An answer to the SPIRO versus ANSA dilemma in cyclophosphazenes Part XVI*. Synthesis and crystal structure of the first SPIRO species from dithiadiamines

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Abstract

Aminolysis of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, by dithiadiamines in suitable conditions yields mono-SPIRO species which constitute new macrocyclic monocyclophosphazenic structures containing sulphur atoms in their loops. Such (S,S) compounds are isologous to previously described oxygenated cyclophosphazenic cages which are commonly capable of inclusion of "hard" metals. Thus, one may expect that (S,S) cages will be useful for inclusion of "soft" metals. The X-ray structure of the (S,S) mono-SPIRO derivative from 3,7-dithianonane-1,9-diamine (coded as SS 232) reveals two crystallographically independent molecules in the unit cell, and also shows the conformations of SPIRO loops.

INTRODUCTION

Reactions of long oxodiamines with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, 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 have been unambiguously elucidated by X-ray investigations [5–11]. Only four configurations have 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 N_3P_3 ring);

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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);

(iv) the BINO configuration (in which the oxodiamino ligand bridges two different N_3P_3 rings).

We recently reported [12] on the possibility of using one of these new macrocyclic compounds, namely the SPIRO (30203) [3,6] (I) obtained from $H_2N-(CH_2)_3-O-(CH_2)_2-O-(CH_2)_3-NH_2$, as a cryptand for lithium (Ia), zinc (Ib) and magnesium (Ic). The three molecular structures reveal three different patterns of metal coordination. In compound (Ia) one of the two hydrogen atoms in SPIRO (30203) is substituted by lithium generating a dimeric structure with pentacoordinated lithium centres. This structure is further stabilized by N-H hydrogen bonds. In (Ib) both hydrogen atoms of the macrocylic loop are replaced by two zinc atoms through a cross-link metallation leading again to a dimeric molecule. In this compound the zinc atom is found to be in a trigonal bipyramidal environment with one very long-range N-Zn interaction. The origin of the dimerization of the magnesium compound (Ic) is analogous to that of (Ib). Magnesium is the centre of a distorted octahedron, coordinated with the O- and N-donors of the macrocyclic loop, and also with one nitrogen atom of the N_3P_3 ring. (Ic) is the first example of a metallic centre coordinated by a neutral phosphazene ligand.

Aluminium cryptates were also obtained from SPIRO (30203) as the cryptand [13] which reveal another pattern of metal coordination where the two hydrogen atoms in SPIRO (30203) are substituted by aluminium for generating monomeric structures with pentacoordinated aluminium centres in the inner cavities.

Thus, cyclophosphazenic compounds such as SPIRO (30203) are capable of the inclusion of "hard" metals. Conversely, inclusion of "soft" metals would need cyclophosphazenic structures containing "soft" coordination sites in their cages. Thus, we were urged to design such (S,S) macrocyclic architectures, and the present contribution reports on the synthesis and the molecular structure of the first (S,S) SPIRO derivatives so obtained upon aminolysis of $N_3P_3Cl_6$ by dithiadiamines.

SYNTHESIS OF DITHIADIAMINES

The dithiadiamines, $H_2N-(CH_2)_m-S-(CH_2)_n-S-(CH_2)_m-NH_2$ (coded as SS mnm), were prepared according to Hay et al. [14] through the following

five-step pathway:

$$Na + EtOH_{absolute} \rightarrow NaOEt + \frac{1}{2}H_{2}$$

$$2NaOEt + 2HS-CH_{2}-CH_{2}-NH_{3}^{+}Cl^{-} \rightarrow 2Na^{+}S^{-}-CH_{2}-CH_{2}-NH_{3}^{+}Cl^{-} + 2EtOH$$

$$(2)$$

$$2 \operatorname{Na}^{+} \operatorname{S}^{-} - \operatorname{CH}_{2} - \operatorname{CH}_{2} - \operatorname{NH}_{3}^{+} \operatorname{Cl}^{-} + \operatorname{Br}_{-} (\operatorname{CH}_{2})_{6}^{-} \operatorname{Br}$$

