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Preparation and Structural Properties of Macrocyclic Phosphonamides. Structural Characterization of a Potassium Complex

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Abstract. A novel class of organophosphorus macrocycles containing one phosphonamide or one thiophosphonamide group was obtained by condensation of bis(dimethylamino)methyl-phosphine with the appropriate oligoether-bisprimary amine, followed by the oxidation of the P(III) species. The structures of two macrocyclic phosphonamide ligands (**3** and **4**) which differ in the length of the oligoether chain, and that of the potassium thiocyanate complex of **4**, were studied by X-ray diffraction. The crystals of **3** and **4** contain two crystallographically independent molecules. A cavity appears in the centre of each uncomplexed molecule, but the oxygen atoms of the longer oligoether chain are better oriented towards the centre of this cavity. An important rearrangement of the molecular conformation of **4** occurs upon complexation as shown in the crystal structure analysis of the complex **4** · KSCN. The phosphoryl O atom of one molecule binds to the metal ion of another complexed molecule, leading to the self assembly of **4** · KSCN complexes.

Key words: Macrocyclic phosphonamide, phosphorus crown ether, crystal structures, potassium complex.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP. 82161 (27 pages).

1. Introduction

Phosphorus containing macrocycles have been the subject of several recent investigations. Most of these include phophines, phosphites or their oxidized forms [1, 2]. Other phosphorus based corands with other heteroatoms have been reported, particularly those including the P-X bond, where X is either O, S or N; some are new receptors for ionic guests [2, 3]. Bis-macrocyclic phosphorus derivatives

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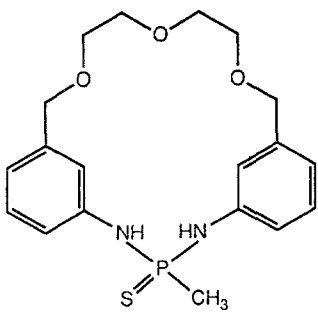
have also been synthesized and their complexing properties towards neutral guests examined [4]. As ligands, phosphorus macrocycles offer several advantages, for two main reasons: first, the complexing properties of phosphorus compounds have been widely extended to transition metal, heavy ions and organic cations, as well as neutral substrate by hydrogen bonding through phosphoryl or phosphoramido groups [5]; second, a variety of oxidation states and substitutions of the phosphorus atom provide a broad family of recognition systems, and lead to a wide range of applications in guest complexation. They have obvious applications in the design of ion extractants [6] and supramolecular assemblies [7].

Recently we described the synthesis of macrocyclic phosphorus compounds where the phosphorus moiety is part of a polyether chain [8, 9]. A common structural feature of these macrocyclic compounds is the introduction of a bis(phenylamino)-phosphane into the cyclic polyether chain. This leads to a particular structural organization of the ligands and furthermore offers the capability of an increased preorganization by further substitution around phosphorus. We now report the convenient synthesis and the solid state structure determination of new phosphonamide macrocyclic ligands with a cavity defined by the phosphorus group and a crown-ether chain of various length (**1–4**, Chart 1). These phospha-crowns have been designed to have one phosphonamide group in the crown backbone that can dramatically change the complexing properties of these ligands. Furthermore they are precursors of rigidified receptors by means of the aminobenzyl moieties [10]. Ligands **1–4** were prepared by our simple ring closure reaction of a bis-dimethylaminophosphine and a diamine [9]. This reaction is a nontemplate method for the production of phosphorus macrocycles in fairly good yields. There is no need to use high dilution condition (10^{-2} M solutions are usual) and compounds are easily recovered. Crystal structures of two new phosphonamide ligands (**3** and **4**) and one potassium complex of **4** were determined by X-ray crystallography.

2. Experimental

2.1. General

All manipulations involving air-sensitive species were carried out under dry nitrogen or argon. Solvents were purified by standard procedures. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on Bruker AC200 and AM300 spectrometers. Chemical shifts are in δ values from Me_4Si (^{1}H and ^{13}C) or H_3PO_4 85% (^{31}P), ^{13}C- and ^{31}P-NMR spectra are proton decoupled unless otherwise noted. The reported multiplicities of ^{13}C-NMR spectra represent ^{31}P-^{13}C couplings. Mass spectra were obtained by the electron impact or chemical ionization methods. Elemental analyses were performed by the Service Central d'Analyses, CNRS. Reactions were monitored by ^{31}P-NMR, thin layer chromatography (Merck Kieselgel $60F_{254}$) and analytical size exclusion chromatography (Merck Lichrogel PS, using



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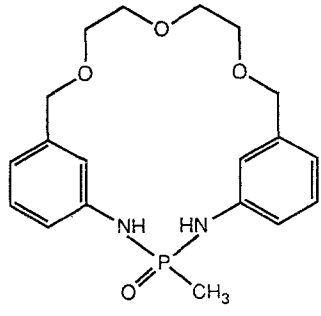

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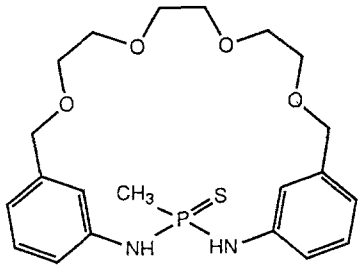

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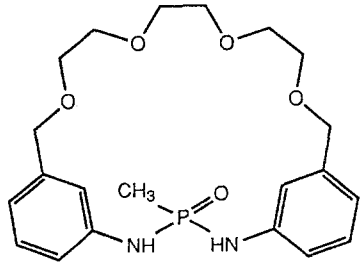

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Chart 1.

dichloromethane as the mobile phase). Silica gel used for column chromatography was Merck Kieselgel 60.

2.2. SYNTHESES

3-*Aminobenzyl alcohol* is commercially available or is obtained by reduction of 3-nitrobenzyl alcohol using hydrazine-Pd-C in ethanol [11]. *Di-* and *triethyleneglycol ditosylate* [12], and *bis(dimethylamino)methylphosphine* [13] were prepared according to literature methods.

2,5,8-*Trioxanonane*-1,9-*diyl-bis*(m-*phenylamine*) **5**. A solution of 3-aminobenzyl alcohol (18.83 g, 153 mmol) in tetrahydrofuran (250 mL) was added to a solution of diethyleneglycol ditosylate (31.69 g, 76.4 mmol) and NaH (7.34 g, 60% in oil, 183.5 mmol) in tetrahydrofuran (350 mL). The mixture was heated under reflux for 3 h and then left overnight at room temperature. A minimum amount of water was added and the solvent was evaporated. The residue was dissolved in dichloromethane, washed with dilute NaOH solution and water, and dried ($MgSO_4$). Removal of the solvent gave a yellowish oil which was subjected to flash chromatography on silica. Elution with dichloromethane-ethyl acetate

(1 : 1) yielded **5** as an oil which crystallized on standing (13.4 g, 55.4%), m.p. 75–76°C; ^{1}H-NMR (300.13 MHz; $CDCl_3$) δ, 3.42 (4H, br s, NH_2), 3.56–3.72 (8H, m, OCH_2CH_2O), 4.46 (4H, s, $ArCH_2O$), 6.50–6.72 (6H, m, ArH), 7.07 (2H, t, J 8Hz, ArH); ^{13}C-NMR (75.46 MHz; $CDCl_3$) δ, 69.45, 70.69, 73.20 (OCH_2), 114.34, 114.34, 117.87, 129.22, 139.57, 146.53 (ArC); *Anal. Calcd.* for $C_{18}H_{24}N_2O_3$: C, 68.33; H, 7.64; N, 8.85%. *Found*: C, 68.06; H, 7.63; N, 8.87%.

