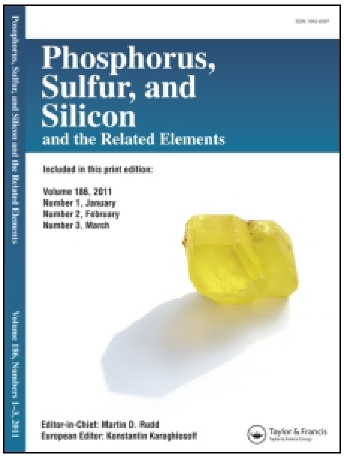

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FORMATION AND X-RAY STRUCTURAL CHARACTERIZATION OF THE CHIRAL

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FORMATION AND X-RAY STRUCTURAL CHARACTERIZATION OF THE CHIRAL AND RACEMIC FORMS OF A BIS-MACROCYCLIC PHOSPHORAMIDE

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The 1,3,2,4-diazadiphosphetidine ring **1**, bearing two macrocyclic units, reacts with ethanol to form the chiral bis-macrocycle **2**, including an asymmetric phosphorus center. **2** has been isolated as its chiral and racemic crystalline forms; both were structurally characterized using X-ray crystallography. The bis-macrocyclic molecule has a similar shape in the two crystal forms. A water molecule is complexed in one of the macrocylic units, inducing strong conformational changes respectively to the uncomplexed one.

Keywords: chiral phosphorus; diazadiphosphetidine; phosphorus macrocycle; X-ray structure

There is considerable current interest in the synthesis of macrocyclic and cage compounds containing phosphorus binding sites which are particularly attractive and important in the design of new phosphorus-based ligands.[1] In previous studies we have designed and synthesized new macrocyclic ligands incorporating a diaminophosphine group in a crown ether backbone.[2,3] Some with phosphoryl or thio-phosphoryl moieties provided interesting structures which exhibited high affinity towards cationic guests such as alkali metal or Ag^{I} and Hg^{II} metal cations.[2,4]

Here we describe the unusual formation and characterization of the bis-macrocyclic phosphoramide **2** bearing a chiral phosphorus center. **2** was obtained from the ring opening reaction of the diazadiphosphetidine

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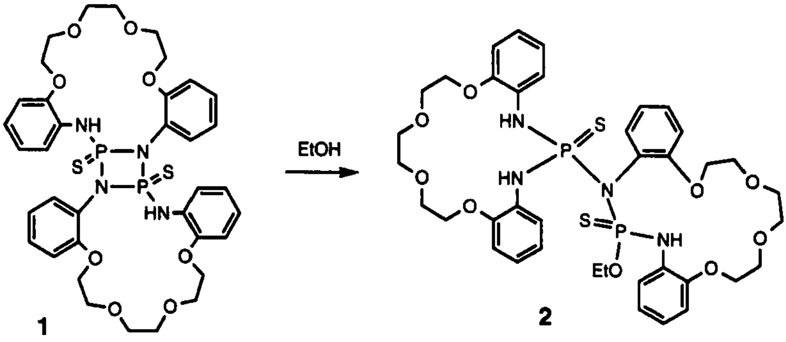
derivative **1**. The outstanding of this reaction lies in the presence of an asymmetric phosphorus center and the formation of **2** as a conglomerate or a racemate in the solid state (crystals I and II, respectively).

RESULTS AND DISCUSSION

Compound **1** was previously described and structurally characterized.[3] **1** exists as two *cis* and *trans* isomers due to the different orientations of the substituents at phosphorus. The chiral *cis* isomer (C_2 symmetry) was obtained as a racemic mixture. **2** was first obtained when recrystallisation of what we hoped to be the complex of **1** and KSCN was carried out in dichloromethane, in the presence of traces of ethanol, affording tiny crystals of **2**•H_2O (crystal I). The structure analysis revealed that **2** clearly arose from the nucleophilic attack of one molecule of ethanol and the cleavage of one P-N bond of the diazadiphosphetidine ring in **1**, leading to a bis-macrocyclic structure with one asymmetric phosphorus center. In the crystal, space group *P1*, Z = 1, **2** underwent spontaneous resolution. The absolute configuration was determined from X-ray data and was consistent with the described and pictured absolute configuration (Figure 1).



