

(the sums of the interior angles are 719.9, 720.0 and 719.9°). The B atom is in the plane of the phenyl ring as shown by the sum of the angles at the C atom bonded to it (359.6, 359.9 and 359.7°). The three pentafluorophenyl groups, instead of being propeller blades about the B—O axis, are each oriented differently. The plane of the first is almost perpendicular to that axis, the plane of the second is at an angle of about 20° and the plane of the third is nearly parallel to it (Fig. 2). The B...O-F distances range from 2.88 to 3.07 Å, all greater than van der Waals contacts, but the O2...F26 and O2...F36 distances are short, 2.723 (6) and 2.671 (7) Å, respectively, compared to 2.75 Å for a van der Waals contact.

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## Bis[di(imidazol-2-yl)phosphinato-*N*<sup>3</sup>,*N*<sup>3'</sup>]platinum(II) Tetrahydrate

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**Abstract.** [Pt{(C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>O<sub>2</sub>P)}<sub>2</sub>].4H<sub>2</sub>O, *M*<sub>r</sub> = 661.4, triclinic, *P* $\bar{1}$ , *a* = 7.473 (1), *b* = 7.779 (2), *c* = 9.787 (2) Å,  $\alpha$  = 109.46(3),  $\beta$  = 98.56(3),  $\gamma$  = 98.29(3)°, *V* = 518.9 (3) Å<sup>3</sup>, *Z* = 1, *D*<sub>m</sub> = 2.11 (1), *D*<sub>x</sub> = 2.116 Mg m<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71073 Å,  $\mu$  = 7.038 mm<sup>-1</sup>, *F*(000) = 320, *T* = 293 (1) K, *R* = 0.0268, *wR* = 0.0324 for 4521 unique reflections and 136 parameters. The ligand molecule is chelated through the *N*(3) atoms of the imidazole rings to the Pt atom, which lies on an inversion centre. Bond lengths and angles are normal.

**Introduction.** We have previously prepared di(imidazol-2-yl)phosphinic acid (Howard-Lock, Lock, Penny & Turner, 1989) and characterized

some of its iron, copper and zinc complexes (Seidel, 1990). Ball, Brown & Cocho (1984) have prepared the zinc complex of a related C(4),C(5)-substituted acid and characterized the compound by X-ray crystallography. In all these complexes the metal is bound to the *N*(3) atom of one of the rings and to one of the O atoms of the phosphinate group. This is hardly surprising, since the acid exists in the zwitterion form. Both N atoms in the second imidazole ring are protonated, and thus unavailable for coordination. It was of interest, therefore, to prepare a platinum(II) complex of this acid in which one might obtain an N<sub>2</sub>O<sub>2</sub> coordination arrangement. We were unsuccessful, however, and the title compound was obtained instead. The compound was prepared by the direct reaction of aqueous solutions of phosphinic acid (0.2 g in 10 mL) and potassium tetrachlo-

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roplatinat(II) (0.2 g in 5 mL). The resulting solution was allowed to evaporate slowly under a nitrogen atmosphere at 295 K and the title compound was obtained as colourless plate-like crystals (0.09 g).

