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Crystalline O,O'-di-*sec*-butyl and O,O'-diethyl dithiophosphate platinum(II) complexes: Synthesis, ¹³C and ³¹P CP/MAS NMR, single crystal X-ray diffraction studies and thermal behaviour

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ABSTRACT

Crystalline bis(O,O'-di-*sec*-butyldithiophosphato)platinum(II) was prepared and studied by means of ¹³C, ³¹P CP/MAS NMR spectroscopy and single-crystal X-ray diffraction. The unit cell of the platinum(II) compound is comprised of one centrosymmetric mononuclear molecule [Pt{S₂P(O-*sec*-C₄H₉)₂}], in which the dithiophosphate groups display structural equivalence in both ³¹P NMR and XRD data. A pair of the dithiophosphate ligands exhibit the same *S*,*S'*-bidentate chelating structural function and form two planar four-membered chelate rings, [PtS₂P], in this molecule. The planar configuration of the [PtS₄] chromophore in structure **1** is governed by the *dsp*²-hybrid state of platinum(II). The structural states of the dithiophosphate groups in two different samples of complex **1** (one crystallised from ethanol and the other one precipitated from an aqueous solution) are all characterised by almost rhombic ³¹P chemical shift tensors. The observed essential dispersion of the ³¹P NMR chemical shift is caused by a coexistence of six optical isomers of molecule **1**. The thermal behaviour of this compound was studied by means of simultaneous thermal analysis (a combination of TG and DSC) under an argon atmosphere. The thermal behaviour shows that the mass of **1** is lost in three steps, involving successive thermal decompositions of the organic and inorganic parts of this compound with platinum(II) dithio-*meta*-phosphate and reduced metallic platinum as the intermediate and the final products, respectively.

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1. Introduction

lonic *O*,*O'*-dialkyl dithiophosphates are the main components of commercial flotation reagents such as Aerofloats, Danafloats, etc. Therefore, dialkylsubstituted derivatives of dithiophosphoric acid are widely used as selective reagents. These derivatives function as collectors in froth flotation enrichment of non-ferrous sulphide ores, including serving a special purpose in improving the recovery of platinum group elements, which are strongly associated with sulphide minerals [1,2]. Furthermore, some *O*,*O'*-dialkyl dithiophosphate transition metal complexes, as well as ashless dithiophosphates, displaying both outstanding antiwear and antioxidant properties, have long been used as lubricating oil additives [3–7] and as antioxidants in polyolefins [8]. Recently, it was also discovered that heteroleptic platinum(II) complexes with other related dithioligands (*i.e.*, dithiocarbamates) display greater

cytotoxic activity against myelogenous leukaemia cell lines compared to cisplatin [9]. Therefore, transition metal complexes with dithioligands have long been a focus of interest in coordination and applied chemistry.

Recently, we have reported the successful use of ¹⁹⁵Pt NMR spectroscopy (both static and MAS) for the study of platinum minerals with single crystal cooperite¹ (natural PtS) as an example [10,11]. In cooperite, platinum(II) is situated in a central position within the square-planar chromophore [PtS₄]. A structurally similar pattern has been established in platinum(II) complexes with various ionic *O*,*O*'-dialkyl dithiophosphates [12–15] and cyclic *O*,*O*'-alkylene dithiophosphates [16]: the central platinum atom is surrounded by four sulphur atoms, forming a slightly distorted square-planar coordination polygon. The final product of thermal decomposition of these dithiophosphate complexes is also PtS [11,15]. However, most of the presently known and characterised *O*,*O*'-dialkyl dithiophosph

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¹ Natural PtS was discovered in South Africa and characterised by R.A. Cooper in 1928.

phate platinum(II) complexes are liquid compounds [12].

The present article describes the preparation, multinuclear (¹³C, ³¹P) CP/MAS NMR and single-crystal X-ray diffraction studies of a novel crystalline platinum(II) complex with a symmetrically substituted O,O'-di-sec-butyl dithiophosphate ligand, -S(S)P(Osec-C₄H₉)₂. In the centrosymmetric molecule of [Pt{S₂P(O-sec- $C_4H_9_2$] (1), the central platinum atom links two Dtph groups in an almost S,S'-isobidentate coordination mode, forming two small-sized four-membered rings [PtS₂P]. Therefore, the platinum atom has four sulphur atoms in its neighbouring environment and two phosphorus atoms in the second coordination sphere. At relatively low spinning frequencies (2.8 and 2.3 kHz), the ³¹P CP/ MAS NMR spectra of the isolated platinum(II) complex display manifolds of spinning sidebands, whose intensities have been used to calculate the ³¹P chemical shift anisotropy (CSA) parameters: δ_{a-1} _{niso} and η . The ³¹P CSA parameters, as well as the isotropic chemical shift (δ_{iso}), were used to characterise the structural state of the terminal *O*,*O*'-di-sec-butyl dithiophosphate groups in the platinum(II) complex 1, in comparison with platinum(II) 0,0'-diethyl dithiophosphate (complex 2). Simultaneous thermal analysis (STA), as a combination of TG and DSC techniques, has been also used to study the thermal behaviour of complex 1 under an argon atmosphere.