SCHEME 1

Improved synthesis of **2** was carried out by treating **1** with an excess of ethanol in toluene at 120°C. The formation of **2** was evidenced by the appearence of an AB quartet in the ^{31}P NMR spectrum ($\delta^{31}P$

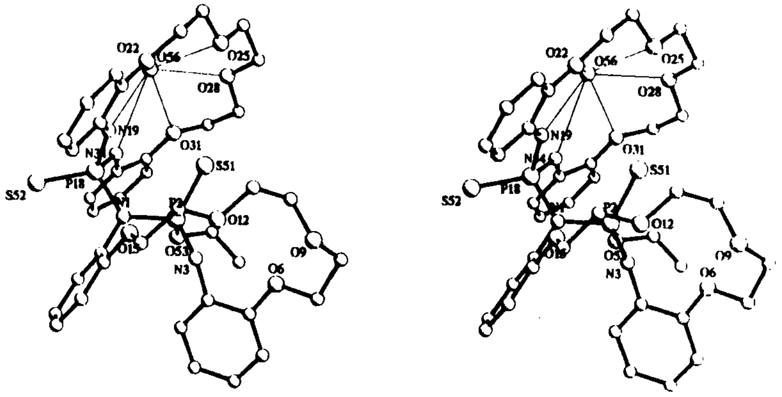


FIGURE 1 Stereoscopic view of **2** in crystal I.[8]

($CDCl_3$) = 60.3 and 48.1 ppm, $^2J_{PP}$ = 22.8 Hz), characteristic of the non equivalence of the phosphorus atoms. Proton NMR and mass spectroscopy indicated the addition of one molecule of ethanol to the starting product **1**. To complete the characterization of the compound thus obtained, a second determination of the X-ray crystal structure of **2** was undertaken (crystal II). Surprisingly, the new data revealed that compound **2** crystallized as a racemate (space group *P-1*, Z = 2).

In both crystals I and II, the bond distances and angles are very similar. The angles around the phosphorus atoms reflect the different conformations around the adjacent bonds (Table I). The main differences arise from the conformations around the C(23)-C(24) and O(25)-C(26) bonds in the polyether chain [respectively (g^-) and (a) in crystal I, (g^+) and (g^+) in crystal II]. The molecule shows two different conformations for the two macrocyclic units. The macrocycle bearing the P(18) phosphorus atom bound to three nitrogen atoms adopts a nearly planar conformation, a consequence of the complexation of a water molecule which lies 1.25 Å above the macrocyclic cavity in crystal I, and 1.40 Å above the macrocycle in crystal II. The involved non-hydrogen atoms deviate from their least-squares plane as depicted in Table II.

The distances of the water oxygen atom to the other heteroatoms of the ring, reported in Table III, indicate an interaction of the bounded water molecule with all donor atoms of the macroring.

TABLE I Selected interatomic distances (Å) and angles (°) around the phosphorus atoms in **2** (crystals I and II)

	crystal I	*crystal II*
P(2)-N(1)	1.695(4)	1.695(3)
P(18)-N(1)	1.709(4)	1.702(3)
P(2)-N(3)	1.636(4)	1.645(3)
P(18)-N(19)	1.644(4)	1.641(3)
P(18)-N(34)	1.634(4)	1.652(3)
P(2)-S(51)	1.928(2)	1.931(2)
P(18)-S(52)	1.931(2)	1.924(1)
P(2)-O(53)	1.569(4)	1.577(3)
C(17)-N(1)-P(2)	118.8(3)	117.0(2)
P(18)-N(1)-P(2)	122.0(2)	123.7(2)
P(18)-N(1)-C(17)	119.0(3)	118.9(2)
S(51)-P(2)-N(1)	114.3(2)	113.8(1)
O(53)-P(2)-N(1)	100.0(2)	100.7(1)
O(53)-P(2)-S(51)	117.3(2)	116.8(1)
N(3)-P(2)-N(1)	108.5(2)	107.6(2)
S(51)-P(2)-N(3)	111.5(2)	112.0(1)
O(53)-P(2)-N(3)	104.1(2)	104.8(2)
N(19)-P(18)-N(1)	110.6(2)	111.1(2)
N(34)-P(18)-N(19)	97.4(2)	97.2(2)
S(52)-P(18)-N(19)	113.8(2)	114.9(1)
N(34)-P(18)-N(1)	105.6(2)	105.6(2)
S(52)-P(18)-N(1)	110.8(2)	109.5(1)
S(52)-P(18)-N(34)	117.7(2)	117.7(1)
P(2)-N(3)-C(4)	129.8(3)	128.0(3)
P(18)-N(19)-C(20)	128.8(4)	131.5(3)
P(18)-N(34)-C(33)	129.9(3)	127.7(3)

