SYNTHESIS AND STRUCTURE OF METALLATED MACROCYCLE-BEARING CYCLOPHOSPHAZENES
Part I. The (Li, Mg, Zn)/SPIRO(3O2O3)* derivatives

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ABSTRACT

Syntheses and molecular structures of three metallated (Li, Zn, Mg) derivatives of the macrocycle-bearing cyclophosphazene $N_3P_3Cl_4$ [HN–$(CH_2)_3$–O–$(CH_2)_2$–O–$(CH_2)_3$–NH] (coded as SPIRO 3O2O3, **1**) are reported. These three molecular structures reveal three different patterns of metal coordination. In compound **2** one of the two hydrogen atoms in SPIRO 3O2O3 is substituted by lithium generating a dimeric structure with pentacoordinated lithium centers. This structure is further stabilized by N–H hydrogen bonds. In **3** 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 **4** is analogous to **3**. Magnesium is in the center 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. **4** is the first example of a metallic center coordinated by a neutral phosphazene ligand. Typical metal–N and metal–O distances are (in Å): Li–O, 2.05–2.07; Li–N, 2.07–2.36; Zn–O, 2.08–2.14; Zn–N, 1.94–1.95 (2.49); Mg–O, 2.09–2.14; Mg–N, 2.07–2.31.

INTRODUCTION

An exciting and rapidly growing development in the chemistry of host molecules capable of molecular recognition has occurred in the last few years. Numerous factors seem to influence the selectivity of such compounds in binding host molecules or host cations. Among them are the cavity size, the conformational freedom and the nature of coordination sites.

Reactions of long polyglycolamines, $H_2N–(CH_2)_m–O–(CH_2)_n–O–(CH_2)_m–$
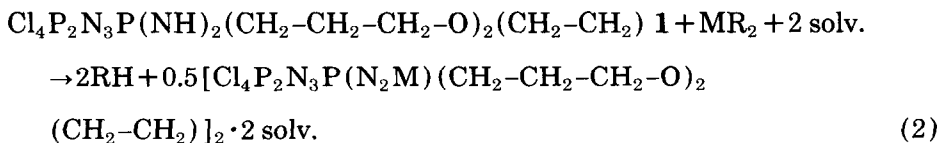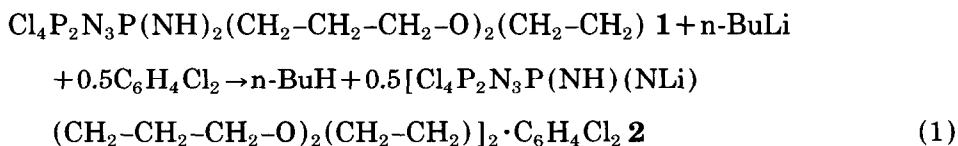
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*For nomenclature, see ref. 3.

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NH$_2$ and H$_2$N–(CH$_2$)$_m$–O–(CH$_2$)$_n$–O–(CH$_2$)$_n$–O–(CH$_2$)$_m$–NH$_2$, with hexachlorocyclotriphosphazene, N$_3$P$_3$Cl$_6$, in suitable conditions lead to mono-BINO (bridged, [1]) and non-gem di-BINO (di-bridged, [2]) di-cyclophosphazenic derivatives which may be considered, at least for the latter type of compound, as crown-ether-shaped cyclophosphazenic species. These syntheses proceed cleanly in ethyl ether with a Na$_2$CO$_3$/water interface. Incidentally, the same reactions may also lead to *cis*-MACRO-ANSA [3] and *cis*-MEGA-ANSA [4] derivatives (i.e. mono-cyclophosphazenic species in which the polyglycolamine ligand is grafted on one side of the N$_3$P$_3$ ring as an ANSA arch on two different P atoms) when achieved in THF without a second phase. It may lead also in toluene/Na$_2$CO$_3$/water to MACRO-SPIRO [3, 5] and MEGA-SPIRO [4, 5] moieties (i.e. mono-cyclophosphazenic species in which the polyglycolamine ligand is grafted as a SPIRO loop onto one phosphorus atom of the N$_3$P$_3$ ring). These winsome macrocyclic one- and two-ring architectures have been unambiguously proven by several X-ray structure investigations [5–10].

We have been interested in the possibility of using one of these new bicyclic compounds, namely the SPIRO (3O2O3) [3, 6] obtained from H$_2$N–(CH$_2$)$_3$–O–(CH$_2$)$_2$–O–(CH$_2$)$_3$–NH$_2$, as a ligand to metallic elements such as the monovalent lithium and the divalent magnesium and zinc. So we attempted the replacement of the hydrogen atoms in the SPIRO loop of the SPIRO (3O2O3) by these electrophiles without changing the cyclophosphazene moiety nor replacing the chlorine atoms on the phosphorus atoms. At the same time we were interested to know how the oxygen-containing ligand would respond to the incorporation of the electrophile. Constitutions were hinted at by elemental analyses as well as by three-dimensional structures from single-crystal X-ray diffractions.

SYNTHESES

The incorporation of metallic elements into the bicyclic SPIRO (3O2O3), **1**, can easily be performed by reacting it with organometallic compounds of Li, Mg and Zn as summarized in the eqns. (1) and (2).

$$Cl_4P_2N_3P(NH)_2(CH_2-CH_2-CH_2-O)_2(CH_2-CH_2) \; \mathbf{1} + n\text{-BuLi}$$

$$+ 0.5 C_6H_4Cl_2 \rightarrow n\text{-BuH} + 0.5[Cl_4P_2N_3P(NH)(NLi)$$

$$(CH_2-CH_2-CH_2-O)_2(CH_2-CH_2)]_2 \cdot C_6H_4Cl_2 \; \mathbf{2} \tag{1}$$

$$Cl_4P_2N_3P(NH)_2(CH_2-CH_2-CH_2-O)_2(CH_2-CH_2) \; \mathbf{1} + MR_2 + 2 \, \text{solv.}$$

$$\rightarrow 2RH + 0.5[Cl_4P_2N_3P(N_2M)(CH_2-CH_2-CH_2-O)_2$$

$$(CH_2-CH_2)]_2 \cdot 2 \, \text{solv.} \tag{2}$$

M=Zn, R=Et (solv.=C_6H_5Cl) **3**
M=Mg, R=Et (solv.=C_7H_8) **4**

The products are obtained in high yields and characterized completely. In reactions (1) and (2) the molarities of the reactants have to be strictly followed according to the equation.

All experiments were performed under dry nitrogen in a Stock apparatus (high vacuum techniques). Compound **1** was carefully dried in vacuo after synthesis. Elemental analyses (C, H, N) were performed by Beller, Göttingen (F.R.G.), lithium was determined by flame-photolysis, and magnesium by standard complexometric methods.

Synthesis of **2**

0.6093 g (1.35 mmol) **1** are dissolved in 22 ml 1,3-dichlorobenzene. Dropwise addition of 0.563 ml of a 2.40 M solution of n-butyllithium in hexane causes some precipitation of the product and evolution of butane. Stirring of the solution is continued for 12 h at 80°C, after which the reaction mixture is allowed

TABLE 1

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

Formula	$[C_8H_{17}Cl_4LiN_5O_2P_3]_2 \cdot C_6H_4Cl_2$
Crystal	Plate-like (0.4 mm × 0.5 mm × 1.1 mm)
Mol. wt. (g)	1060.86
Cryst. system	Monoclinic
Space group	$P2_1/n$
a (Å)	8.748(9)
b (Å)	15.128(14)
c (Å)	17.293(16)
β (°)	102.9(2)
V (Å^3)	2230(2)
Z	2
d_X (g cm^{-3})	1.579
$F(000)$	1076
$\mu(MoK\alpha)$ (cm^{-1})	8.06
Temperature (K)	291
λ (Å)	0.71069
θ range (°)	3–45
No. of meas. refl.	1911
No. of observed refl., NO	1260 ($F \geq 3\sigma$)
No. of variables, NV	207
Agreement factors	
R	0.071
R_w	0.077

$w = 1.9926/(\sigma_{F^2} + 0.001 \cdot F^2)$

to cool to room temperature. 0.566 g (79% yield) colourless, plate-like crystals of **2** are formed.

