The crystal structure of (*N,N*-diethyldithiocarbamato)-bis(2-diphenylphosphinoethyl)phenylphosphineplatinum(II)-tetraphenylborate

Ray Colton, Maureen F. Mackay*
Chemistry Department, La Trobe University, Bundoora 3083 (Australia)

and Vanda Tedesco
Inorganic Chemistry Section, School of Chemistry, University of Melbourne, Parkville 3052 (Australia)

(Received October 26, 1992; revised January 18, 1993)

Abstract

The structure of $[Pt(Et_2dtc)(P_2P')]BPh_4$ ($Et_2dtc = S_2CNEt_2$ and $P_2P' = PhP(CH_2CH_2PPh_2)_2$) has been determined from three-dimensional X-ray data. Monoclinic crystals of the complex belong to the space group $P2_1/c$ with cell dimensions $a = 18.375(2)$, $b = 15.724(2)$, $c = 20.426(3)$ Å, $\beta = 108.85(1)°$, $V = 5585(3)$ Å^3, $Z = 4$. Residuals are $R = 0.034$ and $R_w = 0.044$ for 4092 observed data. The phosphine ligand is chelated via all three phosphorus atoms while the dithiocarbamate ligand is monodentate, through one sulfur atom, to give a distorted square planar arrangement about the platinum atom. The short non-bonding distance (2.754(3) Å) between the platinum and other sulfur atom indicates there may be some interaction between these two atoms in the solid state.

Introduction

There have been numerous studies on the reactions of platinum(II) bis(dithiolate) compounds, $Pt(S\text{-}S)_2$ (S-S = dithiocarbamate (dtc), dithiophosphate (dtp), xanthate (xan) with monodentate [1], bidentate [2–4] and recently tridentate [5, 6] phosphine ligands. These investigations have generally been carried out using NMR (^1H, ^{13}C, ^{31}P, ^{195}Pt) spectroscopic methods although some crystal structures have been determined, including $Pt(S\text{-}S)_2PPh_3$ (S-S = dtc, dtp) [1] where there is one bidentate and one monodentate dithiolate ligand.

There are several reports on platinum(II) complexes containing bidentate dtc ligands [1, 7–13]. In contrast, however, there are only three [1, 7, 14] structural analyses on platinum(II) compounds with a monodentate dtc ligand and only one [15] with a bridging dtc ligand. The crystal structure of $NaEt_2dtc3H_2O$ which contains an ionic dtc group has also been reported [16, 17].

The title compound has been studied previously, in solution, by both NMR spectroscopy [5] and electrospray mass spectrometry [6] methods. The principal ion detected in mass spectrometry investigations [6] was at *m/z* 877 and confirmed the identity of the cation whilst the multi-NMR (^{31}P and ^{195}Pt) spectroscopic studies [5] showed that, in dichloromethane solution, the complex contained the phosphine ligand coordinated to platinum in a tridentate mode to give $[Pt(dtc)(\eta^3\text{-}P_2P')]^+$. The coordination of the dithiocarbamate ligand could not be ascertained by NMR spectroscopic methods but monodentate coordination was suggested by comparison of its NMR data with those for similar compounds. Thus in solution, the cation $[Pt(dtc)(P_2P')]^+$ behaves as a four-coordinate square planar platinum(II) entity.

Crystals of the compound were grown and diffraction data obtained in an effort to determine its structure in the solid state. This paper reports the crystal structure of $[Pt(dtc)(P_2P')]B(C_6H_5)_4$ which is the first for a platinum(II) compound containing the potentially tridentate phosphine ligand P_2P'.

Experimental

Preparation

The title compound was prepared as described previously [5]. Equimolar amounts of $Pt(dtc)_2$ [2, 18] and P_2P' (STREM) were mixed in dichloromethane. The solvent was removed under vacuum and the resulting solid dissolved in acetone. $NaB(C_6H_5)_4$ (BDH) in acetone was then added, the solvent removed and the

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

solid extracted into dichloromethane. The solvent was finally removed to yield the desired yellow crystalline product.

