COMPLEXES OF MERCURY(II) WITH TETRAETHYL 2,2′-BIPYRIDYL-4,4′-DIPHOSPHONATE

Pavel VOJTISEK[1], Jan ROHOVEC and Ivan LUKES[2]

Department of Inorganic Chemistry, Charles University, 128 40 Prague 2, Czech Republic;
e-mail: [1] pavojt@prfdec.natur.cuni.cz; [2] lukes@ prfdec.natur.cuni.cz

Dedicated to Professor Miroslav Ebert on the occasion of his 70th birthday.

Complexes $[Hg(bipyP_2)Br_2]$ (**2**), $[Hg(bipyP_2)BrCl]$ (**3**), and $[Hg(bipyP_2)Cl_2]$ (**4**), where bipyP$_2$ is tetraethyl 2,2′-bipyridyl-4,4′-diphosphonate (**1**), were prepared and their crystal structures were determined. Coordination of the phosphonate group was only found in **4**. In this compound, the coordination sphere of Hg(II) contains two Cl atoms, two N atoms from the bipyridine chelate and O atom from phosphonate group and thus, the coordination number is five. The presence of Br atoms in the coordination sphere of complexes **2** and **3** results in the formation of tetrahedral environment (coordination number four) without any interaction with phosphonate. The coordination of the phosphonate group in **4** was also confirmed by IR spectroscopy.
Key words: Chelates; Phosphonates; Bipyridines; Complexes of Hg(II); Complexes of substituted 2,2′-bipyridine; X-Ray diffraction; IR spectroscopy; NMR spectroscopy.

The 2,2′-bipyridine bearing an additional group with a potential coordination ability is of considerable interest due to different behaviour towards "soft" and "hard" metals. Mercury(II), as a typically soft cation, forms complexes with 2,2′-bipyridine[1–4], and also with substituted 2,2′-bipyridines[5], involving various and interesting types of coordination. The 2,2′-bipyridines are mostly bonded as *N,N′*-chelates[1–4] and the coordination towards Hg(II) depends mainly on the nature of other ligands present and/or on sterical requirements of a substituent in the bipyridine ligand. Monodentate N-coordination was only observed in the structure of (3,3′-dimethyl-2,2′-bipyridyl)(methyl)mercury(II) nitrate[5].

Investigating coordination ability of tetraethyl 2,2′-bipyridyl-4,4′-diphosphonate (**1**) (bipyP$_2$) towards Pt(II), Pd(II) and Ru(II) (ref.[6]), we also decided to study the detailed behaviour of HgX$_2$–**1** systems (where X = Cl or Br) containing anions with relatively good coordination abilities towards Hg(II) and with different ionic radii ($r_{Br^-} = 1.82$ Å and $r_{Cl^-} = 1.67$ Å; ref.[7]). The ligand chosen was described[8,9]; however, its coordination chemistry has not been investigated so far. In addition to the mentioned coordination ability of 2,2′-bipyridine, the phosphonate can be also coordinated to a transition metal

and thus, it forms a polymeric chain. The formation of polymeric structures is a typical feature of the phosphonate chemistry. Here we report a study of the influence of the halogenide size on the formation of the coordination sphere of Hg(II) bonded to tetra-ethyl 2,2′-bipyridyl-4,4′-diphosphonate (**1**).

EXPERIMENTAL

Measurements

Infrared spectra in both the Nujol and Fluorolube mulls were recorded on an ATI Mattson Genesis FTIR spectrometer (2 cm^{-1} resolution, Beer–Norton medium apodization) in the region 400–4 000 cm^{-1} at room temperature. ^{31}P{^{1}H} NMR (80.98 MHz) and ^{1}H NMR (200.06 MHz) spectra of CDCl$_3$ solutions were recorded on a Varian Unity 200 spectrometer at room temperature with H$_3$PO$_4$ as external standard or TMS as internal standard. ^{31}P{^{1}H} NMR spectra of solid samples were measured at a Bruker 400 spectrometer (80.010 MHz) at room temperature using the CP/MAS technique and standard procedure (spinning 3.9–4 kHz, contact time 1.5 ms, the pulse repetition time 4 s and CaHPO$_4$ reference).

Mercury was determined by titration with KSCN solution. All melting points were uncorrected.