2,5,8,11-*Tetraoxadodecane*-1,12-*diyl-bis*(m-*phenylamine*) **6** was prepared as above from 3-aminobenzyl alcohol (6.34 g, 51.5 mmol) in THF (150 mL); triethyleneglycol ditosylate (11.83 g, 25.8 mmol) and NaH (2.27 g, 60% in oil, 56.7 mmol) in THF (200 mL). Reflux for 48 h. Chromatography on silica eluting with CH_2Cl_2-ethyl acetate (1 : 1) afforded **6** (5.57 g, 60%) as a pale yellow oil; ^{1}H-NMR (200.13 MHz; $CDCl_3$) δ, 3.55–3.69 (16H, br m, OCH_2CH_2O and NH_2), 4.44 (4H, s, $ArCH_2O$), 6.50–6.69 (6H, m, ArH), 7.07 (2H, t, J 7.9 Hz, ArH); ^{13}C-NMR (50.32 MHz; $CDCl_3$) δ, 69.03, 70.33, 70.37, 72.89 (OCH_2), 113.99, 114.01, 117.34, 128.93, 139.18, 146.55 (ArC); *Anal. Calcd.* for $C_{20}H_{28}N_2O_4$: C, 66.64; H, 7.83; N, 7.77%; *Found*: C, 66.27; H, 7.79; N, 7.86%.

Preparation of the macrocyclic ligands **1** *and* **2**. A typical experimental procedure is as follows.

3-*Methyl*-11,14,17-*trioxa*-2,4,3-*diazaphosphatricyclo*[17,3,1,$1^{5,9}$]*tetracosa*-1(23),5,7,9(24),19,21-*hexaene*-3-*sulfide* **1**. A solution of bis(dimethylamino)methylphosphine (0.011 mol) and the diamine **5** (0.01 mol) in toluene (500 mL) was stirred for 4 days at reflux temperature. The dimethylamine formed during the reaction was removed by a stream of dry nitrogen. After completion of the reaction, sulfur (400 mg, excess) was added and the heating stopped. The mixture was further stirred until it reached room temperature. The solvent was rotary evaporated and the residue was recrystallized from dichloromethane-hexane at −20°C yielding **1** (44%), m.p. 171–172°C; m/z 393 (M+1; chemical ionization m.s.); ^{1}H-NMR ($CDCl_3$; 300.13 MHz) δ, 2.05 (3H, d, PCH_3, J_{PH} 14.2 Hz), 3.54–3.69 (8H, m, OCH_2CH_2O), 4.46, 4.52 (4H, AB d, $ArCH_2$, J_{AB} 12.3 Hz), 5.06 (2H, d, NH, J_{PH} 8.7 Hz), 6.84–6.88 (2H, m, Ar), 7.12–7.24 (6H, m, Ar); ^{13}C-NMR ($CDCl_3$; 75.46 MHz) δ, 20.89 (PCH_3, J 90.4 Hz), 69.46, 70.68, 72.71 (OCH_2), 118.81 (Ar, J 5.8 Hz), 119.47 (Ar, J 6.4 Hz), 122.19, 129.15, 139.98 (Ar), 139.92 (Ar, J 3.4 Hz); ^{31}P-NMR ($CDCl_3$; 32 MHz) δ, 55.8 ppm.; *Anal. Calcd.* for $C_{19}H_{25}N_2O_3PS \cdot 1.5H_2O$: C, 54.40; H, 6.73; N, 6.68; P, 7.38; S, 7.64%; *Found*: C, 54.43; H, 6.04; N, 6.35; P, 6.82; S, 7.71%.

3-*Methyl*-11,14,17,20-*tetraoxa*-2,4,3-*diazaphosphatricyclo*[20,3,1,$1^{5,9}$]-*heptacosa*-1(26),5,7,9(27),22,24-*hexaene*-3-*sulfide* **2** was similarly prepared from the appropriate diamine **6**. The crude product was first purified by column chromatography on silica with first 9 : 1 dichloromethane-ethyl acetate as eluent

followed by increasing quantities of ethyl acetate (up to 1 : 1). Recrystallization from dichloromethane-hexane gave **2** (38%), m.p. 143–144°C; m/z 437 (M+1; chemical ionization m.s.); ^{1}H-NMR ($CDCl_3$; 200.13 MHz) δ, 2.13 (3H, d, PCH_3, J_{PH} 14.5 Hz), 3.49–3.74 (12H, m, OCH_2CH_2O), 4.46, 4.50 (4H, AB d, $ArCH_2$, J_{AB} 13.3 Hz), 5.93 (2H, d, NH, J_{PH} 11.3 Hz), 6.68–6.73 (2H, m, Ar), 7.02–7.24 (6H, m, Ar); ^{13}C-NMR ($CDCl_3$; 50.32 MHz) δ, 22.21 (PCH_3, J 91.7 Hz), 69.18, 69.98, 70.40, 72.07 (OCH_2), 116.49 (Ar, J 6.8 Hz), 117.35 (Ar, J 6.8 Hz), 120.26, 128.96, 139.39 (Ar), 140.32 (Ar, J 3.4 Hz); ^{31}P-NMR ($CDCl_3$; 81 MHz) δ, 52.5 p.p.m.; *Anal. Calcd.* for $C_{21}H_{29}N_2O_4PS \cdot H_2O$: C, 55.49; H, 6.87; N, 6.16; P, 6.81; S, 7.05%; *Found*: C, 55.80; H, 6.93; N, 6.16; P, 6.46%.

Preparation of the macrocyclic phosphonamides **3** *and* **4** (Method A). Typically bis(dimethylamino)methylphosphine (1.1 equiv.) and the appropriate diamine (1 equiv.) were heated in toluene (150 mL/mmol of diamine) at reflux temperature. The reaction was monitored as described above. After completion of the reaction, the mixture was cooled down to −15°C. A solution of hydrogen peroxide (30 wt.-% solution in water; 0.1 mL/mmol of phosphine) in 100 mL of acetone was slowly added. The resulting solution was evaporated and the residue was subjected to column chromatography on silica. Elution with 9 : 1 dichloromethane-acetone followed by increasing quantities of acetone (up to 1 : 1), afforded the product which was recrystallized from acetone-hexane.

3-*Methyl*-11, 14, 17-*trioxa*-2, 4, 3-*diazaphosphatricyclo*[17, 3, 1, $1^{5,9}$]*tetracosa*-1(23), 5, 7, 9(24), 19, 21-*hexaene*-3-*oxide* **3**. (31%), m.p. 172–173°C; m/z 376 (M+; electron impact m.s.); ^{1}H-NMR ($CDCl_3$; 300.13 MHz) δ, 1.73 (3H, d, PCH_3, J_{PH} 15.5 Hz), 3.58–3.68 (8H, m, OCH_2CH_2O), 4.45, 4.53 (4H, AB d, $ArCH_2$, J_{AB} 12.3 Hz), 5.50 (2H, d, NH, J_{PH} 8.0 Hz), 6.81 (2H, br d, Ar), 7.03–7.19 (6H, m, Ar); ^{13}C-NMR ($CDCl_3$; 75.47 MHz) δ, 13.92 (PCH_3, J 117.8 Hz), 69.5, 70.70, 72.74 (OCH_2), 117.60 (Ar, J 5.5 Hz), 118.87 (Ar, J 5.8 Hz), 121.46, 129.23, 139.89, 140.14 (Ar); ^{31}P-NMR ($CDCl_3$; 121.5 MHz) δ, 23.4 p.p.m.; *Anal. Calcd.* for $C_{19}H_{25}N_2O_4P \cdot 0.5H_2O$: C, 59.22; H, 6.79; N, 7.26; P, 8.03%; *Found*: C, 59.67; H, 6.80; N, 6.84; P, 7.20%.

