



## Syntheses, crystal structure and spectroscopic characterization of new platinum(II) dithiocarbimato complexes

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### ABSTRACT

The reaction of 4-iodobenzenesulfonamide or 4-fluorobenzenesulfonamide with CS<sub>2</sub> and KOH in dimethylformamide yielded the potassium *N*-R-sulfonyldithiocarbimates, K<sub>2</sub>(RSO<sub>2</sub>N=CS<sub>2</sub>) [R = 4-IC<sub>6</sub>H<sub>4</sub> (**1**) and 4-FC<sub>6</sub>H<sub>4</sub> (**2**)]. These salts reacted with K<sub>2</sub>[PtCl<sub>4</sub>] in water/methanol to yield complex anions bis(*N*-R-sulfonyldithiocarbimato)platinate(II), which were isolated as their tetrabutylammonium salts, (Bu<sub>4</sub>N)<sub>2</sub>[Pt(RSO<sub>2</sub>N=CS<sub>2</sub>)<sub>2</sub>] [R = 4-IC<sub>6</sub>H<sub>4</sub> (**3**) and 4-FC<sub>6</sub>H<sub>4</sub> (**4**)]. The structures of **2–4** were determined by X-ray crystallography. The Pt<sup>2+</sup> in both complexes **3** and **4** lies at the inversion centre and the PtS<sub>4</sub> moiety has a distorted square-planar configuration. The compounds were also characterized by IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopies, and elemental analyses. The molar conductance data are consistent with the fact that **3** and **4** are dianionic complexes.

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### 1. Introduction

Dithiocarbamate salts and dithiocarbamate complexes are well known compounds, their wide range of applications being described in the literature. For example, dithiocarbamate and their derivatives are very active accelerators in vulcanization [1,2]. Many dithiocarbamates, anions and complexes show biological activity and are used as fungicides [1,3].

Hundreds of platinum(II) complexes involving dithiocarbamate ligands have been reported [1]. The interest in this kind of complexes has increased in recent years, with the aim of synthesizing anti-tumor drugs of reduced toxicity with respect to cisplatin [1,4]. On the other hand, reports about the synthesis and characterization of platinum(II)-dithiocarbimato complexes are much more rare in the literature [5–10]. These papers include the description of only two complexes containing dithiocarbimates derived from sulfonamides [10]. The characterization of salts of *N*-R-sulfonyldithiocarbimates by single crystal X-ray diffraction experiments is also rare, probably due to their low stability at ambient conditions. To our knowledge, only two potassium salts of this kind have had their structures described [11,12].

The bis(dithiocarbimato)-platinum(II) complexes are much more stable than the potassium salts of their free ligands. Furthermore, differently from the dithiocarbamate complexes, they are, necessarily, anionic species. So the applications of these complexes will also depend on the counter ion. Thus, the use of active cations might improve their biological activity and different cations should also allow a variation in their solubility. Another important aspect to be considered is the possibility of variation in the R groups, what might change their solubility in the biological medium, interfering in the effectiveness of their action in within the cells. In a recent work we reported on the structures of compounds (Bu<sub>4</sub>N)<sub>2</sub>[Pt(C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>N=CS<sub>2</sub>)<sub>2</sub>] and (Bu<sub>4</sub>N)<sub>2</sub>[Pt(4-BrC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>N=CS<sub>2</sub>)<sub>2</sub>] [10]. These compounds were insoluble in water and soluble in organic solvents, which might enable their interactions with the lipophilic parts of the cell membranes. So, we decided to prepare new complexes keeping the same cation, but changing the aromatic substituents, obtaining similar complexes, with anions of different sizes, for posterior studies on their anti-tumoral activities.

