

# Synthesis and structure of metallated macrocycle-bearing cyclophosphazenes

## Part II: The (Al)/SPIRO (3O2O3)\* derivatives

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### Abstract

Synthesis and molecular structures of two metallated (aluminium) derivatives,  $[\text{C}_9\text{H}_{19}\text{Cl}_4\text{AlN}_5\text{O}_2\text{P}_3] \cdot 1.5\text{C}_7\text{H}_8$  and  $[\text{C}_8\text{H}_{16}\text{Cl}_5\text{AlN}_5\text{O}_2\text{P}_3] \cdot 1.5\text{C}_7\text{H}_8$ , of the macrocycle-bearing cyclophosphazene  $\text{N}_3\text{P}_3\text{Cl}_4[\text{HN}-(\text{CH}_2)_3-\text{O}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_3-\text{NH}]$  (coded as SPIRO 3O2O3) are reported. These two molecular structures reveal the same pattern of metal coordination where the two hydrogen atoms in SPIRO 3O2O3 are substituted by aluminium generating monomeric structures with pentacoordinated aluminium centres in the inner cavities. In the first compound the exocyclic ligand at aluminium is a methyl group, in the second a chlorine atom. Typical Al-N, Al-O and Al-X distances are (Å): 1.84–1.89, 1.97–2.04 and 1.93 in the former, 1.81–1.86, 1.93–2.01 and 2.12 in the latter, respectively.

### INTRODUCTION

Reactions of long polyglycolamines,  $\text{H}_2\text{N}-(\text{CH}_2)_m-\text{O}-(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m-\text{NH}_2$  and  $\text{H}_2\text{N}-(\text{CH}_2)_m-\text{O}-(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m-\text{NH}_2$ , with hexachlorocyclotriphosphazene,  $\text{N}_3\text{P}_3\text{Cl}_6$ , lead to macrocyclic host molecules, the conformation, cavity size and number of coordination sites of which depend drastically on experimental conditions [1–11]. Most of these attractive one- and two-ring architectures were unambiguously evidenced by X-ray investigations [5–11] and only the following four configurations have ever been observed up to now: (i) the SPIRO configuration (in which the oxodiamino ligand is grafted as a SPIRO loop onto one phosphorus atom of one  $\text{N}_3\text{P}_3$  ring);

\*For nomenclature see ref. 3.

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(ii) the *cis*-ANSA configuration (in which the oxodiamino ligand is grafted on one side of one  $N_3P_3$  ring as an ANSA arch onto two different phosphorus atoms); (iii) the *trans*-ANSA configuration (in which the oxodiamino ligand is grafted on both sides of one  $N_3P_3$  ring as an ANSA arch onto two different phosphorus atoms); and (iv) the BINO configuration (in which the oxodiamino ligand bridges two different  $N_3P_3$  rings).

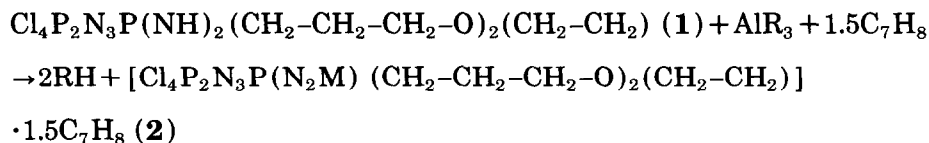
We recently reported [12] the possibility of using one of these new bicyclic compounds, namely the SPIRO (3O2O3) (**1**) [3,6] obtained from  $H_2N-(CH_2)_3-O-(CH_2)_2-O-(CH_2)_3-NH_2$ , as a ligand to metallic elements such as monovalent lithium (**1a**) and divalent zinc (**1b**) and magnesium (**1c**). These three molecular structures reveal three different patterns of metal coordination. In compound (**1a**) one of the two hydrogen atoms in SPIRO 3O2O3 is substituted by lithium generating a dimeric structure with pentacoordinated lithium centres. This structure is further stabilized by N-H hydrogen bonds. In (**1b**) both hydrogen atoms of the macrocyclic loop are replaced by two zinc atoms through a cross-link metallation leading again to a dimeric molecule. In this compound the Zn atom is found to be in a trigonal bipyramidal environment with one very long N-Zn interaction. The origin of the dimerization of the magnesium compound (**1c**) is analogous to (**1b**). Magnesium is in the centre of a distorted octahedron, coordinated with the O- and N-donors of the macrocyclic loop and also one nitrogen atom of the  $N_3P_3$  ring. (**1c**) is the first example of a metallic centre coordinated by a neutral phosphazene ligand.

The present contribution deals with two aluminium cryptates, (**2**) and (**3**), from SPIRO 3O2O3 as the cryptand.

## SYNTHESIS

All experiments have been performed under dry nitrogen in a Stock apparatus (high vacuum techniques). Compound (**1**) has been carefully dried in vacuo after synthesis. Elemental analyses (C,H,N) have been performed by BELLER, Göttingen, Germany; aluminium was determined by standard complexometric methods.  $^1H$  NMR spectra ( $\delta$  values) were recorded on a Bruker-80-MHz-Ft spectrometer and  $^{31}P$  NMR spectra on a Bruker AM 400 spectrometer. For  $^1H$  NMR spectra toluene (Ph-Me, 2.12 ppm) was used both as internal standard and solvent, while for  $^{31}P$  NMR spectra 85% phosphoric acid was used as external standard and 1,2-dichlorobenzene as solvent.

The incorporation of aluminium into the bicyclic SPIRO (3O2O3) (**1**) can be easily performed by reacting it with suitable organoaluminic compounds as summarized in the equation



where R=Me and for product (2) M=Al-Me.

Product (2) is obtained in high yields and can be characterized completely. The molarities of the reactants have to be strictly followed according to the equation.