Crystals suitable for a single crystal X-ray structure determination were obtained by slow evaporation of a dichloromethane/n-hexane solution. The yellow crystal used was a regular six-sided prism.

Structure determination

Integrated intensity data were measured on a RIGAKU-AFC four-circle diffractometer with Cu Kα radiation (graphite crystal monochromator, $\lambda = 1.5418$ Å). The crystal data together with details of the data collection are given in Table 1. Accurate unit cell parameters were determined by least-squares from 2θ values ($35 < 2\theta < 54°$) for 25 independent reflections well separated in reciprocal space. The intensities were recorded by a $\omega/2\theta$ scan, scan rate 2° min^{-1}, scan range ($\Delta\omega$) $1.2° + 0.5°\ \tan\theta$ and 10 second stationary background counts. Three reflections were monitored every 50 reflections and they showed no significant variation in intensity during data collection. The intensities were corrected for Lorentz and polarisation effects and an analytical absorption correction was also made.

The coordinates of the platinum atom were derived from the vector map. Subsequent difference-Fourier syntheses revealed the sites of the remaining non-hydrogen atoms. The hydrogen atom sites were included at calculated positions (C–H 1.08 Å); the methyl and methylene H atoms were given a common isotropic temperature factor (8.2(7) Å^2) and the phenyl H atoms were also assigned an isotropic temperature factor (10.6(7) Å^2). The atomic parameters were refined in two blocks with SHELX-76 [19]; one block contained the cation atoms (418 variables), the other block contained the platinum and anion atoms (238 variables). The function minimised was $\Sigma w\Delta^2$ where $\Delta = (|F_0| - |F_c|)$, and with weights $(\sigma^2|F_0| + 0.000556|F_0|^2)^{-1}$. An isotropic extinction correction of the form $F_c = F[1 - 1.0 \times 10^{-6}\text{-}(F^2/\sin\theta)]$ was applied to the calculated structure amplitudes. Complex neutral scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion [20]. The major calculations were made on a VAX8800 computer. The atomic positional coordinates and equivalent isotropic thermal parameters are given in Table 2. Figure 1 which contains the atom numbering was prepared from the output of ORTEPII [21].

TABLE 1. Crystal data for $[Pt(dtc)(P_2P')]B(C_6H_5)_4$

Formula	$C_{63}H_{63}BNP_3PtS_2$
Formula weight	1197.2
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	18.375(2)
b (Å)	15.724(2)
c (Å)	20.426(3)
β (°)	108.85(1)
V (Å^3)	5585(3)
Z	4
ρ_{calc} (g cm^{-1})	1.424
ρ_{meas} (g cm^{-1})	1.423(5) (by flotation in aq. K_2HgI_4)
Crystal dimensions (distance in mm from the centroid)	$\bar{1}$ 0 0, 0.135; 1 0 0, 0.135; 0 1 0, 0.321; 1 0 $\bar{1}$, 0.135; $\bar{1}$ 0 1, 0.135; 1 $\bar{1}$ 1, 0.090
T (°C)	18(1)
Radiation	Cu Kα, $\lambda = 1.5418$ Å monochromatic
F (000)	2432
Absorption coefficient (cm^{-1})	64.64
Transmission factors	min. 0.2085 max. 0.3865
2θ limits	$0 < \theta < 115°$
No. reflections measured	6119
No. unique reflections	4347 (h −15 to 15, k 0 to 13, l 0 to 17)
Unique reflections used	4092 ($I > 3\sigma(I)$)
Highest residual peak (e Å^{-3})	0.55, −0.73
R_{merg}	0.012
$R = \Sigma(\lvert F_0\rvert - \lvert F_c\rvert)/\Sigma\lvert F_0\rvert$	0.034
$R_w = [\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_0\rvert^2]^{1/2}$	0.044
Max. (variable shift)/(e.s.d.)	0.05
Goodness of fit	1.37