$$\rightarrow \operatorname{Cl}^{-}_{H_{3}} \operatorname{N}_{-} (\operatorname{CH}_{2})_{2}^{-} \operatorname{S}_{-} (\operatorname{CH}_{2})_{6}^{-} \operatorname{S}_{-} (\operatorname{CH}_{2})_{2}^{-} \operatorname{NH}_{3}^{+} \operatorname{Cl}^{-} + 2 \operatorname{NaBr}$$
(3)
$$\operatorname{Cl}^{-}_{H_{3}} \operatorname{N}_{-} (\operatorname{CH}_{2})_{2}^{-} \operatorname{S}_{-} (\operatorname{CH}_{2})_{2}^{-} \operatorname{NH}_{3}^{+} \operatorname{Cl}^{-} + 2 \operatorname{NaI}$$

$$\rightarrow \operatorname{I}^{-}_{H_{3}} \operatorname{N}_{-} (\operatorname{CH}_{2})_{2}^{-} \operatorname{S}_{-} (\operatorname{CH}_{2})_{6}^{-} \operatorname{S}_{-} (\operatorname{CH}_{2})_{2}^{-} \operatorname{NH}_{3}^{+} \operatorname{I}^{-} + 2 \operatorname{NaI}$$
(4)
$$\operatorname{I}^{-}_{H_{3}} \operatorname{N}_{-} (\operatorname{CH}_{2})_{2}^{-} \operatorname{S}_{-} (\operatorname{CH}_{2})_{6}^{-} \operatorname{S}_{-} (\operatorname{CH}_{2})_{2}^{-} \operatorname{NH}_{3}^{+} \operatorname{I}^{-}$$

$$\rightarrow \operatorname{H}_{2} \operatorname{N}_{-} (\operatorname{CH}_{2})_{2}^{-} \operatorname{S}_{-} (\operatorname{CH}_{2})_{6}^{-} \operatorname{S}_{-} (\operatorname{CH}_{2})_{2}^{-} \operatorname{NH}_{2}^{+} 2 \operatorname{HI}$$
(5)

Five dithiadimines, namely SS 222, SS 232, SS 242, SS 252 and SS 262, were obtained in this way giving high yields, i.e. larger than 85%. Their purity was checked by high-field $^{1}\text{H}^{-13}\text{C}$ 2D NMR measurements using a Bruker AC 200 spectrometer. Mass spectra of SS 222, SS 232, SS 242, SS 252 and SS 262 (Ribermag 1010 H quadrupole mass spectrometer) reveal molecular ions at expected values of m/z, i.e. 181, 195, 209, 223 and 237 respectively.

SYNTHESIS OF (S,S) SPIRO DERIVATIVES

For this synthesis we moved to the technique we previously found as favouring gem disubstitution and generating SPIRO derivatives [1,2]. Aminolysis of $N_3P_3Cl_6$ by SS *mnm* was then achieved in a heterogeneous medium (interface process) constituted by toluene and a saturated aqueous solution of sodium carbonate. In such conditions, one SS *mnm* equivalent is enough, hydrogen chloride now being captured from the organic phase by Na_2CO_3 through a sort of phase-transfer mechanism

 $N_3P_3Cl_6 + SS mnm \rightarrow SPIRO [SS mnm] + 2HCl$

Reactions for SS 232, SS 242, SS 252 and SS 262 took four days at room temperature and were stopped when the ³¹P NMR singlet of $N_3P_3Cl_6$ at 20.09 ppm (in CDCl₃, with 85% H₃PO₄ as the standard) remained unchanged over time. The organic phases were then dried over Na_2SO_4 and solvent was removed in vacuo at 25°C to give white powders. ³¹P NMR spectra of crude final products reveal a doublet centred around 21–22 ppm and a triplet centred on 9–10 ppm (with ²J_{PP} about 45–46 Hz), together with the 20.09 ppm