### *Synthesis of (2)*

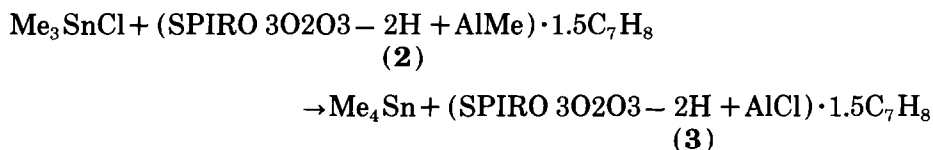
4.46 g (9.89 mmole) (1) are dissolved in 80 ml toluene. Dropwise addition of 4.94 ml of a 2 M solution of trimethylaluminium in toluene causes some precipitation of the product and evolution of methane. Stirring of the mixture is continued for 15 h at 100°C, after which half of the solvent is removed in vacuo at 25°C to spontaneously give 9.7 g (78% yield) of colourless plate-like crystals of (2).

$C_9H_{19}AlCl_4N_5O_2P_3 \cdot 1.5C_7H_8$  (mol.wt., 629.21) (2); m.p. 210°C (dec.);  $^1H$  NMR,  $-0.5776$  ppm (s) Al-Me.  $^{31}P$  NMR: P(2),  $\delta=8.88$  ppm (dd,  $^2J_{PP}=23$  Hz,  $^2J_{PP}=8$  Hz); P(1) or P(3),  $\delta=18.10$  ppm (dd,  $^2J_{PP}=79$  Hz,  $^2J_{PP}=23$  Hz); P(1) or P(3),  $\delta=20.05$  ppm (dd,  $^2J_{PP}=79$  Hz,  $^2J_{PP}=8$  Hz). Elemental analysis: calc.; C, 37.22%; H, 4.97%; Al, 4.29%; N, 11.13%; found; C, 31.55%; H, 4.86%; Al, 4.04%; N, 10.84%.

The deviation in experimental C and H values from the calculated values is partly due to loss of the solvent trapped in the crystal (see below).

### *Reactivity of (2) and synthesis of (3)*

The methyl group of (2) can be exchanged by a halogen as exemplified in the reaction



A suspension of 0.146 g (0.232 mmole) (1) is prepared in 8 ml toluene at room temperature. Dropwise addition of 2.7 ml of a 0.168 M solution of trimethyltinchloride in toluene and stirring of the mixture for 24 h at 80°C gives a clear solution. After slow cooling at room temperature colourless crystals are obtained. Recrystallization of the product from toluene gives 1.43 g (95% yield) of colourless plate-like crystals of (3).

$C_8H_{16}AlCl_5N_5O_2P_3 \cdot 1.5C_7H_8$  (mol.wt. 649.62) (3), m.p. 280°C (dec.). Elemental analysis: calc.; C, 34.21%; H, 4.34%; Al, 4.15%; N, 10.78%; found; C, 33.49%; H, 4.56%; Al, 3.98%; N, 10.32%.

The reaction was done with an excess of trimethyltinchloride as it was an equilibrium reaction [13].

## X-RAY STUDY

*Data collection*

Transparent colourless blocks of compounds (**2**) and (**3**) have been chosen for data collections using a Siemens AED2 diffractometer. 25 *hkl* reflections were used to give the lattice parameters. Details of data collections together with morphologies and sizes of single crystals used are reported in Tables 1 and 2. Lorentz and polarization corrections were applied. Absorption corrections were not necessary.

*Structural analyses and refinements*

Structures were determined using direct methods leading to the location of all non-hydrogen atoms. Hydrogen atoms were added to the structure factors calculations as fixed at 1.08 Å from their related attached atoms. Scattering

TABLE 1

Physical properties and parameters for data collection and refinement of compound (**2**)

Formula	$[\text{C}_9\text{H}_{19}\text{Cl}_4\text{AlN}_5\text{O}_2\text{P}_3] \cdot 1.5\text{C}_7\text{H}_8$
Crystal	Plate-like ( $0.05 \times 0.5 \times 0.9 \text{ mm}^3$ )
Mol. wt. (g)	629.2
Crystal system	Monoclinic
Space group	$P 2_1/n$
$a$ (Å)	7.675(6)
$b$ (Å)	11.919(8)
$c$ (Å)	33.025(2)
$\beta$ (deg.)	94.75(13)
$V$ (Å <sup>3</sup> )	3010.4
$Z$	4
$d_x$ (g cm <sup>-3</sup> )	1.388
$F(000)$	1300
$\mu(\text{MoK}\alpha)$ (cm <sup>-1</sup> )	5.49
Temperature (K)	291
$\lambda$ (Å)	0.71069
$\theta$ range (deg.)	3–45
No. of measured refl.	4189
No. of observed refl., NO	1681 ( $F \geq 3\sigma$ )
No. of variables, NV	253
<i>Agreement factors</i>	
$R$	0.073
$R_w$	0.078
$w = 1.4267 / (\sigma F^2 + 0.002636 F^2)$	

TABLE 2

Physical properties and parameters for data collection and refinement of compound (3)

Formula	[C <sub>8</sub> H <sub>16</sub> Cl <sub>5</sub> AlN <sub>5</sub> O <sub>2</sub> P <sub>3</sub> ] · 1.5C <sub>7</sub> H <sub>8</sub>
Crystal	Plate-like (0.05 × 0.3 × 0.1 mm <sup>3</sup> )
Mol. wt. (g)	649.6
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	7.607(2)
<i>b</i> (Å)	11.918(2)
<i>c</i> (Å)	33.132(9)
$\beta$ (deg.)	95.86(3)
<i>V</i> (Å <sup>3</sup> )	2988.0
<i>Z</i>	4
<i>d</i> <sub>x</sub> (g cm <sup>-3</sup> )	1.444
<i>F</i> (000)	1332
$\mu$ (MoK $\alpha$ ) (cm <sup>-1</sup> )	6.37
Temperature (K)	291
$\lambda$ (Å)	0.71069
$\theta$ range (deg.)	3–45
No. of measured refl.	3057
No. of observed refl., NO	1459 ( $F \geq 3\sigma$ )
No. of variables, NV	235
<i>Agreement factors</i>	
<i>R</i>	0.085
<i>R</i> <sub>w</sub>	0.072
$w = 2.5875 / (\sigma F^2 + 0.000010 F^2)$	

factors were taken from ref. 14. Details for refinements are gathered in Tables 1 and 2. Both calculations with SHELX-76 [15] or SHELX-86 [16] and illustrations with SHAKAL-88 [17] softwares were performed on a Microvax VMS 4.3 computer.

