

Hence, the hydrogen bonds in the KHSeO_4 crystal are much stronger than in the KHSO_4 crystal, where the $\text{O}\cdots\text{O}$ distances are 2.619 (3) and 2.573 (3) Å for dimer and polymer, respectively (Payan & Haser, 1976).

Although the positions of the H atoms were not found in our work, taking into account the Se—O distances one may suppose that the H is closer to the O(11) atom [the Se—O(11) length is 1.737 (6) Å] in the dimer hydrogen bond and closer to the O(22) atom [the Se—O(22) distance is 1.712 (6) Å] in the polymer-chain hydrogen bond. The other O atoms involved in the hydrogen bonding (acceptors) make shorter bonds with the Se atoms of lengths 1.638 (6) and 1.654 (7) Å for the dimer and chain, respectively. The lengths of the remaining two Se—O bonds are very similar in both SeO_4 groups (Table 2). The Se—O distances obtained correspond to the distances observed in RbHSeO_4 (Waškowska, Olejnik, Łukaszewicz & Głowiak, 1978; Waškowska, Olejnik, Łukaszewicz & Czaplą, 1980; Roziere, Brach, & Jones, 1983) and NH_4HSeO_4 (Kruglik, Misjul & Aleksandrov, 1980; Aleksandrov, Kruglik, Misjul & Simonov, 1980).

The environments of both K^+ cations are similar to those observed in the sulfate analogue (Loopstra & MacGillavry, 1958). Each K^+ cation is surrounded by nine O atoms and only the K(1)—O(14) distance is significantly longer than 3 Å (see Table 2).

The authors thank the Polish Academy of Sciences for financial support (Project MR.I.9).

References

- ALEXSANDROV, K. S., KRUGLIK, A. I., MISJUL, S. W. & SIMONOV, M. A. (1980). *Kristallografiya*, **25**, 1142–1147.
 COTTON, F. A., FRENZ, B. A. & HUNTER, D. L. (1975). *Acta Cryst.* **B31**, 302–304.
 CRUICKSHANK, D. W. J. (1964). *Acta Cryst.* **17**, 682–683.
 GOYPRON, A., DE VILLEPIN, J. & NOVAK, A. (1980). *J. Raman Spectrosc.* **9**, 297–303.
 GROTH, P. (1908). *Chem. Krystalogr.* **2**, 313.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 KRUGLIK, A. I., MISJUL, S. W. & ALEXSANDROV, K. S. (1980). *Dokl. Akad. Nauk SSSR*, **255**, 344–348.
 LOOPSTRA, L. H. & MACGILLAVRY, C. H. (1958). *Acta Cryst.* **11**, 349–354.
 MADAR, J. (1960). *Czech. J. Phys.* **10**, 259.
 PAETZOLD, R. & AMOULONG, H. (1962). *Z. Anorg. Allg. Chem.* **317**, 166–175.
 PAYAN, F. & HASER, R. (1976). *Acta Cryst.* **B32**, 1875–1879.
 ROZIERE, J., BRACH, I. & JONES, D. J. (1983). *J. Solid State Chem.* **8**, 401–406.
 Syntex (1976). *XTL/XTLE Structure Determination System*. Syntex Analytical Instruments, Cupertino, California.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.
 WAŠKOWSKA, A., OLEJNIK, S., ŁUKASZEWICZ, K. & CZAPLA, Z. (1980). *Cryst. Struct. Commun.* **9**, 963–969.
 WAŠKOWSKA, A., OLEJNIK, S., ŁUKASZEWICZ, K. & GŁOWIAK, T. (1978). *Acta Cryst.* **B34**, 3344–3347.

Acta Cryst. (1986). **C42**, 272–274

Structure of a Homoleptic Bis(diphenylphosphino)methanide Complex, $[\text{Pt}\{(\text{C}_6\text{H}_5)_2\text{PCHP}(\text{C}_6\text{H}_5)_2\}_2]\cdot\text{C}_6\text{H}_6$

BY LJUBICA MANOJLOVIĆ-MUIR AND KENNETH W. MUIR

Chemistry Department, Glasgow University, Glasgow G12 8QQ, Scotland

(Received 31 July 1985; accepted 16 October 1985)