TABLE II Deviations of the non-hydrogen atoms from their least-squares plane (in Å)

	Crystal I	*Crystal II*
N(19)	0.18	0.04
O(22)	−0.22	0.14
0(25)	0.14	−0.20
0(28)	−0.02	0.12
0(31)	−0.05	0.04
N(34)	−0.03	−0.14

TABLE III Bond distances of the water oxygen atom to the heteroatoms of the ring (in Å)

	Crystal I	*Crystal II*
N(19)	3.09	3.21
O(22)	3.12	3.30
O(25)	2.90	2.97
O(28)	2.80	2.88
O(31)	2.97	2.99
N(34)	2.94	3.00

The folded conformation of the other macrocycle, that contains the asymetric P(2) phosphorus atom, seems to be related to intramolecular hydrogen bonding between the NH and the crown ether part of the macrocycle (N(3)H...O(12) 2.31 Å in crystal I and 2.26 Å in crystal II). Thence, on complexation to water the conformation of the involved crown part of the molecule differs dramatically from the uncomplexed one. In the S(51)P(2)N(1)P(18)S(52) moiety, the phosphorus substituents are in Z/E-positions. Angles around the N(1) nitrogen atom summed 360° in both crystalline forms. Figure 2 shows the similar organization of the bis-macrocyclic phosphoramide in both racemic and enantiomeric crystal forms. Nevertheless, we must point out the different conformations of the ring in the C(23)---C(26) region, and the POCC dihedral angles involving the ethoxy substituent which are different in both structures (90° and 173° in crystals I and II respectively).

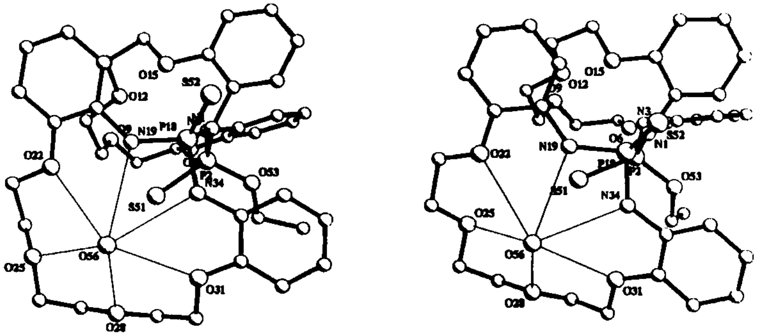


FIGURE 2 Comparison of the conformation of the macrocycle which binds the water molecule: right crystal I, left crystal II.[8]

The reaction leading to the formation of **2** suggests that other nucleophilic addition to **1** would be possible. The treatment of the diazadiphosphetidine disulfide compound $[(C_6H_5NH)P(S)NC_6H_5]_2$, with benzylamine was earlier reported to afford thiophosphoric triamide.[5] Preliminary results showed that with primary amines, under experimental conditions similar to that used for the preparation of **2**, **1** is mainly converted to bis-phosphorus derivatives with non equivalent phosphorus atoms.[4] On the other hand, **1** proved to be stable toward H_2O under neutral conditions. The stereochemistry of the diazadiphosphetidine **1** imposes several possibilities regarding to the final products obtained from the ring opening by nucleophilic agents. Our results indicate that the nucleophilic attack on the P_2N_2 cycle, leading to **2**, takes place at the P-N bond not involved in the macrocyclic structure (the P-NH bonds of the macrocyclic moieties are unaffected). Interestingly, the bis-macrocycle **2** was isolated in two different crystalline forms. However, we cannot predict which factors direct the formation of the racemate versus the conglomerate.