**Experimental.** Density was measured by suspension in carbon tetrachloride/bromofrom mixture. A colourless plate crystal of dimensions 0.17 × 0.33 × 0.50 mm was chosen for diffraction. Unit-cell parameters were refined by least-squares fit of positional parameters for 38 reflections (10.81 ≤ 2θ ≤ 24.96°) on a Siemens P4 rotating-anode diffractometer, with use of graphite-monochromated Mo Kα radiation. Intensities for -1 ≤ h ≤ 12, -11 ≤ k ≤ 11, -15 ≤ l ≤ 11 (2θ<sub>max</sub> = 45°) were measured by an ω-2θ scan technique at scan rates from 2.00 to 29.3° min<sup>-1</sup> in 2θ. The ratio of total background time to scan time was 1.0. Three standard reflections measured every 100 reflections showed no instrument instability or crystal decay. 5675 measured reflections averaged to give 4521 independent reflections; R<sub>int</sub> = 0.015. Reflections with 3σ<sub>I</sub> ≥ I ≥ -3σ<sub>I</sub> were treated by the method of French & Wilson (1978). Lp corrections were made, as was an empirical correction for absorption (correction factors 2.68 ≤ A\* ≤ 9.45) by the program DIFABS (Walker & Stuart, 1983). The structure was solved by direct methods. Not all H atoms could be detected, so they were placed in calculated positions and not refined, except for the water molecules to which no H atoms were added. Anisotropic full-matrix least-squares refinement of non-H atoms except for O(3), O(4) and O(5), which had isotropic temperature factors, minimized Σw(|F<sub>o</sub> - |F<sub>c</sub>||<sup>2</sup>), where w = 1/(σ<sub>F</sub><sup>2</sup>). Scale, positional parameters for all atoms, anisotropic temperature factors for all non-H atoms, except O(3), O(4), O(5), were varied; 136 parameters. Final R = 0.0268 and wR = 0.0324, S = 2.22. Refinement ended when (Δ/σ)<sub>max</sub> = 0.001. The final difference map revealed an electron density maximum of 2.73, and minimum of -1.28 e Å<sup>-3</sup>. Scattering factors were obtained from Cromer & Waber (1974). Corrections for anomalous dispersion were made for N, O, P and Pt atoms (Cromer & Ibers, 1974). Calculations employed SHELXTL-PC (Sheldrick, 1990) and Laser 386 or IBM 486 computers. O(4) and O(5) were about 1.0 Å apart and were treated as a disorder problem. Refinement of the occupancy with fixed isotropic temperature factors, U = 0.10 Å<sup>2</sup>, gave almost identical values of about 0.60. Since the total occupancy cannot add up to more than one, both atoms were given occupancies of 0.5 in further refinements which varied the temperature factors. There may be a disorder problem with O(3) since the only significant peak in the final difference map lies 0.14 Å from O(3), but attempts to refine various disordered models did not give better answers.

Table 1. Atomic coordinates (× 10<sup>4</sup>) and isotropic or equivalent isotropic displacement coefficients (Å<sup>2</sup> × 10<sup>3</sup>)

The equivalent isotropic temperature factor, U<sub>eq</sub>, is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor. Atoms O(4) and O(5) were each given a site occupancy of one half, and were treated isotropically.

	x	y	z	U <sub>iso</sub> /U <sub>eq</sub>
Pt	5000	0	0	21 (1)
P	1610 (1)	-3938 (1)	-2343 (1)	27 (1)
N(1)	1948 (4)	-2030 (4)	-4304 (3)	33 (1)
C(2)	2509 (4)	-2121 (4)	-2963 (3)	26 (1)
N(3)	3751 (4)	-570 (3)	-2128 (3)	25 (1)
C(4)	4007 (5)	527 (4)	-2957 (4)	31 (1)
C(5)	2887 (6)	-390 (5)	-4322 (4)	36 (1)
N(1')	-149 (4)	-2743 (4)	49 (3)	32 (1)
C(2')	1327 (4)	-2512 (4)	-544 (3)	25 (1)
N(3')	2573 (4)	-1011 (3)	394 (3)	25 (1)
C(4')	1849 (5)	-282 (5)	1623 (4)	32 (1)
C(5')	162 (5)	-1358 (6)	1425 (4)	37 (1)
O(1)	3036 (4)	-5021 (4)	-2174 (3)	42 (1)
O(2)	-260 (4)	-4901 (4)	-3279 (3)	39 (1)
O(3)	3442 (9)	3498 (8)	4692 (7)	115 (2)
O(4)	3551 (10)	4960 (9)	756 (8)	50 (2)
O(5)	3218 (11)	5218 (10)	1791 (9)	58 (2)

Table 2. Interatomic distances (Å), bond angles (°) and hydrogen-bond geometry (Å, °)

