Crystal structure of ethyl-{3-thioxo-2-(3-thioxo-11,14,17,20-tetraoxa-2,4-diaza-3λ^5-phospha-tricyclo [19.4.0.0^{5,10}]pentacosa-1(25),5(10),6,8,21,23-hexaene-3-yl)-11,14,17,20-tetraoxa-2,4-diaza-3λ^5-phospha-tricyclo-[19.4.0.0^{5,10}]pentacosa-1(25),5(10),6,8,21,23-hexaene-3-yl}-amine monohydrate, ($C_{38}H_{49}N_5O_8P_2S_2$) · H_2O

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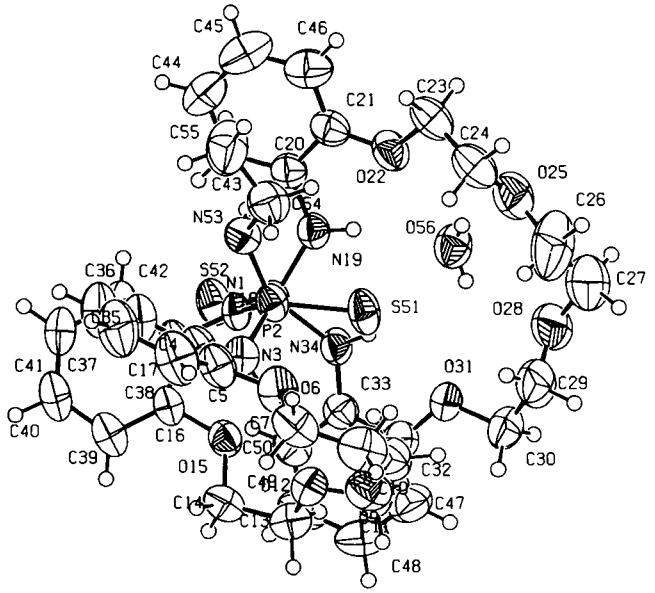

Abstract

$C_{38}H_{51}N_5O_9P_2S_2$, triclinic, $P\bar{1}$ (No. 2), a = 9.444(2) Å, b = 11.017(3) Å, c = 21.138(5) Å, α = 79.23(2)°, β = 84.09(2)°, γ = 71.35(3)°, V = 2044.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.072, $wR_{ref}(F^2)$ = 0.214, T = 293 K.

Source of material

The synthesis of the title compound was carried out by heating the diazadiphosphetidine precursor [1], with an excess of ethylamine in toluene. Under these conditions, we isolated a solid compound, which gave suitable crystals for X-ray diffraction analysis.

Discussion

In the course of our investigations to produce macrocyclic phosphorus ligands, we have been particularly interested by the cyclic derivatives obtained from the reaction of diamines with a diaminophosphine that can lead to macrocyclic phosphoramides [2-6]. From such compounds, nucleophilic attack at phosphorus could lead to new interesting structures. Recently, a diazadiphosphetidine disulfide derivative bearing two macrocyclic moieties was allowed to react with ethanol to produce a bis-macrocyclic compound with one asymmetric phosphorus center [7]. We thus showed by X-ray analysis that one molecule of ethanol was added, following the cleavage of one P—N bond of the diazadiphosphetidine ring.

The structure of the title compound shows that one molecule of ethylamine was added, breaking one P—N bond of the P_2N_2 cycle of the precursor. The bis-macrocyclic structure remains, and the two macrocyclic units in the molecule adopt two different conformations. The structure is isomorphous to that one reported for the parent compound bearing an ethoxy substituent at phosphorus P2 [7]. The macrocycle bearing the P18 phosphorus atom adopts an extended conformation, a consequence of the complexation of a water molecule which lies 1.39 Å above the macrocyclic cavity. The involved non-hydrogen atoms deviate from their least-squares plane by 0.16 Å, –0.04 Å, –0.14 Å, 0.22 Å, –0.13 Å and –0.07 Å for N19, O22, O25, O28, O31 and N34, respectively. The distances of the water oxygen atom to the other heteroatoms of the ring, indicate an interaction of the bounded water molecule with all donor atoms of the macroring. The folded conformation of the other macrocycle, that contains the asymetric P2 phosphorus atom, is related to intramolecular hydrogen bonding between the NH and the crown ether part of the macrocycle (d(N3···O12) = 3.107 Å, d(H3···O12) = 2.29 Å, ∠N3–H3···O12 = 166°). Thence, on complexation to water the conformation of the involved crown part of the molecule differs dramatically from the uncomplexed one. This feature is often encountered in similar macrocyclic structures and shows that the entrapped water molecule imposes a nearly planar conformation for the macrocyclic part of the ligand due to the formation of strong hydrogen bonds with water and the heteroatoms [8]. The absence of water as guest, implies a self-folding of the macrocycle with the formation of intramolecular H-bonds. This is characterized by the different conformations around the P—N bonds, which are *anti* and *gauche* respectively in the complexed and unbound macrocycle. In the S51–P2–N1–P18–S52 moiety, the phosphorus substituents are in Z/E-positions, with a planar N1 nitrogen atom (angles around N1 sum to 359°).