2. Experimental

2.1. Materials

Potassium tetrachloroplatinate(II), K_2 [PtCl₄] >99% ('Merck'), was used without additional purification. Two potassium salts of symmetrically disubstituted *O*,*O*'-dialkyl dithiophosphoric acids, which constitute the major components of the commercial Danafloat collectors, were provided by 'CHEMINOVA AGRO A/S':

 $O,O'-di\mbox{-sec-butyl}$ dithiophosphate – $K[S_2P(O\mbox{-sec-}C_4H_9)_2]$ – Danafloat-345 K. $O,O'\mbox{-diethyl}$ dithiophosphate – $K[S_2P(OC_2H_5)_2]$ – Danafloat-123 K.

Both original potassium salts were additionally characterised by solid state ¹³C CP/MAS NMR (δ , ppm):

 $\begin{array}{l} K\{S_2P(O\text{-sec-}C_4H_9)_2\} \ (1:1:1:1): \ 77.5 \ (-OCH=); \ 31.7, \ 31.5, \ 31.1 \\ (-CH_2-); \ 22.0, \ 21.2 \ (-CH_3); \ 12.0 \ (-CH_3). \\ K\{S_2P(OC_2H_5)_2\} \ (1:1): \ 63.2 \ (-OCH_2-); \ 18.1, \ 18.0 \ (1:1, \ -CH_3). \end{array}$

2.2. Synthesis of complexes 1 and 2

The crystalline complexes **1** and **2** were prepared by reacting aqueous solutions of K₂[PtCl₄] with the appropriate dithiophosphate salts, K{S₂P(OR)₂} (R = *sec*-C₄H₉ and C₂H₅, respectively). The reaction mixtures were heated at 60 °C for 10 min and left overnight. The resulting yellow precipitates were filtered off, washed with water, and air-dried. Additional crops were obtained by extraction of the complexes from the mother liquors using chloroform. For X-ray diffraction studies, suitable single crystals of bis(*O*,*O*'-di-*sec*-butyldithiophosphato-*S*,*S*')platinum(II), [Pt{S₂P(O-*sec*-C₄H₉)₂]₂] (**1**) were isolated by means of slow evaporation of ethanol at room temperature. Complex **1** was isolated as transparent, yellowish prismatic crystals. The yield was 92% (the structural data on complex **2** were previously established in [12]). Solid state ¹³C CP/MAS NMR data (δ , ppm) for compounds **1** and **2** are given below:

1, $[Pt{S_2P(O-sec-C_4H_9)_2}]$ (1:1:1:1): 78.2, 77.4 (1:1, -OCH=); 31.8, 31.1 (-CH₂-); 23.9, 22.3, 22.7 (-CH₃); 12.1 (-CH₃).

1a, $[Pt{S_2P(O-sec-C_4H_9)_2}_2]$ (1:1:1:1): 78.3, 77.2 (-OCH=); 32.1, 31.1 (-CH₂-); 24.0, 22.6 (-CH₃); 12.1, 11.4 (-CH₃) (powdered sample).

2, [Pt{S₂P(OC₂H₅)₂}₂] (1:1): 65.5, 65.4 (1:1, -OCH₂-); 18.7, 17.5 (1:1, -CH₃).

2.3. Physical measurements

2.3.1. ¹³C and ³¹P NMR spectroscopy

Solid state ¹³C and ³¹P magic-angle-spinning (MAS) NMR spectra were recorded on a Varian/Chemagnetics InfinityPlus CMX-360 (B_0 = 8.46 T) spectrometer, using cross-polarisation (CP) from the protons together with phase modulated proton decoupling [17]. The ¹³C/³¹P operating frequencies were 90.52/145.72 MHz, respectively. The proton $\pi/2$ pulse durations were 6.0/7.0 µs, the CP contact time was 2.0/3.0 ms and the nutation frequency of protons during decoupling was $\omega_{nut}/2\pi = 38/32$ kHz. For the studied sample, 100– 2400/32–600 transients, spaced by relaxation delays of 3/3 s, were accumulated. The polycrystalline sample (ca. 80–100 mg) was packed in zirconium dioxide standard double bearing 7.5 mm rotors. The spinning frequencies ranged from 3600 to 4600/2300 to 3800 Hz and were stabilised to ±2 Hz using a built-in stabilisation device. All ¹³C and ³¹P MAS NMR spectra were recorded at room temperature (ca. 295 K).