Structure Determination

The crystals of [Hg(bipyP$_2$)Br$_2$] (**2**) and [Hg(bipyP$_2$)Cl$_2$] (**4**) suitable for X-ray diffraction were picked up from crops of these compounds after recrystallization, the crystals of Hg(bipyP$_2$)BrCl (**3**) were obtained by a slow recrystallization of the microcrystallic sample from MeOH–H$_2$O (1 : 1; v/v) using a temperature gradient. The transparent air-stable crystals of all complexes were mounted on glass fibres (using a fast epoxy glue) at random orientations for the unit cell and space group determinations and for the data collections. The data collection and processing parameters are listed in Table I.

The structures of all three complexes were solved by the Patterson and Fourier methods and refined by the least squares treatment (full-matrix, based on F^2; SHELX86, SHELXL93, refs[10,11]). The hydrogen atoms were placed at the theoretical positions (for **3**) or found on the difference map and refined isotropically (for **2**). In the case of **4** the aromatic hydrogen atoms were isotropically refined and the others placed at theoretical positions.

Syntheses

Tetraethyl 2,2′-bipyridyl-4,4′-diphosphonate (bipyP$_2$) (**1**). **1** was synthesized in a quite good yield using the procedure which will be described in the following paper[8], m.p. 104–106 °C. For C$_{18}$H$_{26}$N$_2$O$_6$P$_2$ (428.4) calculated: 50.42% C, 6.12% H, 6.54% N; found: 49.94% C, 6.40% H, 6.43% N. ^{1}H NMR (CDCl$_3$): 1.37 t, 12 H, ^3J(H,H) = 7.2 Hz (CH$_2$**CH**$_3$); 4.1–4.3 m, 8 H (POC**H**$_2$CH$_3$); 7.78–8.9 m, 6 H (NC$_5$**H**$_3$).

*Hg(bipyP$_2$)X$_2$ (**2**) and (**4**).* The complexes Hg(bipyP$_2$)X$_2$ (X = Br (**2**), X = Cl (**4**)) were prepared from saturated solutions of corresponding HgX$_2$ (0.72 g of HgBr$_2$ or 0.54 g of HgCl$_2$; 0.002 mol) in mixture MeOH : H$_2$O (1 : 1; v/v) at room temperature. The stoichiometric amount of the ligand (0.86 g, 0.002 mol) in the same solvent was added and the heavy white precipitates obtained were filtered after about 10 h. They were washed with water and air-dried at room temperature. The crude compounds were recrystallized from MeOH–H$_2$O before analysis. Compound **2**: yield 1.45 g (92%); m.p. 131–132 °C. For C$_{18}$H$_{26}$Br$_2$HgN$_2$O$_6$P$_2$ (788.8) calculated: 27.41% C, 3.32% H, 3.55% N, 25.4% Hg; found: 26.92% C, 2.84% H, 3.23% N, 25.5% Hg. Compound **4**: yield 1.33 g (above 95%); m.p. 143–145 °C.

For $C_{18}H_{26}Cl_2HgN_2O_6P_2$ (699.8) calculated: 30.89% C, 3.74% H, 4.00% N, 28.7% Hg; found: 29.84% C, 3.73% H, 3.78% N, 28.0% Hg.

Hg(bipyP$_2$)BrCl (3). The mixed complex **3** was prepared by the following procedure: Equimolar amounts of $HgBr_2$ (0.36 g, 1 mmol) and $HgCl_2$ (0.27 g, 1 mmol) were mixed and refluxed about one hour in the mixture MeOH : H_2O (1 : 1; v/v). The stoichiometric amount of the ligand (0.86 g, 0.002 mol) was added after cooling to room temperature. The heavy, white precipitate obtained was isolated and recrystallized as described above. Yield 0.87 g (58%); m.p. 167–168 °C. For $C_{18}H_{26}BrClHgN_2O_6P_2$ (754.4) calculated: 29.05% C, 3.52% H, 3.76% N; found: 28.88% C, 3.31% H, 3.59% N.