3-*Methyl*-11, 14, 17, 20-*tetraoxa*-2, 4, 3-*diazaphosphatricyclo*[20, 3, 1, $1^{5,9}$]-*heptacosa*-1(26), 5, 7, 9(27), 22, 24-*hexaene*-3-*oxide* **4**. (47%), m.p. 146–147°C; m/z 420 (M+; electron impact m.s.); ^{1}H-NMR ($CDCl_3$; 300.13 MHz) δ, 1.81 (3H, d, PCH_3, J_{PH} 15.6 Hz), 3.50–3.80 (12H, m, OCH_2CH_2O), 4.48, 4.51 (4H, AB d, $ArCH_2$, J_{AB} 11.5 Hz), 5.91 (2H, br d, NH, J_{PH} 9.5 Hz), 6.72 (2H, br d, Ar), 7.0–7.16 (6H, m Ar); ^{13}C-NMR ($CDCl_3$; 75.47 MHz) δ, 15.9 (PCH_3, J 117.9 Hz), 69.26, 70.27, 70.69, 72.25 (OCH_2), 116.17 (Ar, J 4.0 Hz), 117.35 (Ar, J 5.9 Hz), 120.23, 129.28, 139.67, 140.28 (Ar); ^{31}P-NMR ($CDCl_3$; 121.5 MHz) δ, 18.9 p.p.m.; *Anal. Calcd.* for $C_{21}H_{29}N_2O_5P$: C, 59.99; H, 6.95; N, 6.66; P, 7.37%; *Found*: C, 59.58; H, 7.02; N, 6.79; P, 7.30%.

TABLE I. Crystal data and data collection parameters.

Compounds	**3**	**4**	**4** · KSCN
Formula	$C_{19}H_{25}N_2O_4P \cdot 0.25CHCl_3$	$C_{21}H_{29}N_2O_5P$	$C_{21}H_{29}N_2O_5P \cdot KSCN$
M	406.24	420.45	517.64
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\text{-}1$	$Pn2_1a$	Cc
Temp./K	293	293	293
a/Å	9.357(2)	10.021(1)	19.071(2)
b/Å	13.918(5)	22.539(2)	9.946(1)
c/Å	16.142(5)	19.752(1)	13.938(2)
α/°	90.17(3)	90.0	90.0
β/°	91.59(2)	90.0	108.59(1)
γ/°	75.80(2)	90.0	90.0
V/Å^3	2037(1)	4461.1(6)	2505.7(4)
Z	4	8	4
D_c/g cm^{-3}	1.32	1.25	1.37
Crystal size/mm	0.3 × 0.3 × 0.1	0.2 × 0.15 × 0.15	0.26 × 0.08 × 0.08
Radiation	MoK_α	CuK_α	CuK_α
λ/Å	0.71069	1.54178	1.54178
F(000)	858	1792	1088
scan mode	ω	ϑ–2ϑ	ϑ–2ϑ
μ/mm^{-1}	0.265	1.37	3.50
(sin ϑ/λ)max/Å^{-1}	0.65	0.60	0.65
h range	−11; 10	0; 12	0; 22
k range	−16; 16	0; 26	0; 11
l range	0; 19	0; 23	−15; 15
standard reflection	1 3 6	−1 −1 −9	1 1 2
No. of reflns. measd.	7168	4116	2257
No. of reflns. obserd.	3121	3176	1947
No. of variables	635	698	384
R/%	0.0616	0.0392	0.0464
R_w/%	0.0555	0.0399	0.0479
S	1.36	1.16	1.31
$(\Delta/\sigma)_{max}$	0.1	0.16	0.002
$\Delta\rho_{max}$/e Å^{-3}	0.48	0.23	0.32
$\Delta\rho_{min}$/e Å^{-3}	−0.34	−0.28	−0.48

Conversion of the thiophosphonamide (P=S) into the phosphonamide (P=O) (Method B). A solution of *m*-chloroperbenzoic acid (2 equiv.) in 30 mL of dichloromethane was added dropwise with stirring at 0°C, to a solution of the thiophosphonamide (**1** or **2**) (1.65 mmol) in dichloromethane (80 mL). After addi-

tion, the mixture was refluxed for one day, cooled and washed with 100 mL of a concentrated solution of potassium carbonate. The aqueous layer was extracted with CH_2Cl_2 (30 mL). Combined CH_2Cl_2 solutions were washed with brine (2×50 mL), dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography and recrystallization as reported in Method A. Yields are 58% and 60% for **3** and **4**, respectively.

2.3. X-Ray Crystallography

X-ray diffraction measurements were performed at 293 K on a Huber four-circle diffractometer. Crystal data and data collection parameters are collected in Table I. For each compound a standard reflection was checked every 50 reflections which showed no significant deviation. The structures were solved by SHELXS 86 [14]. Non-hydrogen atoms were refined anisotropically using F; hydrogen atoms were refined isotropically with a common temperature factor. Calculations were performed using full-matrix least-squares methods using SHELX 76 [15]. Scattering factors were taken from *The International Tables for X-Ray Crystallography* [16].

Crystal data and structure analysis of **3**. Suitable crystals of **3** were obtained by slow diffusion of isooctane through a dichloromethane solution of **3**. Lattice parameters were determined by least squares from 16 reflections ($5° \leq \vartheta \leq 13°$). Of the 7168 independent reflections collected ($\sin \vartheta/\lambda \leq 0.65$ Å^{-1}), 3121 had $I \geq 2.5\sigma(I)$. Refinement with a weighting scheme $w = 1/(\sigma^2 + 0.00035\, F^2)$ converged at $R = 0.0616$ ($R_w = 0.0555$) for 3121 observed reflections. A disordered solvent molecule (chloroform) appears around the inversion center with 0.5 occupation factor and originates from previous attempts to get suitable X-ray crystals from miscellaneous solvent mixtures. The atoms are labelled C(1S) to Cl(3S).

Crystal data and structure analysis of **4**. Crystals of **4** were obtained by slow diffusion of isooctane through a chloroform solution of **4**. Lattice parameters were determined by least squares from 21 reflections ($3° \leq \vartheta \leq 24°$). 4116 Independent reflections were recorded ($\sin \vartheta/\lambda \leq 0.60$ Å^{-1}), of which 3176 had $I \geq 3.0\sigma(I)$. Hydrogen atoms were included in calculated positions (C-H 1.08 Å). Refinement converged at $R = 0.0392$ ($R_w = 0.0399$) for 3176 observed reflections ($w = 1/(\sigma^2 + 0.001\, F^2)$).

Crystal data and structure analysis of $4 \cdot KSCN$. The complex was crystallized by slow evaporation of a solution of **4** in acetone with an excess of potassium thiocyanate. Lattice parameters were refined using 19 reflections ($8° \leq \vartheta \leq 24°$). Of the 2257 independent reflections collected ($\sin \vartheta/\lambda \leq 0.65$ Å^{-1}), 1947 had