¹³C isotropic chemical shifts (in the deshielding, δ-scale) were externally referenced to the least shielded resonance of solid adamantane [18] at 38.48 ppm [19] relative to tetramethylsilane. Chemical shifts and integrated intensity ratios for overlapping signals in the ¹³C NMR spectra were additionally refined by fragmentby-fragment simulation with consideration of line positions and line widths, as well as of the Lorentzian and Gaussian contributions to the line shapes. All ³¹P chemical shift data are given with respect to 85.5% H₃PO₄ [20] (here, 0 ppm, externally referenced), which was mounted in a short 1 mm glass tube and placed in a 7.5 mm rotor to avoid errors due to differences in the magnetic susceptibility. Drifts in the ¹³C/³¹P frequencies (*B*₀-drift) were 0.051/0.11 Hz h⁻¹, respectively. The homogeneity of the magnetic field was monitored by measuring the width of the reference signal of crystalline adamantane at δ (¹³C) = 38.48 ppm, which was 2.6 Hz.

The anisotropy, $\delta_{aniso} = \delta_{zz} - \delta_{iso}$, and the asymmetry parameter of the ³¹P chemical shift tensor (CST), $\eta = (\delta_{yy} - \delta_{xx})/(\delta_{zz} - \delta_{iso})$, were estimated from the determined ratios between the integrated sideband intensities for each phosphorous site in the NMR spectra recorded at two different spinning frequencies [21,22] using a simulation program in the Mathematica front end [23]. To increase the number of spinning sidebands in the ³¹P NMR spectra, which are needed for more accurate estimation of CSA parameters, the spectra were recorded at relatively low spinning frequencies (2.3 and 2.8 kHz).

2.3.2. Crystal structure determination

A suitable single crystal of $[Pt{S_2P(O-sec-C_4H_9)_2}]$ was selected and mounted on a glass capillary with epoxy glue. Experimental intensity data were collected at T = 173(2) K on a BRUKER SMART 1000 CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) in the range of a semi-sphere [24] (crystal-detector distance 45 mm). Intensity data were corrected for absorption using the crystal face indices. The unit cell dimensions, additional crystallographic data and refinement results of complex 1 are given in Table 1.

The structure was solved by direct methods and refined by leastsquares calculations in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were added at ideal positions and refined using a riding model. Each dithiophosphate ligand has both

Table I	Table	1	
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Selected crystal data for $[Pt{S_2P(O-sec-C_4H_9)_2}_2]$ (1).

Empirical formula	$C_{16}H_{36}O_4P_2S_4Pt$
Formula weight	677.72
Crystal system	triclinic
Space group	ΡĪ
Crystal shape	prism
Crystal size (mm)	$0.21 \times 0.17 \times 0.15$
Unit cell dimensions	
a (Å)	7.2213(7)
b (Å)	8.7625(8)
<i>c</i> (Å)	11.9319(1)
α (°)	106.2410(1)
β(°)	90.863(2)
γ (°)	111.483(2)
V (Å ³)	668.66(1)
Ζ	1
D_{calc} (g cm ⁻³)	1.683
T (K)	173(2)
μ (Mo K α) (mm ⁻¹)	5.696
θ Range	2.62-28.31
Range of h, k and l	$-9 \rightarrow 8$,
	$-10 \to 11$,
	-14 ightarrow 15
F(0 0 0)	336
R _{int}	0.0129
Number of observations	3228
Criterion of significance	$I > 2\sigma(I)$
Number of parameters	224
Weighting scheme	$W = 1/[s^2(F_0^2) + (0.0251P)^2 + 0.2529P]$
	where $P = (F_{0}^{2} + 2F_{0}^{2})/3$
S (Goodness-of-fit)	1.087
$R_1, WR_2 (F^2 > 2\sigma(F^2))$	0.0206, 0.0486
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} (e/Å^3)$	0.897, -0.463
,	

sec-C₄H₉O– groups that were modelled as disordered. Oxygen atoms O(1A), O(2A), O(1B), O(2B) and carbon atoms C(1A), C(2A), C(3A), C(4A), C(5A), C(6A), C(7A), C(8A) and C(1B), C(2B), C(3B), C(4B), C(5B), C(6B), C(7B), C(8B) have the same (0.50) site occupation factors. Compared to the space group $P\bar{1}$, the refinement of the structure in the non-centrosymmetric space group P1 does not allow us to remove the disorder of the *sec*-C₄H₉O– groups or to improve *R*-values essentially, while the refined (using SHELXTL) BASF parameter was close to 0.50. Therefore, the final refinement of the structure has been executed in the centrosymmetric space group $P\bar{1}$.