Here we describe the synthesis of a new potassium *N*-R-sulfonyldithiocarbimato salt: K<sub>2</sub>(4-FC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>N=CS<sub>2</sub>) (**2**) and two new bis(*N*-R-sulfonyldithiocarbimato)platinate(II) tetrabutylammonium salts: (Bu<sub>4</sub>N)<sub>2</sub>[Pt(4-IC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>N=CS<sub>2</sub>)<sub>2</sub>] (**3**) and (Bu<sub>4</sub>N)<sub>2</sub>[Pt(4-FC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>N=CS<sub>2</sub>)<sub>2</sub>] (**4**). These compounds were characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra, elemental analyses and by single X-ray diffraction techniques.

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## 2. Experimental

### 2.1. Materials and methods

Solvents (dichloromethane, dimethylformamide, ethanol and methanol) were purchased from Merck and were used as supplied. 4-Fluorobenzenesulfonamide, 4-iodobenzenesulfonyl chloride, potassium tetrachloroplatinate(II) and tetrabutylammonium bromide were purchased from Aldrich. KOH and CS<sub>2</sub> were purchased from Vetec. The 4-iodobenzenesulfonamide was prepared from 4-iodobenzenesulfonyl chloride in reaction with concentrated ammonia solution, according to the methodology applied for the syntheses of similar compounds [13] and potassium *N*-4-iodophenylsulfonyldithiocarbamate was prepared from the parent sulfonamide as described in the literature [12]. This salt, which is soluble in H<sub>2</sub>O and insoluble in most organic solvents, was recrystallized from a hot mixture of ethanol and water. IR spectra were recorded with a Perkin–Elmer 1000 FT-IR spectrophotometer using CsI pellets. The NMR spectra were recorded with a Bruker DPX-200-AVANCE or a VARIAN-300 spectrophotometers in D<sub>2</sub>O (**1**, **2**), DMSO-*d*<sub>6</sub> (**3**) and CDCl<sub>3</sub> (**4**) with TMS as internal standard. Microanalyses for C, H and N were obtained from a Perkin–Elmer 2400 CHN elemental analyzer. Platinum was analyzed by atomic absorption on a Hitachi Z-8200 atomic absorption spectrophotometer. Uncorrected melting points were measured with a Mettler FP5 melting point apparatus. The molar conductances ( $\Lambda_m$ ) were measured in acetonitrile solutions at 25 °C with a Conductivity Meter Jenway 4010.

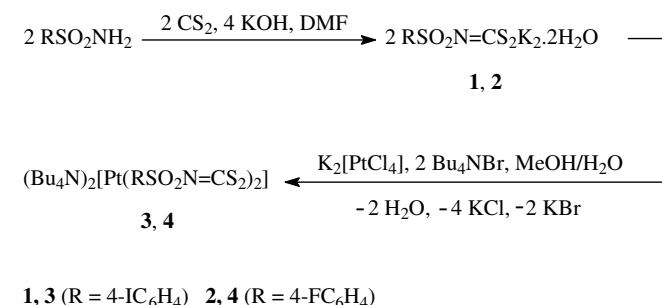
### 2.2. Syntheses of the dithiocarbamate potassium salts

Compound **1** was prepared as described in the literature [12]. Compound **2** was prepared as described, see Scheme 1.

Carbon disulfide (0.02 mol) and potassium hydroxide (0.01 mol) were added to a solution of 4-fluorobenzenesulfonamide (0.02 mol) in DMF (20 mL). The mixture was stirred at room temperature for 2 h previous to the addition of a second portion of potassium hydroxide (0.01 mol). After stirring for further 1 h, the yellow solid formed was filtered, washed with DMF, ethanol and ethyl acetate and dried under reduced pressure yielding the potassium *N*-4-fluorophenylsulfonyldithiocarbamate (80% based on the sulfonamide). Suitable crystals for X-ray structure analysis were obtained after recrystallization in ethanol:water 1:1 mixture.