TABLE 2. Fractional coordinates of Pt ($\times 10^5$) and B, C, N. S and P ($\times 10^4$) and equivalent isotropic temperature factors (Å^2) for the non-hydrogen atoms of $[Pt(dtc)(P_2P')]B(C_6H_5)_4$ with e.s.d.s in parentheses

Atom	x	y	z	B_{eq}^{a}
Pt	21694(2)	27866(2)	−5185(2)	2.55(1)
P(1)	1446(1)	3813(2)	−1229(1)	3.29(6)
P(2)	2737(1)	3883(2)	146(1)	3.42(6)
P(3)	3318(1)	2096(2)	−42(1)	3.78(6)
S(1)	1731(1)	1637(2)	−1319(1)	3.63(6)
S(2)	1263(1)	1667(2)	−89(1)	3.71(6)
N(1)	884(4)	421(5)	−1031(4)	4.4(2)
C(1)	1247(4)	1145(6)	−826(4)	3.0(2)
C(2)	815(6)	38(7)	−1725(6)	6.2(4)
C(3)	1442(7)	−557(8)	−1689(6)	7.3(4)
C(4)	494(5)	−47(7)	−604(5)	5.1(3)
C(5)	974(6)	−701(8)	−165(6)	7.3(4)
C(6)	3953(5)	2797(6)	597(5)	4.8(3)
C(7)	3774(4)	3723(7)	349(5)	4.4(3)
C(8)	2437(5)	4885(6)	−318(4)	4.1(2)
C(9)	2102(5)	4716(6)	−1098(4)	4.2(3)
C(11)	3588(5)	2317(7)	−1302(5)	5.4(3)
C(12)	4027(7)	2241(8)	−1737(6)	7.7(4)
C(13)	4706(8)	1821(11)	−1511(9)	9.1(6)
C(14)	4966(7)	1445(9)	−880(10)	8.8(6)
C(15)	4534(5)	1521(7)	−441(6)	6.4(4)
C(16)	3851(5)	1960(6)	−643(5)	4.3(3)
C(21)	3217(5)	347(11)	8(7)	6.3(4)
C(22)	3107(6)	−425(10)	299(9)	7.0(5)
C(23)	3058(7)	−431(12)	950(10)	8.6(6)
C(24)	3100(7)	302(13)	1311(8)	8.1(5)
C(25)	3229(6)	1054(9)	1022(7)	7.2(4)
C(26)	3287(4)	1080(8)	358(7)	4.7(3)
C(31)	2917(5)	4768(7)	1358(5)	4.8(3)
C(32)	2877(5)	4881(8)	2017(5)	5.4(3)
C(33)	2553(6)	4277(8)	2313(5)	5.3(3)
C(34)	2258(5)	3551(7)	1953(5)	4.8(3)
C(35)	2292(5)	3412(6)	1280(4)	3.9(3)
C(36)	2634(4)	4032(6)	991(4)	3.1(2)
C(41)	470(5)	3062(6)	−2416(4)	4.4(3)
C(42)	230(5)	2814(7)	−3104(5)	5.6(3)
C(43)	650(7)	3061(7)	−3521(5)	5.6(3)
C(44)	1295(7)	3545(7)	−3267(5)	5.6(3)
C(45)	1542(5)	3781(6)	−2577(5)	4.5(3)
C(46)	1122(5)	3556(6)	−2152(4)	3.4(2)
C(51)	269(5)	3810(7)	−658(5)	4.8(3)
C(52)	−398(6)	4128(9)	−571(6)	6.4(4)
C(53)	−726(6)	4837(10)	−899(6)	6.9(4)
C(54)	−408(7)	5294(9)	−1308(6)	7.9(5)
C(55)	256(6)	4977(8)	−1404(5)	6.6(4)
C(56)	603(4)	4233(6)	−1071(4)	3.8(2)
B(1)	6731(6)	3069(7)	1530(5)	4.1(3)
C(61)	7859(6)	3842(7)	2521(5)	6.1(3)
C(62)	8556(7)	3864(9)	3080(5)	7.0(4)
C(63)	8894(6)	3116(10)	3352(6)	7.5(4)
C(64)	8546(6)	2375(8)	3093(5)	6.7(3)
C(65)	7852(5)	2359(7)	2539(5)	5.1(3)
C(66)	7503(5)	3103(6)	2231(4)	3.8(2)
C(71)	6235(7)	1501(9)	1207(5)	7.4(4)
C(72)	5837(8)	756(9)	1247(6)	8.2(5)
C(73)	5408(6)	750(8)	1662(7)	6.7(4)
C(74)	5395(9)	1432(11)	2041(9)	10.3(7)
C(75)	5802(8)	2158(8)	1978(7)	9.9(6)
C(76)	6240(4)	2219(7)	1569(4)	3.8(2)
C(81)	5995(11)	4161(10)	2026(6)	17.6(8)
C(82)	5510(14)	4835(13)	2017(7)	21(1)
C(83)	5270(8)	5368(9)	1511(8)	8.7(5)
C(84)	5487(7)	5174(10)	975(8)	9.1(5)
C(85)	5927(6)	4457(8)	971(7)	7.5(4)
C(86)	6205(6)	3911(7)	1505(5)	5.3(3)
C(91)	7792(7)	2981(6)	884(5)	5.5(3)
C(92)	8039(8)	2926(7)	310(6)	7.4(4)
C(93)	7502(11)	2879(9)	−345(8)	9.4(6)
C(94)	6750(10)	2907(9)	−408(6)	9.6(5)
C(95)	6484(7)	2955(7)	166(5)	7.7(4)
C(96)	7031(6)	3010(6)	842(4)	4.9(3)