Data collection and editing, as well as the refinement of the unit cell parameters, was performed with the SMART and SAINT-PLUS program packages [24]. The structure solution and refinement were performed with the SHELXTL/PC program packages [25]. Selected bond lengths, bond angles and torsion angles are listed in Table 2. Complete crystallographic details are included in the Supporting Information.

2.3.3. Thermal analysis

The thermal behaviour of complex **1** was studied using the simultaneous thermal analysis (STA) technique for parallel recording of TG (thermogravimetry) and DSC (differential scanning calorimetry) curves. The study was performed on an STA 449C Jupiter instrument ('NETZSCH') in corundum crucibles under a lid with a hole to ensure a vapour pressure of 1 atm during the thermal decomposition of the sample. The rate of heating to 1200 °C was 5 °C min⁻¹ under an argon atmosphere. The sample mass was in the range of 3.43–5.47 mg. The accuracy of the temperature measurements was ±0.7 °C, and that of mass changes was ±1 × 10⁻² mg.

2.3.4. Elemental microanalysis

Qualitative determination of the elements was carried out on the basis of electron-probe X-ray microanalysis. The energy

Table 2	2
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Selected bond lengths (Å), bond angles (°) and torsion angles (°) in the molecule of $[Pt{S_2P(O-sec-C_4H_9)_2}]$ (1).

Bond lengths			
Pt-S(1)	2.3210(7)	Pt-S(2)	2.3244(7)
S(1)-P	1.9900(1)	S(2)-P	1.9984(1)
P-O(1A)	1.582(3)	P-O(1B)	1.578(3)
P-O(2A)	1.606(3)	P-O(2B)	1.575(3)
O(1A)-C(1A)	1.445(5)	O(1B)-C(1B)	1.483(6)
C(1A)-C(2A)	1.475(8)	C(1B)-C(2B)	1.569(1)
C(1A)-C(3A)	1.504(7)	C(1B)-C(3B)	1.451(8)
C(3A)-C(4A)	1.532(8)	C(3B)-C(4B)	1.504(1)
O(2A)-C(5A)	1.474(5)	O(2B)-C(5B)	1.477(5)
C(5A)-C(6A)	1.486(8)	C(5B)-C(6B)	1.493(8)
C(5A)-C(7A)	1.491(6)	C(5B)-C(7B)	1.498(7)
C(7A)-C(8A)	1.545(9)	C(7B)-C(8B)	1.510(8)
Bond angles			
$S(1)-Pt-S(1)^{a}$	180.0	$S(2)-Pt-S(2)^{a}$	180.0
S(1)-Pt-S(2)	83.32(3)	$S(1)-Pt-S(2)^{a}$	96.68(3)
$S(1)^{a}-Pt-S(2)$	96.68(3)	$S(1)^{a}$ -Pt- $S(2)^{a}$	83.32(3)
P-S(1)-Pt	87.23(3)	P-S(2)-Pt	86.94(3)
S(1)-P-S(2)	101.47(4)	O(1B)-P-O(1A)	16.46(2)
O(1A) - P - S(1)	121.18(2)	O(1B) - P - S(1)	108.02(2)
O(1A)-P-S(2)	107.91(1)	O(1B) - P - S(2)	122.69(1)
O(2A)-P-S(1)	124.12(9)	O(2B) - P - S(1)	106.34(1)
O(2A)-P-S(2)	105.82(1)	O(2B) - P - S(2)	124.40(1)
O(1A)-P-O(2A)	95.15(2)	O(1B)-P-O(2B)	92.73(2)
O(1A)-P-O(2B)	97.29(2)	O(1B)-P-O(2A)	96.64(2)
C(1A)-O(1A)-P	125.0(3)	C(1B)-O(1B)-P	118.5(3)
O(1A)-C(1A)-C(2A)	108.3(5)	O(1B)-C(1B)-C(2B)	105.4(5)
O(1A)-C(1A)-C(3A)	109.6(4)	O(1B)-C(1B)-C(3B)	107.0(5)
C(2A)-C(1A)-C(3A)	112.6(4)	C(2B)-C(1B)-C(3B)	106.0(6)
C(1A)-C(3A)-C(4A)	114.7(4)	C(1B)-C(3B)-C(4B)	109.7(7)
C(5A)-O(2A)-P	124.0(2)	C(5B)-O(2B)-P	121.3(3)
O(2A)-C(5A)-C(6A)	109.6(3)	O(2B)-C(5B)-C(6B)	110.1(4)
O(2A)-C(5A)-C(7A)	106.5(3)	O(2B)-C(5B)-C(7B)	106.6(3)
C(5A)-C(7A)-C(8A)	114.1(5)	C(5B)-C(7B)-C(8B)	114.5(4)
C(6A)-C(5A)-C(7A)	113.5(4)	C(6B)-C(5B)-C(7B)	111.4(5)
Torsion angles			
Pt-S(1)-S(2)-P	-168.79(5)	S(1)-Pt-P-S(2)	-169.44(4)

^a -x, -y, -z + 2.

dispersive X-ray (EDX) spectra were recorded using a JEOL JSM-6390 LV scanning electron microscope attached to an Oxford INCAEnergy EDX instrument.

