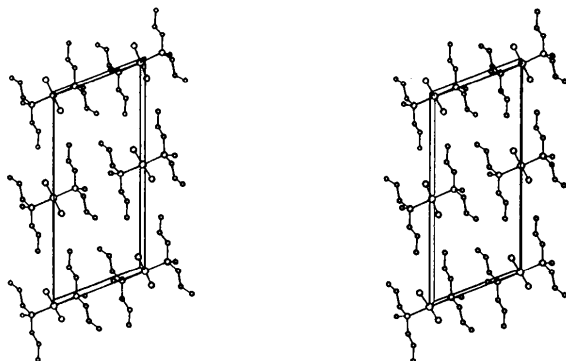


Table 2. Bond distances (Å) and angles (°)

Pt—Cl	2.292 (3)	C(1)—C(2)	1.53 (2)
Pt—S	2.292 (2)	C(2)—C(3)	1.54 (2)
S—C(1)	1.799 (9)	C(4)—C(5)	1.51 (1)
S—C(4)	1.795 (9)	C(5)—C(6)	1.55 (1)
S—O	1.473 (7)		
Cl—Pt—S	90.3 (1)	O—S—C(4)	109.4 (4)
S—Pt—Cl'	89.7 (1)	C(1)—S—C(4)	100.4 (4)
Pt—S—C(1)	112.7 (3)	S—C(1)—C(2)	111.7 (7)
Pt—S—C(4)	108.7 (3)	S—C(4)—C(5)	111.5 (6)
Pt—S—O	116.7 (3)	C(1)—C(2)—C(3)	109.9 (10)
O—S—C(1)	107.6 (4)	C(4)—C(5)—C(6)	109.6 (8)

Fig. 2. Stereoscopic drawing of the packing in the *trans*-[Pt(dps)<sub>2</sub>Cl<sub>2</sub>] crystal (*c* axis vertical, view down *b* axis).

multiple-bond character of the Pt—S bonds in the *cis* compounds would be more important than in the corresponding *trans* isomers. The stronger Pt—S bonds in the *cis* isomer would explain the rapid isomerization of *trans* disulfoxide compounds (if the sulfoxide ligand is not too bulky).

The S atoms in the sulfoxide ligands are in approximate tetrahedral environment. The Pt—S—O

angle [116.7 (3)°] is larger than the tetrahedral value while the C(1)—S—C(4) [100.4 (4)°] is smaller, as observed in the Pt-sulfoxide structures described above. The S—O, S—C and C—C bond distances agree well with published values.

The packing of the molecules is shown in Fig. 2. It consists of layers of molecules parallel to the *ab* plane and centered at *z* = 0 and  $\frac{1}{2}$ . No strong hydrogen bonds are expected in this compound, but one intermolecular distance is slightly shorter than the sum of the van der Waals radii. The C(4)···O distance is 3.19 (1) Å and the angles S—C(4)···O = 132.1 (4) and C(5)—C(4)···O = 112.4 (6)°.

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada and to the Ministère de l'Éducation (FCAR) for financial support.

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## The Structure of Bis(acetonitrile)bis(*cis*-1,2-diphenylphosphinoethene)iron(II) Diperchlorate

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(Received 5 April 1988; accepted 22 June 1988)

**Abstract.** [Fe(CH<sub>3</sub>CN)<sub>2</sub>{(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCHCHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (1), *M<sub>r</sub>* = 1129.7, tetragonal, *P*4<sub>2</sub>/*m*, *a* = 13.183 (2), *c* = 16.040 (3) Å, *V* = 2788 (1) Å<sup>3</sup>, *Z* = 2,

*D<sub>m</sub>* = 1.38 (2), *D<sub>x</sub>* = 1.35 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 0.531 mm<sup>-1</sup>, *F*(000) = 1168, room temperature, *R* = 0.070 for 1092 reflections. The cation

0108-2701/88/111895-03\$03.00

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has crystallographic  $2/m$  symmetry and a pseudo-octahedral coordination with the Fe and four P atoms in a plane with the acetonitrile ligands bound perpendicular to the plane. The Fe atom is in the low-spin state. The perchlorate anions occupy two crystallographically distinct special positions and are disordered.