$C_{16}H_{34}Cl_8Li_2N_{10}O_4P_6 \cdot C_6H_4Cl_2$ (mol. wt.1060.86) **2**, m.p. 170–200°C (dec.). Elemental analysis. Calc. (%): C, 24.91; H, 3.61; Li, 1.31; N, 13.20. Found (%): C, 26.38; H, 4.78; Li, 1.23; N, 13.64.
(The deviation in experimental C and H values from the calculated values is due partly to loss of solvent trapped in the crystal (see below).)

Synthesis of 3

0.2633 g (0.5838 mmol) of **1** are dissolved in 6 ml toluene. Dropwise addition of 0.584 ml of a 1 M solution of diethylzinc in hexane causes evolution of ethane. The solution is stirred during 1 day at 90°C. Removal of the solvent in vacuo at 25°C gives a white powder. After recrystallization of the product from chlorobenzene, 0.3 g (82% yield) of colourless plate-like crystals of **3** are obtained.

$C_{16}H_{32}Cl_8N_{10}O_4P_6Zn_2 \cdot 2C_6H_5Cl$ (mol. wt.1253.86) **3**, m.p. 240°C (dec.). El-

TABLE 2

Physical properties and parameters for data collection and refinement of compound **3**

Formula	$[C_8H_{16}Cl_4ZnN_5O_2P_3]_2 \cdot 2C_6H_5Cl$
Crystal	Plate-like (0.05 mm $\times$ 0.3 mm $\times$ 0.7 mm)
Mol. wt. (g)	1253.86
Cryst. system	Monoclinic
Space group	$P2_1/n$
a (Å)	8.439(6)
b (Å)	16.782(10)
c (Å)	17.574(9)
$\beta(°)$	96.92(4)
V (Å^3)	2471(2)
Z	2
d_X (g cm^{-3})	1.685
$F(000)$	1264
$\mu(MoK\alpha)$ (cm^{-1})	16.21
Temperature (K)	291
λ (Å)	0.71069
θ range (°)	3–45
No. of meas. refl.	3362
No. of observed refl., NO	2148 ($F \geq 2\sigma$)
No. of variables, NV	261
Agreement factors	
R	0.061
R_w	0.062

$w = 0.887/(\sigma_{F^2} + 0.001725 \cdot F^2)$

emental analysis. Calc (%): C, 26.82; H, 3.38; N, 11.17. Found (%): C, 29.23; H, 4.10; N, 10.65.
(The deviation in experimental C and H values from the calculated values is due partly to loss of the solvent trapped in the crystal (see below).)

Synthesis of 4

A suspension of 0.053 g (0.64 mmol) diethylmagnesium and 0.2887 g (0.64 mmol) 1 is prepared in 7 ml toluene at room temperature. The reaction mixture is stirred during 2 days at 90°C and evolution of ethane is observed. After removal of the solvent in vacuo at 25°C a white powder is obtained. Recrystallization of the product from toluene gives 0.289 g (80% yield) of colourless cube-like crystals of 4.

$C_{16}H_{32}Cl_8Mg_2N_{10}O_4P_6 \cdot 2C_7H_8$ (mol. wt.1130.85) 4, m.p. 230°C (dec.). Elemental analysis. Calc. (%): C, 31.86; H, 4.28; Mg, 4.30; N, 12.39. Found (%): C, 31.53; H, 5.06; Mg, 3.95; N, 13.25.

TABLE 3

Physical properties and parameters for data collection and refinement of compound 4

Formula	$[C_8H_{16}Cl_4MgN_5O_2P_3]_2 \cdot 2C_7H_8$
Crystal	Cube-like (0.45 mm × 0.5 mm × 0.6 mm)
Mol. wt. (g)	1130.85
Cryst. system	Monoclinic
Space group	$C2/c$
a (Å)	22.745(12)
b (Å)	16.158(8)
c (Å)	15.930(9)
β(°)	122.69(4)
V (Å^3)	4927(2)
Z	4
d_X (g cm^{-3})	1.524
$F(000)$	2320
μ(MoKα) (cm^{-1})	6.56
Temperature (K)	291
λ (Å)	0.71069
θ range (°)	3–45
No. of meas. refl.	3362
No. of observed refl., NO	2110 ($F \geq 2\sigma$)
No. of variables, NV	281
Agreement factors	
R	0.062
R_w	0.070
$w = 0.889/(\sigma_{F^2} + 0.005758 \cdot F^2)$	

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

Then, composition and nomenclature of the metallated compounds described here is as follows: **2**, [SPIRO 3O2O3–H+Li]$_2 \cdot$C$_6$H$_4$Cl$_2$; **3**, [SPIRO 3O2O3–2H+Zn]$_2 \cdot$2C$_6$H$_5$Cl; **4**, [SPIRO 3O2O3–2H+Mg]$_2 \cdot$2C$_7$H$_8$.

TABLE 4

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

Atom	x	y	z	B (Å^2)
Cl(1)	0.0514(7)	0.8201(2)	0.7389(3)	7.7(3)
Cl(2)	−0.0324(5)	0.6711(3)	0.8423(2)	6.2(2)
Cl(3)	0.5035(9)	0.5444(4)	0.8497(3)	11.8(5)
Cl(4)	0.5602(5)	0.6989(4)	0.7532(5)	11.1(4)
P(1)	0.0962(4)	0.6919(2)	0.7612(2)	3.7(2)
P(2)	0.1324(3)	0.5696(2)	0.6427(2)	2.7(1)
P(3)	0.3819(4)	0.6230(2)	0.7669(2)	4.3(2)
O(1)	−0.289(1)	0.5226(5)	0.5869(5)	4.2(2)
O(2)	−0.215(1)	0.6316(5)	0.4696(5)	3.8(2)
N(1)	0.272(1)	0.6839(8)	0.8051(7)	5.6(7)
N(2)	0.318(1)	0.5707(6)	0.6904(6)	3.5(5)
N(3)	0.033(1)	0.6361(6)	0.6866(5)	3.3(5)
N(4)	0.109(1)	0.5846(5)	0.5501(5)	2.8(2)
N(5)	0.055(1)	0.4699(6)	0.6460(6)	3.0(2)
C(1)	−0.008(2)	0.4383(9)	0.7133(8)	4.2(2)
C(2)	−0.181(2)	0.4200(9)	0.6917(9)	4.8(3)
C(3)	−0.283(2)	0.5009(9)	0.6677(9)	4.4(3)
C(4)	−0.383(2)	0.603(1)	0.565(1)	5.2(3)
C(5)	−0.377(2)	0.621(1)	0.481(1)	5.2(3)
C(6)	−0.146(2)	0.7129(9)	0.4958(8)	4.2(3)
C(7)	0.009(2)	0.7210(9)	0.4715(8)	4.0(2)
C(8)	0.146(2)	0.6703(9)	0.5275(8)	4.1(2)
Li	−0.111(3)	0.519(1)	0.527(1)	3.5(3)
Cl(5)	0.029(4)	0.349(2)	0.915(2)	12.3(7)[a]
Cl(6)	0.241(6)	0.419(3)	0.936(3)	9.8(9)[b]
Cl(7)	0.194(7)	0.549(3)	1.021(3)	19.(1)[a]
Cl(8)	−0.177(5)	0.371(2)	0.910(2)	8.2(7)[b]
C(9)	0.030(5)	0.445(2)	0.967(2)	5.3(6)[c]
C(10)	0.127(5)	0.483(3)	0.987(3)	12.2(8)
C(11)	−0.058(7)	0.431(3)	0.955(3)	7.(1)[c]
C(12)	0.149(5)	0.390(2)	0.924(2)	5.9(8)[c]
C(13)	−0.058(4)	0.343(2)	0.908(2)	4.6(6)[c]

[a]Occupation factor, 0.3333. [b]Occupation factor, 0.1667. [c]Occupation factor, 0.5

X-RAY STUDIES

Data collection

Transparent colourless blocks of compounds **2–4** have been chosen for data collection using a Siemens AED2 diffractometer. 25 *hkl* reflections were used to give the lattice parameters. Details of data collection together with morphologies and sizes of single crystals used are reported in Tables 1–3. Lorentz and polarization corrections were applied. Absorption corrections were not necessary.