Pt-N(3)	2.023 (3)	Pt-N(3')	2.014 (3)
P-C(2)	1.799 (4)	P-C(2')	1.803 (3)
P-O(1)	1.474 (3)	P-O(2)	1.488 (3)
N(1)-C(2)	1.345 (4)	N(1')-C(2')	1.337 (5)
C(2)-N(3)	1.334 (3)	C(2')-N(3')	1.338 (3)
N(3)-C(4)	1.372 (5)	N(3')-C(4')	1.374 (5)
C(4)-C(5)	1.362 (5)	C(4')-C(5')	1.357 (5)
C(5)-N(1)	1.371 (5)	C(5')-N(1')	1.377 (4)
O(4)···O(5)	1.040 (12)		
C(2)-P-C(2')	99.0 (1)	C(2)-P-O(2)	108.3 (2)
C(2')-P-O(2)	108.1 (2)	C(2)-P-O(1)	109.4 (2)
C(2)-P-O(1)	109.9 (2)	O(1)-P-O(2)	120.1 (2)
Pt-N(3)-C(3)	124.4 (2)	Pt-N(3')-C(2')	125.3 (2)
Pt-N(3)-C(4)	127.2 (2)	Pt-N(3')-C(4')	127.5 (2)
C(5)-N(1)-C(2)	108.4 (3)	C(5')-N(1')-C(2')	108.4 (3)
N(1)-C(2)-N(3)	108.6 (3)	N(1')-C(2')-N(3')	109.4 (3)
C(2)-N(3)-C(4)	108.4 (3)	C(2')-N(3')-C(4')	107.2 (3)
N(3)-C(4)-C(5)	107.5 (3)	N(3')-C(4')-C(5')	108.6 (3)
C(4)-C(5)-N(1)	107.0 (4)	C(4')-C(5')-N(1')	106.4 (3)
P-C(2)-N(1)	125.9 (2)	P-C(2')-N(1')	126.2 (2)
P-C(2)-N(3)	125.4 (2)	P-C(2')-N(3')	124.4 (3)
N(3)-Pt-N(3')	89.7 (1)	N(3)-Pt-N(3A)	180.0 (1)
N(3')-Pt-N(3A)	90.3 (1)		
N(1)-H(1A)···O(2)	2.714 (4)	H(1A)···O(2')	1.87
N(1')-H(1A')···O(4 <sup>ii</sup> )	2.70 (1)	H(1A')···O(4 <sup>ii</sup> )	1.84
N(1)-H(1A)···O(5 <sup>v</sup> )	2.72 (1)	H(1A')···O(5 <sup>v</sup> )	1.86
O(1)···O(4 <sup>iii</sup> )	2.70 (1)		
O(1)···O(5 <sup>iii</sup> )	2.80 (1)		
O(1)···O(3 <sup>iv</sup> )	2.98 (1)		
O(3)···O(3')	2.88 (1)		
O(1)···O(4 <sup>iv</sup> )	2.84 (1)		

Symmetry code: (i) -x, -1-y, -1-z; (ii) -x, -y, -z; (iii) 1-x, -y, -z; (iv) x, y-1, z-1; (v) 1-x, 1-y, 1-z; (vi) x, y-1, z. N(3A) is related to N(3) by the inversion centre at ½,0,0.

Atomic positional parameters are given in Table 1.\* Bond lengths, bond angles and hydrogen-bond geometry are listed in Table 2.

\* Lists of anisotropic temperature factors, H-atom positional parameters, torsion angles and the moduli of F<sub>o</sub> and F<sub>c</sub> have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55855 (15 pp.) Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester, CH1 2HU, England. [CIF reference: BR1016]

**Discussion.** The complex prepared was not the one desired; the N(3) atom of the second ring had been deprotonated and the Pt atom was coordinated to the two imidazole rings through the N(3) positions, giving an  $N_4$  coordination arrangement. The molecule is shown in Fig. 1. The Pt atom lies on an inversion centre and the environment is planar and almost exactly square; both the chelate and non-chelate *cis*-N—Pt—N angles are close to  $90^\circ$ . The Pt—N bond lengths [2.023 (3), 2.014 (3) Å] do not differ significantly and agree well with those we have measured previously, where Pt was bound to the imidazole ring in purine derived molecules (Beyerle-Pfnur, Brown, Faggiani, Lippert & Lock, 1985; Faggiani, Lippert, Lock & Speranzini, 1982; Faggiani, Lock & Lippert, 1980; Lippert, Lock & Pilon, 1984; Lock, Speranzini, Turner & Powell, 1976).

