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THE CRYSTAL STRUCTURE OF FOUR PHOSPHORUS-CONTAINING POLYOXAMACROCYCLES

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GRAPHICAL ABSTRACT



Abstract The crystal structures of four phosphorus-containing polyoxamacrocycles 2,4, 6,11,13-Pentachloro-dibenzo[d,g][1,3,9,2]trioxaphosphacycloundecan-2-thione (1),2,4,9,14, 16-Pentachloro-dibenzo[d,g]][1,3,6,12,2]tetraoxaphosphacyclotetra-decan-2-thione (2), 2,4, 10,16,18-Pentachloro-dibenzo[h,h][1,3,7,12,2]tetraoxa-phosphacyclohexadecan-2-thione (3) and 2,4,6,12,14,18,20,28,30—Nona-chloro-tetrabenzo[d,g,p,s] [1,3,9,13,15,21,2,14]hexaoxa diphosphacyclotetracosan-2,14-dithione (4) have been determined by X-ray diffraction. The result shows that compound 4 has a center of symmetry, and compounds 1, 2, and 3 have no elements of symmetry. The molecules of compounds 2 and 4 form inclusion complex with neutral molecule guest (CHCl₃) which is outside of the phosphorus-containing macrocycle in the ratio of 1:1, and compounds 1 and 3 do not form inclusion complexes with CHCl₃. The result obtained in this paper lays a foundation for further research on the complexing properties of phosphorus-containing polyoxamacrocycles.

[Supplementary materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfer, and Silicon and the Related Elements for the following free supplemental files: Additional text, figures, and tables.]

Keywords Crystal structure; phosphorus-containing macrocycle; inclusion complex

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INTRODUCTION

A great deal of attention has been paid to the synthesis and chemistry of phosphoruscontaining macrocycles in recent years¹⁻⁶ due to their complexing ability, molecular recognizing ability, and their bioactivity. The size of the holes formed by macrocycles, and the type and number of heteroatoms are important factors that influence their complexing and recognizing properties. We reported the synthesis, bioactivity, and complexing property of substituted dibenzo [1, 3, 2]-dioxaphosphocins.⁷⁻¹⁰ One of the interesting phenomina we observed in our work is that some of these eight-membered compounds easily form complexes with some solvents. In view of the property of phosphane oxides serving as strong hydrogen-bond acceptors and as a continuation of our work, we intend to increase the size of the cycle and the number of oxygen atom based on the dibenzo [1, 3, 2]-dioxaphosphocin to improve their complexing ability. We reported the synthesis of four phosphorus-containing polyoxamacrocycles with one or two reactive thiophosphoryl chloride groups, namely, 2,4,6,11,13-Pentachlorodibenzo[d,g][1,3,9,2]trioxaphosphacycloundecan-2-thione (1), 2,4,9,14,16-Penta- chlorodibenzo[g,j][1,3,6,12,2]tetraoxaphosphacyclotetradecan-2-thione (2), 2,4,10,16,18-Pentachlorodibenzo[h,k][1,3,7,12,2]tetraoxaphosphacyclohexadecan-2-thione (3), and 2,4,6,12, 14,18,20,28,30-Nonachlorotetrabenzo[d,g,p,s] [1,3,9,13,15,21,2,14]hexaoxadiphosphacyc lotetracosan-2,14-dithione (4) by introducing CH₂CH₂O or CH₂CH₂CH₂O units into bis(3,5-dichloro-2-hydroxylphenyl)methan, followed by reaction with thiophosphoryl chloride,¹¹ and retaining reactive thiophosphoryl chloride groups to benefit their derivation. In this paper, we would like to report their crystal structures.