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

Atom	x	y	z	U_{eq}
Molecule **3a**				
C(1)	3706(6)	1676(4)	10170(4)	34(2)
N(2)	5241(5)	1239(3)	10176(3)	35(2)
P(3)	6401(2)	1410(1)	9482(1)	32(1)
N(4)	6314(5)	2618(3)	9538(3)	36(2)
C(5)	6712(5)	3256(4)	8960(3)	31(2)
C(6)	7339(6)	2931(4)	8205(4)	36(2)
C(7)	7687(7)	3602(5)	7664(4)	43(3)
C(8)	7432(7)	4594(5)	7862(4)	44(3)
C(9)	6815(6)	4935(4)	8615(4)	35(2)
C(10)	6552(8)	6004(5)	8882(5)	48(3)
O(11)	5010(4)	6495(3)	8862(2)	44(2)
C(12)	4482(8)	6845(5)	8050(5)	57(3)
C(13)	2842(9)	7177(6)	8034(5)	68(4)
O(14)	2102(5)	6405(4)	7902(3)	83(2)
C(15)	2356(8)	5685(6)	8513(5)	63(3)
C(16)	1214(8)	5098(5)	8433(5)	61(3)
O(17)	1661(5)	4325(3)	9031(3)	66(2)
C(18)	866(8)	3580(5)	8972(5)	55(3)
C(19)	1532(6)	2806(4)	9594(4)	40(2)
C(20)	711(7)	2570(5)	10236(5)	52(3)
C(21)	1391(8)	1904(6)	10824(5)	60(3)
C(22)	2881(7)	1454(5)	10815(4)	48(3)
C(23)	3014(7)	2330(4)	9568(4)	40(2)
C(24)	6465(6)	4294(4)	9150(4)	32(2)
C(25)	8148(7)	764(5)	9910(4)	44(3)
O(26)	6132(4)	1107(3)	8625(2)	41(2)
Molecule **3b**				
C(1)	3178(6)	1946(5)	7060(4)	43(2)
N(2)	3577(5)	1025(3)	7487(3)	38(2)
P(3)	2549(2)	255(1)	7696(1)	36(1)
N(4)	1928(5)	−141(4)	6826(3)	41(2)
C(5)	2763(7)	−668(4)	6184(4)	39(2)
C(6)	4280(7)	−1052(5)	6255(4)	58(3)
C(7)	5044(8)	−1549(6)	5604(5)	78(3)
C(8)	4301(8)	−1706(6)	4880(5)	71(3)
C(9)	2795(7)	−1327(5)	4795(4)	53(3)
C(10)	1972(9)	−1455(7)	3995(5)	67(4)
O(11)	1336(5)	−537(4)	3589(3)	61(2)
C(12)	2431(9)	−88(7)	3298(5)	85(4)

TABLE II. Continued.

Atom	x	y	z	U_{eq}
Molecule **3b**				
C(13)	1810(1)	860(1)	2951(6)	126(7)
O(14)	1192(8)	1508(7)	3534(5)	132(4)
C(15)	940(2)	2520(1)	3268(8)	175(8)
C(16)	250(1)	3150(1)	3924(9)	192(8)
O(17)	1181(8)	3061(7)	4631(6)	166(5)
C(18)	570(1)	3250(1)	5350(1)	149(7)
C(19)	1773(8)	3062(7)	6037(5)	83(4)
C(20)	2500(1)	3768(7)	6268(6)	90(4)
C(21)	3600(1)	3566(6)	6882(6)	80(4)
C(22)	3937(7)	2649(5)	7278(4)	53(3)
C(23)	2119(8)	2155(6)	6435(5)	63(3)
C(24)	2029(7)	−834(5)	5456(4)	45(3)
C(25)	868(7)	949(5)	8116(4)	48(3)
O(26)	3432(4)	−527(3)	8246(2)	46(2)
Solvent				
C(1S)	4900(2)	4440(1)	4850(1)	101(9)
Cl(1S)	3620(2)	5540(1)	4700(1)	260(1)
Cl(2S)	5840(1)	4028(6)	4048(5)	213(5)
Cl(3S)	6120(2)	4820(2)	5634(8)	320(1)

$I \geq 2.5\sigma(I)$. Refinement with a weighting scheme $w = 1/(\sigma^2 + 0.0014\ F^2)$ converged at $R = 0.0464$ ($R_w = 0.0479$) for 1947 observed reflections.

The final atomic coordinates and equivalent isotropic thermal parameters for the three compounds are given in Tables II, III and IV (**3**, **4** and **4** · KSCN, respectively). Bond distances and angles appear as Supplementary Material (Tables VII–XII).

3. Results and Discussion

3.1. SYNTHESIS

The synthetic route utilized in the preparation of the macrocyclic ligands **1–4** is illustrated in Chart 2. Di- and triethyleneglycol bis(3-aminobenzyl) ether **5** and **6** were prepared in 55% and 60% yields, respectively, by reaction of 3-aminobenzyl alcohol with the appropriate oligoethylene glycol ditosylate.

Ring closure occurred by a condensation reaction of bis(dimethylamino)methylphosphine ($CH_3P[N(CH_3)_2]_2$) with the appropriate diamine **5** or **6** in refluxing toluene. The macrocyclic diaminophosphines **7** and **8** were formed but not isolated, although they are of particular interest as macrocyclic ligands e.g. for transition metals. The *in situ* treatment of **7** and **8** with solid sulfur provided **1** ($\delta^{31}P = 55.8$

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

Atom	x	y	z	U_{eq}
Molecule **4a**				
C(1)	4526(3)	4079(2)	2839(2)	45(1)
N(2)	4766(3)	3518(1)	2547(2)	49(1)
P(3)	3687(1)	3079(1)	2174(1)	45(1)
N(4)	3563(3)	3342(1)	1393(2)	50(1)
C(5)	2702(3)	3142(2)	874(2)	49(1)
C(6)	1770(4)	2693(2)	988(3)	67(2)
C(7)	961(6)	2518(3)	464(3)	95(2)
C(8)	1025(6)	2779(3)	−166(3)	92(2)
C(9)	1941(4)	3230(2)	−276(2)	64(1)
C(10)	2037(6)	3542(3)	−951(3)	77(2)
O(11)	1636(3)	4151(1)	−909(2)	66(1)
C(12)	300(5)	4233(2)	−674(3)	67(2)
C(13)	−96(5)	4855(3)	−770(3)	71(2)
O(14)	771(3)	5220(1)	−377(1)	64(1)
C(15)	433(5)	5827(2)	−407(3)	71(2)
C(16)	1474(5)	6166(2)	−23(3)	77(2)
O(17)	1345(3)	6036(2)	683(2)	78(1)
C(18)	2300(6)	6325(3)	1074(3)	85(2)
C(19)	2086(6)	6181(2)	1791(3)	72(2)
O(20)	2802(3)	5671(1)	1982(2)	67(1)
C(21)	2385(5)	5448(2)	2619(2)	62(1)
C(22)	3409(4)	5024(2)	2884(2)	54(1)
C(23)	4192(4)	5188(2)	3430(2)	61(1)
C(24)	5118(5)	4794(2)	3683(2)	68(2)
C(25)	5299(4)	4245(2)	3395(2)	56(1)
C(26)	3582(4)	4468(2)	2597(2)	50(1)
C(27)	2782(4)	3402(2)	244(2)	52(1)
C(28)	4529(4)	2380(2)	2135(3)	63(2)
O(29)	2363(2)	3031(1)	2497(1)	58(1)
Molecule **4b**				
C(1)	2520(3)	−636(2)	2156(2)	44(1)
N(2)	2713(3)	−66(2)	2444(2)	50(1)
P(3)	1628(1)	362(1)	2810(1)	43(1)
N(4)	1533(3)	128(2)	3606(2)	50(1)
C(5)	622(3)	312(2)	4104(2)	44(1)
C(6)	−368(4)	730(2)	3981(2)	53(1)
C(7)	−1262(4)	875(2)	4490(3)	62(2)
C(8)	−1172(5)	610(2)	5122(2)	61(1)
C(9)	−182(4)	200(2)	5253(2)	54(1)

TABLE III. Continued.