Abstract. Bis[bis(diphenylphosphino)methanido]platinum(II) benzene solvate, $[\text{Pt}(\text{C}_{25}\text{H}_{21}\text{P}_2)_2]\cdot\text{C}_6\text{H}_6$, $M_r = 1040.0$, triclinic, $P\bar{1}$, $a = 9.780$ (1), $b = 9.817$ (2), $c = 12.898$ (1) Å, $\alpha = 93.09$ (1), $\beta = 109.51$ (1), $\gamma = 95.68$ (1)° (reduced cell), $V = 1157$ (1) Å³, $Z = 1$, $D_x = 1.493$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 32.4$ cm⁻¹, $F(000) = 522$, $T = 295$ K, $R = 0.016$ for 6723 unique observed intensities. The structure is built from molecules of the bis(chelate) square-planar platinum(II) complex and of benzene, both of which straddle sites of crystallographic $\bar{1}$ symmetry. The ligand is attached to Pt through both P atoms and contains a delocalized $\text{P}\cdots\text{C}\cdots\text{P}$ system with a mean P—C(methanido) bond length of

1.729 (2) Å. The PtP_2C chelate rings are significantly non-planar.

Introduction. The title complex (1) contains the first example of a transition-metal ion stabilized only by chelating bis(diphenylphosphino)methanide ligands. Products of composition $[\text{M}\{(\text{C}_6\text{H}_5)_2\text{PCHP}(\text{C}_6\text{H}_5)_2\}_2]$, $M = \text{Pd}, \text{Pt}$, have been reported previously but were deemed intractable and probably polymeric (Schmidbauer & Mandl, 1977; Bassett, Mandl & Schmidbauer, 1980). The preparation and spectroscopic characterization of (1), together with preliminary details of its structure, have been described earlier (Brown, Yavari, Manojlović-Muir, Muir, Moulding & Seddon, 1982).

Table 1. Atomic fractional coordinates and isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U*</i>
Pt	0.0000	0.0000	0.0000	0.025
P(1)	0.03077 (4)	0.23430 (3)	0.05366 (3)	0.029
P(2)	0.04868 (4)	0.12772 (3)	-0.13272 (3)	0.030
C(1)	0.0393 (2)	0.2852 (2)	-0.0706 (1)	0.037
C(2)	0.0929 (3)	0.3670 (2)	0.5275 (2)	0.070
C(3)	0.8942 (3)	0.4505 (3)	0.5415 (2)	0.069
C(4)	1.0988 (3)	0.4167 (3)	0.4860 (2)	0.067
C(11)	0.1936 (2)	0.2960 (1)	0.1726 (1)	0.033
C(12)	0.2281 (2)	0.4348 (2)	0.2118 (2)	0.047
C(13)	0.3558 (2)	0.4799 (2)	0.2987 (2)	0.057
C(14)	0.4506 (2)	0.3894 (3)	0.3475 (2)	0.059
C(15)	0.4174 (2)	0.2517 (3)	0.3098 (2)	0.063
C(16)	0.2902 (2)	0.2058 (2)	0.2226 (2)	0.049
C(21)	-0.1145 (2)	0.3046 (1)	0.0898 (1)	0.034
C(22)	-0.1100 (2)	0.3261 (2)	0.1984 (2)	0.048
C(23)	-0.2293 (3)	0.3678 (3)	0.2212 (2)	0.062
C(24)	-0.3542 (3)	0.3874 (3)	0.1368 (2)	0.064
C(25)	-0.3605 (2)	0.3654 (3)	0.0286 (2)	0.064
C(26)	-0.2413 (2)	0.3247 (2)	0.0052 (2)	0.049
C(31)	0.2187 (2)	0.1169 (2)	-0.1597 (1)	0.036
C(32)	0.3051 (2)	0.0143 (2)	-0.1219 (2)	0.052
C(33)	0.4312 (2)	0.0057 (3)	-0.1477 (3)	0.067
C(34)	0.4725 (2)	0.1003 (3)	-0.2091 (2)	0.071
C(35)	0.3890 (3)	0.2038 (3)	-0.2459 (2)	0.076
C(36)	0.2619 (2)	0.2135 (2)	-0.2216 (2)	0.058
C(41)	-0.0818 (2)	0.0944 (1)	-0.2739 (1)	0.033
C(42)	-0.2057 (2)	0.1619 (2)	-0.3046 (1)	0.040
C(43)	-0.3102 (2)	0.1338 (2)	-0.4096 (2)	0.050
C(44)	-0.2908 (2)	0.0393 (2)	-0.4848 (2)	0.052
C(45)	-0.1676 (2)	-0.0280 (2)	-0.4558 (2)	0.053
C(46)	-0.0635 (2)	-0.0012 (2)	-0.3505 (1)	0.044
H(1)	0.068 (3)	0.374 (3)	-0.086 (2)	0.042 (7)
H(2)	0.995 (3)	0.273 (3)	0.556 (2)	0.090 (7)
H(3)	0.814 (3)	0.405 (3)	0.565 (2)	0.090 (7)
H(4)	1.171 (3)	0.359 (3)	0.480 (2)	0.089 (7)
H(12)	0.156 (3)	0.495 (3)	0.179 (2)	0.084 (7)
H(13)	0.379 (3)	0.576 (3)	0.328 (2)	0.086 (7)
H(14)	0.541 (3)	0.418 (3)	0.411 (2)	0.070 (7)
H(15)	0.498 (3)	0.190 (3)	0.343 (2)	0.082 (7)
H(16)	0.265 (3)	0.109 (3)	0.194 (2)	0.065 (7)
H(22)	-0.020 (3)	0.316 (3)	0.257 (2)	0.070 (7)
H(23)	-0.222 (3)	0.381 (3)	0.297 (2)	0.086 (7)
H(24)	-0.443 (3)	0.413 (3)	0.151 (2)	0.072 (6)
H(25)	-0.455 (3)	0.374 (3)	-0.034 (2)	0.079 (7)
H(26)	-0.244 (3)	0.312 (3)	-0.065 (2)	0.069 (7)
H(32)	0.272 (3)	-0.056 (3)	-0.077 (2)	0.052 (7)
H(33)	0.499 (3)	-0.067 (3)	-0.120 (2)	0.083 (7)
H(34)	0.567 (3)	0.100 (3)	-0.227 (2)	0.075 (7)
H(35)	0.411 (3)	0.272 (3)	-0.286 (2)	0.095 (7)
H(36)	0.200 (3)	0.293 (3)	-0.243 (2)	0.071 (7)
H(42)	-0.219 (3)	0.226 (3)	-0.252 (2)	0.048 (7)
H(43)	-0.400 (3)	0.182 (3)	-0.433 (2)	0.068 (7)
H(44)	-0.359 (3)	0.022 (3)	-0.561 (2)	0.060 (7)
H(45)	-0.150 (3)	-0.084 (3)	-0.508 (2)	0.077 (7)
H(46)	0.021 (3)	-0.051 (3)	-0.325 (2)	0.049 (7)