Compounds	1	2	3	4
Empirical formula	C ₁₅ H ₁₀ Cl ₅ O ₃ PS	C ₁₇ H ₁₄ Cl ₅ O ₄ PS· CHCl ₃	$C_{19}H_{18}Cl_5O_4PS$	$C_{32}H_{24}Cl_{10}O_6P_2S_2$. CHCl ₃
Formula weight	478.54	641.97	550.65	1104.52
Crystal system/ Space group	Triclinic/P-1	Monoclinic/P2(1)/n	Monoclinic/P2(1)/c	Triclinic/P-1
a/Å	8.8145(10)	14.9760(5)	12.3919(6)	8.3269(6)
b/Å	10.8876(10)	9.1188(4)	13.6990(5)	9.8261(7)
c/Å	11.8022(10)	18.0492(9)	14.0032(6)	15.8216(10)
$\alpha /^{\circ}$	101.863(7)	90	90	94.680(2)
βI°	111.921(2)	91.609(2)	100.369(2)	102.939(4)
γI°	108.376(4)	90	90	94.898(2)
V/Å ³	927.52(16)	2463.88(18)	2338.31(17)	1250.28(15)
Ζ	1	4	4	2
D_{calc} (g/cm ³)	1.713	1.731	1.564	1.623
$\mu (\text{mm}^{-1})$	0.994	1.090	0.803	1.066
Crystal size (mm)	$0.48\times0.29\times0.15$	$0.41 \times 0.24 \times 0.19$	$0.38 \times 0.34 \times 0.12$	$0.55\times0.37\times0.34$
Color/shape	Colorless/flaky	Colorless/flaky	Colorless/flaky	Colorless/flaky
Theta range for collection/°	2.32 to 27.36	2.26 to 27.43	2.10 to 27.46	2.09 to 27.41
Reflections collected	5963	9919	10038	8778
Independent reflections	3976 [R(int) = 0.0330]	5442 [R(int) = 0.0278]	5279 [R(int) = 0.0651]	5511 [R(int) = 0.0326]
Data/restraints/	3976/0/226	5442/0/290	5279/0/271	5511/0/272
Goodness of fit on F^2	0.968	0.786	0.547	0.863
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0292, wR2 = 0.0727	R1 = 0.0256, wR2 = 0.0400	R1 = 0.0341, wR2 = 0.0323	R1 = 0.0484, wR2 = 0.1239
R indices (all data)	R1 = 0.0388, wR2 = 0.0746	R1 = 0.0476, wR2 = 0.0418	R1 = 0.1940, wR2 = 0.0399	R1 = 0.1043, wR2 = 0.1353
Largest difference peak/hole (e. Å ³)	0.397 and -0.298	0.338 and -0.334	0.256 and -0.285	0.624 and -0.412

Table 1 Crystal structures and data refinement parameters for the compounds 1, 2, 3, and 4

RESULTS AND DISCUSSION

Crystal structures and Data refinement parameters for the compounds **1**, **2**, **3**, and **4** are summarized in Table 1, The crystal of compound **1** belongs to the triclinic system, space group P-1 with a = 8.8145(10), b = 10.8876(10), c = 11.8022(10) Å, $\alpha = 101.863(7)$, $\beta = 111.921(2)$, $\gamma = 108.376(4)^{\circ}$. The crystal of compound **2** belongs to the monoclinic system, space group P2(1)/*n* with a = 14.9760(5), b = 9.1188(4), c = 18.0492(9) Å, $\alpha = 90$, $\beta = 91.609(2)$, $\gamma = 90^{\circ}$. The crystal of compound **3** belongs to the monoclinic system, space group P2(1)/*c* with a = 12.3919(6), b = 13.6990(5), c = 14.0032(6) Å, $\alpha = 90$, $\beta = 100.369(2)$, $\gamma = 90^{\circ}$. The crystal of compound **4** belongs to the triclinic system, space group P-1 with a = 8.3269(6), b = 9.8261(7), c = 15.8216(10) Å, $\alpha = 94.680(2)$, $\beta = 102.939(4)$, $\gamma = 94.898(2)^{\circ}$.



Figure 1 Crystal structure of compound 1.

The selected bond lengths and bond angles for the compounds 1, 2, 3, and 4 are listed in Tables 2–5 respectively, and the crystal structures of compounds 1, 2, 3, and 4 revealed in Figures 1–4 respectively.

Table 2 Selected bond lengths (Å) and bond angles (°) for the compound 1

Bond	Dist.	Bond	Dist.	Bond	Dist.
P(1)-O(2)	1.5617(13)	O(2)–C(14)	1.466(2)	C(7)–C(8)	1.518(2)
P(1)-O(1)	1.5976(13)	O(3)–C(1)	1.374(2)	C(8)–C(13)	1.381(3)
P(1)-S(1)	1.8978(7)	O(3)–C(15)	1.441(2)	C(14)–C(15)	1.494(3)
P(1)-Cl(5)	2.0045(7)	C(1)–C(6)	1.402(2)		
O(1)–C(13)	1.399(2)	C(6)–C(7)	1.520(2)		
Angle	(°)	Angle	(°)	Angle	(°)
O(2)-P(1)-O(1)	104.80(7)	C(13)-O(1)-P(1)	124.29(12)	C(1)-C(6)-C(7)	119.14(16)
O(2)-P(1)-S(1)	112.72(6)	C(14)-O(2)-P(1)	123.16(12)	C(8)–C(7)–C(6)	113.90(15)
O(1)-P(1)-S(1)	118.17(5)	C(1)-O(3)-C(15)	117.92(14)	C(13)-C(8)-C(7)	120.73(16)
O(2)-P(1)-Cl(5)	104.04(6)	O(3)-C(1)-C(6)	118.22(16)	C(8)-C(13)-O(1)	118.81(16)
O(1)-P(1)-Cl(5)	98.91(5)	O(3)-C(1)-C(2)	123.28(16)	O(2)-C(14)-C(15)	108.54(15)
S(1)-P(1)-Cl(5)	116.28(3)	C(6)-C(1)-C(2)	118.30(16)	O(3)-C(15)-C(14)	113.95(15)



Figure 2 Crystal structure of compound 2.