Atom	x	y	z	U_{eq}
Molecule **4b**				
C(10)	−98(6)	−111(2)	5931(2)	66(2)
O(11)	−421(3)	−721(1)	5901(1)	56(1)
C(12)	−1739(4)	−830(2)	5654(3)	64(2)
C(13)	−2051(5)	−1472(2)	5756(3)	66(2)
O(14)	−1142(3)	−1805(1)	5364(1)	63(1)
C(15)	−1450(6)	−2409(2)	5351(3)	73(2)
C(16)	−396(6)	−2742(2)	4991(3)	69(2)
O(17)	−427(3)	−2598(1)	4293(2)	72(1)
C(18)	506(6)	−2916(2)	3899(3)	81(2)
C(19)	229(6)	−2788(2)	3174(3)	80(2)
O(20)	930(3)	−2262(2)	2978(2)	80(1)
C(21)	455(5)	−2023(2)	2366(2)	64(2)
C(22)	1436(4)	−1591(2)	2100(2)	51(1)
C(23)	2265(4)	−1747(2)	1569(2)	56(1)
C(24)	3222(4)	−1351(2)	1322(2)	59(1)
C(25)	3325(4)	−797(2)	1614(2)	53(1)
C(26)	1570(4)	−1028(2)	2394(2)	50(1)
C(27)	706(4)	57(2)	4746(2)	49(1)
C(28)	2426(4)	1072(2)	2812(3)	65(2)
O(29)	303(2)	391(1)	2489(1)	57(1)

ppm) and **2** ($\delta^{31}P = 52.4$ ppm) in 44% and 38% yields, respectively, after purification and recrystallization. A number of methods for the oxidation of phosphorus compounds are readily available. The most common synthetic procedure requires the *in situ* oxidation of the P(III) compounds. We performed this reaction by adding a hydrogen peroxide solution in acetone at −15°C to the crude reaction mixture containing **7** or **8**. This afforded **3** ($\delta^{31}P = 23.4$ ppm) and **4** ($\delta^{31}P = 18.9$ ppm) in 31% and 47% yields, respectively, after recrystallization (method A).

Oxidation of thiophosphoryl derivatives to their oxo analogues were extensively studied and it has been demonstrated that a variety of oxidizing agents can smoothly oxidize thio- and selenophosphoryl compounds [17]. *m*-Chloroperbenzoic acid (*m*-CPBA) in methylene chloride is an efficient nonaqueous oxidizing agent for the conversion of thiophosphoryl compounds to phosphoryl compounds [18]. The oxidation of compounds **1** and **2** was carried out by adding an excess of *m*-chloroperbenzoic acid in solution in dichloromethane to a solution of the thiophosphonamide in the same solvent (method B). The ^{31}P-NMR analysis of the reaction mixture showed that the reaction was complete after one day at reflux temperature. Yields, after chromatography and recrystallization, reached 58% (**3**) and 60% (**4**), indicating that this route is as efficient as the direct oxidation of the parent P(III) species. The macrocyclic ligands **1**–**4** are crystalline compounds

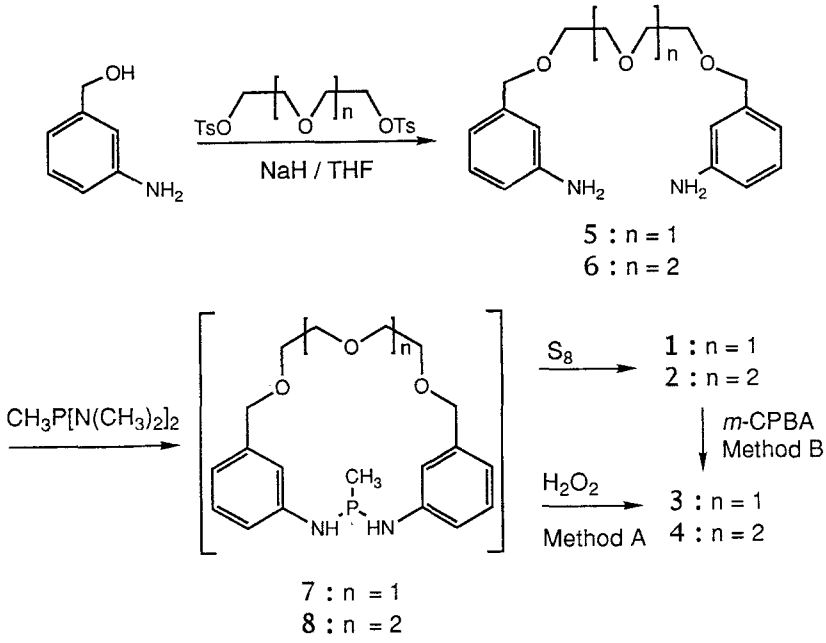

Chart 2.

that contained water of hydration and/or solvent molecules originating from the solvents of recrystallization.

The ^{1}H-NMR spectra of ligands **1–4** in chloroform-*d* show the expected two doublets for the methyl and NH protons coupled to the phosphorus nucleus. A characteristic AB pattern is observed for the diastereotopic methylene protons of the benzylic groups with higher $\Delta\delta = (\delta_A - \delta_B)$ values for the 18-membered rings **1** and **3** ($\Delta\delta = 0.06$ and 0.08 ppm, respectively). This indicates different conformations in solution for the 21-membered rings **2** and **4** ($\Delta\delta = 0.04$ and 0.03 ppm, respectively), and probably a release of strain in the structure of the latter two macrocycles. ^{1}H and ^{13}C downfield shifts are observed for the methyl groups bound to the phosphorus atom of the thiophosphoryl compounds as compared to the phosphoryl derivative. ^1J phosphorus-carbon coupling constants are larger in the P(O) (117.8 and 117.9 Hz for **3** and **4**, respectively) than in the P(S) compounds (90.4 and 91.7 Hz for **1** and **2**, respectively). The phosphorus-coupled aromatic carbon atoms are assigned to the quaternary N*C* carbon and the two carbon atoms *ortho* to the nitrogen substituent, corresponding to $^2J_{P\text{-}C}$ and $^3J_{P\text{-}C}$ coupling constants, respectively. The ^{1}H- and ^{13}C-NMR spectra reflect the flexibility of the macrocycles and emphasize the C_s symmetry averaged conformations of the molecules in solution, a situation different from that observed in the solid state.

The potassium complex of the phosphonamide **4** was prepared from a solution of **4** in acetone containing an excess of potassium thiocyanate. The complex **4** · KSCN

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

Atom	x	y	z	U_{eq}
C(1)	−1317(3)	−1507(5)	1725(4)	37(2)
N(2)	−1591(3)	−637(5)	2325(5)	46(2)
P(3)	−1226(1)	763(1)	2904(2)	40(1)
N(4)	−1124(3)	1806(5)	2025(4)	42(2)
C(5)	−1581(3)	2035(5)	1032(4)	36(2)
C(6)	−2276(4)	1447(7)	617(5)	50(2)
C(7)	−2680(4)	1697(8)	−391(6)	57(3)
C(8)	−2408(4)	2494(7)	−985(5)	46(2)
C(9)	−1740(3)	3120(6)	−592(4)	40(2)
C(10)	−1438(4)	4000(7)	−1243(5)	45(2)
O(11)	−659(2)	3880(4)	−928(3)	47(1)
C(12)	−343(4)	4530(7)	−1603(5)	50(2)
C(13)	480(4)	4299(8)	−1224(6)	59(3)
O(14)	613(2)	2906(5)	−1196(4)	54(2)
C(15)	1353(5)	2610(1)	−1080(8)	71(3)
C(16)	1489(5)	1150(1)	−896(7)	68(3)
O(17)	1421(3)	828(5)	73(4)	55(2)
C(18)	1614(4)	−530(7)	382(7)	63(3)
C(19)	1472(4)	−728(8)	1383(6)	61(3)
O(20)	716(2)	−813(4)	1292(4)	47(2)
C(21)	404(4)	−2105(6)	975(6)	52(3)
C(22)	−346(3)	−2228(5)	1083(5)	40(2)
C(23)	−778(4)	−3305(6)	626(5)	47(2)
C(24)	−1481(4)	−3472(7)	692(5)	49(2)
C(25)	−1758(4)	−2554(6)	1226(5)	44(2)
C(26)	−610(3)	−1334(6)	1661(4)	39(2)
C(27)	−1331(3)	2908(5)	427(4)	35(2)
C(28)	−1943(5)	1408(9)	3332(7)	63(3)
O(29)	−499(3)	619(4)	3689(4)	52(2)
K(1)	0(1)	1371(1)	0(1)	45(1)
S(1A)	1480(2)	4440(3)	1687(2)	88(1)
C(1A)	905(8)	3410(1)	1904(6)	100(5)
N(1A)	616(3)	2606(6)	2192(4)	46(2)

crystallized as suitable crystals for X-ray analysis. Its structure is described in the following section.