3. Results and discussion

3.1. Heteronuclear (¹³C, ³¹P) CP/MAS NMR data

Fig. 1 shows the ¹³C CP/MAS NMR spectra of the polycrystalline dialkyl dithiophosphate platinum(II) complexes **1** [Pt{S₂P(O-sec- $C_4H_9_{2}_2$ (Fig. 1a and b) and **2**, $[Pt\{S_2P(OC_2H_5)_2\}_2]$ (Fig. 1c). There are four and two sets of expected resonance lines (see Fig. 1a-c, respectively), which can be attributed to ${}^{13}C$ sites in CH₃-, -CH₂-, -OCH₂- and -OCH= groups of the alkyl substituents in the Dtph ligands of compounds 1 and 2. However, these spectra also reveal that the samples of di-sec-butyl platinum(II) dithiophosphate, which were crystallised from ethanol solution (1) and precipitated from aqueous solution (1a), are spectrally non-identical. Fig. 2 exhibits the ³¹P CP/MAS NMR spectra of the recrystallised complexes 1 (Fig. 2a and a') and 2 (Fig. 2b and b'). Single ³¹P resonance multiplet lines (²J(³¹P-¹⁹⁵Pt)-couplings are also clearly visible) are observed in these experimental CP/MAS NMR spectra as central bands flanked by spinning sidebands. This observation indicates that there is structural equivalence of the Dtph groups in both compounds 1 and 2. It is also necessary to note that there is a superposition of two resonance lines in the ³¹P CP/MAS NMR spectrum of the sample 1a, which was precipitated from aqueous solution (see Fig. 3). The central band of this spectrum was



Fig. 1. ¹³C CP/MAS NMR spectra (90.51 MHz) of O,O'-dialkyl dithiophosphate platinum(II) complexes, $[Pt{S_2P(OR)_2}]$: $R = sec-C_4H_9$ (a and b) and $R = C_2H_5$ (c). In the cases of 'a' and 'b', the samples of complex **1** were precipitated from aqueous solution and crystallised from ethanol, respectively. The MAS frequencies were 4.6 (a and b) and 3.6 kHz (c); the number of transients being 1600 (a), 3700 (b) and 100 (c). The sidebands are denoted by 's'.

de-convoluted as two ³¹P resonances at 104.1 and 102.9 ppm ²J(³¹P–¹⁹⁵Pt)-couplings were also taken into account) with almost equal line widths and integral intensities. The former, less shielded resonance is characterised by the same chemical shift value (*i.e.*, 104.1 ppm) as the phosphorus sites in sample **1**, which was crystal-lised from ethanol. The latter ³¹P resonance line at 102.9 ppm demonstrates the existence of the second polymorph of complex **1**, which shows complete transformation to the first polymorph, **1** (104.1 ppm) in the crystallisation course from ethanol. Comparing the isotropic ³¹P chemical shift values for the above-mentioned platinum(II) complexes and the initial potassium dithiophosphates [26] (see Table 3), more shielded phosphorus sites (smaller values in the deshielded δ -scale) were revealed in the former case. This



Fig. 3. ³¹P CP/MAS NMR (145.72 MHz) spectra of platinum(II) 0,0'-di-sec-butyl dithiophosphate, whose sample was precipitated from aqueous solution. The MAS frequencies were 2.8 (a) and 2.3 kHz (b); the number of transients being 1024 in the each case. The central band is denoted by an asterisk.

result is consistent with our previous ³¹P NMR studies of other dithiophosphate transition and post-transition metal complexes [26–43]: nickel(II) [26–28], zinc(II) [26,29,30], cadmium(II) [31–34], lead(II) [35–37], silver(I) [38], thallium(I) [39,40] and antimony(V) [41–43]. Therefore, the additional shielding of the ³¹P nuclei arises due to the formation of covalent linkages between the Dtph groups and platinum atoms in complexes **1** and **2**.