Crystal structures of compounds 1, 2, and 3 (Figures 1–3 and Tables 2–4) show that two phenyl rings are approximately perpendicular to each other and there are no elements of symmetry in the molecules. It is safe to predict that compounds 1, 2, and 3 can exist in two enantiomeric forms. Crystal structure of compound 4 (Figure 4 and Table 5) shows that it has a center of symmetry which is the centre of the phosphorus-containing macrocycle and is therefore optically inactive although two phenyl rings are approximately perpendicular to each other in two phenyl-methylene-phenyl units.

Bond	Dist.	Bond	Dist.	Bond	Dist.
S(1)–P(1)	1.9078(7)	O(3)–C(15)	1.374(2)	C(8)–C(9)	1.504(2)
P(1)–O(2)	1.5704(12)	O(3)-C(16)	1.440(2)	C(9)–C(10)	1.522(2)
P(1)–O(1)	1.5720(12)	O(4) - C(3)	1.389(2)	C(10)–C(15)	1.402(2)
P(1)–Cl(1)	2.0125(6)	O(4)–C(2)	1.4481(19)	C(16)-C(17)	1.491(2)
O(1)–C(1)	1.4591(19)	C(1)-C(2)	1.495(2)		
O(2)–C(17)	1.4583(19)	C(3)–C(8)	1.396(2)		
Angle	(°)	Angle	(°)	Angle	(°)
O(2) - P(1) - O(1)	102.44(6)	C(17)–O(2)–P(1)	122.93(11)	C(3)–C(8)–C(9)	120.52(16)
O(2) - P(1) - S(1)	118.71(5)	C(15)-O(3)-C(16)	113.59(12)	C(8)-C(9)-C(10)	112.65(14)
O(1) - P(1) - S(1)	116.91(5)	C(3)-O(4)-C(2)	114.86(12)	C(15)-C(10)-C(9)	120.33(16)
O(2) - P(1) - Cl(1)	99.71(5)	O(1)-C(1)-C(2)	108.27(14)	O(3)-C(15)-C(10)	120.90(15)
O(1) - P(1) - Cl(1)	102.45(5)	O(4)-C(2)-C(1)	108.82(14)	O(3)-C(16)-C(17)	106.89(14)
S(1)-P(1)-Cl(1)	113.99(3)	C(4)-C(3)-C(8)	120.28(16)	O(2)-C(17)-C(16)	109.66(14)
C(1)-O(1)-P(1)	120.28(10)	O(4)-C(3)-C(8)	117.95(15)		

Table 3 Selected bond lengths (Å) and bond angles (°) for the compound 2



Figure 3 Crystal structure of compound 3.



Figure 4 Crystal structure of compound 4.

Bond	Dist.	Bond	Dist.	Bond	Dist.
P(1)–O(4)	1.553(2)	O(2)–C(13)	1.372(3)	C(7)–C(8)	1.510(3) 1.387(4)
P(1)–O(3)	1.5594(19)	O(2)–C(14)	1.434(3)	C(8)–C(13)	1.493(3) 1.517(3)
P(1)-S(1)	1.9078(13)	O(3)–C(16)	1.458(3)	C(14)–C(15)	1.441(4) 1.451(3)
P(1)–Cl(5)	1.9785(13)	O(4)–C(17)	1.443(3)	C(15)-C(16)	
O(1)–C(1)	1.371(3)	C(1)–C(6)	1.391(4)	C(17)–C(18)	
O(1)-C(19)	1.452(3)	C(6) - C(7)	1.516(4)	C(18)–C(19)	
Angle	(°)	Angle	(°)	Angle	(°)
O(4)–P(1)–O(3)	101.98(12)	C(16)–O(3)–P(1)	120.93(19)	C(13)-C(8)-C(7)	120.1(4) 117.9(4)
O(4)–P(1)–S(1)	115.62(11)	C(17)–O(4)–P(1)	123.5(2)	O(2)-C(13)-C(8)	109.8(3) 114.7(3)
O(3)-P(1)-S(1)	111.32(10)	O(1)-C(1)-C(6)	119.5(4)	O(2)-C(14)-C(15)	105.9(2) 110.8(3)
O(4)–P(1)–Cl(5)	106.38(10)	O(1)-C(1)-C(2)	120.5(4)	C(14)-C(15)-C(16)	120.3(4) 109.7(3)
O(3)–P(1)–Cl(5)	107.50(10)	C(3)-C(2)-Cl(1)	119.5(3)	O(3)-C(16)-C(15)	
S(1)–P(1)–Cl(5)	113.16(7)	C(4)-C(3)-C(2)	117.5(4)	C(18)-C(17)-O(4)	
C(1)-O(1)-C(19)	114.3(2)	C(1)-C(6)-C(7)	119.4(3)	C(17)-C(18)-C(19)	
C(13)-O(2)-C(14)	115.9(3)	C(8)-C(7)-C(6)	114.5(3)	C(18)-C(19)-O(1)	