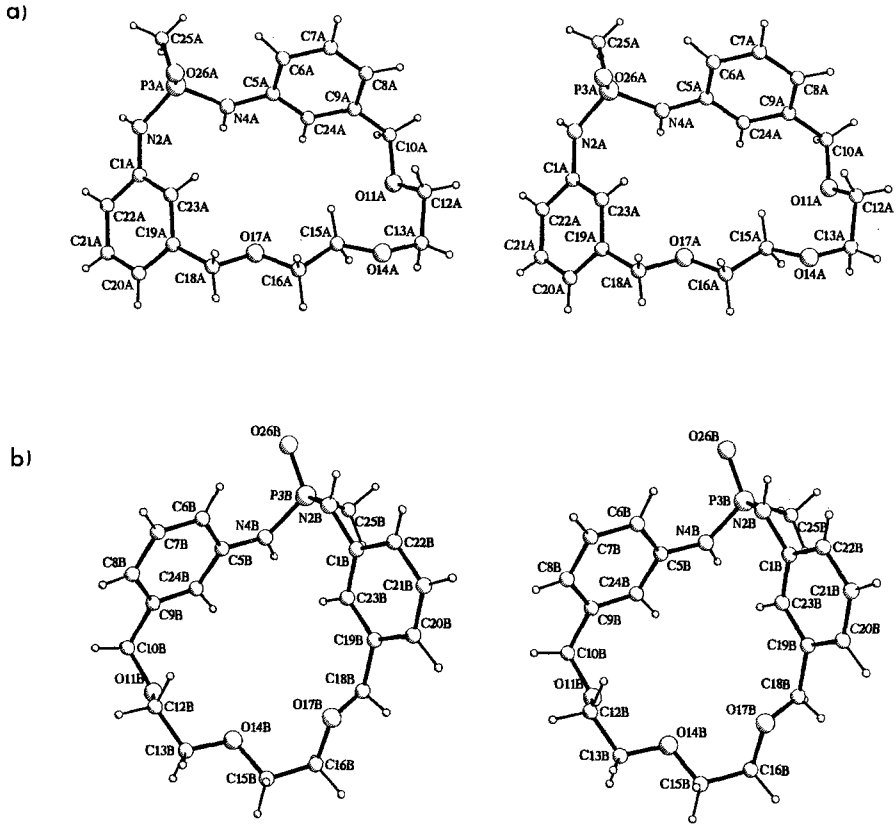

Fig. 1. Stereoview of **3** (a) molecule **3a**; (b) molecule **3b**.

3.2. X-RAY STRUCTURES

The solid-state structures of the compounds **3**, **4**, and **4** · KSCN, were determined by X-ray crystallography. Details of the structure determinations are given in the experimental section. Stereoscopic views [19] of the structures, including atom numbering, are shown in Figures 1–3. Table I contains the crystal data and data collection parameters. Bond distances and bond angles (Tables VII–XII) are available as supplementary materials.

Molecule **3** adopts two different conformations in the crystal, **3a** and **3b**, as shown in the computer drawing (Figure 1). The final atomic coordinates of the non-hydrogen atoms are listed in Table II. According to Dale [20], the conformation of the oligoether moiety can be described qualitatively as a succession of groups of three torsion angles in each oxyethylene unit. Molecule **3a** is characterized by the succession (ag^-g^+) (aaa), a 'pseudo-corner' followed by an all-*trans* sequence, implying that the central oxygen atom O(14) points away from the cavity of the molecule. The conformation of **3b** differs principally in the neighbourhood of the

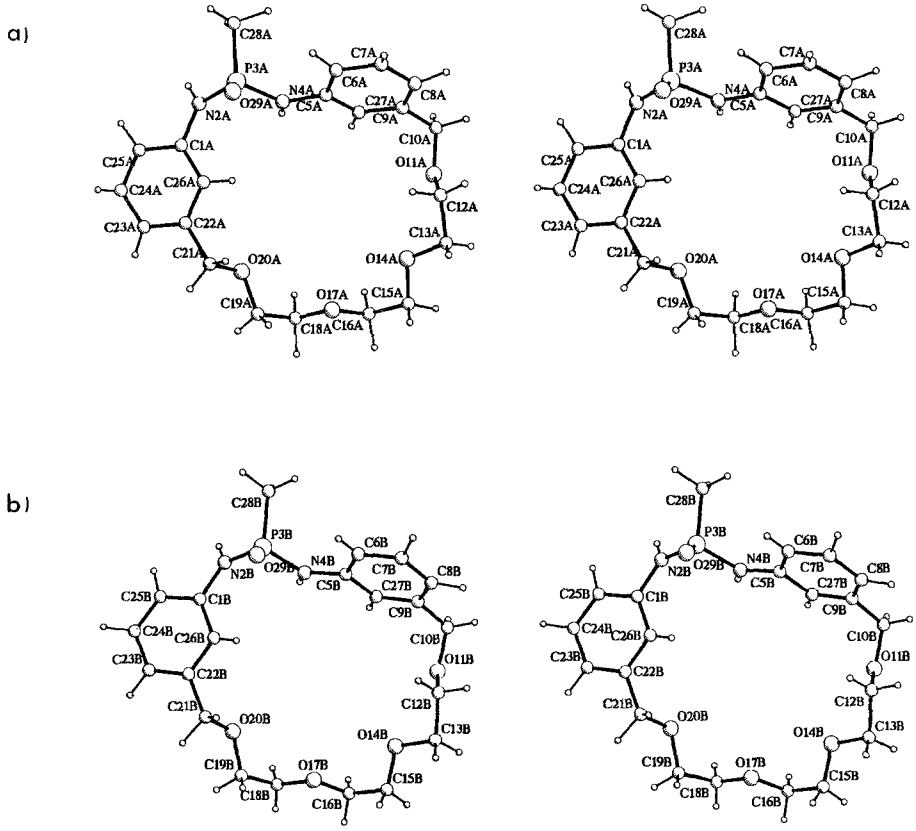

Fig. 2. Stereoview of **4** (a) molecule **4a**; (b) molecule **4b**.

O(14) oxygen atom, with a succession (ag^+a) (ag^+a). With such a conformation, the oxygen atoms are much better oriented towards the centre of the cavity. A second important conformational difference arises from the torsional angles around the phosphorus atoms. In **3a**, due to the (g^+a) N-P-N arrangement, the two NH bonds are located on the same side of the plane defined by the atoms N(2), P(3) and N(4) and opposite to the P=O bond. In **3b**, the NH hydrogens are located on opposite sides of the NPN plane due to the isoclinal (g^+g^+) situation of the N-P-N group. Consequently, different relative orientations of the phenyl rings are observed within the molecules. The fact that in the same crystal structure two very different conformations are observed, demonstrates the conformational flexibility of the molecule. A disordered chloroform solvent molecule is associated with one molecule of **3** in the crystal lattice but does not interact strongly with the ligand.