EXPERIMENTAL

^1H NMR spectra were recorded on a Varian Unity$^{\oplus}$ 500 NMR spectrometer. ^{13}C and ^{31}P NMR spectra were obtained with a Bruker AC200 operating at 50.3 and 81.02 MHz respectively. Chemical shifts are given in ppm and *J* coupling constants in Hz. ^{1}H and ^{13}C chemical shifts are referenced internally to residual protonated-solvent resonances. δ^{31}P are from H_3PO_4 85%. ^{13}C and ^{31}P NMR spectra are proton decoupled and the reported multiplicities of ^{13}C NMR resonances represent ^{31}P – ^{13}C couplings. ^{13}C assignments were mainly based on the DEPT spectrum. Some of the ^{1}H and ^{13}C resonances were assigned by means of 2D NMR correlation experiments.

Preparation of **2**: Typically a suspension of **1**^{3} in a 1:1 mixture of toluene and ethanol was heated to 120°C for several hours in a sealed tube. The solid starting material was generally only partially dissolved. The resulting solution was evaporated and the residue was chromatographied on silica gel [chloroform-ethyl acetate (1:1 v/v)] to give **2** as the main product together with some starting **1** and minor unidentified phosphorus derivatives. Recrystallization from dichloromethane afforded pure **2** (dec above 190°C). No attempts were made to optimize the yield. The product was identified from NMR spectroscopy, mass spectroscopy and X-ray analysis. ^{1}H NMR ($C_2D_2Cl_4$), δ: 0.76 (3H, t, $J = 7.0$, CH_3), 3.55 and 3.76 (2H, m, $POCH_2$), 3.42 – 4.33 (24H, m, OCH_2CH_2O), 6.52 (1H, d, $J_{PH} = 10.5$, NH), 6.65 (1H, d, $J_{PH} = 8.0$, ArH), 6.75 (1H, t, $J_{PH} = 7.8$, ArH) 6.80–6.90 (7H, m, ArH), 6.96 (3H, m, ArH + NH), 7.17 (3H, m, ArH + NH), 7.45 (1H, d, $J_{PH}= 7.7$, ArH), 8.01 (1H, br, ArH), 8.07 (1H, d, $J_{PH} = 7.7$, ArH); ^{13}C NMR ($C_2D_2Cl_4$), δ: 14.86 (d, $J = 9.0$, CH_3), 63.95 (d, $J = 5.8$, $POCH_2$), 68.12, 68.42, 68.49, 68.55, 68.80, 69.36, 69.52, 69.60, 70.29, 70.45, 70.45, and 71.20 (OCH_2CH_2O), 111.28, 111.96, 112.13, 112.13, 118.41 (br d), 118.88 (br d), 120.00 (br), 120.22 (br), 120.51, 120.61, 120.76, 121.40, 121.59, 122.02, 129.07 (br) and 133.14 (br) (tertiary aromatic C), 127.46 (d, $J = 2.2$), 129.46, 130.25 (d, $J = 2.3$), 130.60 (d, $J = 2.6$), 147.34 (d, $J= 9.7$), 147.90 (d, $J = 9.9$), 148.55 (d, $J = 9.3$), and 156.32 (t, $J= 2.8$) (quaternary aromatic C); ^{31}P NMR ($CDCl_3$) δ: 60.3 and 48.1 ($^2J_{PP} = 22.8$); FAB MS *m/z* 831.4 (MH^+).