**Introduction.** In the course of studies of the coordination complexes of the ligand (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCHCHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> the title compound was isolated by reaction of iron(II) perchlorate with the ligand in acetonitrile. The crystal structure of the compound is reported and compared with that of the related compound [Fe{(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCHCHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>}] (2) which shows a high-spin to low-spin phase transition at low temperatures when crystallized from acetone (Ceconi, Di Vaira, Midollini, Orlandini & Sacconi, 1981).

**Experimental.** Preparation of crystals: To a warm solution of *cis*-1,2-bis(diphenylphosphino)ethene (0.80 g) in acetonitrile (50 ml) was added a solution of 0.36 g Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in acetonitrile (20 ml). On cooling and slow evaporation fine red crystals were formed. If required the compound may be recrystallized from acetonitrile. Density was measured by flotation.

A parallelepiped 0.10 × 0.12 × 0.12 mm was measured using a Philips PW 1100 diffractometer,  $\omega/2\theta$  scan, scan width  $1.2 + 0.3(\tan\theta)^\circ$ , scan speed  $1.2^\circ \text{ min}^{-1}$ . Graphite-monochromated Mo  $K\alpha$  radiation. 2667 reflections measured ( $6 < 2\theta < 47^\circ$ ;  $h = 0, 14$ ;  $k = -9, 10$ ;  $l = 0, 17$ ). 2140 unique reflections ( $R_{\text{int}} = 0.021$ ) of which 1048 were taken as unobserved [ $I < 3\sigma(I)$ ]. Three standard reflections measured every 120 min showed a variation of less than  $2.5\sigma(I)$  and no correction for change in intensity was applied. Cell parameters from least-squares refinement of 22 centred reflections ( $27 < 2\theta < 41^\circ$ ). Data corrected for Lorentz and polarization effects but not for absorption. The structure was solved by heavy-atom methods. All calculations used a local version of XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) or ORTEPII (Johnson, 1976). Scattering factors for neutral atoms from Cromer & Mann (1968), and anomalous-dispersion corrections for Fe, P and Cl from *International Tables for X-ray Crystallography* (1974). Least-squares refinement on  $|F|$  (full matrix) with Fe, P, Cl and O anisotropic, all H atoms in calculated positions and unit weights gave final values of  $R = 0.070$ ,  $S = 1.85$  for 1092 reflections with 127 variables,  $(\Delta/\sigma)_{\text{max}} = 0.36$ ,  $(\Delta/\sigma)_{\text{ave}} = 0.08$ . The final difference Fourier map showed maxima and minima of  $+0.50$  and  $-0.41 \text{ e } \text{Å}^{-3}$ .

**Discussion.** Atomic coordinates and equivalent isotropic temperature factors are given in Table 1, and

Table 1. Fractional coordinates, equivalent isotropic atomic displacement factors  $U_{\text{eq}}$  ( $\text{Å}^2 \times 10^3$ ) and population parameters (PP)