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Table 1. Data collection and handling.

Crystal:	colourless parallelepiped, size 0.08 × 0.18 × 0.32 mm
Wavelength:	Cu K_α radiation (1.54180 Å)
μ:	24.21 cm^{-1}
Diffractometer, scan mode:	Huber, $\theta/2\theta$
$2\theta_{max}$:	135°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7371, 7371
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5233
$N(param)_{refined}$:	525
Programs:	SHELXS-86 [9], SHELXL-97 [10], PLATON [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(7A)	2*i*	1.1088(5)	0.0605(4)	0.7571(3)	0.107(3)
H(7B)	2*i*	1.2280(5)	0.1267(4)	0.7671(3)	0.107
H(8A)	2*i*	1.1799(5)	0.2568(5)	0.6662(3)	0.107
H(8B)	2*i*	1.2355(5)	0.1095(5)	0.6593(3)	0.107
H(10A)	2*i*	0.9748(6)	0.3664(4)	0.5895(2)	0.107
H(10B)	2*i*	0.9337(6)	0.3710(4)	0.6631(2)	0.107
H(11A)	2*i*	0.7251(5)	0.4164(5)	0.5950(2)	0.107
H(11B)	2*i*	0.7788(5)	0.2669(5)	0.5923(2)	0.107
H(13A)	2*i*	0.5502(5)	0.2436(4)	0.6497(2)	0.107
H(13B)	2*i*	0.4997(5)	0.3955(4)	0.6448(2)	0.107
H(14A)	2*i*	0.3755(5)	0.2945(4)	0.7328(2)	0.107
H(14B)	2*i*	0.5312(5)	0.2270(4)	0.7644(2)	0.107
H(23A)	2*i*	0.8971(5)	0.9502(4)	0.7617(3)	0.107
H(23B)	2*i*	0.8207(5)	1.0780(4)	0.7145(3)	0.107
H(24A)	2*i*	1.0029(5)	0.9333(5)	0.6595(3)	0.107
H(24B)	2*i*	0.9187(5)	0.8293(5)	0.6808(3)	0.107
H(26A)	2*i*	0.9855(7)	0.9151(9)	0.5508(4)	0.107
H(26B)	2*i*	0.9100(7)	0.8078(9)	0.5793(4)	0.107
H(27A)	2*i*	0.8710(8)	0.8949(9)	0.4739(4)	0.107
H(27B)	2*i*	0.7756(8)	1.0256(9)	0.4962(4)	0.107
H(29A)	2*i*	0.7623(7)	0.7047(6)	0.5437(3)	0.107
H(29B)	2*i*	0.7605(7)	0.7455(6)	0.4685(3)	0.107
H(30A)	2*i*	0.4968(6)	0.7939(5)	0.4756(2)	0.107
H(30B)	2*i*	0.5778(6)	0.6460(5)	0.4998(2)	0.107
H(35)	2*i*	0.7025(5)	0.3670(5)	0.9267(2)	0.107
H(36)	2*i*	0.8496(7)	0.2209(6)	1.0054(3)	0.107
H(37)	2*i*	1.0766(7)	0.0848(6)	0.9782(3)	0.107
H(38)	2*i*	1.1551(6)	0.0803(5)	0.8708(3)	0.107
H(39)	2*i*	0.3477(5)	0.2636(4)	0.8492(2)	0.107
H(40)	2*i*	0.2953(6)	0.2823(5)	0.9574(2)	0.107
H(41)	2*i*	0.3348(5)	0.4477(5)	0.9973(2)	0.107
H(42)	2*i*	0.4317(4)	0.5969(4)	0.9305(2)	0.107
H(43)	2*i*	0.3836(5)	0.8469(4)	0.8880(2)	0.107
H(44)	2*i*	0.4856(7)	0.9005(5)	0.9699(2)	0.107
H(45)	2*i*	0.6710(7)	0.9950(6)	0.9468(3)	0.107
H(46)	2*i*	0.7714(6)	1.0263(5)	0.8430(3)	0.107
H(47)	2*i*	0.3483(6)	0.6316(5)	0.5071(2)	0.107
H(48)	2*i*	0.1688(6)	0.5366(5)	0.5473(3)	0.107
H(49)	2*i*	0.0863(5)	0.5325(5)	0.6537(3)	0.107
H(50)	2*i*	0.1846(4)	0.6262(4)	0.7208(2)	0.107
H(54A)	2*i*	0.9352(5)	0.6625(5)	0.8166(2)	0.107
H(54B)	2*i*	0.9810(5)	0.5115(5)	0.8394(2)	0.107
H(55A)	2*i*	1.0516(7)	0.6088(7)	0.9132(3)	0.107
H(55B)	2*i*	0.9310(7)	0.5437(7)	0.9455(3)	0.107
H(55C)	2*i*	0.8851(7)	0.6943(7)	0.9228(3)	0.107
H(3)	2*i*	0.756(7)	0.380(5)	0.765(2)	0.107
H(19)	2*i*	0.498(6)	0.899(5)	0.730(2)	0.107
H(34)	2*i*	0.470(4)	0.765(5)	0.670(2)	0.107
H(53)	2*i*	0.714(6)	0.672(3)	0.854(3)	0.107
H(56A)	2*i*	0.482(7)	0.967(6)	0.602(2)	0.107
H(56B)	2*i*	0.586(4)	0.993(6)	0.635(3)	0.107