The crystals were examined at 20 °C on a Huber four circle diffractometer and Rigaku RU200 rotating anode generator equipped with graphite monochromatized CuKα radiation ($\lambda = 1.54178$ Å). Crystal measurement and refinement data are summarized in Table IV. The lattice parameters were refined using 30 reflections for crystal I and 17 reflections for crystal II in the range $5° \leq 2\Theta \leq 20°$. Intensities were measured with ω scans. One standard reflection was checked every 50 reflections and no significant deviation was observed. The intensity data were corrected for Lorentz-polarization but not for absorption. Both structures were solved from direct methods using the program SHELX86.[6] They were refined by full-matrix least-squares on F with anisotropic temperature factors for all non hydrogen atoms with SHELXL93.[7] For crystal I, all the hydrogen atoms positions were calculated; the hydrogens of the water molecule were not included. For crystal II, H(3), H(34), H(56a) and H(56b) were located from a difference Fourier synthesis. The positions of the other H atoms were calculated and refined with a common isotropic temperature factor. At the end of the refinement of crystal I the Flack absolute structure parameter was –0.02(2). The absolute configuration was confirmed by sorting the reflexions according to $w^{1/2}\|Fc(h, k, l)|-|Fc(-h, -k, -l)\|$. Among the 100 most sensitive reflexions, the sign of 96 were consistent with the described and pictured absolute configuration. Atomic scattering factors are from reference 9.

The final atomic coordinates and equivalent isotropic thermal parameters for **2** are given in Tables V and VI (crystals I and II, respectively). Additional material available from the Cambridge Crystallographic Data Centre comprises full list of bond lengths and angles, H-atom coordinates, and thermal parameters.

TABLE IV Data collection and refinement parameters

	crystal I	*crystal II*
Formula	$C_{38}H_{48}N_4O_9P_2S_2.H_2O$	$C_{38}H_{48}N_4O_9P_2S_2.H_2O$
Mr	848.88	848.88
System	triclinic	triclinic
Space group	P1	P-1
a(Å)	9.544(2)	9.341(2)
b(Å)	11.193(2)	11.148(2)
c(Å)	10.738(2)	21.100(4)
(α°)	87.52(2)	78.88(2)
(β°)	109.07(2)	84.66(2)
(γ°)	113.16(2)	71.31(2)
V(Å^3)	992.0(4)	2041.7(7)

	crystal I	*crystal II*
Z	1	2
Dx(gcm^{-3})	1.42	1.38
λ (Å)	1.54178	1.54178
F(000)	448	896
μ (mm^{-1})	2.44	2.44
Approximate crystal size (mm)	0.10 × 0.10 × 0.12	0.10 × 0.10 × 0.16
Collection range		
(sinΘ/λ)max Å^{-1}	0.60	0.53
Range of *hkl*	$-11 \leq h \leq 9$	$0 \leq h \leq 9$
	$-13 \leq k \leq 13$	$-11 \leq k \leq 10$
	$-12 \leq l \leq 12$	$-21 \leq l \leq 22$
Indices of standard refl.	0 4 0	−3 −3 2
N° of collected refl.	5779	5129
N° of observed refl.		
$(I \geq 2\sigma(\mathbf{I}))$	5009	3567
N° of parameters	507	521
U of the H atoms (Å^2)	0.094	0.100
R $(I \geq 2\sigma(I))$	0.055	0.048
(all data)	0.062	0.074
wR_2	0.145	0.114
weigth	$1/[\sigma^2 Fo^2 + 0.0976P^2 + 0.3P]$	$1/[\sigma^2 Fo^2 + 0.0662P^2]$
S	1.088	1.052
Extinction parameter	0.015	no correction
Shift/esd max	0.001	0.002
(max,min) (e/Å^3)	0.54 −0.38	0.49 −0.29