There are clearly visible two equidistant satellite signals symmetrically located from both sides of the ³¹P resonance line in the latter case (Fig. 2b and b'). The discussed ³¹P resonance line was de-convoluted as a triplet with relative integral intensities of 1:4:1. Platinum has one naturally occurring NMR active nuclide with nuclear spin $I = \frac{1}{2} - \frac{195}{Pt}$ ($\mu = 0.60950 \ \mu/\mu_N$), therefore the two-bond spin–spin interaction $^2J(^{31}P-^{195}Pt)$ is the basis of the observed multiplicity of the ³¹P resonance. The integral intensities of the discussed satellites are also in good agreement with the natural abundance of the ¹⁹⁵Pt nuclide (33.832 at.%). In contrast, the expected multiplicity of the ³¹P resonance is not directly visible for the considerably broadened ³¹P CP/MAS NMR spectra of complex **1**, [Pt{S₂P(O-*sec*-C₄H₉)₂]₂] (Figs. 2a and a' and 3a and b). For example, the discussed ³¹P NMR signal (Iw = 370 Hz) is broadened approximately tenfold with respect to the spectra of the diethyl dithiophosphate platinum(II) complex (Iw = 35 Hz). This unusually



Fig. 2. ³¹P CP/MAS NMR spectra (145.72 MHz) of platinum(II) 0,0'-dialkyl dithiophosphates, [Pt{S₂P(OR)₂}]: $R = sec-C_4H_9$ (a and a') and $R = C_2H_5$ (b and b'). The MAS frequencies were 2.8 (a), 3.8 (b) and 2.3 kHz (a' and b'); the number of transients being 600 and 32 for the cases a, a' and b, b', respectively. The central bands are denoted by asterisks.

large broadening can be explained by the presence of two chiral centres in the $(sec-C_4H_9O)_2P(S)S^-$ ligand (*i.e.*, the asymmetric carbon atoms of the $-OCH(CH_3)(C_2H_5)$ groups bound to a tetrahedral array of four different substituents). Inasmuch as the original ligand is not stereospecific and is represented, according to the random distribution of *l* and *d* groups, by a mixture of three optical isomers: *ld* (50%), *ll* (25%) and *dd* (25%), the sample of the complex theoretically should be a set of six isomers: (*ll*)–(*ll*) (6.25%), (*ll*)–(*ld*) (25.0%), (*ll*)–(*dd*) (12.5%), (*ld*)–(*ld*) (25.0%), (*ld*)–(*dd*) (25.0%) and (*dd*)–(*dd*) (6.25%). The coexistence of these structurally similar optical isomers results in the aforementioned dispersion of the ³¹P NMR chemical shift.

To characterise quantitatively the Dtph groups with terminal chelating structural functions in complexes 1 and 2, both ³¹P isotropic chemical shifts $(\delta_{\rm iso})$ and the chemical shift anisotropy (CSA) parameters were used. From the relative intensities of the sidebands in the spinning sideband manifolds (see Figs. 2 and 3). χ^2 -statistics as a function of the two ³¹P CSA parameters: the chemical shift anisotropy, δ_{aniso} = $\delta_{zz} - \delta_{iso}$, and the asymmetry parameter of the chemical shift tensor (CST), $\eta = (\delta_{yy} - \delta_{xx})/(\delta_{yy} - \delta_{xx})/(\delta_{yy} - \delta_{yy})/(\delta_{yy} - \delta_{yx})/(\delta_{yy} - \delta_{yy})/(\delta_{yy} - \delta_{y$ $(\delta_{zz} - \delta_{iso})$, were calculated using the MATHEMATICA program [23]. The global minimum of this statistic, χ^2_{min} , gives values for the two CSA parameters, δ_{aniso} and η , while the joint confidence limit is the measure of the errors for these parameters [23]. Fig. 4 shows joint confidence limits for δ_{aniso} and η , while the ³¹P CSA data given in Table 3 correspond to the minima of the χ^2 -plots [23] (it is necessary to note that the zero asymmetry parameter, $\eta = 0$, corresponds to the axially symmetric CST, while an increase in the η -value from 0 to 1 reflects an enhanced contribution of rhombicity). The ³¹P CSTs of both samples of complex 1 (both crystallised from ethanol and precipitated from water solution) are close to being rhombic (η = 0.89 and 0.85). These data are very similar to the η -values of the previously studied crystalline di-cyclo-hexyl- (0.98) [14], di-iso-propyl- (0.75) [14] and di-isobutyl (0.73) dithiophosphate platinum(II) complexes [15]. However, complex **2**, unexpectedly, shows the least contribution of the rhombic component to CST ($\eta = 0.57$) among all of the studied crystalline platinum(II) dialkyl dithiophosphates.

In order to confirm the validity of these conclusions derived from heteronuclear (³¹P, ¹³C) CP/MAS NMR, the crystal and molecular structure of the mononuclear *O*,*O*'-di-*sec*-butyl dithiophosphate platinum(II) complex has been successfully resolved using single-crystal X-ray diffraction analysis.