TABLE 5

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

Atom	x	y	z	B (Å^2)
Zn	0.0505(1)	0.02557(8)	0.08010(6)	2.84(5)
Cl(1)	−0.5106(4)	0.2720(2)	−0.0512(3)	8.0(2)
Cl(2)	−0.4590(4)	0.1875(2)	−0.2000(2)	7.4(2)
Cl(3)	0.0931(4)	0.3396(3)	−0.1508(3)	9.3(3)
Cl(4)	−0.0608(5)	0.4044(2)	−0.0155(3)	10.0(3)
Cl(5)	0.3035(8)	0.0526(4)	0.6793(4)	14.0(2)
P(1)	−0.3321(3)	0.2247(2)	−0.1037(2)	4.1(2)
P(2)	−0.0712(3)	0.1504(1)	−0.0176(1)	2.7(1)
P(3)	−0.0581(3)	0.3054(1)	−0.0772(2)	3.9(1)
O(1)	0.2955(8)	0.0453(4)	0.0957(4)	4.1(4)
O(2)	0.089(1)	0.0326(4)	0.2026(4)	4.7(4)
N(1)	−0.2267(9)	0.2965(5)	−0.1265(5)	4.5(5)
N(2)	0.0139(9)	0.2375(4)	−0.0267(5)	3.3(4)
N(3)	−0.2556(9)	0.1530(4)	−0.0591(5)	3.5(4)
N(4)	−0.0686(9)	0.1244(4)	0.0693(4)	3.1(4)
N(5)	0.0309(8)	0.0806(4)	−0.0524(4)	2.6(4)
C(1)	0.182(1)	0.0976(6)	−0.0857(6)	3.8(6)
C(2)	0.327(1)	0.0613(6)	−0.0375(7)	4.1(6)
C(3)	0.363(1)	0.0964(6)	0.0398(8)	4.5(6)
C(4)	0.349(1)	0.0677(8)	0.1754(8)	6.1(8)
C(5)	0.253(2)	0.0194(8)	0.2238(7)	6.0(8)
C(6)	0.026(2)	0.1064(8)	0.2355(7)	6.5(9)
C(7)	−0.143(2)	0.1239(8)	0.1987(7)	5.8(8)
C(8)	−0.153(1)	0.1676(6)	0.1246(6)	4.4(6)
C(11)	0.110(2)	0.094(1)	0.658(1)	8.8(5)
C(12)	0.068(2)	0.156(1)	0.6984(9)	8.9(4)
C(13)	−0.085(2)	0.191(1)	0.690(1)	10.4(5)
C(14)	−0.185(3)	0.157(1)	0.631(1)	12.1(6)
C(15)	−0.140(2)	0.089(1)	0.593(1)	11.3(5)
C(16)	0.010(3)	0.044(1)	0.601(1)	11.7(6)

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 factor

TABLE 6

Positional parameters and isotropic B values calculated from u_{ij} for non-hydrogen atoms of compound **4**

Atom	x	y	z	B (Å^2)
Cl(1)	0.2195(2)	−0.0355(2)	0.2281(2)	6.8(3)
Cl(2)	0.0845(1)	−0.0383(2)	0.0234(3)	7.4(3)
Cl(3)	0.1917(2)	0.1439(2)	−0.1022(3)	8.8(4)
Cl(4)	0.3318(2)	0.1308(2)	0.0925(3)	9.5(4)
P(1)	0.1888(1)	−0.0345(1)	0.0851(2)	3.8(2)
P(2)	0.2396(1)	−0.1088(1)	−0.0263(1)	3.5(2)
P(3)	0.2460(1)	0.0620(1)	0.0079(2)	4.4(2)
Mg	0.2305(1)	−0.2602(1)	−0.1107(2)	3.3(2)
O(1)	0.1535(3)	−0.2791(3)	−0.2655(4)	5.0(5)
O(2)	0.2878(3)	−0.2341(3)	−0.1752(4)	4.5(5)
N(1)	0.2052(4)	0.0546(3)	0.0615(5)	4.5(6)
N(2)	0.2652(4)	−0.0146(3)	−0.0296(5)	4.3(6)
N(3)	0.2159(3)	−0.1125(3)	0.0581(4)	3.8(5)
N(4)	0.3002(3)	−0.1794(3)	0.0176(4)	3.3(5)
N(5)	0.1825(3)	−0.1468(3)	−0.1305(4)	4.0(5)
C(1)	0.1128(5)	−0.1138(6)	−0.1958(7)	5.5(8)
C(2)	0.0818(6)	−0.1523(7)	−0.2998(8)	8.(1)
C(3)	0.0847(6)	−0.2435(7)	−0.3056(8)	8.(1)
C(4)	0.1825(6)	−0.2720(6)	−0.3246(7)	6.0(9)
C(5)	0.2422(6)	−0.2101(6)	−0.2778(7)	5.9(9)
C(6)	0.3487(6)	−0.1790(7)	−0.1245(8)	6.(1)
C(7)	0.3935(5)	−0.1984(6)	−0.0178(8)	5.6(8)
C(8)	0.3726(5)	−0.1602(5)	0.0476(7)	5.0(8)
C(9)	0.5000(0)	0.236(1)	0.2500(0)	9.2(5)[a]
C(10)	0.5000(0)	0.385(2)	0.2500(0)	13.5(7)[a]
C(11)	0.490(1)	0.312(1)	0.113(2)	15.2(6)
C(12)	0.487(2)	0.243(2)	0.138(2)	9.5(7)[a]
C(13)	0.492(1)	0.301(2)	0.203(2)	9.1(7)[a]
C(14)	0.505(2)	0.391(2)	0.175(2)	11.0(8)[a]
C(15)	0.570(2)	0.036(2)	0.563(4)	8.2(8)[a]
C(16)	0.530(2)	0.027(1)	0.450(3)	5.6(4)[a]
C(17)	0.500(3)	0.015(3)	0.389(4)	13.(1)[a]
C(18)	0.473(2)	−0.006(2)	0.415(2)	7.4(6)[a]
C(19)	0.433(2)	−0.024(2)	0.376(4)	12.(1)[a]
C(20)	0.434(2)	−0.013(2)	0.307(3)	13.(1)[a]
C(21)	0.446(2)	−0.032(1)	0.489(4)	5.7(5)[a]

[a]Occupation factor 0.5

calculations as fixed at 1.08 Å from their related attached atoms. Scattering factors were taken from ref. 11. Details for refinements are gathered in Tables 1–3. Both calculations with SHELX-76 [12] or SHELX-86 [13] and illustrations with SHAKAL-88 [14] programs were performed on a Microvax VMS 4.3 computer.

Packing

Packing in the three 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 [15]. These closed packings are achieved by incorporating solvent molecules in unit cells, namely 2 molecules of 1,3-dichlorobenzene for **2**, 4 molecules of chlorobenzene for **3** and 8 molecules of toluene for **4**. All these molecules of solvent are detected at centers of symmetry (thus randomly distributed) except for those in **3**. It must be pointed out that these clathrated species are so hugely wobbling at room temperature that they could not be accurately located as we could do for non-hydrogen atoms of metallated species. Then, molecules of solvents were introduced in structure factor calculations of **2**, **3** and **4** with occupation factors as indicated at the bottom of Tables 4 and 6.

