be transformed to the previously determined triclinic cell.

The molecular geometry of (**II**) is shown in Fig. 1. The differences in geometry between (**II**) and (**I**) are depicted in Fig. 2. The 16-membered crown ring of (**II**) is more ordered than in (**I**) and adopts the conformation $ac^- ap(ap\,sc^+\,ap\,ap\,sc^-\,ap)_2\,ap\,ac^-$ in opposition to (**I**) which exhibits the conformation $ac^-\,ap\,ap\,sc^-\,ap\,ap\,sc^-\,ap\,ac^-\,sc^-\,ap\,ap\,sc^+\,ac^+\,ap\,ac^+$ [10]. In addition, in (**II**) a *pseudo* plane of symmetry passes through N(1) and O(3) atoms, which is perpendicular to the ring plane. The crown ether shows a partial pseudo threefold axis of symmetry $(ap\,sc^+\,ap\,ap\,sc^-\,ap)_2$, and two *pseudo* mirror planes $(ap\,sc^+\,ap\,ap\,sc^-\,ap)$. This can be explained by a more stabilized K^+ ion, which is coordinated by an additional H_2O molecule (Table III).

The least squares plane calculated through five oxygen atoms of the "crown", with maximum deviation of 0.242(3) for O(3) atom, makes an angle 75.50(9)° with the cyclophosphazene ring. All these oxygen atoms are directed into the interior of the ring. The ether oxygen atoms exist in almost ideal envelope conformation with O(3) at the flap. It can be detected by asymmetry parameters [11] $\Delta C_s = 1.290(7)$, $\Delta C_2 = 9.995(8)$. Values of torsion angles and placement of asymmetry parameters are shown in Fig. 3. The oxygen atoms create a pentagonal cavity with the size of edges O(1)–O(2) = 2.788(7),

TABLE II Selected bond lengths [Å], angles and torsion angles [deg] for **II**

I(1)–K(1)	3.5656(15)
K(1)–O(5)	2.809(4)
K(1)–O(3)	2.810(6)
K(1)–O(2)	2.893(5)
K(1)–O(1)	2.900(4)
K(1)–O(4)	2.983(5)
K(1)–O(11)	3.023(5)
K(1)–O(10)	3.053(6)
P(3)–N(1)–P(1)	121.0(3)
O(1)–P(1)–N(2)	113.0(3)
O(1)–P(1)–N(1)	103.2(3)
N(2)–P(1)–N(1)	116.6(3)
O(1)–P(1)–N(4)	103.1(3)
N(2)–P(1)–N(4)	107.8(3)
N(1)–P(1)–N(4)	112.5(3)
P(1)–N(2)–P(2)	124.1(3)
N(2)–P(2)–N(3)	115.4(3)
N(2)–P(2)–N(6)	106.4(3)
N(3)–P(2)–N(6)	113.6(3)
N(2)–P(2)–N(5)	113.9(3)
N(3)–P(2)–N(5)	105.2(3)
N(6)–P(2)–N(5)	101.7(3)
P(3)–N(3)–P(2)	123.6(3)
N(3)–P(3)–N(1)	117.7(3)
N(3)–P(3)–O(5)	117.7(3)
N(1)–P(3)–O(5)	102.6(2)
N(3)–P(3)–N(7)	107.5(3)
N(1)–P(3)–N(7)	113.2(3)
O(5)–P(3)–N(7)	103.1(3)
P(3)–N(1)–P(1)–O(1)	−109.1(4)
N(1)–P(1)–O(1)–C(1)	175.0(5)
P(1)–O(1)–C(1)–C(2)	−161.3(5)
O(1)–C(1)–C(2)–O(2)	61.4(7)
C(1)–C(2)–O(2)–C(3)	172.6(6)
C(2)–O(2)–C(3)–C(4)	−179.9(6)
O(2)–C(3)–C(4)–C(3)	−65.6(7)
C(3)–C(4)–O(3)–C(5)	175.5(6)
C(4)–O(3)–C(5)–C(6)	−173.0(6)
O(3)–C(5)–C(6)–O(4)	67.2(8)
C(5)–C(6)–O(4)–C(7)	−175.4(7)
C(6)–O(4)–C(7)–C(8)	−177.0(6)
O(4)–C(7)–C(8)–O(5)	−62.0(8)
C(7)–C(8)–O(5)–P(3)	161.0(5)
C(8)–O(5)–P(3)–N(1)	176.1(5)
O(5)–P(3)–N(1)–P(1)	112.4(4)

O(2)–O(3) = 2.811(7), O(3)–O(4) = 2.802(8), O(4)–O(5) = 2.751(6) and O(5)–O(1) = 3.929(6) Å. The C(9), C(10) atoms and the pyrrolidine N(6)–C(17)–C(18)–C(19)–C(20) carbon atoms show symptoms of disorder. All attempts to model this disorder were unsuccessful. Distortion of the pyrrolidine ring manifests in shortening of the C(18)–C(19) distance which is equal to 1.356(13) Å.