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	2*i*	0.5086(3)	0.6109(3)	0.8066(1)	0.043(2)	0.051(2)	0.048(2)	–0.014(1)	0.006(1)	–0.002(1)
P(2)	2*i*	0.6970(1)	0.56247(9)	0.78928(5)	0.0429(5)	0.0500(5)	0.0610(6)	–0.0121(4)	0.0096(4)	–0.0061(4)
N(3)	2*i*	0.7564(3)	0.4027(3)	0.8005(2)	0.046(2)	0.058(2)	0.062(2)	–0.006(1)	–0.002(1)	–0.006(1)
C(4)	2*i*	0.8425(4)	0.3152(4)	0.8511(2)	0.057(2)	0.051(2)	0.071(2)	–0.014(2)	–0.002(2)	0.000(2)
C(5)	2*i*	0.9792(5)	0.2288(4)	0.8342(2)	0.061(2)	0.053(2)	0.084(3)	–0.011(2)	0.000(2)	0.004(2)
O(6)	2*i*	1.0200(3)	0.2431(3)	0.7698(2)	0.066(2)	0.059(2)	0.088(2)	0.004(1)	0.011(2)	–0.006(1)
C(7)	2*i*	1.1353(5)	0.1403(4)	0.7469(3)	0.056(2)	0.058(2)	0.118(4)	–0.008(2)	0.011(2)	–0.020(2)
C(8)	2*i*	1.1538(5)	0.1768(5)	0.6757(3)	0.053(2)	0.092(3)	0.123(4)	–0.013(2)	0.017(3)	–0.041(3)
O(9)	2*i*	1.0208(4)	0.1940(3)	0.6434(2)	0.075(2)	0.072(2)	0.106(2)	–0.019(2)	0.013(2)	–0.034(2)
C(10)	2*i*	0.9332(6)	0.3251(4)	0.6282(2)	0.086(3)	0.070(3)	0.082(3)	–0.024(2)	0.018(2)	–0.016(2)
C(11)	2*i*	0.7772(5)	0.3315(5)	0.6181(2)	0.083(3)	0.075(3)	0.061(2)	–0.018(2)	0.006(2)	–0.010(2)
O(12)	2*i*	0.7005(3)	0.3085(3)	0.6784(1)	0.065(2)	0.068(2)	0.058(2)	–0.019(1)	0.000(1)	–0.012(1)
C(13)	2*i*	0.5511(5)	0.3140(4)	0.6711(2)	0.072(3)	0.068(3)	0.073(3)	–0.019(2)	–0.008(2)	–0.018(2)
C(14)	2*i*	0.4735(5)	0.3029(4)	0.7362(2)	0.069(3)	0.056(2)	0.088(3)	–0.024(2)	–0.002(2)	–0.014(2)
O(15)	2*i*	0.4594(3)	0.4174(2)	0.7612(1)	0.067(2)	0.050(1)	0.060(2)	–0.019(1)	0.002(1)	–0.004(1)
C(16)	2*i*	0.4229(4)	0.4197(4)	0.8255(2)	0.055(2)	0.053(2)	0.057(2)	–0.017(2)	0.004(2)	0.004(2)
C(17)	2*i*	0.4470(4)	0.5201(3)	0.8495(2)	0.043(2)	0.054(2)	0.056(2)	–0.012(2)	0.007(2)	0.001(2)
P(18)	2*i*	0.38775(9)	0.74928(8)	0.76801(4)	0.0424(5)	0.0481(5)	0.0513(5)	–0.0138(4)	0.0054(4)	–0.0044(4)
N(19)	2*i*	0.4690(3)	0.8621(3)	0.7645(2)	0.053(2)	0.054(2)	0.053(2)	–0.017(1)	0.004(1)	–0.007(1)