TABLE 7

Bond lengths in **2**

Bond	Length (Å)	Bond	Length (Å)
P(1)⋯Cl(1)	2.000(5)	C(3)⋯C(2)	1.52(2)
P(1)⋯Cl(2)	2.008(6)	C(4)⋯O(1)	1.48(2)
P(3)⋯Cl(3)	1.979(5)	C(5)⋯O(2)	1.48(2)
P(3)⋯Cl(4)	1.992(7)	C(5)⋯C(4)	1.49(3)
N(1)⋯P(1)	1.562(9)	C(6)⋯O(2)	1.40(1)
N(1)⋯P(3)	1.58(1)	C(7)⋯C(6)	1.52(2)
N(2)⋯P(2)	1.648(8)	C(8)⋯N(4)	1.41(2)
N(2)⋯P(3)	1.537(8)	C(8)⋯C(7)	1.56(2)
N(3)⋯P(1)	1.537(8)	Li⋯O(1)	2.05(3)
N(3)⋯P(2)	1.63(1)	Li⋯O(2)	2.07(2)
N(4)⋯P(2)	1.584(9)	Li⋯N(4)	2.13(2)
N(5)⋯P(2)	1.661(9)	Li⋯N(4)'	2.07(2)
C(1)⋯N(5)	1.47(2)	Li⋯N(5)	2.36(2)
C(2)⋯C(1)	1.50(2)	H⋯O(2)'	2.02(1)
C(3)⋯O(1)	1.42(2)	H⋯N(5)	1.08(0)

Results

Final positions and *B* values for the non-hydrogen atoms are given in Tables 4–6. Bond lengths and angles are given in Tables 7–12. Chlorine atoms from phosphazenic rings are found to have relatively high *B* values; this is attributed to their terminal positions in the molecules.

TABLE 8

Bond angles in **2**

Angle	Value (deg)	Angle	Value (deg)
Cl(2)–P(1)–Cl(1)	99.8(3)	Li–N(4)–P(2)	91.6(7)
N(1)–P(1)–Cl(1)	107.3(5)	Li'–N(4)–P(2)	121.7(7)
N(1)–P(1)–Cl(2)	107.1(6)	Li–N(4)–C(8)	128.9(8)
N(3)–P(1)–Cl(1)	110.6(4)	Li'–N(4)–C(8)	119.0(8)
N(3)–P(1)–Cl(2)	110.2(5)	Li–N(4)–Li'	70.4(8)
N(3)–P(1)–N(1)	119.9(6)	P(2)–N(5)–H	106(1)
N(3)–P(2)–N(2)	109.4(4)	C(1)–N(5)–H	125(1)
N(4)–P(2)–N(2)	113.2(5)	Li–N(5)–H	84(2)
N(4)–P(2)–N(3)	115.0(4)	C(1)–N(5)–P(2)	123.3(8)
N(5)–P(2)–N(2)	110.9(4)	Li–N(5)–P(2)	81.9(5)
N(5)–P(2)–N(3)	106.2(6)	Li–N(5)–C(1)	121.8(9)
N(5)–P(2)–N(4)	101.8(4)	C(2)–C(1)–N(5)	113.3(9)
Cl(4)–P(3)–Cl(3)	97.1(4)	C(3)–C(2)–C(1)	115(1)
N(1)–P(3)–Cl(3)	109.1(6)	C(2)–C(3)–O(1)	110(1)
N(1)–P(3)–Cl(4)	106.2(5)	C(5)–C(4)–O(1)	105(1)
N(2)–P(3)–Cl(3)	110.3(4)	C(4)–C(5)–O(2)	113(1)
N(2)–P(3)–Cl(4)	109.8(5)	C(7)–C(6)–O(2)	109(1)
N(2)–P(3)–N(1)	121.5(4)	C(8)–C(7)–C(6)	114(1)
C(4)–O(1)–C(3)	110(1)	C(7)–C(8)–N(4)	116(1)
Li–O(1)–C(3)	128.6(9)	O(1)–Li–N(4)'	117(1)
Li–O(1)–C(4)	109(1)	O(2)–Li–O(1)	85.6(9)
C(5)–O(2)–H'	131(1)	O(2)–Li–N(4)'	112.4(8)
C(6)–O(2)–C(5)	114(1)	N(4)–Li–O(1)	131(1)
C(6)–O(2)–H'	112(1)	N(4)–Li–O(2)	89.5(8)
Li–O(2)–C(5)	100(1)	N(4)–Li–N(4)'	109.6(6)
Li–O(2)–C(6)	117.1(7)	N(5)–Li–O(1)	87.5(8)
Li–O(2)–H'	74(1)	N(5)–Li–O(2)	142.8(9)
P(3)–N(1)–P(1)	117.8(6)	N(5)–Li–N(4)	68.1(6)
P(3)–N(2)–P(2)	124.4(7)	N(5)–Li–N(4)'	103.2(6)
P(2)–N(3)–P(1)	126.8(6)	N(5)–H–O(2)'	171(2)
C(8)–N(4)–P(2)	115.2(7)		

TABLE 9

Bond lengths in **3**

Bond	Length (Å)	Bond	Length (Å)
N(5)···Zn	2.492(7)		
Zn···N(5)'	1.950(7)		
P(1)···Cl(1)	2.022(4)	N(5)···P(2)	1.618(7)
P(1)···Cl(2)	1.990(4)	C(1)···N(5)	1.49(1)
P(3)···Cl(3)	2.007(5)	C(2)···C(1)	1.53(1)
P(3)···Cl(4)	1.985(4)	C(3)···O(1)	1.47(1)
O(1)···Zn	2.080(6)	C(3)···C(2)	1.48(2)
O(2)···Zn	2.141(6)	C(4)···O(1)	1.47(1)
N(1)···P(1)	1.578(8)	C(5)···O(2)	1.41(1)
N(1)···P(3)	1.582(8)	C(5)···C(4)	1.48(2)
N(2)···P(2)	1.646(7)	C(6)···O(2)	1.49(1)
N(2)···P(3)	1.524(7)	C(7)···C(6)	1.53(2)
N(3)···P(1)	1.536(7)	C(8)···N(4)	1.46(1)
N(3)···P(2)	1.638(7)	C(8)···C(7)	1.49(2)
N(4)···Zn	1.937(7)		
N(4)···P(2)	1.586(8)		

TABLE 10

Bond angles in **3**

Angle	Value (deg)	Angle	Value (deg)
O(2)-Zn-O(1)	80.3(3)	N(2)-P(3)-N(1)	121.2(4)
N(4)-Zn-O(1)	111.9(3)	C(3)-O(1)-Zn	117.8(5)
N(4)-Zn-O(2)	93.7(3)	C(4)-O(1)-Zn	110.6(7)
N(5)-Zn-O(1)	91.0(2)	C(4)-O(1)-C(3)	112.9(9)
N(5)-Zn-O(2)	154.7(2)	C(5)-O(2)-Zn	106.3(7)
N(5)-Zn-N(4)	67.4(3)	C(6)-O(2)-Zn	114.7(6)
N(5)'-Zn-N(5)	97.0(2)	C(6)-O(2)-C(5)	114.1(9)
N(5)'-Zn-O(1)	119.5(2)	P(3)-N(1)-P(1)	115.5(5)
N(5)'-Zn-O(2)	107.9(2)	P(3)-N(2)-P(2)	125.0(5)
N(5)'-Zn-N(4)	126.4(3)	P(2)-N(3)-P(1)	124.6(5)
Cl(2)-P(1)-Cl(1)	99.1(2)	P(2)-N(4)-Zn	106.1(4)
N(1)-P(1)-Cl(1)	106.9(4)	C(8)-N(4)-Zn	130.3(6)
N(1)-P(1)-Cl(2)	106.6(4)	C(8)-N(4)-P(2)	123.5(6)
N(3)-P(1)-Cl(1)	111.4(4)	P(2)-N(5)-Zn	83.9(3)
N(3)-P(1)-Cl(2)	109.8(3)	C(1)-N(5)-Zn	118.3(5)
N(3)-P(1)-N(1)	120.8(4)	C(1)-N(5)-P(2)	121.9(6)
N(3)-P(2)-N(2)	109.6(4)	P(2)'-N(5)'-Zn	124.5(3)
N(4)-P(2)-N(2)	112.5(4)	C(1)'-N(5)'-Zn	111.5(5)
N(4)-P(2)-N(3)	109.8(4)	Zn'-N(5)'-Zn	82.9(2)
N(5)-P(2)-N(2)	110.4(4)	C(2)-C(1)-N(5)	111.8(8)
N(5)-P(2)-N(3)	111.9(4)	C(3)-C(2)-C(1)	114.6(9)
N(5)-P(2)-N(4)	102.7(4)	C(2)-C(3)-O(1)	109.0(8)
Cl(4)-P(3)-Cl(3)	99.4(2)	C(5)-C(4)-O(1)	106.3(9)
N(1)-P(3)-Cl(3)	105.8(4)	C(4)-C(5)-O(2)	110.6(9)
N(1)-P(3)-Cl(4)	108.0(4)	C(7)-C(6)-O(2)	111(1)
N(2)-P(3)-Cl(3)	110.4(3)	C(8)-C(7)-C(6)	115(1)
N(2)-P(3)-Cl(4)	109.8(3)	C(7)-C(8)-N(4)	110.9(9)