TABLE 1

Formula	$Cl_4S_2P_3N_5C_7H_{16}$
Mol. wt. (g)	469.09
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.537(7)
b (Å)	36.10(1)
c (Å)	11.757(9)
β (deg)	108.20(3)
$V(Å^3)$	3845(4)
Ζ	4×2
$\rho_{\rm exp} ({\rm g} {\rm cm}^{-3})$	1.61(2)
$\rho_{\rm x} (\rm g \rm cm^{-3})$	1.621(2)
F(000)	1904
μ (Mo K α)(cm ⁻¹)	10.7
Temperature (K)	293
λ (Å)	0.71069
Take-off (deg)	3.5
Detector width (mm)	4×4
Scan type	$\theta/2\theta$
Scan width (deg)	$0.80 + 0.35 \tan \theta$
θ range (deg)	0-22 ($h \ 0 \rightarrow 10, \ k \ 0 \rightarrow 38, \ l - 12 \rightarrow 12$)
No. of measured reflections	5138
No. of unique reflections, NO	$2762 \ (I \ge 2\sigma)$
No. of variables, NV	379
R	0.078
R _w	0.098

Physical properties and parameters for data collection and refinement

singlet of the unreacted $N_3P_3Cl_6$. The latter was eliminated by a single washing with *n*-hexane in which it is soluble, whereas SPIRO SS *mnm* are not. $N_3P_3Cl_6$ free final samples were crystallized by a slow evaporation of CH_2Cl_2 -petroleum ether or CH_2Cl_2 -CCl₄ solutions.

It must be noticed that "dangling" intermediates, that is moieties in which only one amino function of the dithiadiamine is linked to the cyclophosphazenic ring, were observed at J + 1, their NMR patterns (doublet centred on 21.6 ppm, triplet centred on 18.6 ppm, ${}^{2}J_{PP} = 47.5$ Hz) disappearing gently from J + 1 to J + 4 for the A₂X systems of SPIRO entities. Thus, aminolysis of N₃P₃Cl₆ by dithiadiamines is slow enough to reveal "dangling" intermediates, in contrast to oxodiamines [1,2] where such monofunctional intermediates could not be detected owing to the high rate of these reactions.

Incidentally, aminolysis of $N_3P_3Cl_6$ by SS 222 does not occur at all, even after 18 days at room temperature or above. This amazing behaviour is analogous to that previously observed with $H_2N-(CH_2)_2-O-(CH_2)_2-O$