#### 2.2.1. Potassium *N*-4-fluorophenylsulfonyldithiocarbamate dihydrate (**2**)

Elemental Anal. Calc. for C<sub>7</sub>H<sub>8</sub>FNO<sub>4</sub>S<sub>3</sub>K<sub>2</sub>: C, 23.13; H, 2.22; N, 3.85. Found: C, 23.10; H, 2.02; N, 3.85%. IR (most important bands) (cm<sup>-1</sup>): 3340 (water), 1259 (νCN) + (νSO<sub>2</sub>asym), 1135 (νSO<sub>2</sub>sym), 977 (νCS<sub>2</sub>asym). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O), (δ), J (Hz): 7.72–7.65 (m, 4H, H2 and H6), 7.15–7.07 (m, 4H, H3 and H5). <sup>13</sup>C NMR (δ), J (Hz): 225.29



Scheme 1. Syntheses of **1–4**.

(N=CS<sub>2</sub>), 164.35 (d, <sup>1</sup>J<sub>C,F</sub> = 248.4, C4), 137.96 (C1), 129.31 (d, <sup>3</sup>J<sub>C,F</sub> = 9.8, C2 and C6), 115.90 (d, <sup>2</sup>J<sub>C,F</sub> = 22.9, C3 and C5).

### 2.3. Syntheses of the platinum complexes

The syntheses of the platinum complexes were performed according to Scheme 1. Potassium tetrachloroplatinate(II) (0.001 mol) and tetrabutylammonium bromide (0.002 mol) were added to a solution of potassium *N*-R-sulfonyldithiocarbamate dihydrate (**1** or **2**, 0.002 mol) in methanol/water 1:1 (10 mL). The reaction mixture was stirred for 3 h at room temperature. The yellow solid obtained was filtered, washed with distilled water and dried under reduced pressure for one day, yielding (Bu<sub>4</sub>N)<sub>2</sub>[Pt(N-RSO<sub>2</sub>N=CS<sub>2</sub>)<sub>2</sub>] (ca. 70% based on the K<sub>2</sub>[PtCl<sub>4</sub>]). Suitable crystals for X-ray structure analyses were obtained after slow evaporation of the solutions of compounds **3** and **4** (R = 4-IC<sub>6</sub>H<sub>4</sub> and 4-FC<sub>6</sub>H<sub>4</sub>, respectively) in methanol/water 4:1.

#### 2.3.1. Tetrabutylammonium bis(*N*-4-iodophenylsulfonyldithiocarbamate)platinate(II) (**3**)

Elemental Anal. Calc. for (C<sub>16</sub>H<sub>36</sub>N)<sub>2</sub>C<sub>14</sub>H<sub>8</sub>I<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub>Pt: C, 39.62; H, 5.78; N, 4.02; Pt, 13.99. Found: C, 39.68; H, 5.63; N, 3.96; Pt, 13.72%. M.p. (°C): 168.3–169.7. Molar conductance [ $\Lambda_m$  (Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>)]: 220. IR (most important bands) (cm<sup>-1</sup>): 1384 (νCN), 1287 (νSO<sub>2</sub>asym), 1143 (νSO<sub>2</sub>sym), 936 (νCS<sub>2</sub>asym), 334 (νPtS). <sup>1</sup>H NMR (200 MHz, DMSO-*d*<sub>6</sub>, complex anion signals) (δ), J (Hz): 7.86 (d, 4H, J = 8.4, H3 and H5), 7.52 (d, 4H, J = 8.4, H2 and H6). <sup>13</sup>C NMR (50 MHz, DMSO-*d*<sub>6</sub>, complex anion signals) (δ): 212.37 (N=CS<sub>2</sub>), 142.82 (C1), 137.03 (C3 and C5), 128.76 (C2 and C6), 98.96 (C4).