* *U* is the mean latent root of the anisotropic displacement tensor for non-H atoms. For H atoms it is the refined isotropic displacement parameter.

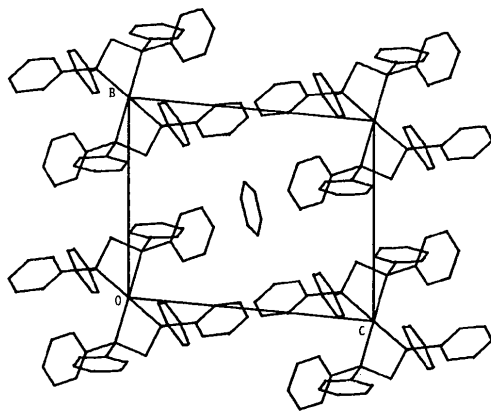


Fig. 1. The contents of the unit cell viewed down the *a* axis. H atoms are omitted for clarity.

Experimental. Straw-coloured centrosymmetric plate, forms exhibited and distances (cm) from specimen centroid: $\{001\}$ 0.008_g, $\{010\}$ 0.024, $\{10\bar{1}\}$ 0.027, $\{100\}$ 0.030. Enraf-Nonius CAD-4F diffractometer, Mo X-rays, graphite monochromator, dimensions of the reduced cell by least-squares fit to setting angles of 25 automatically centred reflections with $15 \leq \theta(\text{Mo } K\alpha) \leq 19^\circ$. Intensities of 7014 $h \pm k \pm l$ reflections ($h - 12 \rightarrow 12$, $k - 12 \rightarrow 12$, $l 0 \rightarrow 16$ with $2 \leq \theta(\text{Mo } K\alpha) \leq 30^\circ$ from $\theta/2\theta$ scans of 1.41° in θ , correction for Lp, linear decay (maximum 14% of *I*) of intensities of 012 and 121 standard reflections, and absorption (Gaussian quadrature, 256 grid points, F^2 transmission factors 0.24–0.56), $R_{\text{int}} = 0.010$ for merging 274 duplicates, 6740 independent structure amplitudes, 17 (*sic*) with $I < 3\sigma(I)$ not used subsequently. Patterson and difference syntheses. H atoms from $\Delta\rho$ synthesis and subsequent least-squares refinement. Full-matrix least-squares refinement on F , $w^{-1} = \sigma^2(F) + 0.0016F^2$, anisotropic Pt, P and C, isotropic H, 373 parameters (non-H and H parameters adjusted in alternate cycles), $R = 0.016$, $wR = 0.021$, $S = 1.0$ on F , $\Delta/\sigma < 0.004$, final $\Delta\rho$ values -0.9 to $1.1 \text{ e } \text{\AA}^{-3}$ near Pt and -0.26 to $0.37 \text{ e } \text{\AA}^{-3}$ elsewhere. Extinction correction not deemed necessary. Anomalous-dispersion corrections (Pt, P, C) and neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), GX crystallography program package (Mallinson & Muir, 1985). Space group $P\bar{1}$ confirmed by successful analysis. Atomic coordinates are in Table 1.*