C(20)	2*i*	0.5222(4)	0.8978(3)	0.8159(2)	0.061(2)	0.043(2)	0.063(2)	–0.011(2)	0.002(2)	–0.011(2)
C(21)	2*i*	0.6400(5)	0.9518(4)	0.8031(2)	0.068(2)	0.049(2)	0.074(3)	–0.016(2)	–0.007(2)	–0.009(2)
O(22)	2*i*	0.6904(3)	0.9633(3)	0.7405(2)	0.063(2)	0.079(2)	0.076(2)	–0.036(1)	–0.005(1)	–0.002(1)
C(23)	2*i*	0.8342(5)	0.9856(4)	0.7250(3)	0.054(2)	0.063(3)	0.111(4)	–0.022(2)	–0.003(2)	–0.002(2)
C(24)	2*i*	0.9050(5)	0.9217(5)	0.6696(3)	0.062(3)	0.073(3)	0.117(4)	–0.028(2)	–0.004(3)	–0.004(3)
O(25)	2*i*	0.8178(4)	0.9727(4)	0.6153(2)	0.079(2)	0.110(3)	0.097(2)	–0.049(2)	0.015(2)	–0.011(2)
C(26)	2*i*	0.8901(7)	0.8998(9)	0.5631(4)	0.075(4)	0.235(9)	0.104(5)	–0.052(5)	0.028(4)	–0.006(5)
C(27)	2*i*	0.8066(8)	0.9319(9)	0.5087(4)	0.126(6)	0.171(7)	0.120(6)	–0.079(5)	0.060(5)	–0.043(5)
O(28)	2*i*	0.6761(4)	0.8899(4)	0.5154(2)	0.104(3)	0.108(3)	0.103(3)	–0.053(2)	0.045(2)	–0.036(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(29)	2*i*	0.7036(7)	0.7616(6)	0.5086(3)	0.107(4)	0.101(4)	0.092(4)	–0.037(3)	0.041(3)	–0.027(3)
C(30)	2*i*	0.5589(6)	0.7331(5)	0.5087(2)	0.117(4)	0.088(3)	0.056(2)	–0.039(3)	0.020(2)	–0.018(2)
O(31)	2*i*	0.4848(4)	0.7446(3)	0.5701(1)	0.108(2)	0.099(2)	0.050(2)	–0.058(2)	0.014(2)	–0.014(1)
C(32)	2*i*	0.3763(5)	0.6855(4)	0.5894(2)	0.074(3)	0.063(2)	0.059(2)	–0.020(2)	–0.009(2)	–0.004(2)
C(33)	2*i*	0.3261(4)	0.6862(3)	0.6542(2)	0.055(2)	0.052(2)	0.057(2)	–0.013(2)	–0.007(2)	–0.004(2)
N(34)	2*i*	0.3922(4)	0.7483(3)	0.6898(2)	0.056(2)	0.075(2)	0.049(2)	–0.032(2)	–0.001(1)	–0.003(1)
C(35)	2*i*	0.7944(5)	0.3109(5)	0.9152(2)	0.074(3)	0.077(3)	0.072(3)	–0.015(2)	0.007(2)	0.007(2)
C(36)	2*i*	0.8825(7)	0.2233(6)	0.9623(3)	0.101(4)	0.100(4)	0.076(3)	–0.024(3)	0.001(3)	0.019(3)
C(37)	2*i*	1.0166(7)	0.1411(6)	0.9460(3)	0.101(4)	0.099(4)	0.095(4)	–0.024(3)	–0.020(3)	0.033(3)