(*continued*)

TABLE 2. (*continued*)

$^{a}B_{eq} = 8\pi^2 U_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

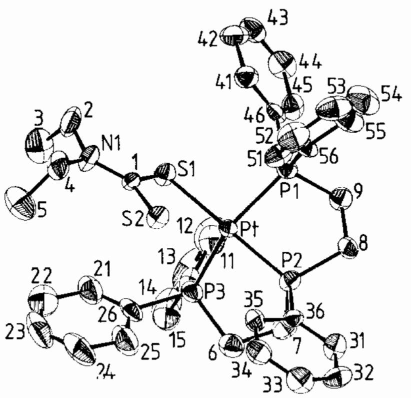

Fig. 1. ORTEP [21] diagram of the cation $[Pt(dtc)(P_2P')]^+$ with ellipsoids scaled to 40% probability (carbon atoms are denoted by their number only).

Results and discussion

Description of structure

A perspective view of the complex cation $[Pt(dtc)(P_2P')]^+$ is shown in Fig. 1, while selected dimensions are given in Table 3. Table 4 lists some relevant parameters of previously reported platinum(II) structures for comparison with those of the title compound.

The platinum is coordinated to the three phosphorus atoms of the potentially tridentate phosphine ligand but to only one sulfur atom of the dithiocarbamate ligand, which in this case is monodentate, to give a distorted square planar arrangement. Although the second sulfur of the dithiocarbamate ligand is not directly bonded to the platinum, the Pt· · ·S(2) distance of 2.754(3) Å is indicative of a weak interaction since it lies between the reported values for bonded (~2.3 Å) [1,7–13] and non-bonded (~3.4 Å) [1, 7, 14] distances and is significantly less than the sum of the van der Waal's radii for sulfur [22] and platinum [23] (3.92 Å).