### Packing

Packing in the two structures is most efficient, as from the space groups of the crystals and the number of molecules per unit cell it follows that a closed packed van der Waals lattice is built up [18]. These closed packings are achieved by incorporating solvent molecules in unit cells, namely six molecules of toluene for both compounds (2) and (3). In both cases, four of these molecules of solvent are detected in general positions, whereas two of them are situated at inversion centres in the unit cells. It must be pointed out that the atoms of these clathrated species are so highly vibrating at room temperature that they could not be accurately located as could be done for non-hydrogen atoms of

metallated species. Then, molecules of solvents were only introduced in structure factor calculations of (2) and (3) with occupation factors as indicated at the bottom of Tables 3 and 4.

TABLE 3

Positional parameters and isotropic  $B$  values calculated from  $u_{ij}$  for non-hydrogen atoms of compound (2)

Atom	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
Cl(1)	0.7351(5)	0.4357(4)	0.1215(2)	8.9(3)
Cl(2)	0.5566(7)	0.3995(4)	0.0375(1)	9.7(3)
Cl(3)	0.0543(5)	0.2313(3)	0.0940(2)	8.0(3)
Cl(4)	0.2232(6)	0.2684(5)	0.1801(2)	10.1(3)
P(1)	0.4956(4)	0.4311(3)	0.0943(1)	5.2(2)
P(2)	0.2192(4)	0.5734(3)	0.1124(1)	4.7(2)
P(3)	0.2159(4)	0.3389(3)	0.1249(1)	5.1(2)
Al	0.0466(5)	0.7583(3)	0.1151(1)	4.6(2)
O(1)	-0.185(1)	0.7798(8)	0.0809(3)	6.8(6)
O(2)	-0.122(1)	0.7463(7)	0.1568(3)	6.2(5)
N(1)	0.401(1)	0.3228(9)	0.1084(4)	6.7(7)
N(2)	0.132(1)	0.4549(8)	0.1265(3)	5.1(6)
N(3)	0.410(1)	0.5472(9)	0.0967(4)	5.8(6)
N(4)	0.211(1)	0.6691(8)	0.1465(3)	5.0(6)
N(5)	0.097(1)	0.6443(8)	0.0804(3)	4.4(5)
C(1)	0.036(2)	0.607(1)	0.0393(5)	6.7(4)
C(2)	-0.096(2)	0.692(1)	0.0209(5)	6.8(3)
C(3)	-0.245(2)	0.719(1)	0.0461(6)	7.1(4)
C(4)	-0.321(2)	0.815(1)	0.1069(5)	7.7(4)
C(5)	-0.309(2)	0.750(1)	0.1436(5)	7.2(4)
C(6)	-0.080(2)	0.689(1)	0.1950(5)	7.9(4)
C(7)	0.099(2)	0.710(1)	0.2117(5)	8.1(4)
C(8)	0.234(2)	0.649(1)	0.1902(6)	8.2(4)
C(9)	0.122(2)	0.913(1)	0.1140(5)	8.(1)
C(10)	0.025(3)	0.494(2)	0.7000(8)	13.4(7)
C(11)	0.213(4)	0.450(3)	0.699(1)	15.5(9)
C(12)	0.355(4)	0.476(2)	0.7229(9)	13.7(8)
C(13)	0.349(4)	0.546(2)	0.7571(9)	14.6(8)
C(14)	0.176(5)	0.585(2)	0.7557(9)	15.6(8)
C(15)	0.032(4)	0.565(2)	0.734(1)	15.1(8)
C(16)	0.180(4)	0.391(3)	0.670(1)	19.(1)
C(17)	0.437(3)	0.046(2)	0.0289(7)	10.7(6)
C(18)	0.737(5)	0.078(3)	0.024(1)	21.(1)
C(19)	0.698(5)	-0.003(3)	-0.014(1)	9.(1) <sup>a</sup>
C(20)	0.594(6)	0.090(4)	0.042(1)	10.(1) <sup>a</sup>
C(21)	0.587(6)	0.037(4)	0.005(2)	12.(1) <sup>a</sup>

<sup>a</sup>Occupation factor, 0.5.

TABLE 4

Positional parameters and isotropic  $B$  values calculated from  $u_{ij}$  for non-hydrogen atoms of compound (3)

Atom	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
Cl(1)	0.7361(7)	0.4439(5)	0.1236(2)	10.8(5)
Cl(2)	0.5605(9)	0.4065(6)	0.0390(2)	11.3(5)
Cl(3)	0.0567(7)	0.2294(5)	0.0944(2)	9.0(4)
Cl(4)	0.2290(9)	0.2759(6)	0.1798(2)	11.1(5)
Cl(5)	0.1190(8)	0.9240(5)	0.1139(2)	9.6(4)
P(1)	0.4936(6)	0.4372(6)	0.0947(2)	6.1(4)
P(2)	0.2141(7)	0.5751(5)	0.1115(2)	5.0(3)
P(3)	0.2179(8)	0.3419(5)	0.1242(2)	5.7(4)
Al	0.0341(8)	0.7550(5)	0.1146(2)	5.1(1)
O(1)	-0.196(2)	0.782(1)	0.0807(4)	8.(1)
O(2)	-0.127(2)	0.752(1)	0.1563(4)	6.8(9)
N(1)	0.405(2)	0.328(1)	0.1081(5)	7.(1)
N(2)	0.133(2)	0.457(1)	0.1253(5)	6.(1)
N(3)	0.407(2)	0.554(1)	0.0968(5)	7.(1)
N(4)	0.204(2)	0.669(1)	0.1451(4)	4.9(4)
N(5)	0.092(2)	0.650(1)	0.0788(5)	5.0(4)
C(1)	0.023(3)	0.616(2)	0.0373(7)	7.0(6)
C(2)	-0.110(3)	0.706(2)	0.0212(6)	7.9(6)
C(3)	-0.247(3)	0.725(2)	0.0436(8)	6.9(6)
C(4)	-0.327(3)	0.819(2)	0.107(1)	9.4(7)
C(5)	-0.319(3)	0.762(2)	0.1438(8)	8.6(6)
C(6)	-0.085(3)	0.694(2)	0.1954(8)	8.2(6)
C(7)	0.094(4)	0.713(2)	0.2099(7)	8.2(6)
C(8)	0.222(3)	0.649(2)	0.1907(9)	9.2(7)
C(10)	0.015(4)	0.492(2)	0.6988(8)	11.8(8)
C(11)	0.204(5)	0.459(3)	0.704(1)	16.(1)
C(12)	0.380(4)	0.464(3)	0.720(1)	17.(1)
C(13)	0.329(4)	0.541(2)	0.7529(9)	12.5(9)
C(14)	0.163(5)	0.591(3)	0.7599(9)	14.(1)
C(15)	0.023(4)	0.562(2)	0.734(1)	12.3(8)
C(16)	0.191(5)	0.395(3)	0.670(1)	19.(1)
C(17)	0.445(4)	0.047(2)	0.0331(8)	10.0(7)
C(18)	0.714(5)	0.079(3)	0.016(1)	18.(1)
C(19)	0.698(7)	0.004(4)	-0.020(2)	9.(1) <sup>a</sup>
C(20)	0.600(8)	0.103(4)	0.045(1)	9.(1) <sup>a</sup>
C(21)	0.588(6)	0.027(4)	0.005(2)	9.(1) <sup>a</sup>