A computer drawing of **4** is shown in Figure 2. The molecule adopts two very close independent conformations, **4a** and **4b**, in the solid state. Table III contains the final positional and equivalent isotropic thermal parameters. In both molecules,

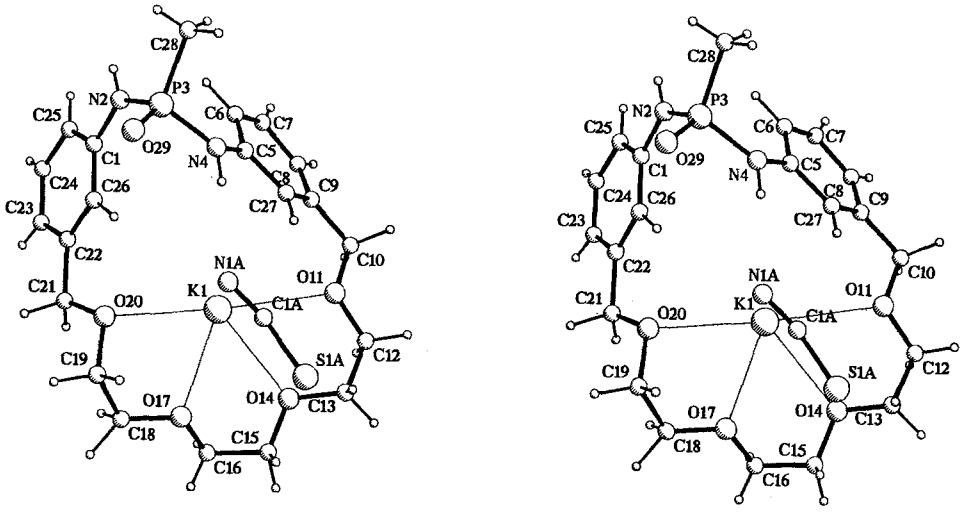

Fig. 3. Stereoview of **4** · KSCN.

the sequence of torsion angles (O-C, C-C, C-O, etc) for the polyether part of the ring is (ag^-a) (ag^-a) (ag^+a) leading to a relatively good convergence of the oxygen atoms towards the cavity. Such a situation seems to be favoured by the lengthening of the oligoether chain. In **4a** and **4b** the geometry around the phosphorus atom implies a (g^+a) conformation of the N-P-N group, so that the NH bonds are located on the same side of the plane defined by the atoms N(2), P(3) and N(4).

Ligands **3** and **4** feature a central cavity in each conformation. In the two compounds the phosphorus group is located outside the macrocyclic cavity. However, except for molecule **3b** where the P=O bond is directed away from the other binding sites, in conformations **3a**, **4a** and **4b** the phosphoryl group lies in the vicinity of the cavity and would be available for interaction with a cation complexed within the cavity. Torsion angles for the polyether part reflect the favorable orientation of the oxygen donor atoms. From this point of view, molecule **4** seems to be a better candidate for complexation than molecule **3**.

In the complex **4** · KSCN, there is only one molecule in the asymmetric unit. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table IV. A rearrangement around the P(3)-N(4) bond (+38° as compared to the average −174° value in the free molecule) makes the conformation of the macrocycle rather different from that observed in the free ligand (Figure 3). The oligoether part is characterized by the $(ag^+a)(ag^-a)(ag^+g^+)$ conformation which maintains the favorable convergence of the polyether oxygen atoms. These atoms lie at the corners of a nearly regular hexagon, the two remaining corners being empty and the potassium cation being located at the center. These four oxygen atoms define an equatorial plane, the largest deviation from their best mean plane being 0.15 Å.

TABLE V. Geometrical parameters involving the K^+ cation in the complex **4** · KSCN.

bond distances (Å):		bond angles (°):	
K...O(11)	2.906(4)	O(11)...K...O(14)	57.7(1)
K...O(14)	2.778(5)	O(14)...K...O(17)	61.9(1)
K...O(17)	2.733(5)	O(17)...K...O(20)	63.9(1)
K...O(20)	2.874(5)	O(11)...K...O(20)	168.4(1)
K...O=P	2.656(4)	P=O...K...O(11)	109.0(1)
K...NCS	3.152(5)	P=O...K...O(14)	97.1(1)
		P=O...K...O(17)	90.7(1)
		P=O...K...O(20)	82.1(1)
		P=O...K...NCS	153.9(1)

The potassium ion is displaced by 0.27 Å out of this plane in the positive direction. For comparison, in the uncomplexed molecule, the deviation of the polyether oxygen atoms from their best mean plane is 0.17 Å. In addition to the four equatorial oxygen atoms of the polyether chain, the cation is coordinated on the positive side of the equatorial plane, through the oxygen atom of the phosphoryl group belonging to a symmetry related molecule. The P=O...K^+ distance (2.656 Å) is slightly shorter than the sum of the corresponding ionic and van der Waals radii (2.73 Å for K^+...O) [21] whereas the other K^+...O distances (mean, 2.823 Å) are slightly longer (Table V).

The P=O...K^+ ion-dipole interaction is probably the main factor in the stability of the complex [22]. The nitrogen atom of the thiocyanate ion completes the coordination of the potassium ion on the negative side of the equatorial plane with a rather long SCN^-...K^+ distance of 3.152 Å. The thiocyanate ion is nearly parallel to the equatorial plane with a C-N...K^+ angle of 90°. A similar situation was observed in complexes of oligoether compounds with KSCN [23]. The potassium cation has thus a strong fivefold coordination and forms a much weaker bond with a sixth neighbour.

It is interesting that in the crystal the molecules are linked together via a continuous phosphoryl-cation bond system parallel to the *c* axis, forming an endless chain (Figure 4). There are no other obvious contacts between molecules.

The C-C, C-O distances and C-C-O and C-O-C angles compare quite well with those reported for other polyether chains. In the three structures, shortened C-C bond distances and widened C-O-C bond angles are observed. These are common features of polyethers [24]. Mean bond distances and angles around phosphorus were computed from fifteen phosphoramide groups found in the Cambridge Structural Database [25]: P=O (1.48 Å), P-C (1.80 Å), P-N (1.66 Å), C-P=O (110.5°), N-P=O (114.6°), N-P-N (99.6°) and C-P-N (108.4°). These values are comparable with those observed in the present molecules except for the values of the N-P-N bond angles (Table VI). The increase of the N-P-N angle is attributed to the strains

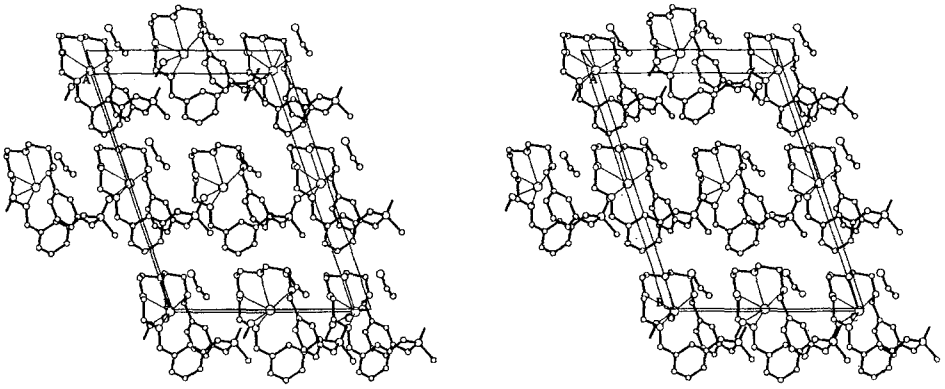

Fig. 4. Stereoview of the self assembly of complexed **4** in the unit cell.

around the phosphorus atom induced by the cyclic structure of the compounds [26]. The differences observed between the two O=P-N, and C-P-N angles belonging to the same molecule are mainly a consequence of the different conformations around the P-N(2) and P-N(4) bonds, involving O=P-N-C_{arom} and C-P-N-C_{arom} dihedral angles. The phosphorus atoms are tetraedric, but most angles involving the P=O bond are widened, while the other angles are narrowed. The low precision on the hydrogen positions does not allow us to evaluate correctly the planarity around the nitrogen atoms, but the large values of the P-N-C angles (about 128°) are indicative of sp^2 hybridization.

4. Conclusions

The synthesis of a family of new phosphonamides and thiophosphonamides macrocycles containing a cavity delineated by a phosphorus-crown ether backbone has been presented. The thioxo derivatives are obtained by addition of elemental sulfur to the reaction mixture containing the P(III) parent compounds. The oxo-compounds are obtained either by addition of hydrogen peroxide to the three-coordinated compounds or by transformation of the sulfide compounds to the oxide by action of *m*-chloroperbenzoic acid. In addition, the X-ray crystal structure of **3**, **4** and **4** · KSCN are reported. The crystal structures of the free ligands and of the potassium complexed form of **4**, demonstrate the conformational flexibility of the molecules. In the solid state, **3** and **4** present a well defined cavity with the phosphorus moieties pointing outwards. In the complex, **4** adopts a different conformation from that observed with the free ligand. The solid state structure of the complex shows a three dimensional arrangement of PO...$K^+ \subset$**4** leading to a supramolecular assembly of macrocycles.