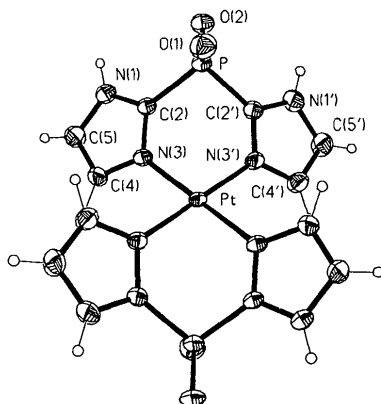


Fig. 1. The molecular complex, showing the atom numbering.

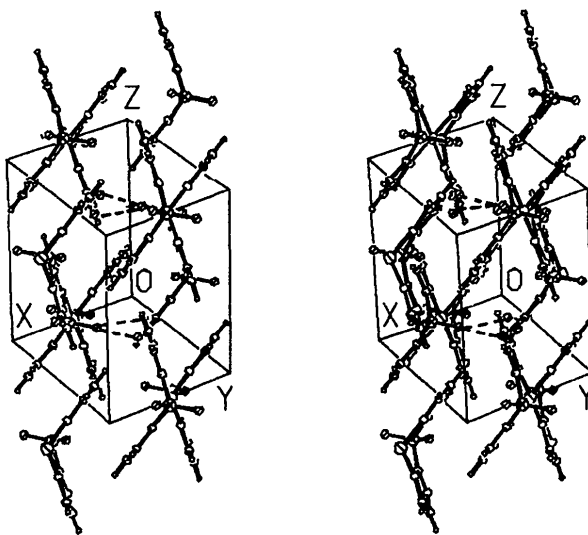


Fig. 2. The packing within the unit cell. The view is approximately down [111]. Hydrogen bonds are indicated by broken lines.

Bond lengths within the bound phosphinic acid agree well with those observed in the free phosphinic acid (Howard-Lock *et al.*, 1989), particularly when compared to the unprotonated ring. Furthermore, most angles agree, although there are some small differences. The binding of the metal to the imidazole rings apparently places some constraints on the ligand and the C—P—C angle is smaller than in the free ligand [99.0 (1) vs 101.9 (1), 104.6 (1)°]. Surprisingly the O(1)—P—O(2) angle is also smaller in the complex than in the free ligand [120.1 (2) vs 121.8 (1), 123.5 (1)°]. The difference is accommodated by an increase in the O—P—C angles, which average  $108.9^\circ$  in the complex vs  $107.3^\circ$  in the free ligand.

As can be seen in Fig. 1, if the complex were completely planar the H atoms attached to C(4), C(4'), and their inversion-related equivalents, would interfere. To accommodate this, the ligand is folded about the Pt...P axis such that the dihedral angle between the two halves is about  $125^\circ$ . The two halves of the ligand are very close to planar [excluding O(1), O(2)]. Because of the fold the six-membered ring Pt—N(3)—C(2)—P—C(2')—N(3') adopts a boat conformation, with Pt and P about 0.7 Å out of the plane of the other four atoms.

The packing is shown in Fig. 2. The molecules of the complex are held together by a hydrogen-bonding network through the water molecules. In the *a* direction, O(4) or O(5) bind N(1') [2.700 (7), 2.720 (7) Å] in one molecule to O(1) in its translational equivalent [2.70 (1), 2.80 (1) Å]. O(4) also acts as a link in the *b* direction from O(1) in one molecule to O(1A) in its translational equivalent [2.70 (1), 2.84 (1) Å]. In the *c* direction, a relatively weak hydrogen-bond chain connects molecules related by the inversion centre at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$  through O(1)...O(3)...O(3)...O(1) [2.98 (1), 2.88 (1), 2.98 (1) Å].