<sup>a</sup>Occupation factor, 0.5.

## Results

Final positions and equivalent isotropic thermal parameters for the non-hydrogen equivalent atoms are given in Tables 3 and 4. Bond lengths and an-

TABLE 5

Bond lengths (Å) in (2)

Bond	Length	Bond	Length
P(1)···Cl(1)	1.979(5)	N(5)···P(2)	1.597(9)
P(1)···Cl(2)	2.007(5)	N(5)···Al	1.840(9)
P(3)···Cl(3)	2.004(5)	C(1)···N(5)	1.47(2)
P(3)···Cl(4)	2.002(6)	C(2)···C(1)	1.53(2)
O(1)···Al	2.041(9)	C(3)···O(1)	1.40(2)
O(2)···Al	1.971(9)	C(3)···C(2)	1.50(2)
N(1)···P(1)	1.57(1)	C(4)···O(1)	1.47(2)
N(1)···P(3)	1.58(1)	C(5)···O(2)	1.46(2)
N(2)···P(2)	1.65(1)	C(5)···C(4)	1.43(2)
N(2)···P(3)	1.527(9)	C(6)···O(2)	1.45(2)
N(3)···P(1)	1.54(1)	C(7)···C(6)	1.46(2)
N(3)···P(2)	1.62(1)	C(8)···N(4)	1.46(2)
N(4)···P(2)	1.606(9)	C(8)···C(7)	1.50(2)
N(4)···Al	1.89(1)	C(9)···Al	1.93(1)

TABLE 6

Bond lengths (Å) in (3)

Bond	Length	Bond	Length
P(1)···Cl(1)	1.991(6)	N(5)···Al	1.81(1)
P(1)···Cl(2)	1.999(8)	O(1)···Al	2.01(1)
P(3)···Cl(3)	2.007(7)	O(2)···Al	1.93(1)
P(3)···Cl(4)	1.999(8)	C(1)···N(5)	1.48(2)
Al···Cl(5)	2.116(8)	C(2)···C(1)	1.54(3)
N(1)···P(1)	1.54(1)	C(3)···O(1)	1.42(2)
N(1)···P(3)	1.58(1)	C(3)···C(2)	1.36(2)
N(2)···P(2)	1.62(1)	C(4)···O(1)	1.46(3)
N(2)···P(3)	1.52(1)	C(5)···O(2)	1.48(2)
N(3)···P(1)	1.54(1)	C(5)···C(4)	1.39(3)
N(3)···P(2)	1.62(1)	C(6)···O(2)	1.48(2)
N(4)···P(2)	1.59(1)	C(7)···C(6)	1.41(3)
N(4)···Al	1.86(1)	C(8)···N(4)	1.52(3)
N(5)···P(2)	1.62(1)	C(8)···C(7)	1.43(3)

gles are given in Tables 5–8. Chlorine atoms are found to have relatively high *B* values; this is attributed to their terminal positions in the molecules.

## DISCUSSION

### *Preliminary remarks*

Ball-and-stick drawings of suitable perspective views of (2) and (3) are



TABLE 7

Bond angles (deg.) in (2)

Angle	Value	Angle	Value
Cl(2)-P(1)-Cl(1)	98.6(2)	C(9)-Al-N(4)	111.1(6)
N(1)-P(1)-Cl(1)	108.9(5)	C(9)-Al-N(5)	127.8(6)
N(1)-P(1)-Cl(2)	105.8(5)	C(3)-O(1)-Al	126.8(8)
N(3)-P(1)-Cl(1)	109.6(4)	C(4)-O(1)-Al	109.9(8)
N(3)-P(1)-Cl(2)	110.6(5)	C(4)-O(1)-C(3)	115(1)
N(3)-P(1)-N(1)	121.0(5)	C(5)-O(2)-Al	118.4(8)
N(3)-P(2)-N(2)	108.8(5)	C(6)-O(2)-Al	122.0(8)
N(4)-P(2)-N(2)	111.8(5)	C(6)-O(2)-C(5)	115(1)
N(4)-P(2)-N(3)	116.6(5)	P(3)-N(1)-P(1)	117.1(6)
N(5)-P(2)-N(2)	114.2(5)	P(3)-N(2)-P(2)	125.9(6)
N(5)-P(2)-N(3)	112.7(5)	P(2)-N(3)-P(1)	126.2(6)
N(5)-P(2)-N(4)	92.0(5)	Al-N(4)-P(2)	94.4(4)
Cl(4)-P(3)-Cl(3)	99.5(3)	C(8)-N(4)-P(2)	124.5(9)
N(1)-P(3)-Cl(3)	106.4(5)	C(8)-N(4)-Al	130.9(9)
N(1)-P(3)-Cl(4)	107.9(5)	Al-N(5)-P(2)	96.9(5)
N(2)-P(3)-Cl(3)	110.6(4)	C(1)-N(5)-P(2)	125.1(8)
N(2)-P(3)-Cl(4)	109.3(5)	C(1)-N(5)-Al	137.3(8)
N(2)-P(3)-N(1)	121.0(6)	C(2)-C(1)-N(5)	108(1)
O(2)-Al-O(1)	78.7(4)	C(3)-C(2)-C(1)	116(1)
N(4)-Al-O(1)	152.2(4)	C(2)-C(3)-O(1)	111(1)
N(4)-Al-O(2)	91.4(4)	C(5)-C(4)-O(1)	110(1)
N(5)-Al-O(1)	88.0(4)	C(4)-C(5)-O(2)	105(1)
N(5)-Al-O(2)	124.5(4)	C(7)-C(6)-O(2)	113(1)
N(5)-Al-N(4)	76.2(4)	C(8)-C(7)-C(6)	114(1)
C(9)-Al-O(1)	96.7(6)	C(7)-C(8)-N(4)	111(1)
C(9)-Al-O(2)	107.3(6)		