3.2. Structural description of $[Pt{S_2P(0-sec-C_4H_9)_2}_2]$ (1)

The unit cell of platinum(II) *O*,*O*'-di-*sec*-butyl dithiophosphate comprises one centrosymmetric molecule of $[Pt{S_2P(O-sec-C_4H_9)_2}]$ (Fig. 5) (selected bond lengths, angles and torsion angles for **1** are given in Table 2) The central platinum atom, exhibiting fourfold coordination, links two Dtph ligands almost in an



Fig. 4. χ^2 Statistics as a function of the ³¹P CSA parameters δ_{aniso} and η . Graphs exhibit simulations for P-sites of $[Pt\{S_2P(O-sec-C_4H_9)_2\}_2]$ samples (a and b) and $[Pt\{S_2P(OC_2H_5)_2\}_2]$ (c). In 'a' and 'b' cases, complex **1** was precipitated from aqueous media and crystallised from ethanol solution, respectively. The 68.3% joint confidence limit (solid) and 95.4% joint confidence limit (dashed) for the two CSA parameters are shown. In each case simulations were performed for one P-site but at two different spinning frequencies: 2.3 kHz (thick lines) and 2.8 kHz (thin lines)

S,S'-isobidentate coordination mode (Fig. 6): Pt–S 2.3210(7) and 2.3244(7) Å. This type of coordination results in the formation of two four-membered chelate rings [PtS₂P] with a common platinum atom. A slight tetrahedral distortion of the planar geometry of these metallocycles is shown by the corresponding Pt–S–S–P and S–Pt–P–S torsion angle values, which deviate noticeably from 180° (see Table 2). This distortion is due to a slight bend in the aforementioned four-membered rings [PtS₂P] along the S–S axis: the dihedral angle between the [PtSS] and [SSP] half-rings is equal to 168.79(5)°. In the dithiophosphate ligands, both values of the P–S bond lengths (1.9900(1) and 1.9984(1) Å) are intermediate

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³¹P NMR chemical shift parameters^a for 0,0'-dialkyl dithiophosphate compounds.

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Compound	$\delta_{ m iso} (m ppm)$	$^{2}f(^{31}P-^{195}Pt)$ (Hz)	δ_{aniso}^{b} (ppm)	$\eta^{\mathbf{b}}$
1 , $[Pt{S_2P(O-sec-C_4H_9)_2}_2]$	104.1	~456	-43.3 ± 0.2	0.89 ± 0.02
1a , $[Pt{S_2P(O-sec-C_4H_9)_2}_2]$	102.9	\sim 443	-42.3 ± 0.2	0.85 ± 0.02
$K{S_2P(O-sec-C_4H_9)_2}$ [26]	113.8		-114.0 ± 1.0	0.33 ± 0.04
	114.8		-112.4 ± 1.7	0.28 ± 0.03
	(1:1)			
2 , $[Pt{S_2P(OC_2H_5)_2}_2]$	105.0	444.4	-35.1 ± 0.2	0.57 ± 0.03
$K{S_2P(OC_2H_5)_2}$ [26]	108.5		-107.6 ± 1.0	0.10 ± 0.06

^a Relative to 85.5% H₃PO₄ (0 ppm, externally referenced), deshielding scale.

^b Definitions: $\delta_{aniso} = \delta_{zz} - \delta_{iso}$; $\eta = (\delta_{yy} - \delta_{xx})/(\delta_{zz} - \delta_{iso})$. (1) The crystalline sample was isolated from ethanol solution. (1a) The powdered sample was precipitated from aqueous solution.



Fig. 5. Crystal structure of [Pt{S₂P(O-sec-C₄H₉)₂] (projection onto the bc plane).

between hypothetical single (2.14 Å) and double (1.94 Å) P–S bonds [44]. This is evidence of delocalisation of the π -electron density over the four-membered metallocycles [PtS₂P], whose small sizes are illustrated by unusually short interatomic Pt…P (2.983 Å) and S…S (3.088 Å) distances. The latter values are much shorter than the sum of the van der Waals radii of the corresponding pairs of atoms: 3.55 and 3.60 Å, respectively [45–47]. Thus, the positions of the platinum and phosphorus atoms are essentially drawn together in the chelate rings, which can be attributed to a direct *trans*-annular interaction between them. The phosphorus atoms in both Dtph groups are in a tetrahedral neighbouring [O₂S₂] environment.

The planar configuration of the $[PtS_4]$ chromophore in structure **1** is due to the dsp^2 -hybrid state of platinum(II). A slight non-equivalence of the Pt–S bonds results in a slight rhombic distortion of the discussed chromophore. In contrast to the $[PtS_4]$ chromophore in cooperite [10,11], the values for both angles

S(1)–Pt–S(2) and S(1)–Pt–S(2)^a (83.32(3)° and 96.68(3)°, respectively) are noticeably deviated from 90° because of the formation of the two sterically strained four-membered chelate rings [PtS₂P]. Complex **1** is also characterised by the lowest value of the S–P–S angle (101.47°) among various platinum(II) dialkyl dithiophosphates: $R = C_2H_5$ (102.4° [12]), *iso*–C₃H₇ (101.9° [13]), *iso*–C₄H₉ (102.39° [15]), *cyclo*–C₆H₁₁ (101.79° [14]).