TABLE 11

Bond lengths in **4**

Bond	Length (Å)	Bond	Length (Å)
P(1)···Cl(1)	1.989(3)	N(4)···Mg	2.212(6)
P(1)···Cl(2)	2.020(3)	N(5)···P(2)	1.578(6)
P(3)···Cl(3)	2.004(3)	N(5)···Mg	2.068(6)
P(3)···Cl(4)	2.005(3)	C(1)···N(5)	1.45(1)
Mg···N(3)'	2.305(6)	C(2)···C(1)	1.54(1)
Mg···N(4)'	2.181(6)	C(3)···O(1)	1.45(1)
O(1)···Mg	2.140(6)	C(3)···C(2)	1.48(2)
O(2)···Mg	2.093(5)	C(4)···O(1)	1.41(1)
N(1)···P(1)	1.583(6)	C(5)···O(2)	1.44(1)
N(1)···P(3)	1.568(6)	C(5)···C(4)	1.52(1)
N(2)···P(2)	1.640(6)	C(6)···O(2)	1.47(1)
N(2)···P(3)	1.536(6)	C(7)···C(6)	1.47(1)
N(3)···P(1)	1.563(6)	C(8)···N(4)	1.48(1)
N(3)···P(2)	1.699(6)	C(8)···C(7)	1.49(1)
N(4)···P(2)	1.626(6)		

TABLE 12

Bond angles in **4**

Angle	Value (deg)	Angle	Value (deg)
Cl(2)–P(1)–Cl(1)	98.7(2)	N(5)–Mg–N(4)	71.0(2)
N(1)–P(1)–Cl(1)	107.3(3)	N(5)–Mg–N(4)'	99.4(2)
N(1)–P(1)–Cl(2)	106.1(3)	C(3)–O(1)–Mg	117.9(5)
N(3)–P(1)–Cl(1)	111.2(2)	C(4)–O(1)–Mg	111.7(5)
N(3)–P(1)–Cl(2)	112.1(3)	C(4)–O(1)–C(3)	117.0(7)
N(3)–P(1)–N(1)	119.3(3)	C(5)–O(2)–Mg	110.8(5)
N(3)–P(2)–N(2)	109.1(3)	C(6)–O(2)–Mg	120.3(5)
N(4)–P(2)–N(2)	115.6(3)	C(6)–O(2)–C(5)	110.4(6)
N(4)–P(2)–N(3)	101.0(3)	P(3)–N(1)–P(1)	118.9(4)
N(5)–P(2)–N(2)	115.6(3)	P(3)–N(2)–P(2)	123.7(4)
N(5)–P(2)–N(3)	112.6(3)	P(2)–N(3)–P(1)	122.0(3)
N(5)–P(2)–N(4)	101.8(3)	Mg–N(3)'–P(1)'	146.0(3)
Cl(4)–P(3)–Cl(3)	98.0(2)	Mg–N(3)'–P(2)'	89.3(3)
N(1)–P(3)–Cl(3)	105.0(3)	Mg–N(4)–P(2)	90.0(3)
N(1)–P(3)–Cl(4)	108.9(3)	C(8)–N(4)–P(2)	121.9(5)
N(2)–P(3)–Cl(3)	111.2(3)	C(8)–N(4)–Mg	122.6(5)
N(2)–P(3)–Cl(4)	109.3(3)	Mg–N(4)'–P(2)'	95.6(3)
N(2)–P(3)–N(1)	121.8(3)	Mg–N(4)'–Mg'	91.7(3)
O(1)–Mg–N(3)'	103.5(2)	Mg–N(4)'–C(8)'	125.6(5)
O(1)–Mg–N(4)'	110.9(2)	Mg–N(5)–P(2)	96.7(3)
O(2)–Mg–O(1)	78.5(2)	C(1)–N(5)–P(2)	124.9(5)
O(2)–Mg–N(3)'	90.6(2)	C(1)–N(5)–Mg	136.0(5)
O(2)–Mg–N(4)'	159.5(2)	C(2)–C(1)–N(5)	108.2(7)
N(3)'–Mg–N(4)'	69.7(2)	C(3)–C(2)–C(1)	117.4(9)
N(4)–Mg–O(1)	151.7(2)	C(2)–C(3)–O(1)	116.1(9)
N(4)–Mg–O(2)	90.5(2)	C(5)–C(4)–O(1)	110.0(7)
N(4)–Mg–N(3)'	102.5(2)	C(4)–C(5)–O(2)	106.6(7)
N(4)–Mg–N(4)'	88.2(2)	C(7)–C(6)–O(2)	111.5(7)
N(5)–Mg–O(1)	85.1(2)	C(8)–C(7)–C(6)	115.9(8)
N(5)–Mg–O(2)	99.5(2)	C(7)–C(8)–N(4)	114.1(7)
N(5)–Mg–N(3)'	167.9(2)		

DISCUSSION

Preliminaries

Ball-and-stick drawings of suitable perspective views of **2–4** are given in Figs. 1–3 which show the lithium **2**, the zinc **3** and the magnesium **4** moieties all to be dimeric. Lithium and zinc appear 5-fold coordinated in **2** and **3**, respectively, whereas magnesium displays coordination number 6 in **4**.

Coordination spheres around metals

More precisely, let us consider coordination polyhedra around the metals (Figs. 4–6). In the case of the lithium compound (Fig. 4), the pentacoordination actually occurs as an addition of the N(5) ligand (Li–N(5) = 2.36 Å; N(5)–Li–O(2) = 142.8°; N(5)–Li–N(4) = 68.1°; N(5)–Li–N′(4) = 103.2°; N(5)–Li–O(1) = 87.5°) to a tetrahedron defined by O(1), O(2), N(4) and N′(4) atoms (Li–O(1) = 2.05 Å; Li–O(2) = 2.07 Å; Li–N(4) = 2.13 Å; Li–N′(4) = 2.07 Å; O(1)–Li–N(4) = 131.0°; O(1)–Li–O(2) = 85.6°; N(4)–Li–N′(4) = 109.6°; O(2)–Li–N(4) = 89.5°; O(1)–Li–N′(4) = 117.0°; O(2)–Li–N′(4) = 112.4°).