TABLE 3. Selected dimensions (lengths (Å), angles (°)) in the cation $[Pt(dtc)(P_2P')]^+$ with e.s.d.s in parentheses

Pt–P(1)	2.287(3)	Pt–P(2)	2.233(3)		
Pt–P(3)	2.292(2)	Pt–S(1)	2.396(3)		
P(1)–C(9)	1.825(10)	P(2)–C(7)	1.832(8)	P(2)–C(8)	1.829(9)
P(3)–C(6)	1.815(8)	C(6)–C(7)	1.542(14)	C(8)–C(9)	1.534(11)
P(1)–C(46)	1.829(8)	P(1)–C(56)	1.806(9)	P(2)–C(36)	1.811(9)
P(3)–C(16)	1.814(11)	P(3)–C(26)	1.804(13)		
S(1)–C(1)	1.727(9)	S(2)–C(1)	1.707(9)	N(1)–C(1)	1.317(12)
N(1)–C(2)	1.507(15)	N(1)–C(4)	1.490(14)	C(2)–C(3)	1.467(17)
C(4)–C(5)	1.459(15)				
P(1)–Pt–P(2)	84.4(1)	P(2)–Pt–P(3)	85.6(1)		
P(1)–Pt–S(1)	95.8(1)	P(3)–Pt–S(1)	89.6(1)		
S(1)–C(1)–S(2)	115.7(5)				
Pt···S(2)	2.754(3)	S(1)···S(2)	2.907(5)		

It is interesting to note that S(2) lies within the plane defined by Pt, S(1) and C(1) (Pt–S(1)–C(1)–S(2) torsional angle 2.4(5)°) and it is approximately 22° from the apical site of an idealised square-based pyramidal configuration. The S···S 'bite' distance of 2.907(5) Å is similar to the 'bite' distances in all three reported Pt complexes with monodentate dtc ligands, 3.000 [1], 2.94 [7] and 2.994 Å [14] compared with the shorter value ~2.8 Å [1, 7–13] when the dtc ligand is bidentate. Moreover, the S···S distance in the title compound is similar to the value of 3.067 Å [16] found in $Nadtc3H_2O$, and the S(1)–C(1)–S(2) angle is 115.7(5)° compared with the values found in the three compounds with monodentate dtc ligands, 120.4° [1], 115.5° [7] and 121.9° [14], and 120.4° in $Nadtc3H_2O$ [16].

The Pt lies 0.4 Å above the P_3S plane (atoms coplanar to within 0.20 Å) as shown in Fig. 2. The two P–Pt–P ligand bite angles are less than 90° (84.4(1) and 85.6(1)°), no doubt a consequence of the strain due to chelation of the P_2P' ligand to form two five-membered rings. These angles are very similar in value to those observed in $Pt(S_2CO)(dpe)$ 86.3° [14] and $Pt(dpe)Cl_2$ 86.3° [24] and compare well with the P–Pd–P angles in $[Pd(P_2P')Cl]^+$ 83.8 and 84.1° [25]. The two P–Pt–S angles in the title compound, as expected, have larger values, i.e. 95.8(1) and 89.6(1)°.

The three Pt–P bond lengths range between 2.233(3) and 2.292(2) Å. The shortest length is Pt–P(2), of the middle phosphorus (P') of the ligand, consistent with previous observations [14] where the *trans* Pt–P lengths are about 0.1 Å less than the *cis* Pt–P lengths. These lengths are normal and comparable to other reported values [1, 7, 9–12, 14, 15]. It is also interesting to note that in $[Pd(P_2P')Cl]^+$ [25], the Pd–P bonds are 2.220(P'), 2.328 and 2.344 Å which compare well with the values found for the title compound. The Pt–S(1) bond length of 2.396(3) Å is marginally longer than other values reported for this bond involving monodentate dithiocarbamate ligands, e.g. $Pt(dtc)_2(PPh_3)$ 2.331 Å [1], $Pt(dtc)_2(PMe_2Ph)$ 2.335 Å [14] and $Pt(dtc)_2(Pchxyl_3)$ 2.329 Å [7].