C(38)	2*i*	1.0654(6)	0.1400(5)	0.8818(3)	0.071(3)	0.065(3)	0.115(4)	0.001(2)	–0.007(3)	0.016(3)
C(39)	2*i*	0.3650(5)	0.3303(4)	0.8654(2)	0.072(3)	0.066(3)	0.082(3)	–0.030(2)	0.007(2)	0.005(2)
C(40)	2*i*	0.3333(6)	0.3422(5)	0.9301(2)	0.092(3)	0.082(3)	0.077(3)	–0.036(3)	0.016(3)	0.013(2)
C(41)	2*i*	0.3573(5)	0.4408(5)	0.9540(2)	0.074(3)	0.091(3)	0.057(2)	–0.028(2)	0.014(2)	0.002(2)
C(42)	2*i*	0.4148(4)	0.5304(4)	0.9140(2)	0.057(2)	0.076(3)	0.056(2)	–0.018(2)	0.006(2)	–0.003(2)
C(43)	2*i*	0.4631(5)	0.8810(4)	0.8787(2)	0.073(3)	0.074(3)	0.063(2)	–0.013(2)	0.008(2)	–0.020(2)
C(44)	2*i*	0.5225(7)	0.9152(5)	0.9276(2)	0.102(4)	0.098(4)	0.064(3)	–0.016(3)	–0.005(3)	–0.027(3)
C(45)	2*i*	0.6344(7)	0.9699(6)	0.9139(3)	0.106(4)	0.125(5)	0.090(4)	–0.020(4)	–0.020(3)	–0.048(4)
C(46)	2*i*	0.6947(6)	0.9889(5)	0.8518(3)	0.087(3)	0.086(3)	0.096(4)	–0.027(3)	–0.019(3)	–0.024(3)
C(47)	2*i*	0.3157(6)	0.6303(5)	0.5502(2)	0.101(4)	0.088(3)	0.070(3)	–0.029(3)	–0.019(3)	–0.019(2)
C(48)	2*i*	0.2088(6)	0.5740(5)	0.5741(3)	0.081(3)	0.094(4)	0.112(4)	–0.023(3)	–0.021(3)	–0.043(3)
C(49)	2*i*	0.1593(5)	0.5717(5)	0.6376(3)	0.059(2)	0.072(3)	0.126(4)	–0.026(2)	–0.004(3)	–0.027(3)
C(50)	2*i*	0.2182(4)	0.6279(4)	0.6778(2)	0.053(2)	0.063(2)	0.079(3)	–0.016(2)	0.004(2)	–0.012(2)
S(51)	2*i*	0.7533(1)	0.6329(1)	0.70307(5)	0.0599(6)	0.0628(6)	0.0728(6)	–0.0148(5)	0.0247(5)	–0.0016(5)
S(52)	2*i*	0.1919(1)	0.7785(1)	0.81038(5)	0.0444(5)	0.0672(6)	0.0787(7)	–0.0110(4)	0.0153(4)	–0.0007(5)
N(53)	2*i*	0.7581(3)	0.5990(3)	0.8492(2)	0.045(2)	0.057(2)	0.067(2)	–0.013(1)	0.005(1)	–0.015(2)
C(54)	2*i*	0.9162(5)	0.5944(5)	0.8493(2)	0.061(3)	0.096(3)	0.093(3)	–0.033(2)	0.006(2)	–0.019(3)
C(55)	2*i*	0.9488(7)	0.6118(7)	0.9133(3)	0.090(4)	0.172(6)	0.082(4)	–0.062(4)	–0.009(3)	0.002(4)
O(56)	2*i*	0.5036(4)	0.9952(4)	0.6293(2)	0.065(2)	0.092(2)	0.069(2)	–0.026(2)	0.008(2)	–0.013(2)

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