TABLE I
Experimental data for X-ray diffraction studies of complexes **2**, **3** and **4**

Parameter	**2**	**3**	**4**
Formula	$C_{18}H_{26}Br_2N_2O_6P_2Hg$	$C_{18}H_{26}BrClN_2O_6P_2Hg$	$C_{18}H_{26}Cl_2N_2O_6P_2Hg$
M.w., g mol^{-1}	788.76	754.38	699.84
Colour and habit	colourless prisms	colourless rods	colourless rods
Crystal sytem	monoclinic	orthorhombic	monoclinic
Space group (No.)	$C2/c$ (No. 15)	$P22_12_1$ (No. 18)	$P2_1/m$ (No. 11)
a, Å	23.1396(6)	8.203(1)	8.195(1)
b, Å	8.355(1)	11.470(2)	14.048(1)
c, Å	13.3323(9)	13.806(2)	11.939(1)
β, °	106.653(4)		109.390(7)
V, Å^3	2 469.44	1 299.00	1 296.50
Z	4	2	2
D_c, g cm^{-3}	2.122	1.929	1.793
$F(000)$	1 504	736	680
μ, mm^{-1}	9.63	7.72	6.30
Crystal size, mm	$0.22 \times 0.10 \times 0.14$	$0.36 \times 0.13 \times 0.13$	$0.58 \times 0.18 \times 0.11$
Collection range: *hkl*	–27, 27; 0, 9; –15, 15	0, 9; 0, 13; –16, 16	–10, 10; 0, 17; –15, 15
$2\theta_{max}$, °	49.95	49.96	53.96
Unique (measured) data	2 176 (4 186)	2 288 (2 563)	2 945 (5 639)
Observed data ($F_o > 4\sigma(F_o)$)	1 933	1 953	2 366
Refined parameters	194	150	195
R_1 (ref.[10])	3.15	3.44	3.04
R_2 (ref.[10])	7.90	9.38	8.20
S (ref.[10])	1.114	1.042	1.036
Residual extrems, e A^{-3}	(+2.64; –1.57)	(+0.43; –0.90)	(+0.86–1.26)
Absorption correction	yes (ref.[15])	yes (ref.[15])	yes (ref.[15])
Second extinction correction (ref.[10])	0.0009(1)	no	0.0028(4)
Coefs in weighting scheme (ref.[10])	0.0559 0.56	0.0541 2.33	0.0435 1.78

RESULTS AND DISCUSSION

The synthesis of **1** (bipyP$_2$) is described in following paper[8]. This compound was prepared as an intermediate in the synthesis of the corresponding diphosphonic acid[8,9].

Complexes **2**, **3** and **4** were prepared according to the procedure described in Experimental by direct reactions of **1** and the corresponding mercury(II) halogenide in MeOH–H$_2$O (1 : 1). The analysis and melting points are given in Experimental, spectroscopic data obtained are listed in Tables II and III. These compounds form colourless crystals, only sparingly soluble in water and in polar organic solvents.

The structure of Hg(bipyP$_2$)Br$_2$ (**2**) is shown in Figs 1 and 2. Tables IV and V list selected bond distances and angles. This structure consists of discrete molecules with the mercury atoms situated on the crystallographic twofold axes. The coordination number of the mercury is four: the structure is formed by two nitrogen atoms of bipyridyl moiety of **1** and by two bromide anions as expected for a soft cation. The shape of the coordination sphere is a distorted tetrahedron. The Hg–Br distances (2.473(1) Å) are typical of the tetrahedral complexes of Hg(II), as nine complexes found by a lit-

TABLE II
Selected IR data (in cm^{-1}) of the compounds studied

Mode	1	2	4	PhPO(OEt)$_2$	MePO(OEt)$_2$[a]
Bending PO(OEt)$_2$	564 vs	506 vw	508 vw	528 s	502
		572 vs	548 s	562 m	715
			571 m		771
Stretching C–C	961 vs	965 sh	946 s	965 vs	965 vs
(of Et groups)	975 vs	972 vs	958 s		
			980 s		
Stretching COPOC	1 015 vs	1 021 vs	1 023 vs	1 025 vs	1 023 vs
	1 045 vs	1 049 vs	1 047 vs	1 054 vs	1 049 s
Stretching P=O	1 245 sh	1 223 s	1 222 s		
	1 254 vs	1 253 vs	1 247 vs	1 252 vs	1 250 vs
			1 256 vs		
Stretching C–O	1 095 m	1 078 m	1 077 m		
		1 097	1 093 m	1 097 m	1 099 s
		1 107 m	1 108 sh		
		1 117 m	1 117 m		
Rocking –CH$_3$	1 145 s	1 152 vs	1 152 vs	1 132 s	
	1 155 s			1 164 m	1 164

[a] Ref.[13].