The two C–S bond lengths of 1.727(9) and 1.707(9) Å lie approximately midway between values expected for single and double bonds, i.e. 1.81 Å and 1.61 Å [26], respectively, and thus have considerable double bond character. The values are in accord with those reported for comparable structures [1, 7, 14]. For example, in $Pt(dtc)_2(PMe_2Ph)_2$ [14], in which the dithiocarbamate ligands are both monodentate, the two C–S distances are unequal having values 1.734 and 1.692 Å, the shorter length involving the non-coordinated sulfur as in the complex cation under study here. The C–N bond length of 1.32(1) Å indicates that this bond also has significant double bond character [27, 28].

Comparison of solution and solid state structures

By comparing the parameters of previously reported platinum(II) complexes containing dithiocarbamate ligands it is possible to ascertain that the mode of coordination of the dithiocarbamate ligand in the complex $[Pt(dtc)(P_2P')]B(C_6H_5)_4$ is monodentate. Therefore, in the solid state the platinum atom retains its square planar geometry. The platinum–sulfur non-bonding distance of 2.754 Å is short indicating that there is some interaction in the solid state. It is well known that the dithiocarbamate ligand prefers to be chelated since chelation allows delocalisation through the C–N bond [29]. However, in the title compound it is competing with a much stronger chelator, the P_2P' ligand, so that one sulfur atom of the dithiocarbamate ligand is bound and the other is close to the platinum atom. It is not surprising that when in solution this cation acts as a four coordinate entity since there is free rotation about the C–S bond (sulfur coordinated to platinum).

TABLE 4. Relevant parameters of previously reported platinum(II) compounds containing dtc ligands

Compound[a]	dtc coord.[h]	Pt–S (Å)	Pt···S (Å)	C–S (Å)	C–N (Å)	S···S (Å)	⟨SCS (°)	Ref.
$[Pt(\eta^1\text{-dtc})(P_2P')]B(C_6H_5)_4$[b]	m	2.396(3)	2.754(3)	1.727(9) 1.707(9)	1.317(12)	2.907(5)	115.7(5)	this work
$Pt(\eta^1\text{-dtc})_2(PMe_2Ph)_2$[c]	m	2.335(2)	3.392(3)	1.734(6) 1.692(8)	1.349(9)	2.994(3)	121.9(4)	14
$Pt(\eta^1\text{-dtc})(\eta^2\text{-dtc})(PPh_3)$[b]	m	2.331(3)	3.457(5)	1.771(17) 1.685(19)	1.331(14)	3.000(8)	120.4(3)	1
	b	2.365(5) 2.313(3)		1.740(18) 1.707(11)	1.329(25)	2.835(5)	110.7(6)	
$Pt(\eta^1\text{-dtc})(\eta^2\text{-dtc})(P(chxyl)_3)$[d]	m	2.329(4)	4.928(5)	1.79(1) 1.68(1)	1.31(2)	2.94(3)	115.5(7)	7
	b	2.364(3) 2.326(4)		1.73(1) 1.72(1)	1.30(2)	2.83(3)	110.3(7)	
$Pt(\eta^2\text{-dtc})_2$[b]	b	2.298 2.283		1.765 1.704	1.304	2.813	108.4	8
$Pt(\eta^2\text{-dtc})(PPh_3)Cl$[b]	b	2.349(7) 2.294(7)		1.714(29) 1.708(24)	1.289(38)	2.823(9)	111.1(4)	9
$[Pt(\eta^2\text{-dtc})(Ph_2PS)][NEt_2H_2]$[b]	b	2.372(9) 2.368(11)		1.72(3) 1.69(2)	1.37(5)	2.865(5)	114(2)	10
$\{Pt(\eta^2\text{-dtc})(Ph_2PS)\}_2.2CDCl_3$[e]	b	2.347(5) 2.299(4)		1.757(16) 1.699(21)	1.319(20)	2.842(4)	109.2(8)	10
$CoPt_2(\eta^2\text{-dtc})(Ph_2PO)(Ph_2PS)H$[e]	b	2.378(5) 2.342(5)		1.752(18) 1.718(18)	1.277(25)	2.843(7)	109.5(9)	11
$PtRh(Ph_2PS)(\eta^2\text{-dtc})(cod)$[b, g]	b	2.377(4) 2.359(4)		1.733(14) 1.700(14)	1.323(18)	2.851(6)	112.3(8)	12
$PtIr(Ph_2PS)(\eta^2\text{-dtc})(cod)$[e, g]	b	2.368(4) 2.352(4)		1.742(15) 1.711(15)	1.313(20)	2.834(7)	110.3(8)	12
$PtCl(\eta^2\text{-dtc})(\eta^1\text{-dtcMe})$[b]	b	2.330(2) 2.327(2)		1.732(7) 1.729(7)	1.305(9)	2.805(2)	108.3(4)	13
	m[i]	2.300(2)		1.741(7) 1.694(5)	1.356(8)	3.043(3)	124.7(4)	
$Pt_2Cl_3(PEt_3)_2(\mu^2\text{-dtc})$[f]	μ	2.370(7)[j] 2.292(7)[j] 2.277(6)		1.742(25) 1.658(26)	1.342(30)	2.822(8)	112(2)	15
$Na(dtc)$[b]	i			1.729(6) 1.712(2)	1.334(8)	3.067(5)	120.4(4)	16