These results extend the capability of our previously reported method for the preparation of macrocyclic phosphonamides. Their potential as ligands for a wide

TABLE VI. Selected bond lengths and bond angles around the phosphorus atom in **3**, **4** and **4** · KSCN.

distances (Å) & angles (°)	**3a**	**3b**	**4a**	**4b**	**4** · KSCN
P=O	1.477(4)	1.476(4)	1.476(2)	1.473(2)	1.475(5)
P-C	1.783(6)	1.782(7)	1.788(5)	1.788(5)	1.776(8)
P-N(2)	1.639(5)	1.647(5)	1.638(3)	1.624(3)	1.647(6)
P-N(4)	1.665(5)	1.650(5)	1.658(3)	1.660(3)	1.664(5)
C-P=O	113.2(3)	115.0(3)	112.2(2)	111.4(2)	115.4(4)
N(2)-P-N(4)	103.8(2)	109.8(3)	104.5(2)	105.7(2)	107.3(3)
O=P-N(2)	116.6(2)	107.5(2)	116.3(2)	115.9(2)	115.6(3)
O=P-N(4)	111.6(2)	115.3(2)	111.1(2)	111.7(2)	107.6(3)
C-P-N(2)	103.2(3)	108.4(3)	103.9(2)	103.4(2)	102.7(3)
C-P-N(4)	107.5(3)	100.5(3)	108.0(2)	108.0(2)	107.8(4)
P-N(2)-C	126.1(4)	129.0(4)	127.8(2)	128.7(3)	128.9(4)
P-N(4)-C	130.2(4)	127.5(4)	127.3(3)	127.3(3)	130.3(4)
Σ[-N(2)-]*	360	357	360	360	359
Σ[-N(4)-]*	360	360	359	359	358

* Sum of the bond angles around the nitrogen atom.

variety of cationic guests is currently being investigated, and is clearly evidenced by the reported solid state structure of the 1 : 1 complex of **4** with a potassium salt. Complexation studies in solution will be presented elsewhere. A subsequent paper will demonstrate that a particularly novel approach to the design of new preorganized ligands based on **1–4**, with phosphonamide binding sites, is readily available [27].

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References

1. L. Wei, A. Bell, K.H. Ahn, M.M. Holl, S. Warner, I.D. Williams and S.J. Lippard: *Inorg. Chem.* **29**, 825 (1990), and references therein.
2. E.I. Sinyavskaya: *Sov. J. Coord. Chem.* (*Engl. Transl.*) **12**, 663 (1986); *Koord. Khim.* **12**, 1155 (1986). E.N. Tsvetkov, A.N. Bovin and V.Kh. Syundyukova: *Russ. Chem. Rev.* (*Engl. Transl.*) **57**, 776 (1988); *Usp. Khim.* **57**, 1353 (1988).
3. M. Badri, J.-P. Majoral, A.-M. Caminade, M. Delmas, A. Gaset, A. Gorgues and J. Jaud: *J. Am. Chem. Soc.* **112**, 5618 (1990). F. Gonce, A.-M. Caminade, F. Boutonnet and J.-P. Majoral: *J. Org. Chem.* **57**, 970 (1992), and references therein.
4. B.P. Friedrichsen, D.R. Powell and H.W. Whitlock: *J. Am. Chem. Soc.* **112**, 8931 (1990).
5. D.R. Armstrong, S. Bennett, M.G. Davidson, R. Snaith, D. Stalke and D.S. Wright: *J. Chem. Soc. Chem. Commun.*, 262 (1992). P. Tecilla, S.K. Chang and A.D. Hamilton: *J. Am. Chem. Soc.*

112, 9586 (1990). M.C. Etter and P.W. Baures: *J. Am. Chem. Soc.* **110**, 639 (1988). F. Toda, K. Mori, Z. Stein and I. Goldberg: *J. Org. Chem.* **53**, 308 (1988).
6. M.I. Kabachnik and Y.M. Polikarpov: *J. Gen. Chem. USSR (Engl. Transl.)* **58**, 1729 (1988); *Zh. Obsh. Khim.* **58**, 1937 (1988). R.M. Izatt, G.C. Lindh, P. Huszthy, G.A. Clark, R.L. Bruening, J.S. Bradshaw and J.J. Christensen: *J. Incl. Phenom.* **7**, 501 (1989).
7. S.J. Geib, S.C. Hirst, C. Vicent and A.D. Hamilton: *J. Chem. Soc. Chem. Commun.*, 1283 (1991).
8. J.-P. Dutasta, J.-P. Declercq, C. Esteban-Calderon and B. Tinant: *J. Am. Chem. Soc.* **111**, 7136 (1989).
9. J.-P. Dutasta and P. Simon: *Tetrahedron Lett.* **28**, 3577 (1987).
10. J.-P. Declercq, J.-P. Dutasta, L. Van Oostenryck, P. Simon and B. Tinant: Unpublished results.
11. A. Furst, R.C. Berlo and S. Hooton: *Chem. Rev.* **65**, 51 (1965).
12. J. Dale and P.O. Kristiansen: *Acta Chem. Scand.* **26**, 1471 (1972).
13. L. Maier: *Helv. Chim. Acta* **46**, 2667 (1963).
14. G.M. Sheldrick: *Crystallographic Computing 3*, eds. G.M. Sheldrick, C. Kruger and R. Goddard, pp. 175–189, Oxford University Press (1985).
15. G.M. Sheldrick: *SHELX 76, Program for Crystal Structure Determination*, University of Cambridge, England (1976).
16. *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, England (1974). Distributed by Kluwer Academic Publishers, Dordrecht, The Netherlands.
17. W.J. Stec, A. Okruszek and J. Michalski: *J. Org. Chem.* **41**, 233 (1976).
18. A.W. Herriott: *J. Am. Chem. Soc.* **93**, 3304 (1971).
19. W.D.S. Motherwell and W. Clegg: *PLUTO, Program for plotting molecular and crystal structures*, University of Cambridge, England (1978).
20. J. Dale: *Isr. J. Chem.* **20**, 3 (1980).
21. L. Pauling: *The Nature of the Chemical Bond* (3rd ed.), Cornell Univ. Press, Ithaca (1960).
22. C.B. Knobler, E.F. Maverick, K.N. Trueblood, R.C. Helgeson and D.J. Cram: *Acta Crystallogr.* **C42**, 156 (1986).
23. D. Moras, B. Metz, M. Herceg and R. Weiss: *Bull. Soc. Chim. Fr.* **II**, 551 (1972). G. Weber and W. Saenger: *Acta Crystallogr.* **B36**, 61 (1980). M.L. Campbell, S.B. Larson and N.K. Dalley: *Acta Crystallogr.* **B37**, 1744 (1981).
24. E. Maverick, P. Seiler, W.B. Schweizer and S.D. Dunitz: *Acta Crystallogr.* **B36**, 615 (1980).
25. F.H. Allen, S.A. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Rodgers and D.G. Watson: *Acta Crystallogr.* **B35**, 2331 (1979).
26. J.-P. Dutasta, C. Esteban-Calderon, B. Tinant and J.-P. Declercq: *Acta Crystallogr.* **C46**, 68 (1990).
27. Preliminary report presented at the XIIth International Conference on Phosphorus Chemistry (Toulouse, France; July 6–10, 1992). J.-P. Dutasta, L. Van Oostenryck, B. Tinant and J.-P. Declercq: *Phosphorus, Sulfur, and Silicon* **75**, 63 (1993).