given in Figs. 1 and 2 which show that the two aluminium derivatives are monomeric. Aluminium appears 5-fold coordinated in both (2) and (3). This 5-fold coordination of aluminium atoms is not very common. There are few compounds previously described with 5-fold coordinated aluminium. For any comparisons, the literature data are given in refs. 19–21 and 27.

#### *Coordination spheres around metals*

Let us focus now on the description of the pentacoordinated aluminium in (2) (Figs. 1 and 3). The coordination polyhedron could be either a tetragonal

TABLE 8

Bond angles (deg.) in (3)

Angle	Value	Angle	Value
Cl(2)-P(1)-Cl(1)	98.1(3)	N(5)-Al-O(2)	131.9(6)
N(1)-P(1)-Cl(1)	107.7(7)	N(5)-Al-N(4)	77.0(6)
N(1)-P(1)-Cl(2)	105.7(7)	C(3)-O(1)-Al	124(1)
N(3)-P(1)-Cl(1)	108.5(6)	C(4)-O(1)-Al	109(1)
N(3)-P(1)-Cl(2)	110.8(7)	C(4)-O(1)-C(3)	121(2)
N(3)-P(1)-N(1)	123.1(8)	C(5)-O(2)-Al	119(1)
N(3)-P(2)-N(2)	109.7(8)	C(6)-O(2)-Al	123(1)
N(4)-P(2)-N(2)	111.6(8)	C(6)-O(2)-C(5)	114(2)
N(4)-P(2)-N(3)	115.6(8)	P(3)-N(1)-P(1)	116.4(9)
N(5)-P(2)-N(2)	117.0(7)	P(3)-N(2)-P(2)	126.9(9)
N(5)-P(2)-N(3)	111.3(8)	P(2)-N(3)-P(1)	123.8(9)
N(5)-P(2)-N(4)	90.8(7)	Al-N(4)-P(2)	95.1(7)
Cl(4)-P(3)-Cl(3)	99.0(3)	C(8)-N(4)-P(2)	125(1)
N(1)-P(3)-Cl(3)	107.1(7)	C(8)-N(4)-Al	128(1)
N(1)-P(3)-Cl(4)	108.4(7)	Al-N(5)-P(2)	95.9(7)
N(2)-P(3)-Cl(3)	112.0(6)	C(1)-N(5)-P(2)	127(1)
N(2)-P(3)-Cl(4)	108.1(7)	C(1)-N(5)-Al	136(1)
N(2)-P(3)-N(1)	120.1(8)	C(2)-C(1)-N(5)	107(2)
O(1)-Al-Cl(5)	95.3(5)	C(3)-C(2)-C(1)	116(2)
O(2)-Al-Cl(5)	103.9(4)	C(2)-C(3)-O(1)	113(2)
O(2)-Al-O(1)	79.9(6)	C(5)-C(4)-O(1)	114(2)
N(4)-Al-Cl(5)	109.4(5)	C(4)-C(5)-O(2)	104(2)
N(4)-Al-O(1)	155.3(6)	C(7)-C(6)-O(2)	110(2)
N(4)-Al-O(2)	93.4(6)	C(8)-C(7)-C(6)	116(2)
N(5)-Al-Cl(5)	123.9(5)	C(7)-C(8)-N(4)	111(2)
N(5)-Al-O(1)	89.8(6)		

pyramid with C(9) at the top or a trigonal bipyramid with O(1) and N(4) in axial positions. A deep comparison of bond lengths and angles according to these possibilities shows that the latter structure has to be preferred. Indeed, the sum of C(9)-Al-O(2), C(9)-Al-N(5) and O(2)-Al-N(5) is equal to 359.6°, i.e. 360°, while O(1)-Al-N(4) is 152.2°. In contrast, the tetragonal pyramid situation would imply C(9)-Al-O(1) (96.7°), C(9)-Al-O(2) (107.3°), C(9)-Al-N(4) (111.1°) and C(9)-Al-N(5) (127.8°) to be equal to 90°. A comparison of bond lengths O(1)-Al with O(2)-Al and N(4)-Al with N(5)-Al also shows the different positions of (O(1), O(2)) and (N(4), N(5)) in the coordination polyhedron in (2).

A similar situation happens in compound (3) where the coordination polyhedron of aluminium is also trigonal bipyramid with O(1) and N(4) in axial positions. Indeed, the sum of Cl(5)-Al-O(2), Cl(5)-Al-N(5) and of O(2)-Al-N(5) is equal to 359.7°, i.e. 360°, while O(1)-Al-N(4) is 155.3°. In contrast, the tetragonal pyramid situation would imply angles near 90° for Cl(5)-