erature search[12] containing Hg–Br bonds in a tetrahedral environment show the average distance of 2.52(3) Å. The Hg–N bonds are rather longer (2.409(3) Å) than the corresponding average value found for Hg(II)–N,N'-bipy-chelates (2.31(6) Å from 8 hits)[12]. The N–Hg–N angle (68.0(2)°) is considerably smaller than tetrahedral one due to the rigid framework of 2,2′-bipyridyl moiety and corresponds to the values found for similar structures[1–4]. On the other hand, the Br–Hg–Br angle (135.90(3)°) is considerably larger than the tetrahedral value. It is expectable for pseudotetrahedral environment of Hg(II) and this C_{2v} distorsion is caused by the rigidity of the bipyridyl system and/or by sterical requirements of the coordinated bromide anion. The Hg–O distance is 3.762(3) Å and thus, –P(O)(OEt)$_2$ groups are not coordinated.

Structure of Hg(bipyP$_2$)BrCl (**3**) is shown with the numbering scheme in Figs 3 and 4. Tables IV and V list selected bond distances and angles. The molecular structure of **3** seems to be similar to the structure of **2**; however these compounds are not isostructural. Different arrangements of both the crystal structures are clear from Figs 2 and 4. We tried to estimate possible hydrophobic or hydrophilic interactions which would result in the structure differences; however, without any evidence. The complex **3** also consists of discrete molecules and the mercury atoms are again situated on crystallographic twofold axes; however, this symmetry can be reached only by an anion dis-

TABLE III
^{31}P {^{1}H} chemical shifts (in ppm) of **1–4**

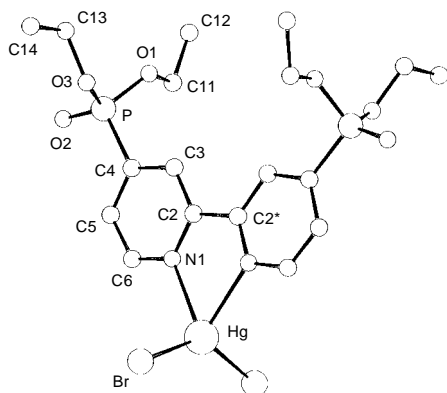| Compound	Solution	Solid state
1	15.4 s	15.9 s
2	14.8 s	14.3 s
3	14.8 s	–
4	14.7 s	15.4 s

FIG. 1
Perspective view of a molecule of **2** with the atom labelling (* –x, y, –1/2z)

order. The halogenide positions are occupied together by the bromide and chloride anions with site occupation factor (s.o.f.) = 0.5 that corresponds to the molar ratio Br : Cl = 1 : 1 in this mixed complex. The coordination environment of the mercury atom is a distorted tetrahedron. Two sites are filled by the *N,N'*-bonded ligand and two by bro-
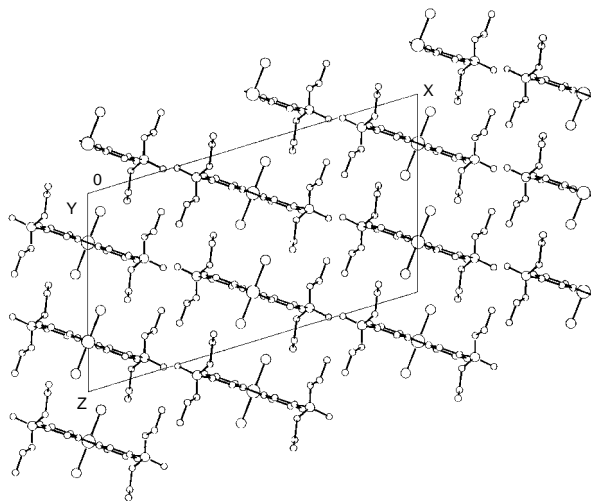

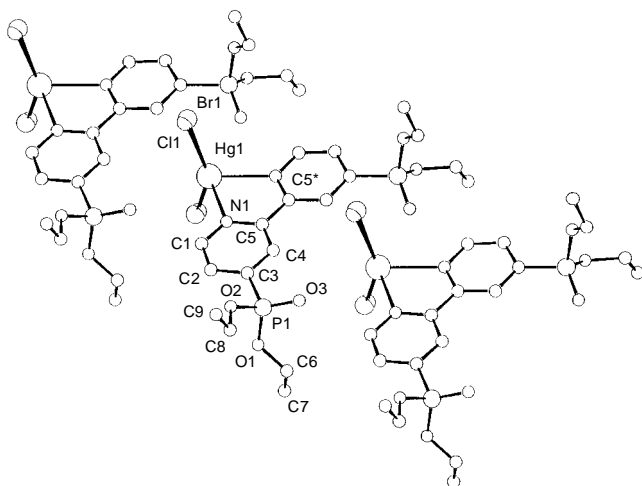
FIG. 2
Crystal packing of **2**

FIG. 3
Perspective view of **3** with atom labelling (* *x*, –*y*, –*z*). Hg atoms are situated on the twofold crystallographic axis representing a "simplex" of Br/Cl disorder