[a] $dtc = S_2CNR_2$. [b] R = Et. [c] R = i–Bu. [d] R = t–Bu. [e] R = i–Pr. [f] R = Me. [g] cod = cyclooctadiene. [h] m = monodentate, b = bidentate, i = ionic, μ = bridging. [i] dtc ester. [j] Sulfur bound to two platinum atoms.

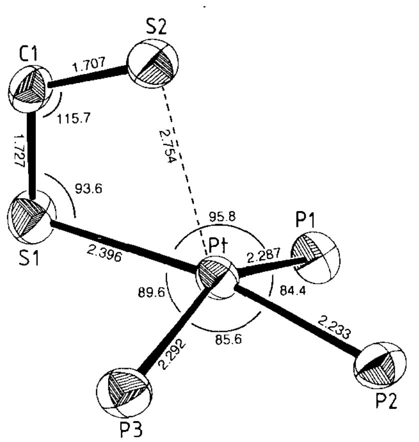

Fig. 2. View of the square plane about the platinum(II) atom.

Conclusions

From the structural data obtained it is possible to conclude that the cation $[Pt(dtc)(P_2P')]^+$ contains the platinum(II) in a distorted square planar environment with some interaction between it and the second sulfur atom of the dithiocarbamate ligand which sits closer to it than previous reports suggest. In the solid state it still retains its four-coordinate structure which is what has been previously observed in solution.

Supplementary material

Anisotropic thermal parameters (Table S.1, 2 pages); calculated positional coordinates for hydrogen atoms (Table S.2, 2 pages); bond lengths in the anion and phenyl rings of the cation (Table S.3); bond angles in the anion and phenyl rings of the cation (Table S.4, 2 pages); selected least-squares planes (Table S.5, 2 pages); short intermolecular contacts (Table S.6); observed and calculated structure amplitudes (Table S.7, 14 pages); crystal packing diagram (Fig. S.1); and an ORTEP diagram of $[B(C_6H_5)_4]^-$ (Fig. S.2), are available from the authors on request.

Acknowledgements

V.T. thanks the Australian Government for an Australian Postgraduate Research Award. We are also grateful to the Australian Research Council for financial support of the platinum chemistry.

References

1 J. P. Fackler, Jr., L. D. Thompson, I. J. B. Lin, T. A. Stephenson, R. O. Gould, J. M. C. Alison and A. J. F. Fraser, *Inorg. Chem., 21* (1982) 2397, and refs. therein.