Rather the same situation seems to happen in **3** (Fig. 5) where the pentacoordination could be a priori described here also through the addition of the N(5) ligand (Zn–N(5) = 2.49 Å) to a pseudo-tetrahedron defined by O(1),
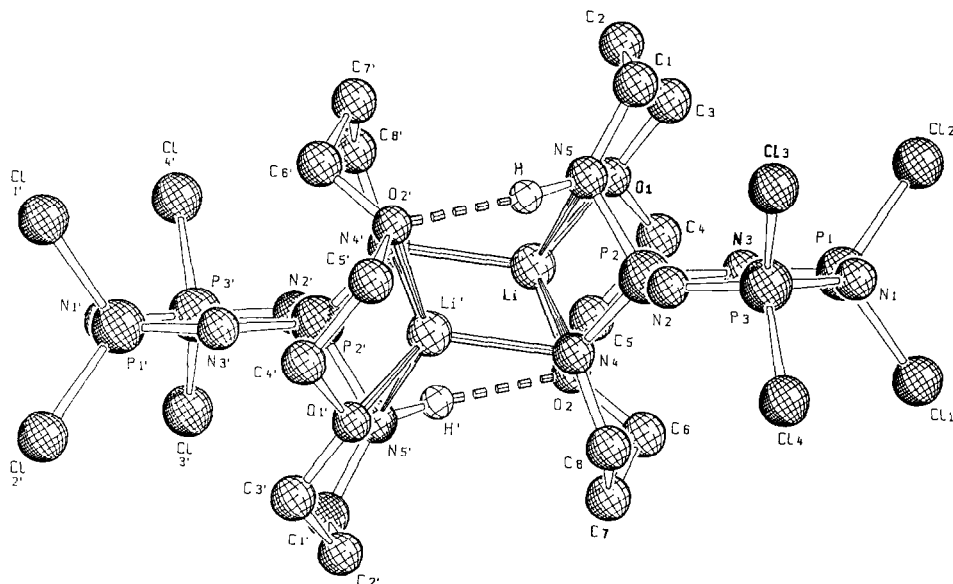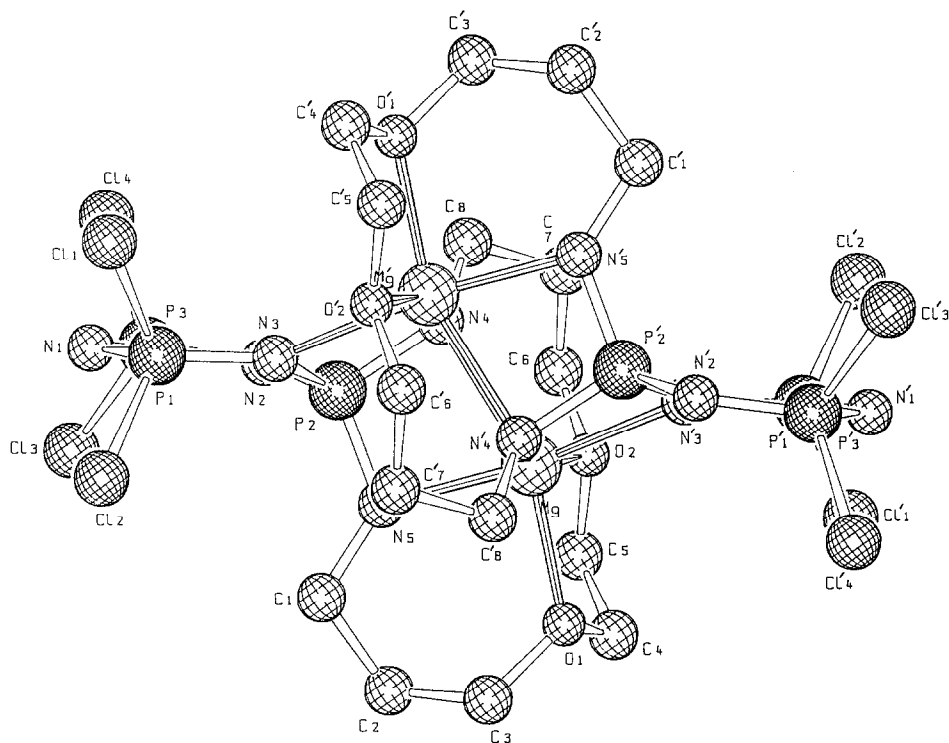

Fig. 1. Perspective view of **2** with numbering of atoms and the N_3P_3 rings perpendicular to the plane of the figure (slightly tilted for clarity).
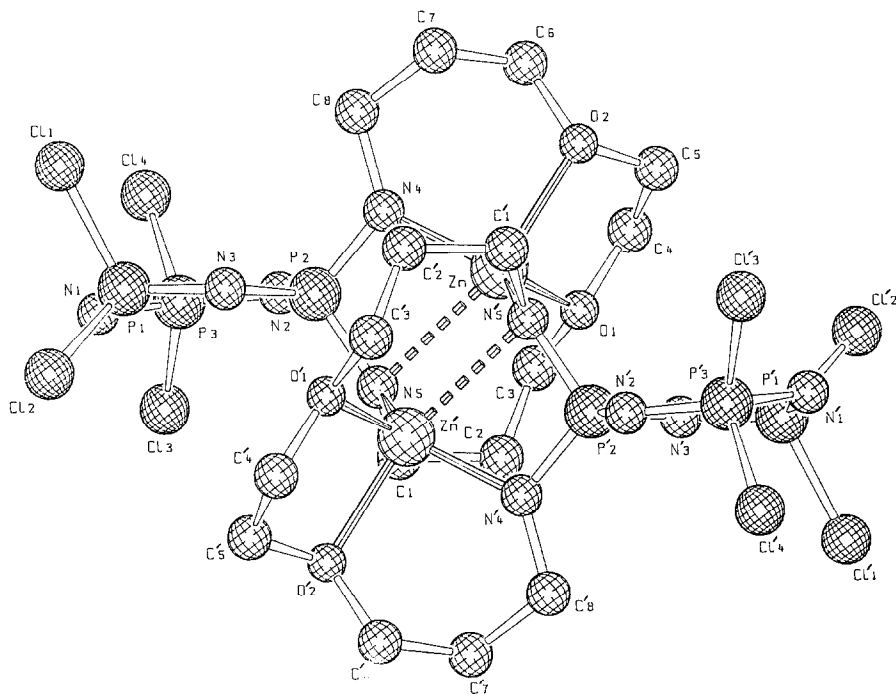
Fig. 2. Perspective view of **3** with numbering of atoms and the N_3P_3 rings perpendicular to the plane of the figure (slightly tilted for clarity).

O(2), N(4) and N'(5) (Zn–O(1) = 2.08 Å; Zn–O(2) = 2.14 Å; Zn–N(4) = 1.94 Å; Zn–N'(5) = 1.95 Å; O(1)–Zn–O(2) = 80.3°; O(2)–Zn–N(4) = 93.7°; O(1)–Zn–N(4) = 111.9°; O(1)–Zn–N'(5) = 119.5°; O(2)–Zn–N'(5) = 107.9°; N(4)–Zn–N'(5) = 126.4°). In fact such a lithium-like description is not satisfactory because the N(5)–Zn bond must be actually considered as a quasi-axial bond of a pseudo-trigonal bipyramid. Indeed, N(5)–Zn–O(1) and N(5)–Zn–N'(5) angles are equal to 91.0 and 97.0°, respectively, that is close to 90°, whereas N(5)–Zn–O(2) is equal to 154.7°, i.e. close to the one of an axial axis. Thus, N(5) and O(2) would occupy axial positions of a pseudo-trigonal bipyramid with O(1), N(4) and N'(5) as equatorial ligands (equatorial distances: Zn–O(1) = 2.08 Å; Zn–N(4) = 1.94 Å; Zn–N'(5) = 1.95 Å, to be compared with axial bond lengths: Zn–N(5) = 2.49 Å and Zn–O(2) = 2.14 Å).

The hexacoordination of magnesium in compound **4** (Fig. 6) looks trivial according to the fact that such an octahedral environment is often found for this element. However, we may notice from Fig. 7 that the sixth ligand in the coordination sphere of Mg comes rather surprisingly from the endocyclic N'(3) atom of N_3P_3 ring which is generally considered as a very poorly donating Lewis base. Incidentally, the N(3)–Mg' bond does not strictly belong to the

Fig. 3. Perspective view of **4** with numbering of atoms and the N₃P₃ rings perpendicular to the plane of the figure (slightly tilted for clarity).