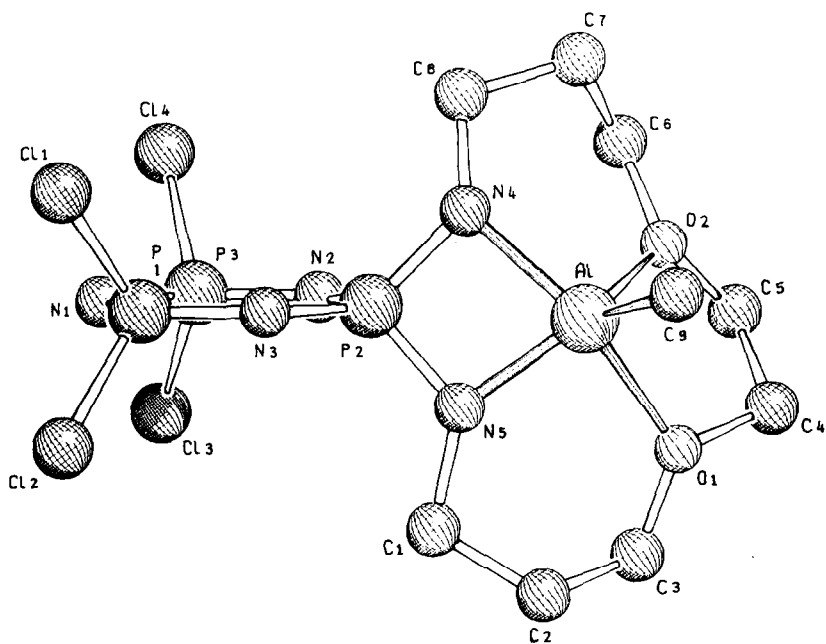


Fig. 1. Perspective view of (2) with numbering of atoms and the  $N_3P_3$  ring perpendicular to the plane of the figure (slightly tilted for sake of clarity).

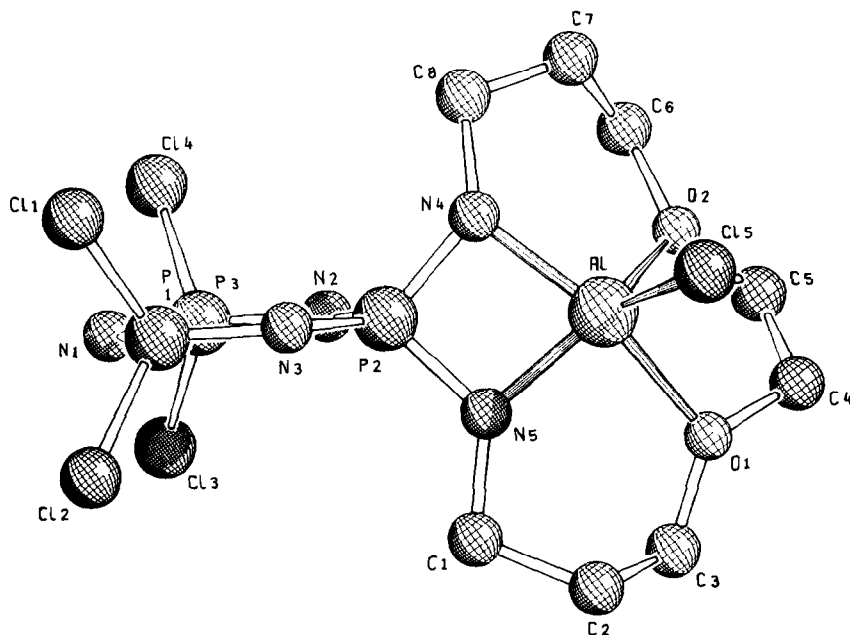


Fig. 2. Perspective view of (3) with numbering of atoms and the  $N_3P_3$  ring perpendicular to the plane of the figure (slightly tilted for sake of clarity).

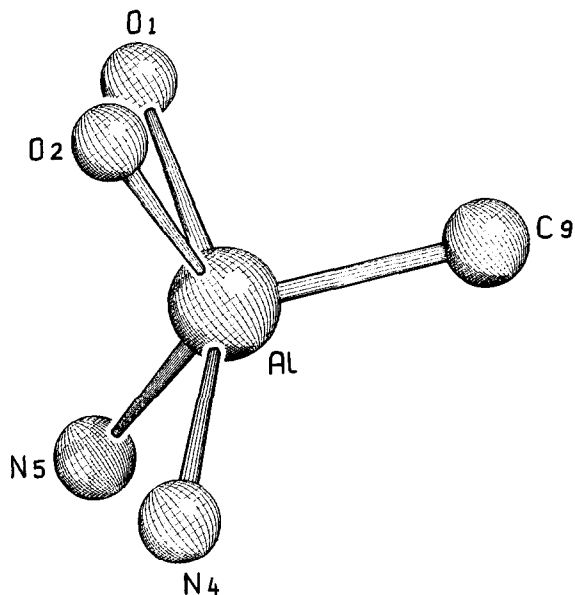


Fig. 3. Coordination polyhedron in (2).

Al-O(1) ( $95.3^\circ$ ), Cl(5)-Al-O(2) ( $103.9^\circ$ ), Cl(5)-Al-N(4) ( $109.4^\circ$ ) and Cl(5)-Al-N(5) ( $123.9^\circ$ ).

Incidentally, the sum of N(4)-P(2)-N(5) ( $92.0^\circ$  in (2) and  $90.8^\circ$  in (3)), P(2)-N(5)-Al ( $96.9^\circ$  in (2) and  $95.9^\circ$  in (3)), P(2)-N(4)-Al ( $94.4^\circ$  in (2) and  $95.1^\circ$  in (3)) and of N(4)-Al-N(5) ( $76.2^\circ$  in (2) and  $77.0^\circ$  in (3)) is equal to  $359.5^\circ$  and  $358.8^\circ$  in (2) and (3) respectively. Then, the P(2)-N(4)-Al-N(5) quadrangles are actually almost square planar. The greater deviation from planarity appears in (3). This can be due to the chlorine atom.

### *Cyclophosphazenic rings*

#### *Compound (2)*

Figure 1 shows that the  $N_3P_3$  ring is planar with P(2)-N(2) ( $1.65 \text{ \AA}$ ) and P(2)-N(3) ( $1.62 \text{ \AA}$ ) longer than in the genuine starting material (1). In that case, this effect must be related only to the coordination of the aluminium atom, no dimerization effect having to be taken into account as in ref. 12. Conversely, P(2)-N(4) and P(2)-N(5) ( $1.61$  and  $1.60 \text{ \AA}$ ) are not really affected upon coordination, despite the fact that aluminium has replaced the two related H-N(4) and H-N(5) hydrogen atoms. The  $^{31}\text{P}$  NMR spectrum of the compound (2) in solution shows that the two phosphorus atoms P(1) and P(3) are not equivalent as in the genuine starting material (1). The different chemical shifts of P(1) and P(3) in solution are consistent with the solid state structure given in Fig. 1. This can be seen as a proof for equal coordination

spheres of aluminium in solution and the solid state. The two phosphorus atoms P(1) and P(3) cannot be assigned to the observed resonances in the  $^{31}\text{P}$  spectrum.