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Molecul	e (a)				Molecule	(q)			
Atom	क्ष	v	N	$U_{\rm eq}$ $({\rm \AA}^2)$	Atom	*	x	N	$U_{\rm eq}$ (Å ²)
Cl1	0.3531(6)	0.1479(2)	0.2294(5)	0.073(7)	CI5	0.5815(8)	0.2282(2)	0.3864(6)	0.084(9)
Cl2	0.3870(8)	0.0641(2)	0.2435(6)	0.084(8)	CI6	0.6540(7)	0.2725(2)	0.6183(5)	0.073(7)
CI3	0.9001(7)	0.1486(2)	0.2531(6)	0.085(9)	CI7	0.0591(8)	0.2393(2)	0.3255(6)	0.087(8)
Cl4	0.8726(7)	0.0641(2)	0.2442(6)	0.076(8)	C18	0.1167(8)	0.2867(2)	0.5508(6)	0.095(9)
SI	0.889(1)	0.0026(2)	0.8016(7)	0.11(1)	S3	0.3672(6)	0.1059(2)	0.9176(5)	0.060(6)
S_2	0.8682(7)	0.1327(2)	0.8826(5)	0.069(7)	S4	0.3918(7)	0.0538(2)	0.6203(7)	0.076(8)
Ы	0.7250(5)	0.1109(2)	0.5191(4)	0.043(5)	P_4	0.3558(5)	0.1847(1)	0.6177(4)	0.040(5)
$\mathbf{P2}$	0.5051(5)	0.1097(2)	0.2977(4)	0.046(5)	P5	0.5002(6)	0.2373(2)	0.5201(5)	0.050(6)
$\mathbf{P3}$	0.7914(6)	0.1087(2)	0.3058(4)	0.048(6)	$\mathbf{P6}$	0.2064(6)	0.2449(1)	0.4879(5)	0.051(6)
N1	0.553(1)	0.1129(4)	0.436(1)	0.04(2)	N4	0.501(2)	0.2002(4)	0.591(1)	0.04(2)
N2	0.624(2)	0.1129(5)	0.229(1)	0.06(2)	N5	0.350(2)	0.2594(5)	0.468(2)	0.07(2)
N3	0.837(1)	0.1060(5)	0.443(1)	0.05(2)	9N	0.211(2)	0.2111(4)	0.563(1)	0.05(2)
N7	0.760(2)	0.0767(4)	0.613(1)	0.05(2)	6N	0.374(2)	0.1812(4)	0.758(1)	0.04(2)
N8	0.751(2)	0.1468(4)	0.600(1)	0.05(2)	01N	0.343(1)	0.1439(3)	0.567(1)	0.03(2)
CI	0.763(3)	0.0379(6)	0.578(2)	0.07(3)	C7	0.894(3)	0.1627(8)	0.672(2)	0.08(3)
C2	0.877(4)	0.0166(8)	0.660(3)	0.12(5)	C8	0.504(2)	0.1630(5)	0.840(1)	0.04(2)
c	0.888(2)	0.0418(6)	0.892(2)	0.07(3)	C9	0.479(2)	0.1482(6)	0.948(2)	0.06(2)
C4	1.021(3)	0.0662(9)	0.921(2)	0.08(4)	C10	0.503(3)	0.0726(7)	0.904(2)	0.08(3)
C5	1.008(2)	0.1006(8)	0.973(2)	0.08(3)	C11	0.433(3)	0.0366(8)	0.857(2)	0.09(4)
8°	0.959(3)	0.148(1)	0.780(3)	0.11(5)	C12	0.317(3)	0.0383(6)	0.734(2)	0.07(3)
C7	0.894(3)	0.1627(8)	0.672(2)	0.08(3)	C13	0.244(2)	0.0807(7)	0.529(2)	0.07(3)
					C14	0.223(2)	0.1183(5)	0.572(2)	0.05(2)

Positional parameters and equivalent isotropic thermal factors for non-hydrogen atoms of (a) and (b)

TABLE 2

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TABLE 3

Molecule (a)				Molecule (b)				
Atom	x	y	z	Atom	x	у	z	
H7	0.783	0.083	0.707	H9	0.289	0.192	0.792	
H8	0.653	0.161	0.603	H10	0.425	0.134	0.528	
H11	0.780	0.037	0.491	H18	0.538	0.141	0.793	
H21	0.658	0.025	0.572	H28	0.592	0.184	0.867	
H12	0.889	- 0.009	0.613	H19	0.584	0.142	1.013	
H22	0.977	0.033	0.672	H29	0.422	0.169	0.984	
H13	0.876	0.032	0.976	H110	0.581	0.068	0.991	
H23	0.793	0.058	0.846	H210	0.557	0.084	0.844	
H14	1.045	0.071	0.839	H111	0.519	0.018	0.850	
H24	1.110	0.052	0.984	H211	0.382	0.025	0.919	
H15	0.984	0.095	1.054	H112	0.272	0.010	0.711	
H25	1.114	0.114	0.992	H212	0.230	0.056	0.739	
H16	1.022	0.125	0.764	H113	0.143	0.066	0.518	
H26	1.037	0.169	0.828	H213	0.261	0.084	0.443	
H17	0.875	0.191	0.684	H114	0.221	0.117	0.663	
H27	0.969	0.160	0.620	H214	0.119	0.130	0.516	

Fractional coordinates of hydrogen atoms for (a) and (b)

 $(CH_2)_2$ -NH₂ oxodiamine (coded as 2O2O2) [1]. Such a failure may be related to the peculiar length of both SS 222 and 2O2O2 (eight links between the two amino functions), which is not suitable for SPIRO loop building.