Table 4 Selected bond lengths (Å) and bond angles (°) for the compound 3

It can also be seen from Figures 2 and 4 that the molecules of compounds **2** and **4** form inclusion complex with neutral molecule guest (CHCl₃) which is outside of the phosphoruscontaining macrocycle in the ratio of 1:1 using CHCl₃ as crystallization solvent. The reason why compounds **1** and **3** did not form inclusion complex with CHCl₃ is not clear. The further work is needed.

EXPERIMENTAL

Preparation of Compounds 1, 2, 3, and 4

(3,5-Dichloro-2-hydroxyphenyl) (3,5-dichloro-2-hydroxyethoxyphenyl)-methane and bis(3,5-dichloro-2-hydroxyethoxyphenyl)methane, prepared starting from bis(3,5-Dichloro-2-hydroxyphenyl)methane by reaction with chloroacetic ester followed by

		-	-	-	
Bond	Dist.	Bond	Dist.	Bond	Dist.
Cl(5)–P(1)	1.9924(14)	O(2)–C(13)	1.376(4)	C(7)–C(8)	1.511(5)
P(1)-O(3)#1	1.568(3)	O(2)–C(14)	1.449(4)	C(14)–C(15)	1.482(5)
P(1)–O(1)	1.582(2)	O(3)–C(16)	1.437(5)	C(15)-C(16)	1.498(6)
P(1)-S(1)	1.8835(14)	O(3)-P(1)#1	1.568(3)		
O(1)-C(1)	1.396(4)	C(6)–C(7)	1.511(4)		
Angle	(°)	Angle	(°)	Angle	(°)
O(3)#1-P(1)-O(1)	99.87(13)	C(1)-O(1)-P(1)	123.10(19)	C(8)-C(7)-C(6)	113.8(3)
O(3)#1-P(1)-S(1)	118.76(14)	C(13)-O(2)-C(14)	113.5(3)	C(13)-C(8)-C(7)	120.4(3)
O(1)-P(1)-S(1)	117.25(10)	C(16)-O(3)-P(1)#1	122.0(3)	O(2)-C(13)-C(8)	119.1(3)
O(3)#1-P(1)-Cl(5)	102.68(13)	C(2)-C(1)-C(6)	121.2(3)	O(2)-C(14)-C(15)	109.8(3)
O(1)-P(1)-Cl(5)	101.06(10)	C(6)-C(1)-O(1)	119.7(3)	C(14)-C(15)-C(16)	117.2(4)
S(1)-P(1)-Cl(5)	114.49(7)	C(1)-C(6)-C(7)	120.5(3)	O(3)-C(16)-C(15)	106.6(4)

Table 5 Selected bond lengths (Å) and bond angles (°) for the compound 4

Symmetry transformations used to generate equivalent atoms: #1 - x, -y, -z + 1.

reduction with lithium aluminum hydride, were allowed to react with thiophosphoryl chloride to give two-component cyclization products **1** and **2** respectively. Bis(3,5-dichloro-2-hydroxypropoxyphenyl)methane and (3,5-Dichloro-2-hydroxypropoxyphenyl)(3,5-dichloro-2-hydroxypropoxyphenyl)methane, prepared starting from bis(3,5-Dichloro-2-hydroxyphenyl)methane by reaction with 3-bromopropene followed by hydroboration, were allowed to react with thiophosphoryl chloride to give two-component cyclization product **3** and four-component cyclization product **4** respectively (for detailed synthetic route, see ref. 11).

X-Ray Crystal Structure Determination of Compounds 1, 2, 3, and 4

The crystals of compounds 1, 2, 3, and 4 were obtained respectively by slow evaporation of a solution of chloroform.

All measurements were made with a Rigaku R-axis RAPID IP four circle area detector using graphite monochromatized Mo K α ($\lambda = 0.071073$ nm) radiation at 293 K. The structures were solved by direct methods using SHELX, and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97. All nonhydrogen atoms were refined with anisotropic displacement parameters. An empirical absorption correction based on Xscans was made on all data. Hydrogen atoms were located from the difference map and were constrained to geometrical estimates. Final refinement was carried out with isotropic displacement parameters applied to hydrogen atoms.

SUPPORTING INFORMATION

CCDC 894570 (compound 4), CCDC 894571 (compound 2), CCDC 894573 (compound 1), and CCDC 894574 (compound 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Telephone: (44) 01223 762910; e-mail: deposit@ccdc.cam.ac.uk

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