TABLE V Atomic coordinates ($*10^4$) and equivalent temperature factors ($Å^2$)($*10^3$) for **2** (crystal I) $U_{eq}=(1/3)\Sigma_i\Sigma_jU_{ij}a^*_ia^*_j\mathbf{a}_i\mathbf{a}_j$

	x	*y*	*z*	*U(eq)*
N(1)	4767(5)	5147(4)	9507(4)	48(1)
P(2)	6810(1)	5681(1)	10033(1)	47(1)
N(3)	7457(5)	5579(4)	11629(4)	52(1)
C(4)	7952(6)	4630(4)	12332(4)	50(1)
C(5)	9510(6)	5065(5)	13280(4)	51(1)
O(6)	10419(4)	6366(3)	13390(3)	61(1)
C(7)	11835(7)	6923(6)	14531(5)	62(1)
C(8)	12523(7)	8373(6)	14483(7)	70(2)
O(9)	11378(5)	8904(4)	14407(4)	67(1)
C(10)	10671(8)	9208(6)	13116(6)	68(2)
C(11)	9201(8)	9396(6)	13054(7)	74(2)
O(12)	7946(5)	8189(3)	13053(4)	63(1)
C(13)	6492(8)	8318(6)	12953(6)	70(2)
C(14)	5221(8)	7005(6)	12911(5)	67(2)
O(15)	4887(5)	6314(3)	11688(3)	58(1)
C(16)	3958(6)	4999(5)	11476(5)	55(1)
C(17)	3902(6)	4376(5)	10343(5)	50(1)
P(18)	3716(1)	5589(1)	8080(1)	43(1)
N(19)	4213(5)	7173(4)	8191(4)	52(1)
C(20)	3857(6)	7922(4)	8976(5)	51(1)
C(21)	4634(7)	9291(5)	9037(5)	59(1)
O(22)	5610(5)	9726(3)	8275(4)	73(1)
C(23)	6790(11)	11034(6)	8585(11)	105(3)
C(24)	7724(11)	11288(6)	7679(12)	109(3)
O(25)	8507(6)	10447(4)	7788(5)	85(1)
C(26)	9529(9)	10729(7)	7021(9)	90(2)
C(27)	10249(8)	9780(7)	7204(8)	84(2)

	x	*y*	*z*	*U(eq)*
O(28)	9120(5)	8574(4)	6453(4)	65(1)
C(29)	9670(7)	7563(6)	6759(6)	68(2)
C(30)	8499(7)	6347(6)	5911(6)	61(1)
O(31)	6994(5)	5997(4)	6137(4)	62(1)
C(32)	5917(6)	4722(5)	5925(5)	51(1)
C(33)	4651(6)	4464(4)	6425(4)	50(1)
N(34)	4578(5)	5543(4)	7005(4)	47(1)
C(35)	10042(8)	4174(5)	14003(5)	65(1)
C(36)	9039(9)	2871(6)	13772(6)	76(2)
C(37)	7520(9)	2434(5)	12842(6)	75(2)
C(38)	6960(8)	3323(5)	12136(6)	65(1)
C(39)	3003(7)	3061(5)	10047(6)	63(1)
C(40)	2142(8)	2357(6)	10850(7)	74(2)
C(41)	2205(9)	2964(7)	11942(8)	84(2)
C(42)	3126(8)	4289(7)	12277(7)	75(2)
C(43)	4380(9)	10082(6)	9797(7)	75(2)
C(44)	3353(9)	9542(7)	10521(7)	82(2)
C(45)	2554(8)	8215(6)	10446(6)	69(1)
C(46)	2818(7)	7411(5)	9686(5)	57(1)
C(47)	3526(7)	3201(5)	6294(6)	65(1)
C(48)	3679(9)	2197(6)	5673(7)	82(2)
C(49)	4873(9)	2472(6)	5158(7)	75(2)
C(50)	6011(8)	3730(6)	5291(6)	68(1)
S(51)	7906(2)	7410(1)	9590(1)	59(1)
S(52)	1419(1)	4560(1)	7612(1)	55(1)
O(53)	6977(4)	4523(3)	9409(3)	55(1)
C(54)	8466(8)	4673(6)	9207(7)	71(2)
C(55)	9552(13)	4408(11)	10212(9)	113(3)
O(56)	5920(5)	8152(4)	6125(4)	70(1)