DCI mass spectra of SPIRO [SS 232] (A), SPIRO [SS 242] (B), SPIRO [SS 252] (C) and SPIRO [SS 262] (D) (Ribermag 1010 H quadrupole mass spectrometer) reveal molecular ions at expected values of m/z, i.e. 470, 484, 498 and 512 respectively, with satellite distributions indicating the presence of four chlorine atoms in the structures.

X-RAY STRUCTURE OF THE SPIRO [SS 232]

Data collection

A colourless single crystal $(0.12 \times 0.15 \times 0.20 \text{ mm})$ was chosen for data collection using an Enraf Nonius CAD4 diffractometer. 25 *hkl* reflections were used to refine the lattice parameters (Table 1). Details of data collection are reported in Table 1. Lorentz and polarization corrections were applied. Absorption corrections were not necessary.

Structural analysis and refinement

The structure was determined using direct methods leading to the

TABLE 4

Molecule (a	a)		Molecule (b)				
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance		
Cl(1)	P(2)	1.980(8)	Cl(5)	P(5)	1.985(9)		
Cl(2)	P(2)	1.985(9)	Cl(6)	P(5)	2.011(8)		
Cl(3)	P(3)	1.984(9)	Cl(7)	P(6)	1.996(9)		
Cl(4)	P(3)	2.015(9)	Cl(8)	P(6)	1.987(9)		
S(1)	C(2)	1.71(3)	S(3)	C(9)	1.83(2)		
S(1)	C(3)	1.77(2)	S(3)	C(10)	1.81(3)		
S(2)	C(5)	1.83(3)	S(4)	C(12)	1.79(3)		
S(2)	C(6)	1.78(3)	S(4)	C(13)	1.77(2)		
P(1)	N(1)	1.63(2)	P(4)	N(4)	1.62(2)		
P (1)	N(3)	1.60(2)	P(4)	N(6)	1.63(2)		
P(1)	N(7)	1.61(2)	P(4)	N(9)	1.61(2)		
P(1)	N(8)	1.58(2)	P(4)	N(10)	1.58(1)		
P(2)	N(1)	1.54(2)	P(5)	N(4)	1.57(2)		
P(2)	N(2)	1.59(2)	P(5)	N(5)	1.59(2)		
P(3)	N(2)	1.57(2)	P(6)	N(5)	1.55(2)		
P(3)	N(3)	1.54(2)	P(6)	N(6)	1.50(2)		
N(7)	C(1)	1.46(3)	N(9)	C(8)	1.46(2)		
N(8)	C(7)	1.48(3)	N(10)	C(14)	1.49(2)		
C(1)	C(2)	1.43(4)	C(8)	C(9)	1.46(3)		
C(3)	C(4)	1.49(4)	C(10)	C(11)	1.49(4)		
C(4)	C(5)	1.41(4)	C(11)	C(12)	1.52(3)		
C(6)	C(7)	1.33(4)	C(13)	C(14)	1.49(3)		

Bond lengths (Å) in (a) and (b)

location of all non-hydrogen atoms. All hydrogen atoms were then identified from the difference Fourier map, but they were added to the structure factor calculations (for consistency with our previous X-ray structures within the series [5–11]) as fixed at 0.97 Å from their relative attached atoms.

Scattering factors were taken from Cromer and Waber [15] and anomalous dispersion effects from Cromer and Liberman [16]. Details for refinement are summarized in Table 1. Both calculations with SHELX **36** [17] and illustrations with ORTEP [18] softwares were performed on an Alliant VFX 80 computer.