The geometry (in Å and °) of the coordination sphere of Hg(II) in complexes **2**, **3** and **4**

Compound	Atoms	Bond distances	Atoms	Bond angles	Atoms	Bond angles
2	Hg–N1	2.409(3)	N1–Hg–N1^i	68.0(2)	N1^i–Hg–Br	107.15(8)
	Hg–N2	2.409(3)^i	N1–Hg–Br	109.12(8)	N1^i–Hg–Br^i	109.12(8)
	Hg–X	2.473(1)	N1–Hg–Br^i	107.15(8)	Br–Hg–Br^i	135.90(3)
	Hg–O1	–				
3	Hg–N1	2.444(7)	N1–Hg–N1^{ii}	67.8(3)	N1–Hg–Cl^{ii,c}	105.4(7)
	Hg–N2	2.444(7)^{ii}	N1–Hg–Br^c	110.4(3)	Br^c–Hg–Br^{ii,c}	138.8(3)
	Hg–X	2.430(6)^a	N1–Hg–Cl^c	108.4(7)	Cl^c–Hg–Cl^{ii,c}	139(1)
		2.39(2)^b				
	Hg–O1	–	N1–Hg–Br^{ii,c}	103.6(3)	Br^c–Hg–Cl^c	3.3(8)
4	Hg–N1	2.360(4)	N1–Hg–N2	68.2(2)	N2–Hg–C1	104.01(6)
	Hg–N2	2.451(5)	N1–Hg–O1^{iii}	81.8(1)	N2–Hg–C1^{iv}	104.01(6)
	Hg–X	2.352(2)	N1–Hg–C1	112.86(5)	O1^{iii}–Hg–C1	87.22(6)
	Hg–O1	2.784(4)^{iii}	N1–Hg–C1^{iv}	112.86(5)	O1^{iii}–Hg–C1^{iv}	87.22(6)
			N2–Hg–O1^{iii}	150.0(1)	C1–Hg–C1^{iv}	132.5(1)

^{a} Br with s.o.f. = 0.5; ^{b} Cl with s.o.f. = 0.5; ^{c} s.o.f. = 0.5.
i = N1 in $–x$, y, $0.5 – z$; ii = N1 in x, $–y$, $–z$; iii = $x – 1$, y, z; iv = x, $0.5 –y$, z
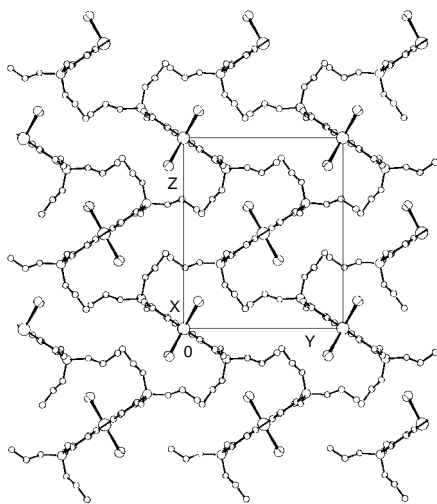
FIG. 4
Crystal packing of **3**

mide and chloride anions statistically disordered along the crystallographic twofold axes. The Hg–Br and Hg–Cl distances (2.430(6) Å and 2.39(2) Å, respectively) can be compared with the distances for dibromo (**2**) and dichloro (**4**) complex. The bond Hg–Br is a little shorter than in $Hg(bipyP_2)Br_2$ (2.473(1) Å) and the Hg–Cl, on the other hand, is longer than that in $Hg(bipyP_2)Cl_2$ (2.352(2) Å). This could be caused by the model used for the description of disorder along the twofold axes which was refined. In general, the Hg–X distances are near to the expected values from a literature search, as well as to the distances for **2** and **4**. The Hg–N distances and the N–Hg–N angles are also similar to the values of $Hg(bipyP_2)Cl_2$ (**4**) and $Hg(bipyP_2)Br_2$ (**2**) (see Table IV). The –$P(O)(OEt)_2$ groups are not coordinated, even through, Fig. 4 points to the coordination. However, the Hg–O distance is about 3.7 Å.