### *Compound (3)*

The same situation is observed in compound **(3)** where the  $\text{N}_3\text{P}_3$  ring stays planar (Fig. 2) with P(2)–N(2) (1.62 Å) and P(2)–N(3) (1.62 Å) longer than in the starting material **(1)**. Again, P(2)–N(4) (1.59 Å) and P(2)–N(5) (1.62 Å) are not really affected upon complexation. The  $^{31}\text{P}$  NMR spectrum of compound **(3)** is also assumed to show different phosphorus atoms P(1) and P(3). The lack of experimental data is due to the extremely low solubility of this compound. In other words, it may be emphasized that aluminium induces only very slight perturbations into the macrocyclic loop when cryptated by this cavity, whatever is its attached ligand (methyl group or chlorine atom).

### *Macrocyclic SPIRO loops*

The most interesting feature comes from the monomeric Al species **(2)** (Fig. 1) in which we neatly observe a “concerted” replacement of the two N–H atoms of the loop by the metal together with a concomitant coordination of the metal to the two oxygen atoms. Figure 4 shows another perspective view of **(2)** with the  $\text{N}_3\text{P}_3$  ring almost equiplanar to the drawing. We may see that the SPIRO loop adopts a sort of “chistera” (i.e. shaped as the gauntlet used when playing Basque pelota) conformation which may protect aluminium from any nucleophilic attack. The same situation is observed in **(3)** (Fig. 5).

Conversely, in dimeric species from lithium, zinc and magnesium [12], the situation seems more intricate, SPIRO loops adopting twisted conformations which are requested both by metal fixation and by dimerization constraints. Anyhow, the SPIRO loop which seemed to be so rigid in the starting material **(1)** [6], appears nicely flexible and capable of adapting itself to any complexing process. Indeed, the four molecular structures obtained up to now reveal four different patterns of metallation: (i) the substitution of one N–H atom of the loop by the metal, the other N–H bond staying unaffected and then free for generating a dimeric architecture (Li); (ii) the substitution of two N–H atoms of the loop by two metal atoms through a sort of cross-link metallation leading to a dimer without hydrogen bonds (Zn); (iii) a pattern analogous to (ii) but in which one N atom from the  $\text{N}_3\text{P}_3$  ring is involved to help at the percoordination of the metal (Mg); and (iv) the substitution of the two N–H atoms of the loop by one metal atom in a monomeric architecture (Al). Incidentally, looking from a mechanistic point of view, it may be anticipated from the distribution of the bond lengths that the dimerization has already occurred at the stage of the replacement of hydrogen atoms of the N–H groups.

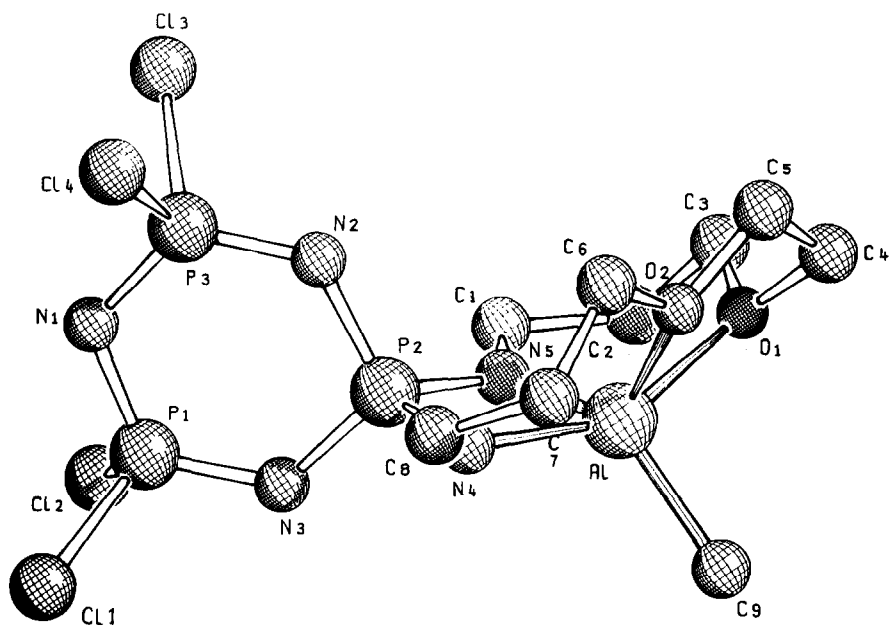


Fig. 4. Perspective view of (2) with numbering of atoms and the  $N_3P_3$  ring parallel to the plane of the figure (slightly tilted for sake of clarity).

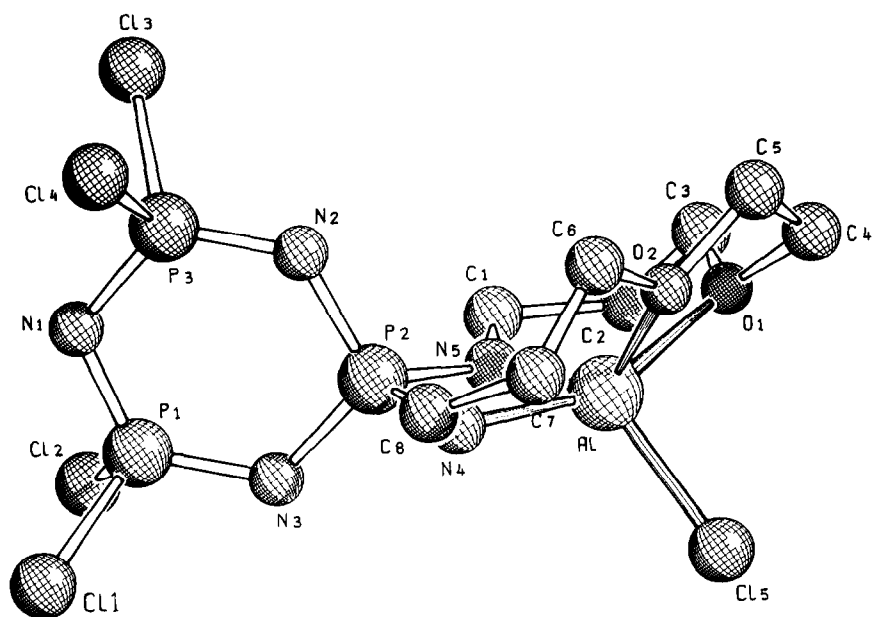


Fig. 5. A perspective view of (3) with the  $N_3P_3$  ring parallel to the plane of the figure (slightly tilted for sake of clarity).