RESULTS

Final positions and equivalent isotropic thermal parameters for all the non-hydrogen independent atoms are given in Table 2. Fractional coordinates of related hydrogen atoms are listed in Table 3. Bond lengths and angles are given in Tables 4 and 5 respectively. All the U_{eq} values of Table 2

Bond	angles	(deg) in	(a)	and (b)

Molecule (a)				Molecule (b)			
Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C(2)	S(1)	C(3)	109(1)	C(9)	S(3)	C(10)	100(1)
C(5)	S(2)	C(6)	100(1)	C(12)	S(4)	C(13)	101(1)
N(1)	P(1)	N(3)	113.0(8)	N(4)	P(4)	N(6)	113.3(8)
N(1)	P(1)	N(7)	113.7(8)	N(4)	P(4)	N(9)	113.8(8)
N(1)	P(1)	N(8)	105.4(8)	N(4)	P(4)	N(10)	102.5(8)
N(3)	P(1)	N(7)	105(1)	N(6)	P(4)	N(9)	104.8(8)
N(3)	P(1)	N(8)	114(1)	N(6)	P(4)	N(10)	116.2(8)
N(7)	P(1)	N(8)	104.8(8)	N(9)	P(4)	N(10)	106.4(8)
Cl(1)	P(2)	Cl(2)	100.2(4)	Cl(5)	P(5)	Cl(6)	99.4(4)
Cl(1)	P(2)	N(1)	108.2(6)	Cl(5)	P(5)	N(4)	109.7(6)
Cl(1)	P(2)	N(2)	107.0(7)	Cl(5)	P(5)	N(5)	107.8(8)
Cl(2)	P(2)	N(1)	110.6(6)	Cl(6)	P(5)	N(4)	110.6(6)
Cl(2)	P(2)	N(2)	108.7(7)	Cl(6)	P(5)	N(5)	108.1(7)
N(1)	P(2)	N(2)	120.2(8)	N(4)	P(5)	N(5)	119(1)
Cl(3)	P(3)	Cl(4)	99.8(4)	Cl(7)	P(6)	Cl(8)	100.2(4)
Cl(3)	P(3)	N(2)	106.6(7)	Cl(7)	P(6)	N(5)	106.3(8)
Cl(3)	P(3)	N(3)	111.7(7)	Cl(7)	P(6)	N(6)	111.5(7)
Cl(4)	P(3)	N(2)	107.8(7)	Cl(8)	P(6)	N(5)	107.6(8)
Cl(4)	P(3)	N(3)	108.2(7)	Cl(8)	P(6)	N(6)	109.5(7)
N(2)	P(3)	N(3)	120(1)	N(5)	P(6)	N(6)	119(1)
P(1)	N(1)	P(2)	122(1)	P(4)	N(4)	P(5)	122(1)
P(2)	N(2)	P(3)	117(1)	P(5)	N(5)	P(6)	120(1)
P(1)	N(3)	P(3)	123(1)	P(4)	N(6)	P(6)	124(1)
P(1)	N(7)	C(1)	124(1)	P(4)	N(9)	C(8)	120(1)
P(1)	N(8)	C(7)	127(1)	P(4)	N(10)	C(14)	122(1)
N(7)	C(1)	C(2)	114(2)	N(9)	C(8)	C(9)	113(2)
S(1)	C(2)	C(1)	128(3)	S(3)	C(9)	C(8)	112(1)
S(1)	C(3)	C(4)	116(2)	S(3)	C(10)	C(11)	111(2)
C(3)	C(4)	C(5)	116(2)	C(10)	C(11)	C(12)	115(2)
S(2)	C(5)	C(4)	116(2)	S(4)	C(12)	C(11)	112(2)
S(2)	C(6)	C(7)	126(2)	S(4)	C(13)	C(14)	117(2)
N(8)	C(7)	C(6)	118(3)	N(10)	C(14)	C(13)	111(2)

are less than 0.1 Å² except those for the S(1), C(2) and C(6) atoms. Moreover, difference Fourier maps reveal a residual electron density equal to $1 e \text{ Å}^{-3}$ at 1.3 Å from S(1). Both observations could suggest that a disorder does exist at the level of these three atoms similar to that previously observed in the case of the *cis*-ANSA (30203) [6]. However, in contrast to what happened for this ANSA structure, attempts for solving such disorders here were unsuccessful.