TABLE VI Atomic coordinates (*10^4) and equivalent temperature factors(Å^2)(*10^3) for **2** (crystal II) $U_{eq}=(1/3)\Sigma_i\Sigma_j U_{ija}{}^*{}_i a^*{}_j \mathbf{a}_i \mathbf{a}_j$

	x	*y*	*z*	*U(eq)*
N(1)	−104(3)	8950(3)	1941(1)	42(1)
P(2)	−1996(1)	9436(1)	2099(1)	48(1)
N(3)	−2576(3)	11017(3)	1975(2)	51(1)
C(4)	−3456(4)	11878(3)	1458(2)	53(1)
C(5)	−4837(5)	12748(4)	1631(2)	63(1)
O(6)	−5224(3)	12617(2)	2270(2)	72(1)
C(7)	−6377(5)	13648(4)	2493(3)	75(1)
C(8)	−6555(5)	13287(5)	3208(3)	85(2)
O(9)	−5213(3)	13104(3)	3529(2)	80(1)
C(10)	−4328(5)	11792(4)	3691(2)	76(1)
C(11)	−2743(6)	11706(4)	3797(2)	74(1)
O(12)	−1990(3)	11946(2)	3194(1)	59(1)
C(13)	−481(5)	11902(4)	3271(2)	66(1)
C(14)	303(5)	11999(4)	2622(2)	67(1)
O(15)	436(3)	10859(2)	2376(1)	53(1)
C(16)	790(4)	10835(4)	1741(2)	49(1)
C(17)	516(4)	9848(3)	1503(2)	45(1)
P(18)	1103(1)	7558(1)	2325(1)	44(1)
N(19)	1073(4)	7545(3)	3105(2)	55(1)
C(20)	1727(4)	8162(3)	3469(2)	50(1)
C(21)	1225(5)	8160(4)	4107(2)	60(1)
O(22)	115(4)	7593(3)	4302(1)	77(1)
C(23)	−607(6)	7675(5)	4920(2)	86(2)
C(24)	−2051(7)	7395(5)	4915(3)	99(2)
O(25)	−1780(4)	6124(4)	4845(2)	97(1)
C(26)	−3058(8)	5669(7)	4911(3)	127(2)
C(27)	−3885(7)	5985(8)	4370(3)	154(3)

	x	y	z	U(eq)
O(28)	−3160(4)	5272(3)	3853(2)	91(1)
C(29)	−4059(6)	5783(5)	3302(3)	87(2)
C(30)	−3332(5)	5167(4)	2754(2)	72(1)
O(31)	−1926(3)	5420(3)	2597(2)	68(1)
C(32)	−1411(5)	5524(4)	1974(2)	58(1)
C(33)	−247(4)	6084(3)	1840(2)	50(1)
N(34)	254(3)	6455(3)	2359(1)	46(1)
C(35)	−5708(5)	13620(4)	1143(3)	85(2)
C(36)	−5239(7)	13607(5)	509(3)	99(2)
C(37)	−3880(7)	12747(5)	349(3)	95(2)
C(38)	−2997(5)	11907(4)	825(2)	71(1)
C(39)	830(4)	9734(4)	865(2)	57(1)
C(40)	1432(5)	10606(5)	457(2)	71(1)
C(41)	1698(5)	11563(5)	696(3)	78(1)
C(42)	1386(5)	11700(4)	1334(2)	69(1)
C(43)	1817(6)	8726(4)	4506(2)	79(1)
C(44)	2904(6)	9292(5)	4259(3)	89(2)
C(45)	3390(5)	9302(4)	3634(3)	78(1)
C(46)	2806(4)	8745(4)	3235(2)	58(1)
C(47)	336(5)	6243(4)	1212(2)	65(1)
C(48)	−211(7)	5848(5)	739(2)	91(2)
C(49)	−1328(7)	5293(5)	875(3)	101(2)
C(50)	−1931(6)	5109(4)	1487(3)	80(1)
S(51)	−2587(1)	8712(1)	2951(1)	65(1)
S(52)	3073(1)	7264(1)	1904(1)	65(1)
O(53)	−2580(3)	9069(2)	1508(1)	57(1)
C(54)	−4122(5)	9048(5)	1507(2)	76(1)
C(55)	−4387(6)	8840(6)	876(2)	98(2)
O(56)	−10(4)	5096(3)	3714(2)	74(1)

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