The inorganic cyclophosphazene ring P_3N_3 of (**II**) is disordered from planarity like in (**I**) but distortion is significantly smaller. It can be indicated by maximum deviation from the least squares plane calculated through all six ring atoms which is −0.082(3) Å for P(1) atom in (**II**) and −0.157(3) Å for P2 atom in (**I**). The P_3N_3 ring

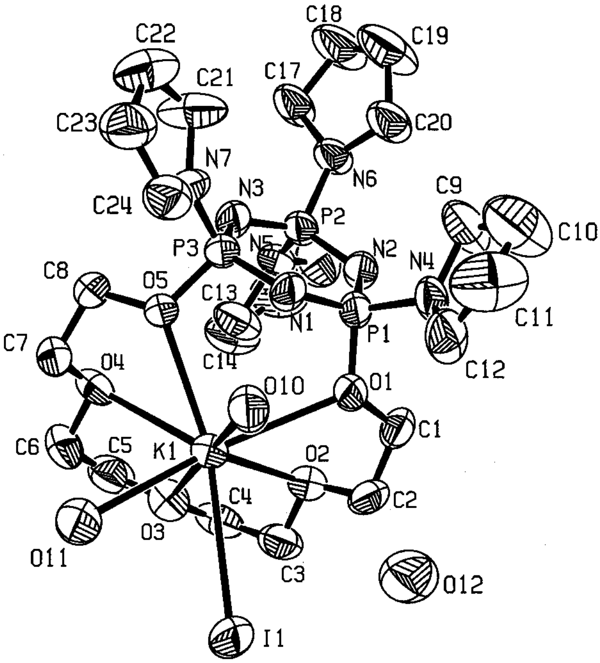

FIGURE 1 Molecular structure of the title compound, hydrogen atoms being omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

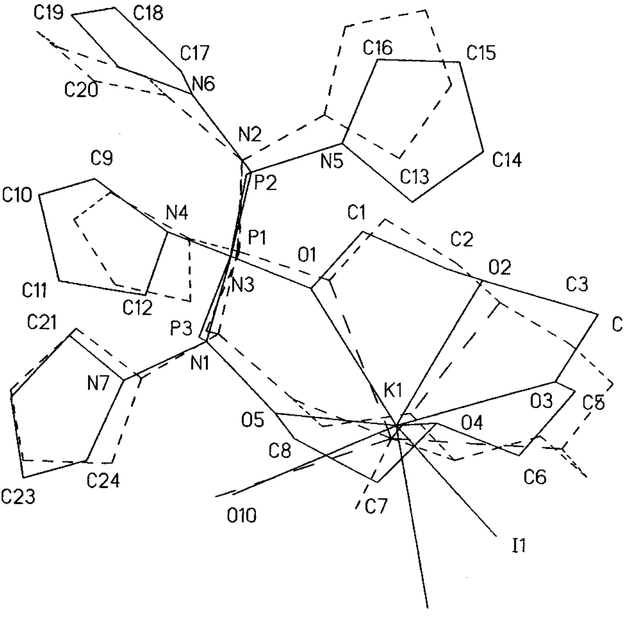

FIGURE 2 Superposition of molecules (**II**) and (**I**). Molecule of (**I**) is indicated by dashed lines.