2 R. Colton and J. Ebner, *Inorg. Chem., 28* (1989) 1559.

3 R. Colton, B. F. Hoskins and J. Ebner, *Inorg. Chem., 27* (1988) 1993.

4 R. Colton and V. Tedesco, *Inorg. Chim. Acta, 183* (1991) 161.

5 R. Colton and V. Tedesco, *Inorg. Chim. Acta, 202* (1992) 95.

6 R. Colton and V. Tedesco, *Inorg. Chem., 31* (1992) 3865.

7 P. C. Christidis and P. J. Rentzeperis, *Acta Crystallogr. Sect. B,* 35 (1979) 2543.

8 A. Z. Amanov, G. A. Kukina and M. A. Porai-Koshits, *Dokl. Akad. Nauk Az. SSR, 33* (1977) 23.

9 L. T. Chan, H. W. Chen, J. P. Fackler, Jr., A. F. Masters and W. H. Pan, *Inorg. Chem., 21* (1982) 4291.

10 D. M. Anderson, E. A. V. Ebsworth, T. A. Stephenson and M. D. Walkinshaw, *J. Chem. Soc., Dalton Trans.* (1982) 2343.

11 D. M. Anderson, A. J. Blake, J. D. Fotheringham, T. A. Stephenson, J. R. Allan and P. M. Veitch, *Acta Crystallogr., Sect. C, 44* (1988) 1305.

12 A. J. Blake, J. D. Fotheringham and T. A. Stephenson, *Acta Crystallogr., Sect. C, 46* (1990) 1102.

13 D. A. Clemente, G. Faraglia, L. Sindellari and L. Trincia, *J. Chem. Soc., Dalton Trans.* (1987) 1823.

14 I. J. B. Lin, H. W. Chen and J. P. Fackler, Jr., *Inorg. Chem., 17* (1978) 394.

15 A. B. Goel, S. Goel, D. van Derveer and C. G. Brinkley, *Inorg. Chim. Acta, 64* (1982) L173.

16 M. Colapietro, A. Domenicano and A. Vaciago, *Chem. Commun.,* (1968) 572.

17 V. D. Khavryuchenko, A. F. Savost'yanova, A. D. Gorbalyuk and V. S. Fundamenskii, *Russ. J. Inorg. Chem., 36* (1991) 281.

18 R. Colton and V. Tedesco, *Inorg. Chem., 30* (1991) 2451.

19 G. M. Sheldrick, *SHELX-76*, a program for crystal structure determination, Cambridge University Press, Cambridge, UK, 1976.

20 J. A. Ibers and W. C. Hamilton (eds.), *International Tables for X-Ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, pp. 99–101 and 149–150 (present distributor: Kluwer, Dordrecht, Netherlands).

21 C. K. Johnson, *ORTEPII,* Fortran thermal ellipsoid plot program, Oak Ridge National Laboratory, TN, USA, 1976.

22 L. Pauling, *The Nature of the Chemical Bond,* Cornell University Press, Ithaca, NY, 3rd edn., 1960, p. 260.

23 N. C. Stephenson, *J. Inorg. Nucl. Chem., 24* (1962) 791.

24 D. H. Farrar and G. Ferguson, *J. Crystallogr. Spectrosc., 12* (1982) 465.

25 C. E. Housecroft, B. A. M. Shaykh, A. L. Rheingold and B. S. Haggerty, *Acta Crystallogr., Sect. C, 46* (1990) 1549.

26 L. Pauling, *The Nature of the Chemical Bond,* Cornell University Press, Ithaca, NY, 3rd edn., 1960, p. 224.

27 D. Coucouvanis, *Prog. Inorg. Chem., 11* (1970) 233.

28 D. Coucouvanis, *Prog. Inorg. Chem., 26* (1979) 301.

29 J. Chatt, L. A. Duncanson and L. M. Venanzi, *Nature (London), 177* (1956) 1042; *Suom. Kemist. B, 29* (1956) 75.