Discussion. The Pt atoms lie on the 1(*a*) centres of symmetry at (0, 0, 0). The packing of the molecules of (1) which results (Fig. 1) leaves channels in the crystal running parallel to the *a* axis. The ordered benzene solvate molecules lie in these channels, straddling the 1(*g*) (0, $\frac{1}{2}$, $\frac{1}{2}$) centres of symmetry. Intermolecular contacts [minimum C...H and H...H distances 2.76 (3) and 2.40 (3) \AA respectively] are consistent with van der Waals packing.

The Pt atom has the square-planar arrangement expected for the dipositive oxidation state but the formation of two PtP_2C chelate rings leads to substantial in-plane distortion of its valency angles (Table 2). In the crystal, molecules of (1) approximate to C_{2h} point symmetry, with a non-crystallographic mirror plane passing through Pt, C(1) and H(1) normal to the Pt coordination plane (Fig. 2). The most significant distortion from C_{2h} symmetry arises from the orientation of the phenyl rings: corresponding Pt–P–

* Lists of anisotropic displacement parameters, bond lengths and angles, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42587 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(*n*1)–C torsion angles are 1.5 (2), –76.2 (2), 14.2 (2), and 85.2 (2)° for rings *n* = 1–4. This conformation, together with the acute P(1)–Pt–P(2) angle avoids short non-bonded intramolecular contacts between atoms of different ligands.

R₂PCHPR₂[–] ligands can chelate a metal ion in two ways: either an $\overline{MP\cdots CH\cdots P}$ ring is formed in which the charge is delocalized over the two P–C bonds, or, alternatively, a three-membered $\overline{MP-CH-P}$ ring is obtained (Schmidbauer, Lauteschläger & Milewski-Mahrla, 1983). The former arrangement is found in (1) and also in [Pt{(C₆H₅)₂PCHP(C₆H₅)₂}{(CH₂)₂-P(CH₃)₂}] (2) (Bassett *et al.*, 1980) and [PtCl{(PEt₃)-(C₆H₅)₂PCHP(C₆H₅)₂}] (3) (Browning, Bushnell & Dixon, 1980). However, there are significant differences in geometry between the PtP₂C chelate rings in (1)–(3). Thus the mean Pt–P bond length in (1), 2.324 (3) Å,* is longer than the value of 2.276 (5) Å in (2), while in (3) distances of 2.317 (2) and 2.252 (2) Å are found

* Weighted means are given throughout this paper. Their standard deviations are the greater of the estimates from the range of individual values and from the pooled individual standard deviations.

Table 2. Selected interatomic distances (Å) and angles (°)

Pt–P(1)	2.326 (1)	P(1)–C(11)	1.825 (2)
Pt–P(2)	2.321 (1)	P(1)–C(21)	1.820 (2)
P(1)–C(1)	1.730 (2)	P(2)–C(31)	1.821 (2)
P(2)–C(1)	1.727 (2)	P(2)–C(41)	1.831 (2)
C(1)–H(1)	0.94 (3)	P(1)⋯P(2)	2.636 (1)
P(1)–Pt–P(2)	69.1 (1)	Pt–P(1)–C(1)	95.0 (1)
Pt–P(1)–C(11)	115.4 (1)	Pt–P(1)–C(21)	117.9 (1)
C(1)–P(1)–C(11)	114.0 (1)	C(1)–P(1)–C(21)	112.1 (1)
C(11)–P(1)–C(21)	103.0 (1)	Pt–P(2)–C(1)	95.3 (1)
Pt–P(2)–C(31)	119.4 (1)	Pt–P(2)–C(41)	117.0 (1)
C(1)–P(2)–C(31)	113.9 (1)	C(1)–P(2)–C(41)	112.4 (1)
C(31)–P(2)–C(41)	99.8 (1)	P(1)–C(1)–P(2)	99.4 (1)
P(1)–C(1)–H(1)	127.5 (17)	P(2)–C(1)–H(1)	129.2 (17)