3.3. Thermal analysis and elemental microanalysis data

Fig. 7 shows both the TG and DSC traces. Thermogravimetry data reflect the thermal stability of complex **1** below 157 °C and the stepwise mass loss in the range of 157–795 °C. There are three distinct steps exhibiting mass loss on the TG curve: (i) in the range 157–170 °C, (ii) at 170–425 °C and (iii) at 425–795 °C (see Fig. 7a). The first and second steps of the TG curve reflect thermal decomposition of the organic parts of the Dtph ligands: a 38.5% total loss



Fig. 6. Molecular structure of $[Pt{S_2P(O-sec-C_4H_9)_2}]$. Displacement ellipsoids are shown at the 50% probability level.



Fig. 7. TG (a) and DSC (c) curves of complex **1**. A close-up view of the inner surface of the crucible with the end-product particles (b). An enlarged fragment of TG curve around the melting endotherm (d).

corresponds to the relative mass of two $sec-C_4H_9-$ and two $sec-C_4H_9O-$ groups (the calculated loss is 38.43%). The mass remaining after the second step at 425 °C (61.5%) corresponds, as expected, to the mass of bis(dithio-*meta*-phosphato)platinum(II), [Pt(S₂PO)₂] (*calc.* 61.57%) as the intermediate product [12]. Hence, a 25.1% loss at the first step is probably connected with the thermal cleavage of the C–C(H)O– bonds when both di-*sec*-butyl dithiophosphate ligands lose alkyl groups of terminal carbon atoms, which are not directly linked to the oxygen atom (*calc.* 26.02%). The third step exhibits a 22.9% loss defining a 38.6% final mass (at 900 °C) of metallic bright rounded particles (Fig. 7b).

Fig. 7c shows a DSC curve with two main endotherms. The first, low-temperature one, which is observed in a region of the thermal stability of **1** (*i.e.*, before the beginning of mass loss), is the melting endotherm of compound **1** (the extrapolated m.p. is 83.5 °C). The second endotherm arises on the DSC curve at 165.1 °C, at the start of the first step of the intense thermal decomposition of the organic part of the Dtph ligands in complex **1**. Besides that, there is one more, very low intense and non-reversible endotherm on the TG curve before the m.p. (see Fig. 7d). This endotherm was attributed to a phase transition of complex **1** at 74.2 °C.



Fig. 8. EDX spectrum of the end-product particles. The central panel shows one of these particles.

The thermal transformations of dialkyldithiophosphate platinum(II) complexes, usually, lead to platinum(II) sulphide as the final product [12]. However, in our case, there was a 38.6% remaining mass that clearly did not correspond to PtS (*calc.* 33.52%). Therefore, to establish qualitatively the elemental composition of the end-product particles, which were characterised by a heterogeneous surface, energy dispersive X-ray analysis was used. The EDX spectral pattern (Fig. 8a) supports the existence of platinum particles as the main end-product with dark inclusions of a slag at its bright metallic surface (Fig. 8b). Form the EDX spectroscopy data, these dark areas are characterised by the presence of the sulphur, phosphorus, oxygen, carbon and platinum.

4. Conclusion

Crystalline bis(0,0'-di-sec-butyldithiophosphato)platinum(II) was prepared and studied by means of heteronuclear ¹³C, ³¹P CP/ MAS NMR spectroscopy and single-crystal X-ray diffraction. The unit cell of this platinum(II) compound comprises of one molecule of $[Pt{S_2P(O-sec-C_4H_9)_2}]$, in which Dtph ligands, playing the same terminal chelating function, exhibit structural equivalence in both solid state ³¹P NMR and XRD data. A terminal S,S'-bidentate coordination of the Dtph groups leads to the formation of two four-membered planar chelate rings [PtS₂P] with a platinum atom displaying a 'spiro' function. In the dithiophosphate complexes, the structural states of the phosphorus atoms are characterised by ³¹P chemical shift tensors that are close to being rhombic. The thermal behaviour of compound 1 was studied by means of the STA method, as a combination of TG and DSC techniques taken under an argon atmosphere. The mass of complex 1 is lost in three steps: first at 157-170 °C and then in the temperature intervals of 170-425 and 425–795 °C. The thermal decomposition of the organic parts of the Dtph ligands over the first and second steps with a 38.5% total loss, corresponding to the relative mass of two sec-C₄H₉- and two sec-C₄H₉O- groups (the calculated loss is 38.43%), yields bis(dithio-meta-phosphato)platinum(II), [Pt(S₂PO)₂] (calc. 61.57%), as the intermediate product; whereas reduced metallic platinum is the main final product.

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Appendix A. Supplementary data

CCDC 821345 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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