N_3P_3 plane, P(2)–N(3)–Mg', P(1)–N(3)–Mg' and P(1)–N(3)–P(2) being equal to 89.3, 146.0 and 122.0°, respectively, their sum being then equal to 357.3° and not to 360°. The N(3)–Mg' bond length is 2.3 Å to be compared with N(4)–Mg' (2.18 Å), N(5)–Mg (2.07 Å) and N'(4)–Mg' (2.21 Å). Moreover, the existence of this N(3)–Mg' dative bond dramatically modifies the genuine structure of the cyclophosphazenic ring which becomes to some extent partly a cyclophosphazanic ring. Indeed, the P(2)–N(3) bond length is 1.70 Å, that is much longer than common endocyclic bond lengths in cyclophosphazenes which are about 1.58 Å [5–10]. Such a P(2)–N(3) bond behaves as a phosphorus–nitrogen single bond which makes the P(2) atom moving out of the N_3P_3 average plane as commonly observed in a cyclophosphazane. As a consequence of such a half-chair conformation, the P(2)–N(2) endocyclic bond length is also increased to 1.64 Å. The only compound previously described with a nitrogen atom of a cyclophosphazene acting as a donor is [(THF)₃Li·N₃P₃ (H, BEt₃, F, F, 2,4-coated cp₂Fe)] [16]. In this compound however, in contrast to **4**, the phosphazene moiety has a negative charge.
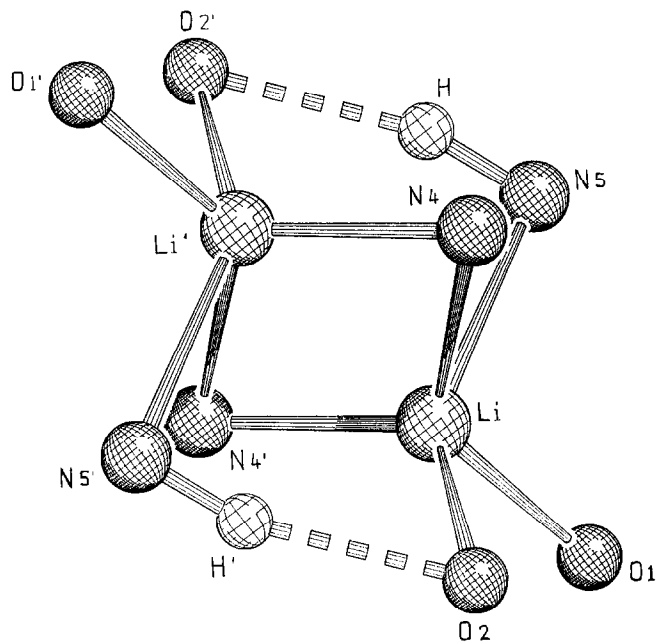
Fig. 4. The coordination polyhedron in **2**.
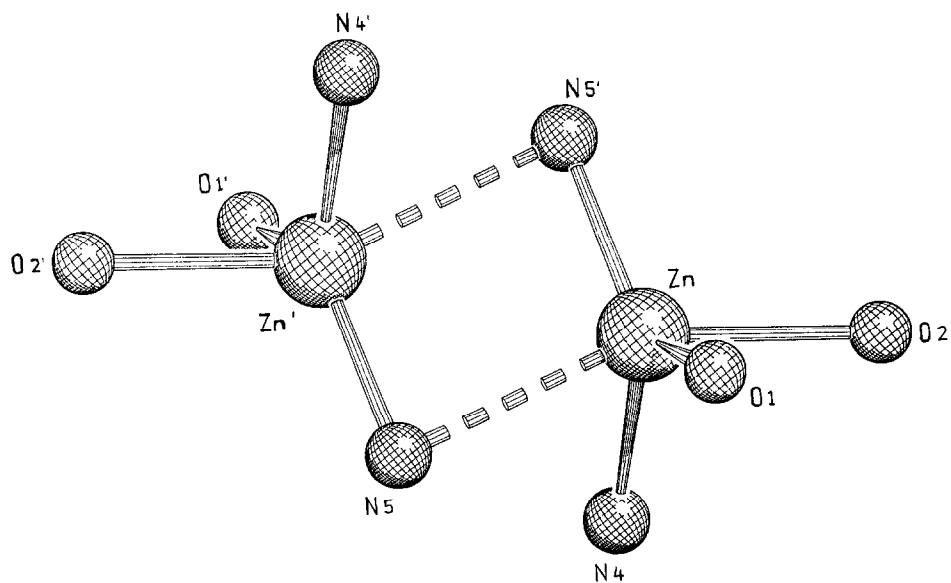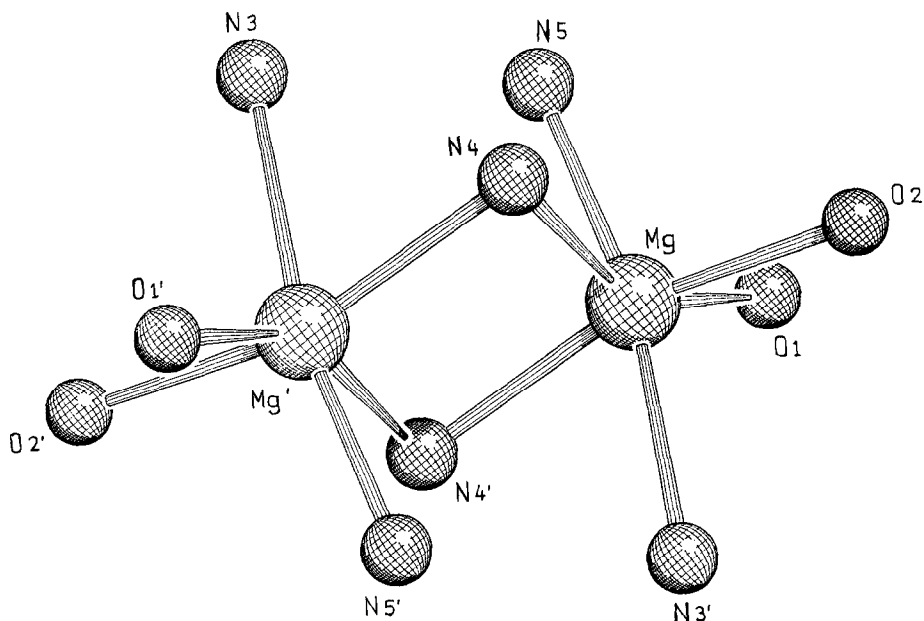

Fig. 5. The coordination polyhedron in **3**.

Fig. 6. The coordination polyhedron in **4**.

Cyclophosphazenic rings

Compound 2

Figure 1 shows that the N_3P_3 rings are strictly planar in **2**. However, two of the endocyclic bonds, namely P(2)–N(2) and P(2)–N(3), are significantly longer (1.65 and 1.63 Å) than others and also slightly longer than in the SPIRO (3O2O3) starting material **1** (1.62 Å). Thus, the fixation of lithium onto the macrocyclic loop gently increases the stretching which had already been induced into the D_{3h} symmetry of the N_3P_3 ring upon grafting of this loop itself.

Within the same frame of mind, exocyclic P(2)–N(4) and P(2)–N(5) (1.58 and 1.66 Å) bonds are respectively shortened and lengthened versus their situation in the genuine starting material **1** (1.616 Å for both). This gap may be reasonably explained by the different charges which do exist on N(4) and N(5) and by the engagement of H–N(5) into hydrogen bonds which stabilize the dimeric form. N(4), being coordinated to two lithium atoms, indeed has the highest negative charge (when compared to N(5) which is coordinated to only one lithium atom) and is then more tightly bound to P(2) than N(5).

Incidentally, P–Cl bonds are not significantly affected by lithium coordination (1.98 to 2.00 Å in **2** versus 2.00 Å in **1**).