$$U_{\text{eq}} = \frac{1}{3} \sum_i U_{ii}$$

	x	y	z	$U_{\text{eq}}$	PP
Fe	0.5	0	0	30.7 (9)	
Cl(1)	0.5	0.5	0.5	90 (4)	
Cl(2)	0.0471 (8)	0.6945 (9)	0	71 (4)	0.5
P	0.38527 (18)	-0.06592 (18)	0.09548 (16)	38.0 (8)	
O(1)	0.5456 (22)	0.482 (3)	0.5719 (14)	156 (18)	0.5
O(2)	0.533 (4)	0.6184 (24)	0.5	160 (22)	0.5
O(3)	0.402 (3)	0.516 (6)	0.5	210 (40)	0.5
O(4)	0.124 (3)	0.6379 (24)	0	146 (19)	0.5
O(5)	-0.021 (4)	0.646 (4)	0	240 (30)	0.5
O(6)	0.0620 (18)	0.745 (3)	0.0554 (20)	240 (21)	0.5
N	0.4257 (8)	0.1249 (8)	0	38 (3)	
C(1)	0.3105 (7)	-0.1602 (7)	0.0408 (6)	47 (3)	
C(10)	0.2973 (13)	0.2724 (13)	0	75 (5)	
C(20)	0.3704 (10)	0.1906 (10)	0	44 (4)	
C(11)	0.2873 (7)	0.0190 (7)	0.1368 (6)	44.2 (24)	
C(12)	0.1882 (9)	0.0096 (9)	0.1123 (8)	72 (3)	
C(13)	0.1144 (10)	0.0803 (10)	0.1407 (9)	90 (4)	
C(14)	0.1415 (10)	0.1561 (10)	0.1921 (8)	80 (4)	
C(15)	0.2391 (10)	0.1664 (10)	0.2165 (8)	83 (4)	
C(16)	0.3127 (8)	0.0998 (8)	0.1872 (7)	61 (3)	
C(21)	0.4263 (7)	-0.1426 (7)	0.1848 (6)	45.4 (25)	
C(22)	0.4622 (8)	-0.2403 (8)	0.1671 (7)	57 (3)	
C(23)	0.4992 (10)	-0.3037 (10)	0.2302 (9)	81 (4)	
C(24)	0.4999 (10)	-0.2679 (10)	0.3087 (9)	87 (4)	
C(25)	0.4623 (11)	-0.1735 (11)	0.3293 (10)	98 (5)	
C(26)	0.4247 (9)	-0.1081 (9)	0.2652 (8)	70 (3)	

Table 2. Selected bond lengths (Å) and angles (°)

Fe-P	2.321 (3)	Fe-N	1.916 (10)
P-C(1)	1.813 (10)	N-C(20)	1.13 (2)
P-C(11)	1.833 (10)	C(20)-C(10)	1.45 (2)
P-C(21)	1.836 (10)	C(1)-C(1)'	1.310 (13)
P-Fe-N	89.4 (2)	P-Fe-P'	82.57 (9)
Fe-P-C(1)	107.0 (3)	C(1)-P-C(11)	102.1 (4)
Fe-P-C(11)	118.0 (3)	C(1)-P-C(21)	99.2 (4)
Fe-P-C(21)	122.0 (3)	C(11)-P-C(21)	105.2 (4)
Fe-N-C(20)	170.6 (11)	N-C(20)-C(10)	178.3 (15)
P-C(1)-C(1)'	118.9 (7)		
N-Fe-P-C(11)	-5.1 (4)	Fe-P-C(11)-C(12)	107.3 (9)
N-Fe-P-C(21)	-138.0 (4)	Fe-P-C(21)-C(22)	-71.0 (8)

P' and C(1)' are related to P and C(1) respectively by the mirror plane bisecting the ligand.

selected bond lengths and bond angles in Table 2.\* Fig. 1 shows the atomic numbering of the asymmetric unit of the cation, and Fig. 2 gives a stereoview of the cation.

The cation has crystallographic  $2/m$  ( $C_{2h}$ ) symmetry, and occupies Wyckoff site *d*: the Fe atom and the C and N atoms of the acetonitrile ligands lie in the mirror

\* Lists of structure factors, atomic positional and anisotropic displacement parameters for atoms and other information in the printed form of the Standard Crystallographic File Structure of Brown (1985) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51176 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane which bisects the C—C double bond of the chelating phosphine ligand. The twofold axis passes between the two chelate ligands. The Fe shows the expected pseudo-octahedral coordination, with the Fe and four coordinated P atoms lying in a plane. The Fe—N bonds are very nearly perpendicular to this plane [ $\text{P—Fe—N} = 89.4(2)^\circ$ ]. Bond distances and angles are normal, with the Fe—P and Fe—N distances close to those previously found for low-spin iron(II) (Ceconi, Di Vaira, Midollini, Orlandini & Sacconi, 1981; Riley, Capshaw, Pettit & Davis, 1978; McCandlish, Santarsiero, Rose & Lingafelter, 1979; Barron, Wilkinson, Motevalli & Hursthouse, 1987). The low-spin character of the iron has been confirmed independently by the Mössbauer spectrum of this compound (Ramseier & Williams, 1981).