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## Structure of (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane)lead(II) Eosin Dihydrate

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**Abstract.** (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane-*N*<sup>1</sup>,*N*<sup>10</sup>,*O*<sup>4</sup>,*O*<sup>7</sup>,*O*<sup>13</sup>,*O*<sup>16</sup>,*O*<sup>21</sup>,*O*<sup>24</sup>)[2-(2,4,6,8-tetrabromo-3,7-dioxo-9-xanthenyl)benzoato-*O*,*O'*]lead dihydrate, [Pb(C<sub>18</sub>H<sub>36</sub>N<sub>2</sub>O<sub>6</sub>)(C<sub>20</sub>H<sub>6</sub>Br<sub>4</sub>O<sub>5</sub>)]·2H<sub>2</sub>O, *M<sub>r</sub>* = 1265.60, triclinic, *P* $\bar{1}$ , *a* = 12.079 (2), *b* = 12.671 (3), *c* = 18.01 (2) Å,  $\alpha$  = 101.46 (5),  $\beta$  = 96.45 (6),  $\gamma$  = 113.60 (3)°, *V* = 2418 (3) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.74 Mg m<sup>-3</sup>, Mo *K* $\alpha$  radiation (graphite-crystal monochromator),  $\lambda$  = 0.71073 Å,  $\mu$  = 6.84 mm<sup>-1</sup>, *F*(000) = 1228, *T* = 293 K, final conventional *R* = 0.078 for 3877 observed reflections and 530 variables. The central Pb<sup>2+</sup> cation is decahedrally coordinated by one eosin and one cryptand organic ligand. Distances: Pb—O(cryptand) 2.62 (2)–3.09 (2) Å; Pb—O(eosin) 2.50 (2) and 2.57 (2) Å; Pb—N 2.81 (3) and 2.97 (3) Å. The Pb<sup>2+</sup> cation is coordinated by two N atoms and four O atoms of the cryptand on a plane; the two eosin O atoms are above this plane and the last two cryptand O atoms are below it, forming a nearly tetrahedral arrangement.

**Introduction.** The diazopolyoxamacrobicycles or cryptands, first synthesized by Lehn (Dietrich, Lehn & Sauvage, 1969), are well known for their ability to form inclusion complexes, called cryptates, with metal ions. Since then, these ligands and related synthetic macrobicyclic compounds have been at the centre of interest to physical, organic, inorganic and biochemists and, to a lesser extent, analytical chemists. From the analytical point of view these host-guest complexes are important because they are readily extractable as colourful ion pairs or fluor-

escent hydrophobic anions into suitable organic solvents and can be used for selective and sensible separation and determination of a variety of metal ions, especially alkali-metal, alkaline-earth-metal and toxic heavy-metal cations.

In an earlier paper we reported a highly sensitive and selective spectrofluorimetric method for the determination of ultratraces of lead, based on solvent extraction with chloroform or 1,2-dichloroethane of the ion pair formed between the positively charged cryptate of lead with cryptand ethers, and the eosinate anion (Blanco-Gomís, Fuente-Alonso & Sanz-Medel, 1985; Blanco-Gomís, Arias-Abrodo, Picinelli-Lobo & Sanz-Medel, 1988). Since the elucidation of the spatial structures of ionophores and their complexes is essential for understanding the detailed mechanisms of selective complex formation and phase transfer of ions, crystallization of a ternary ion-association complex in 1,2-dichloroethane, under the same analytical conditions, has been carried out and an X-ray diffraction single-crystal study has been undertaken. The present paper reports the crystal structure of a new Pb<sup>2+</sup> complex with cryptand ether and eosin.

**Experimental.** A red crystal of size 0.20 × 0.17 × 0.10 mm was used for data collection with Mo *K* $\alpha$  radiation and graphite-crystal monochromator on an Enraf-Nonius CAD-4 single-crystal diffractometer. The unit-cell dimensions were determined from the angular settings of 25 reflections with  $\theta$  between 6 and 18°. Space group *P* $\bar{1}$  was confirmed from structure determination. The intensity data of 9069 reflections, in *hkl* range  $-14, -15, 0$  to  $14, 14, 21$

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