The structure of $Hg(bipyP_2)Cl_2$ (**4**) consists of the parallel polymeric chains containing $\{HgCl_2–OP(OEt)_2C_{10}H_6[PO(OEt)_2]N_2<\}$ repeating units. A part of this chain (with numbering scheme) is shown in Fig. 5, and the selected bond angles and distances are given in Tables IV and V. The coordination around the mercury atom is a highly distorted trigonal bipyramide, the donor atoms being two chlorine atoms, the oxygen atom (O1) of one –$P(O)(OEt)_2$ group from one ligand molecule and two nitrogen atoms of the other ligand. The atoms N2 and O1 are situated in the axial positions of this trigonal bipyramide. The Hg–Cl distance (2.352(2) Å) are typical for chloro complexes of Hg(II), as the 101 compounds containing Hg(II)–Cl bonds, found through a literature search[12], have an average distance of 2.42(12) Å. The Cl–Hg–Cl angle (132.5(1)°) is
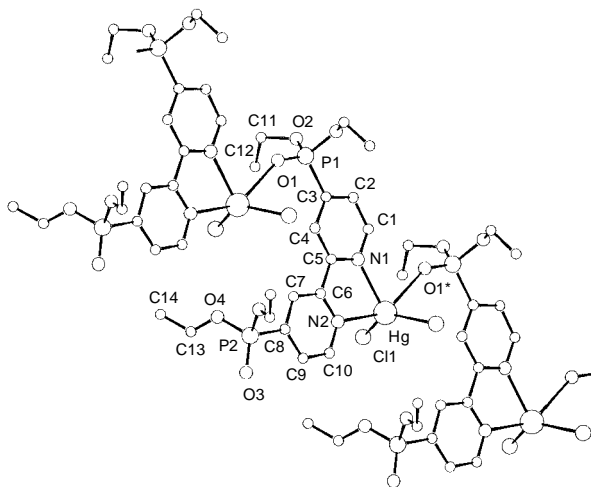

Fig. 5

Perspective view of a part of the endless chain from the structure of **4** with the atom labelling (* $x + 1$, y, z). Hg atoms, bipy moieties, P atoms, O1 and O3 atoms must lie in a plane for the symmetry reason

close to the ones found for distorted tetrahedral complexes **3** and **2** (see Table IV). The geometry of 2,2′-bipyridyl moiety of the ligand is similar to the geometry observed in complexes described above. There is only a difference following from the orientation of the rigid bipyridyl framework of the ligand toward the Hg(II) atom. The distances Hg–N are different (Hg–N1 = 2.360(4) Å and Hg–N2 = 2.451(5) Å, see Table IV) in contrast to the values observed in **2** and **3**. The Hg–N distances in structures of **2** and **3** must to be exactly the same for symmetry reasons. The coordination of –P(O)(OEt)$_2$ group through O1 (the bond distance Hg–O1 = 2.784(4) Å) corresponds to a relatively weak interaction with a predominantly electrostatic character. This interaction probably occurs only in the solid phase and was not observed in complexes **2** and **3** containing bromide anions.

In general, the geometry of the –P(O)(OEt)$_2$ groups is quite similar in all those compounds and even is not changed by coordination in the structure of **4**. The phosphorus

TABLE V
The geometry (in Å and °) of the phosphorus atoms in complexes **2**, **3** and **4**