TABLE III Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \cdot 10^3$) for **II**. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	$U_{(eq)}$
I(1)	866(1)	8275(1)	1445(1)	84(1)
K(1)	– 1054(1)	6989(1)	1171(1)	63(1)
N(1)	– 2594(3)	7813(5)	1792(3)	55(1)
P(1)	– 2856(1)	8881(1)	1230(1)	57(1)
N(2)	– 3611(3)	8626(5)	602(3)	57(1)
P(2)	– 4012(1)	7311(2)	417(1)	55(1)
N(3)	– 3646(3)	6250(5)	956(3)	58(1)
P(3)	– 2934(1)	6454(1)	1631(1)	54(1)
O(1)	– 2093(2)	9103(4)	1013(2)	62(1)
C(1)	– 2097(4)	9951(6)	462(4)	70(2)
C(2)	– 1413(4)	9697(7)	200(4)	73(2)
O(2)	– 1504(3)	8482(4)	– 61(3)	73(1)
C(3)	– 944(4)	8174(8)	– 406(4)	77(2)
C(4)	– 1105(4)	6889(8)	– 654(4)	79(2)
O(3)	– 950(3)	6062(5)	– 83(3)	77(1)
C(5)	– 1144(5)	4821(8)	– 268(5)	87(3)
C(6)	– 1053(5)	4096(7)	361(5)	86(3)
O(4)	– 1642(3)	4488(4)	656(3)	73(1)
C(7)	– 1568(4)	3912(7)	1297(5)	73(2)
C(8)	– 2248(4)	4354(6)	1527(4)	69(2)
O(5)	– 2170(2)	5684(4)	1620(2)	57(1)
N(4)	– 2984(3)	10209(5)	1568(3)	68(2)
C(9)	– -3752(5)	10493(9)	1671(6)	107(3)
C(10)	– 3596(7)	11423(13)	2187(7)	150(5)
C(11)	– 2756(7)	11258(14)	2594(6)	139(4)
C(12)	– 2352(5)	10723(8)	2142(5)	94(3)
N(5)	– 3991(3)	6775(5)	– 324(3)	57(1)
C(13)	– 3238(4)	6335(8)	– 391(5)	84(2)
C(14)	– 3439(6)	6048(11)	– 1139(5)	106(3)
C(15)	– 4199(6)	6622(11)	– 1499(5)	113(4)
C(16)	– 4408(6)	7353(10)	– 979(5)	102(3)
N(6)	– 4955(3)	7515(5)	278(3)	69(2)
C(17)	– 5534(4)	6498(7)	85(6)	106(3)
C(18)	– 6276(5)	7064(11)	109(9)	158(6)
C(19)	– 6115(5)	8077(12)	516(8)	143(5)
C(20)	– 5278(5)	8459(8)	615(6)	109(4)
N(7)	– 3177(3)	5835(5)	2263(3)	62(2)
C(21)	– 3957(5)	5558(11)	2256(5)	108(3)
C(22)	– 3883(5)	4890(10)	2896(6)	111(3)
C(23)	– 3037(5)	5049(9)	3349(5)	99(3)
C(24)	– 2637(4)	5831(8)	2968(4)	76(2)
O(10)	– 944(3)	7929(5)	2605(3)	81(2)
O(11)	318(3)	5403(5)	1972(3)	91(2)
O(12)	– 55(4)	11037(7)	1799(4)	120(2)

forms the angles 76.4(4), 75.3(3), 71.0(4) and 47.2(4)° with the pyrrolidine rings indicated by N(4), N(5), N(6) and N(7) atoms respectively. All endocyclic P–N bond lengths are equal within experimental error with the mean value 1.585(5) Å, and the exocyclic P–N bond lengths are equal with the mean value 1.632(6) Å. The cyclophosphazene ring makes an angle of 77.65(8)°, with the 16-membered ring plane defined by all its atoms.

The potassium ion deviates by 1.291(2) Å from the least-squares plane defined by O1, O2, O3, O4 and O5 atoms. The bond length K–I = 3.5656(16) Å is normal. The assumption that N(1) coordinates to K^+ was rejected because of the large distance, 3.467(6) Å.

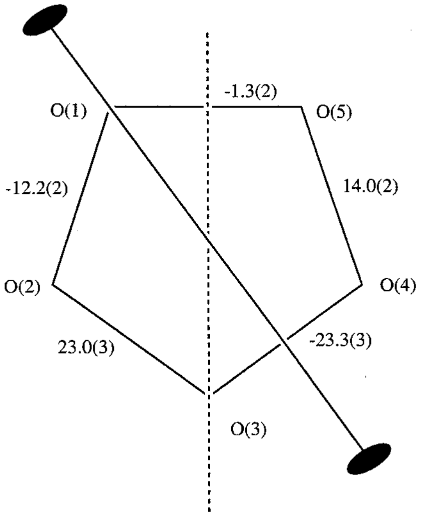

FIGURE 3 Torsion angles and placement of asymmetry parameters for pentagon created by coordinating crown ether oxygen atoms.

In the pure crown ethers K^+ ions are most strongly bonded for 18-crown-6 [2]. In (**II**) the cryptand cavity size is comparable with 18-crown-6 ether, but there are only five oxygen atoms. It does not matter that donor oxygen atoms are in the crown or in the side branches [12]. It is supposed that the water molecules, which lie near the macrocycle, play the same role as hydroxylorganic side branches in the lariat ethers. The presence of two water molecules, instead of one, can be explained by weaker interaction of these molecules with K^+. In addition, water allows for better insertion of the K^+ ion into the crown ether cavity. Weak hydrogen bonds between the oxygen atoms of water molecules can also explain increasing numbers of water molecules coordinating K^+.

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