The bite of the chelate ring is  $82.57(9)^\circ$ , and the crystallographic symmetry requires the four ligand atoms of the chelate ring to be planar; this plane is inclined at  $21.8(5)^\circ$  to the  $\text{FeP}_4$  plane, and the Fe atom

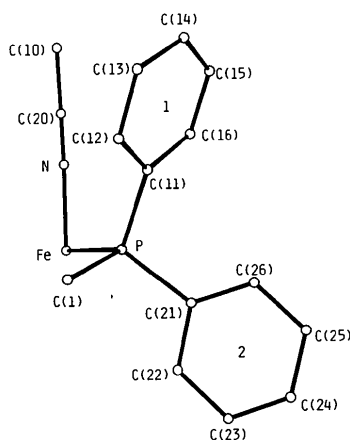


Fig. 1. The asymmetric unit of the cation  $[\text{Fe}(\text{Ph}_2\text{PCHCHPPh}_2)_2(\text{CH}_3\text{CN})_2]^{2+}$  showing the atomic numbering. There is a horizontal twofold axis passing through Fe, N, C(20) and C(10). The disordered perchlorate anions have been omitted.

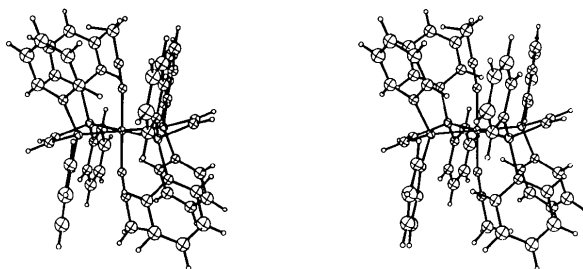


Fig. 2. Stereoview of the cation  $[\text{Fe}(\text{Ph}_2\text{PCHCHPPh}_2)_2(\text{CH}_3\text{CN})_2]^{2+}$ .

lies  $0.647(10) \text{ \AA}$  above one chelate plane and the same distance below the second. No significant non-bonded distances indicative of repulsions between the phenyl groups were found. The acetonitrile ligand is nearly linear but is inclined at  $9.4(11)^\circ$  to the Fe—N bond: comparable bendings have been observed in other acetonitrile complexes (Riley, Capshaw, Pettit & Davis, 1978), but were absent in the closely related complex  $[\text{Fe}(\text{CH}_3\text{CN})_2(\text{dmpe})_2]^{2+}$  [dmpe = 1,2-bis(dimethylphosphino)ethane] (Barron, Wilkinson, Motevalli & Hursthouse, 1987).

The principal structural difference between (1) and (2) lies in the orientation of the phenyl rings. We distinguish the phenyl groups attached to each P as either axial, with the twofold axis of each phenyl nearly perpendicular to the  $\text{FeP}_4$  plane [ring 1 in (1)], or equatorial, with the twofold axis lying closer to the  $\text{FeP}_4$  plane [ring 2 in (1)]. In both (1) and (2) the equatorial phenyls are turned so as to be roughly parallel to a plane bisecting the complex between the two phosphine ligands (the plane of the paper in Fig. 1). In (1) the four axial phenyls are equivalent and oriented so that the ring is roughly perpendicular to the Fe—P bond axis. In (2) the axial phenyls are not equivalent: on one P atom the ring is oriented perpendicular to the Fe—P bond as in (1), but on the other P atom of the ligand the axial phenyl practically eclipses the Fe—P bond, and lies roughly parallel to the axial ring of the other P.

The two crystallographically distinct perchlorate ions both occupy special positions and are disordered. The first [Cl(1)] occupies a site with symmetry  $2/m$  (Wyckoff site *b*) and apparently shows a weak interaction with the methyl carbon of the acetonitrile ligand [distance  $\text{C}(10)\cdots\text{O}(3) (1-y, x, z-\frac{1}{2}) = 2.98(7) \text{ \AA}$ ]. The second perchlorate anion lies on the mirror plane (Wyckoff site *j*) and was taken to have a population of 50%.

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