Fig. 1. A perspective view of (a) with numbering of atoms and the N_3P_3 ring perpendicular to the plane of the figure (slightly tilted for clarity).

DISCUSSION

According to the V, ρ_x and M values from Table 1, the number Z of molecules in the unit cell is equal to eight, which implies that two crystallographically independent molecules, coded as (a) and (b), do exist in it.

Four ball-and-stick drawings of suitable perspective views of (a) and (b) are given in Figs. 1-4 (the hydrogen numbering is omitted for the sake of clarity). The most striking features from these pictures are, as mentioned above, if all the atoms of the SPIRO loop in (b) could be easily located with reasonably small U_{eq} values (see Table 2), several atoms of the SPIRO loop in (a), namely C(2), S(1) and C(6), wobble noticeably at room temperature for unknown reasons. Incidentally, the same obscure wobbling situation was previously observed in cases of di-SPIRO (30403) and di-SPIRO (3020203) [5], and this thermal agitation could not be significantly frozen by X-ray investigations at low temperature, i.e. at 123 K.

Anyhow, the SPIRO configuration of the SS 232 ligand in the title compound is clearly evident, the geometry then developing a 12-membered macrocycle of non-hydrogen atoms. The SPIRO loop adopts a double-twisted conformation in (b) and a "chistera-like" one in (a). For both (a) and (b), the N_3P_3 ring is quite planar, the distances of the various atoms to the average planes being less than 0.1 Å.



Fig. 2. A perspective view of (b) with numbering of atoms and the N_3P_3 ring perpendicular to the plane of the figure (slightly tilted for clarity).



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



Fig. 4. A perspective view of (b) with the N_3P_3 ring parallel to the plane of the figure (slightly tilted for clarity).

Concerning intramolecular contacts, there exists in (a) a hydrogen bond between N(7)-H(7) and S(2) $(N(7) \cdots S(2) = 3.63 \text{ Å}, H(7) \cdots S(2) = 2.67 \text{ Å},$ N(7)-H(7)-S(2) = 147.9°) which induces an intramolecular contact between H(7) and S(1) $(H(7) \cdots S(1) = 3.16 \text{ Å},$ but as N(7)-H(7)-S(1) is equal to 102.3° it is too far from 180° to consider this contact as a hydrogen bond). Incidentally, the second N-H bond in (a), i.e. N(8)-H(8), points towards the outside of the loop and is not at all involved in any intramolecular hydrogen bonding system. Conversely, there does not exist any intramolecular hydrogen bond or contact between N(9)-H(9) and N(10)-H(10) or S(3) and S(4) in (b), both H(9) and H(10) pointing towards the outside of the loop. This situation looks quite different from the common one in isologous oxygenated SPIRO derivatives where at least one N-H bond points systematically towards the inner cavity of the loop [6-9]. In other words, N-H bonds appear noticeably more flexible in (S,S) SPIRO compounds than in their (O,O) homologues.

In contrast, a survey of the molecular packing (Fig. 5) does not reveal any intermolecular hydrogen bonding or contact in the unit cell. However, the eight molecules of the title compound seem to be amalgamated by $[(\mathbf{a}) + (\mathbf{b})]$ pairs, with their loops roughly parallel and their N₃P₃ rings shifted by about 60° from each other. This peculiar paired spatial distribution could not be explained in terms of common stacking effects.



Fig. 5. A perspective view of the molecular packing.

CONCLUSION

X-ray crystallography definitely provides evidence for the SPIRO loop configuration, which exists in the chemical obtained upon reaction of the 3,7-dithianonane-1,9-diamine with $N_3P_3Cl_6$ in a heterogeneous medium (interface process) constituted by toluene and a saturated aqueous solution of sodium carbonate. Two crystallographically independent molecules are observed which are amazing 12-membered macrocycles prone to host suitable small "soft" guest metals.

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