Compound	Atoms	Bond distances	Atoms	Bond angles	Atoms	Bond angles
2[a]	P=O	1.463(3)	C3–P–O1	111.8(2)	O1–P–O3	117.0(2)
	P–O1	1.575(3)	C3–P–O2	107.2(2)	O2–P–O3	102.8(2)
	P–O2	1.550(3)	C3–P–O3	101.1(2)		
	P–C3	1.803(4)	O1–P–O2	115.5(2)		
3[b]	P1-O3	1.452(7)	C3–P1–O1	104.7(5)	O1–P1–O3	115.7(5)
	P1–O2	1.558(9)	C3–P1–O2	100.8(4)	O2–P1–O3	115.3(5)
	P1–O1	1.55(1)	C3–P1–O3	114.1(4)		
	P1–C3	1.806(9)	O1–P1–O2	104.5(6)		
4[c]	P1=O1	1.446(4)	C3–P1–O1	112.7(3)	O1–P1–O2^{iv}	117.2(2)
coordinated	P1–O2	1.55(4)	C3–P1–O2	104.8(2)	O2–P1–O2^{iv}	98.4(4)
–PO(OEt)$_2$	P1–O2^{iv}	1.550(4)	C3–P1–O2^{iv}	104.8(2)		
	P1–C3	1.799(5)	O1–P1–O2	117.2(2)		
4[d]	P2=O3	1.451(6)	C8–P2–O3	111.5(4)	O3–P2–O4^{iv}	117.2(2)
uncoordinated	P2–O4	1.555(9)	C8–P2–O4	105.0(3)	O4–P2–O4^{iv}	98.4(4)
–PO(OEt)$_2$	P2–O4^{iv}	1.555(9)	C8–P2–O4	105.0(3)		
	P2–O8	1.809(7)	O3–P2–O4	117.5(3)		

[a] P is situated 0.048(6) Å away from the bipy plane (N2, C1–C5); [b] P1 is situated 0.058(14) Å away from the bipy plane (N2, C1–C5); [c] P1 is situated in the bipy plane (N1, C1–C5); [d] P2 is situated in the bipy plane (N1, C1–C5).
iv = x, 0.5 − y, z

atoms are situated exactly in the bipyridyl plane for **4** or they lie very close to this plane (0.048(6) Å in structure **2** and 0.058(14) Å in structure **3**).

The selected IR data are listed in Table II. The data for $PhP(O)(OEt)_2$ and $MeP(O)(OEt)_2$ (ref.[13]) are given in this table for comparison. The relevant range 900–1 300 cm^{-1} embraces stretching frequencies of $-P(O)(OEt)_2$ group, according to Hameka[13]. The frequencies C–O–P were observed in a narrow interval of 1 015–1 055 cm^{-1} and the dominant P=O stretching mode was found near 1 250 cm^{-1} (see Table II). The position of the mode is relatively invariable (compare *e.g.* $MeP(O)(OMe)_2$ and $MeP(O)(OEt)_2$ having this mode at 1 250 cm^{-1} in both cases[13] and data in Table II). The spectrum of **2** is similar to the spectra of the free ligand **1** and of the ester $PhP(O)(OEt)_2$ in the selected range; on the other hand, the spectrum of **4** is a little different. The bands in the range considered are split and the splitting of about 23 cm^{-1} was also observed in the band near 565 cm^{-1} which probably corresponds to $O_2P=O$ bending mode[13]. The splitting of the P=O stretching mode is 10 cm^{-1} in **4** (see Table IV) and the intensities of both components are approximately same due to the presence of chemically nonequivalent $-P(O)(OEt)_2$ groups in crystals. These results are well explainable with respect to the structures determined.

The ^{31}P NMR spectra of the compounds were taken in $CDCl_3$ solutions and also in solid phase (using CP/MAS technique) at room temperature. These results are listed in Table III. The values of chemical shifts obtained in solution correspond to the ones of phosphonic acids esters[14]. If we compare chemical shifts of the complexes and of the free ligand, almost the same values were found for all compounds. The lowering of 0.6 ppm points to some changes in the electron densities on phosphorus atoms caused by coordination of the bipyridyl moiety.

Similar results were obtained in solid state (see Table III). The coordination of O1 from one $-P(O)(OEt)_2$ group in complex **4** does not cause any difference in the ^{31}P chemical shift, probably due to the fact that the P–O1–Hg interaction is weak and the electrostatic nature arising from the crystal packing only.

The present study has shown that tetraethyl 2,2′-bipyridyl-4,4′-diphosphonate (bipyP$_2$) (**1**) can exhibit different coordination modes in their mercury(II) complexes. The dominant factor affecting the structures of Hg(bipyP$_2$)X$_2$ complexes might be the size of halogen anion which may "dictate" the coordination number and the shape of coordination sphere of metal atoms. An interesting anion disorder was observed in the structure of compound Hg(bipyP$_2$)BrCl (**3**). The various parameters of the $-P(O)(OEt)_2$ group geometry affecting the IR spectra and solid-state ^{31}P NMR spectra were also discussed*.

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* The tables of atomic coordinates, anisotropic displacement parameters, observed and calculated structure factors and a full list of bond lengths and angles are available on request from the first author.

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