Compound 3

Figure 2 shows that N_3P_3 rings here are distorted, mainly at the level of the N(1) (and of course the N'(1)) atom which is moved out towards the relevant
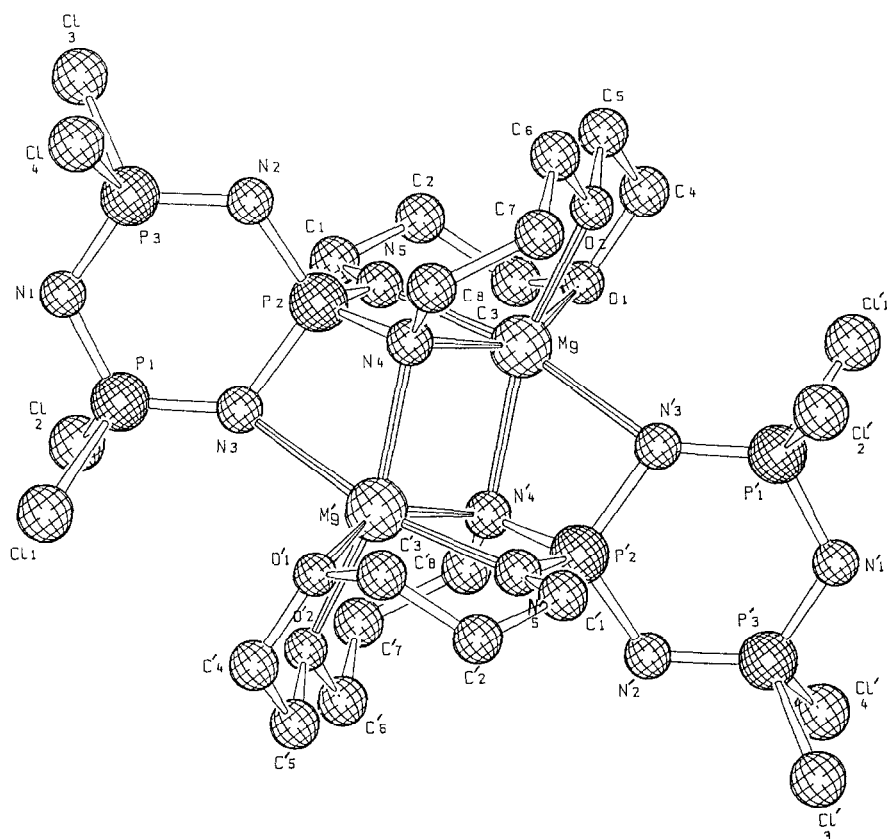
Fig. 7. Perspective view of **4** with the N_3P_3 rings parallel to the plane of the figure (slightly tilted for clarity).

Zn' atom and also at the level of the Cl(1)–P(1)–Cl(2) moiety which is no more symmetrical with respect to the P(1)–N(3)–P(2)–N(2)–P(3) average plane. This could be due to the crowding induced by O'(1), C'(4), C'(5) and O'(2) towards Cl(2) whereas only C(8) may counterbalance this steric hindrance at the level of Cl(1), that is on the other side of the N_3P_3 ring. Then, the Cl(2) atom being pushed up as well as Cl(3), the N(1) atom has to move as it does for mechanical reasons. Consequently, the shortest intramolecular Cl···C contacts are found for C'(5) (C'(5)···Cl(2) = 3.93, C'(5)···Cl(3) = 4.14 Å) whereas C(8) has much longer distances (C(8)···Cl(1) = 5.77, C(8)···Cl(4) = 4.79 Å). Concerning the endocyclic P–N distances, the values are similar to compound **2** (see Tables 7 and 8).

Compound 4

Figure 3 shows that N_3P_3 adopts a half-chair conformation (with P(2) and P'(2) at the top) because of the N(3)–Mg' coordination discussed above. P(2)–

N(4) and P(2)–N(5) (1.63 and 1.58 Å) are significantly lengthened and shortened versus SPIRO (3O2O3) **1** itself (1.616 Å) but in an opposite way as in compound **2**. Although N(4) is coordinated by two Mg atoms and N(5) only by one (see case **2**), the electron gain of magnesium by the bonding of N(3) and the smaller coordination number of N(5) compared to N(4) makes the Mg–N(5) bond shorter than Mg–N(4).

Macrocyclic SPIRO loops

In all the dimeric species, SPIRO loops adopt 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 genuine starting material [6], appears nicely flexible and capable of adapting itself to any coordination process. Indeed, the three molecular structures described here reveal three 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), and (iii) a pattern analogous to (ii) but in which one N atom from the N_3P_3 ring is involved to help at the per-coordination of the metal (Mg). Incidentally, looking from a mechanistical 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.

All three metallated compounds **2**, **3** and **4** have a central tricyclic system in common, consisting of three edge-sharing four-membered rings ($2 \times PN_2M$, $1 \times N_2M_2$) with the overall symmetry $\bar{1}$ (C_i). In **4** two of these "stair-case" structures are interlinked, as a polycyclic system. This system can be deduced from two interpenetrating seco-norcubane like skeletons (see Fig. 7) [17]. Such "stair-case" structures are very common for special silazanes [18–22]. These structures have been examined for structural similarities [19, 20]. It is interesting to note that the same arguments found for the silazanes can also be used for these "phosphazene" compounds **2–4**. In Table 13 a comparison of the bond lengths a and b of the central ring and the average interplanar angle ω are listed for **2–4**. As in the silazane series [19, 20] the ω and a/b values increase in the order $4 \rightarrow 2 \rightarrow 3$ with decreasing group electronegativity (Zn displays a very small value because of its special electronic environment). The tricyclic system in the extreme case **3** can therefore be regarded as an eight-membered ring with transannular N(5)–Zn contacts.

Anyhow, the question arises as to whether the dimeric species we obtained in the solid state have some chance of remaining in solution. The answer is confidently yes for **3** and may be also yes for **2** according to the huge strength of internal hydrogen bonds ($H \cdots O'(2) = 2.02$ Å), at least when working in

TABLE 13

Comparison of the central tricyclic system in **2**, **3** and **4**
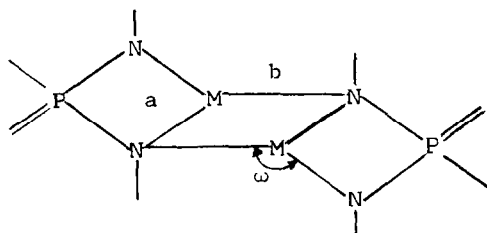
	Compound			
	2	**3**	**4**	**4**
Rings			a	b
M	Li	Zn	Mg	Mg
a (Å)	2.13	2.49	2.21	2.21
b (Å)	2.07	1.95	2.18	2.18
a/b	1.029	1.277	1.014	1.014
ω (deg)	112.5	125.5	97.5	96.3

[a]"Stair-case" P(2), N(5), Mg, N(4)/Mg, N(4), Mg', N'(4)/N'(4), Mg', N'(5), P'(2).
[b]"Stair-case" P(2), N(3), Mg', N(4)/Mg, N(4), Mg', N'(4)/N'(4), Mg, N'(3), P'(2).

non-polar solvents, that is in solvents which cannot be involved in the coordination sphere of the metal. The same positive answer may also be proposed for **4**, owing to the quite spherical morphology of the molecular structure which should even prevent it from any attack by nucleophilic reagents.

Metal–ligand bond lengths

The distances of the metallic atoms Li, Mg and Zn to the non-metal N and O are observed to be in the range of their standard atomic radii (Li–N(O), 2.09 (2.07); Zn–N(O), 1.95 (1.93); Mg–N(O), 2.20 (2.18) Å) [23]. When smaller values are observed, the coordination number at one of the bonding partners is low (e.g. Zn–N(4), 1.94; Mg–N(5), 2.07 Å); higher values are observed for Li–N'(5) in **2**, Zn–N(5) in **3** and Mg'–N(3) in **4**. Explanations for these findings have been given above. In the case of **3** the Zn–O bond lengths are found to be longer than the standard values. This seems to be because zinc is in an unusual 5-fold coordination. For other comparisons some literature data are given in refs. 18–20, 24, 25.

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