*Metal-ligand bond lengths*

The distances of aluminium atoms to the non-metal N, O, C and Cl are observed to be in the range of their standard atomic radii (Al–N, 1.93; Al–O, 1.91; Al–C, 1.95; Al–Cl, 2.17 Å) [22]. When smaller values are observed, the coordination number at one of the bonding partners is low (e.g. Al–N distances in both structures); higher values are observed for Al–O and Al–C. This seems to be because aluminium is in an unusual 5-fold coordination. For other comparisons, some literature data are given in refs. 19 and 23–31.

## REFERENCES

- 1 F. Sournies, P. Castera, A. El Bakili and J.-F. Labarre, *J. Mol. Struct.*, 221 (1990) 239.
- 2 F. Sournies, P. Castera, A. El Bakili, J.-P. Faucher, M. Graffeuil and J.-F. Labarre, *J. Mol. Struct.*, 221 (1990) 245.
- 3 A. El Bakili, P. Castera, J.-P. Faucher, F. Sournies and J.-F. Labarre, *J. Mol. Struct.*, 195 (1989) 21.
- 4 F. Sournies, A. El Bakili, J.-F. Labarre and B. Perly, *J. Mol. Struct.*, 196 (1989) 201.
- 5 F. Sournies, A. El Bakili, B. Zanin, J.-F. Labarre and J. Jaud, *J. Mol. Struct.*, 220 (1990) 43.
- 6 R. Enjalbert, J. Galy, A. El Bakili, P. Castera, J.-P. Faucher, F. Sournies and J.-F. Labarre, *J. Mol. Struct.*, 196 (1989) 207.
- 7 T.S. Cameron, A. Linden, F. Sournies, A. El Bakili and J.-F. Labarre, *J. Mol. Struct.*, 197 (1989) 41.
- 8 T.S. Cameron, A. Linden, A. El Bakili, P. Castera, J.-P. Faucher, M. Graffeuil, F. Sournies and J.-F. Labarre, *J. Mol. Struct.*, 212 (1989) 281.
- 9 J. Jaud, F. Sournies and J.-F. Labarre, *J. Mol. Struct.*, 212 (1989) 305.
- 10 R. Enjalbert, J. Galy, F. Sournies and J.-F. Labarre, *J. Mol. Struct.*, 221 (1990) 53.
- 11 R. Enjalbert, J. Galy, B. Zanin, J.-P. Bonnet, F. Sournies and J.-F. Labarre, *J. Mol. Struct.*, 246 (1991) 123.
- 12 M. Veith, M. Kross and J.-F. Labarre, *J. Mol. Struct.*, 243 (1991) 189.
- 13 (a) L.J. Zakharkin and O.Y. Okhlobystin, *Dokl. Akad. Nauk SSSR*, 116 (1957) 236; *Izv. Akad. Nauk SSSR*, (1959) 1942.  
(b) W.K. Johnson, Monsanto Co., U.S. Patent 3036103, 1959.  
(c) G.J.M. van der Kerk, *J. Appl. Chem.*, 12 (1962) 17.
- 14 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1962, Table 2.2A.
- 15 G. Sheldrick, Program for Crystal Structure Determination, Version SHELEX-76, Cambridge, University Press, Cambridge, 1976.
- 16 G. Sheldrick, Program for Crystal Structure Determination, Version SHELEX-86, Oxford University Press, Cambridge, 1986.
- 17 E. Keller, SHAKAL-88 software, Freiburg, 1988.
- 18 A.I. Kitaigorodsky, *Molecular Crystals and Structures*, Academic Press, New York, 1973, S. 34 ff.
- 19 C.M. Means, S.G. Bott and J.L. Atwood, *Polyhedron*, 9 (1990) 309.
- 20 G.H. Robinson, S.A. Sangokoya, F. Moise and W.T. Pennington, *Organometallics*, 7 (1988) 1887.
- 21 Y. Hirai, T. Aida and S. Inoue, *J. Am. Chem. Soc.*, 111 (1989) 3062.
- 22 L.C. Allen and J.E. Huheey, *J. Inorg. Nucl. Chem.*, 42 (1980) 1523.

- 23 M. Veith, *Chem. Rev.*, 90 (1990) 3.
- 24 D.A. Drew, A. Haaland and J. Weidlein, *J. Organomet. Chem.*, 94 (1975) 345.
- 25 K. Brendhaugen, A. Haaland and D.P. Novak, *Acta Chem. Scand., Ser. A*, 28 (1974) 45.
- 26 N.Ya. Turova, V.A. Kozunov, A.I. Vanovskii, N.G. Bokii, Yu.T. Struchov and B.L. Tarnopol'skii, *J. Inorg. Nucl. Chem.*, 41 (1979) 5.
- 27 A. Haaland, *Angew. Chem.*, 101 (1989) 1017.
- 28 L.V. Interrante, G.A. Sigel, M. Garbaskas, C. Hejna and G.A. Slack, *Inorg. Chem.*, 28(2) (1989) 252.
- 29 M. Veith, H. Lange, O. Recktenwald and W. Frank, *J. Organomet. Chem.*, 294 (1985) 273.
- 30 M. Veith, W. Frank, F. Töllner and H. Lange, *J. Organomet. Chem.*, 326 (1987) 315.
- 31 B. Celinkaya, P.B. Hitchcock, H.A. Jasim, M.F. Lappert and H.D. Williams, *Polyhedron*, 9 (1990) 239.