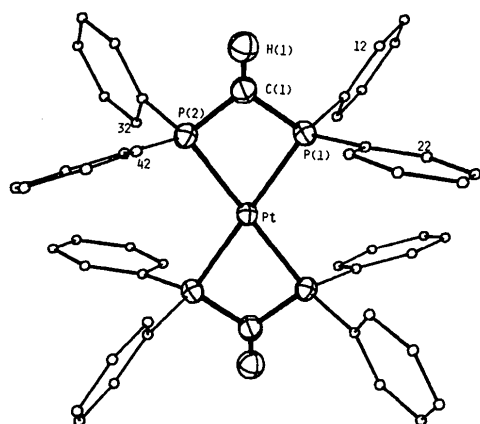


Fig. 2. A view of the [Pt{(C₆H₅)₂PCHP(C₆H₅)₂}] molecule illustrating the atom numbering. Phenyl rings are numbered cyclically C(*n*1)⋯C(*n*6) starting at the P-substituted C atom and only the serial number of C(*n*2) is shown. H atoms are omitted [apart from H(1)]. Phenyl C atoms are represented by spheres of arbitrary size. Otherwise 50% ellipsoids are displayed.

trans to P and Cl respectively. These variations imply a *trans*-influence series P > C > Cl. In all three complexes the charge delocalization reveals itself in shortening of the P–C(ring) bonds: In (1) the mean P–C(1) bond length of 1.729 (2) Å is 0.1 Å shorter than the mean P–C(phenyl) distance of 1.825 (3) Å and compares well with corresponding values of 1.76 (2) and 1.72 Å in (2) and (3). Bond angles within the chelate rings of (1)–(3) are also closely comparable. However, the PtP₂C unit is said to be close to coplanar in (3) and coplanar to ±0.02 Å in (2). By contrast, in (1) C(1) and H(1) are displaced by +0.217 (2) and +0.13 (3) Å from the PtP₂ plane, indicating that rigorous coplanarity is not an essential feature of the PtP₂C rings in these complexes. Moreover, a significant pyramidal distortion of the formally planar *sp*² C(1) atom in (1) is indicated by the displacement of H(1) by 0.27 (3) Å from the weighted plane through C(1), P(1), P(2) and H(1). The reason for this distortion is not obvious.

The dimensions of the phenyl rings are normal: C–C bond lengths are 1.369 (5)–1.395 (3) Å and show the expected effects of thermal shrinkage at the ring peripheries (Domenicano, Vaciago & Coulson, 1975); C–H bond lengths are 0.90 (3)–1.03 (3) Å, with a mean of 0.981 (7) Å. It is worth noting that the mean C–C–C angle of 118.7 (2)° at P-substituted phenyl C is close to the mean value of 118.5 (1)° for P^{III}–C₆H₅ found by Domenicano *et al.* (1975), implying that delocalization of charge onto P does not appreciably change its electronegativity relative to *e.g.* P(C₆H₅)₃.

The benzene solvate molecules contain a regular hexagon of C atoms and the mean C–C bond length of 1.374 (3) Å is not significantly different from that found (before libration correction) in the X-ray study of benzene itself (Cox, Cruickshank & Smith, 1958).

We thank SERC for financial support with equipment.

References

- BASSETT, J. M., MANDL, J. R. & SCHMIDBAUER, H. (1980). *Chem. Ber.* **113**, 1145–1152.
- BROWN, M. P., YAVARI, A., MANOJLOVIĆ-MUIR, L.J., MUIR, K. W., MOULDING, R. P. & SEDDON, K. R. (1982). *J. Organomet. Chem.* **236**, C33–C36.
- BROWNING, J., BUSHNELL, G. W. & DIXON, K. R. (1980). *J. Organomet. Chem.* **198**, C11–C14.
- COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1958). *Proc. R. Soc. London, Ser. A*, **247**, 1–15.
- DOMENICANO, A., VACIAGO, A. & COULSON, C. A. (1975). *Acta Cryst.* **B31**, 221–234; 1630–1641.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
- SCHMIDBAUER, H., LAUTESCHLÄGER, S. & MILEWSKI-MAHRLA, B. (1983). *J. Organomet. Chem.* **254**, 59–68.
- SCHMIDBAUER, H. & MANDL, J. R. (1977). *Angew. Chem. Int. Ed. Engl.* **16**, 640–641.