#### 2.3.2. Tetrabutylammonium bis(*N*-4-fluorophenylsulfonyldithiocarbamate)platinate(II) (**4**)

Elemental Anal. Calc. for (C<sub>16</sub>H<sub>36</sub>N)<sub>2</sub>C<sub>14</sub>H<sub>8</sub>F<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub>Pt: C, 46.88; H, 6.84; N, 4.75; Pt, 16.55%. Found: C, 46.93; H, 6.79; N, 4.75; Pt, 16.52%. M.p. (°C): 163.8–165.0. Molar conductances [ $\Lambda_m$  (Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>)]: 249. IR (most important bands) (cm<sup>-1</sup>): 1376 (νCN), 1283 (νSO<sub>2</sub>asym), 1145 (νSO<sub>2</sub>sym), 934 (νCS<sub>2</sub>asym), 330 (νPtS). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, complex anion signals) (δ), J (Hz): 8.05–7.95 (m, 4H, H2 and H6), 7.04 (br, t, 4H, J ≈ 8, H3 and H5). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, complex anion signals) (δ), J (Hz): 212.96 (N=CS<sub>2</sub>), 164.27 (d, <sup>1</sup>J<sub>C,F</sub> = 249.7, C4), 139.79 (C1), 130.32 (d, <sup>3</sup>J<sub>C,F</sub> = 8.9, C2 and C6), 114.77 (d, <sup>2</sup>J<sub>C,F</sub> = 22.0, C3 and C5).

### 2.4. X-ray diffraction experiments

X-ray intensity data for single crystals were collected using graphite monochromatic Mo Kα radiation on a four-circle κ-geometry KUMA KM-4 diffractometer with a two-dimensional area CCD detector. The ω-scan technique with Δω = 0.80° for each image was used for data collection. The 880 images for six different runs covered about 98% of the Ewald sphere were collected using the CRY-SALIS CCD program [14]. The lattice parameters were refined by least-squares methods based on all the reflections with I > 2σ(I<sup>2</sup>). One image was used as a standard for monitoring of the stability of the crystals as well as for monitoring the data collection after every 50 images, and no correction on the relative intensity variation was necessary. Integration of the intensities, correction for Lorentz and polarization effects and the numerical absorption correction were performed using a CRYSLIS RED program [14]. The structures were solved by direct methods using SHELXS97 [15]. The calculated E map revealed the metals, S, O, N and most of the C atoms. The remaining C atoms were located from the difference Fourier synthesis. The structures were refined with the anisotropic thermal parameters for all non-hydrogen atoms using SHELXL97 [15]. Difference Fourier maps gave electron density concentrations

approximately located for all hydrogen atoms positions; these positions were idealised (HFIX 43 for all H atoms of the phenyl rings with isotropic thermal parameters of 1.2 U<sub>eq</sub> of the carbon atoms joined directly to the hydrogen atoms, and HFIX 137 for the CH<sub>3</sub> and HFIX 23 for the CH<sub>2</sub> with isotropic thermal parameters of 1.5 U<sub>eq</sub> of the carbon atom). Final difference Fourier maps showed no peaks of chemical significance. Details of the data collection parameters and final agreement factors are collected in Table 1. Selected bond lengths and angles and torsion angles are listed in Table 2.

### 2.5. Theoretical calculations

Ab initio molecular orbital calculations full geometry optimizations were performed with the GAUSSIAN98 program package [16]. The calculations were performed for the isolated 4-fluorophenylsulfonilydithiocarbamate(2-) ligand by the density functional three-parameters hybrid (B3LYP) methods [17,18] with the 6-31+G(d) basis set starting from the X-ray geometry. As convergence criterion the threshold limits of 0.00025 and 0.0012 a.u. were applied for the maximum force and the displacement, respectively.

## 3. Results and discussion

Compounds **1** and **2** are yellow solids. They are insoluble in organic solvents and soluble in water. They are not very stable and a white solid is obtained from their aqueous solutions after some days at room temperature. At ambient temperature, the yellow solids are also converted into white solids after several months. Both, **3** and **4**, are yellow crystalline solids insoluble in water and very

**Table 2**

Selected bond lengths (Å) and angles (°)

Compound <b>2</b>					
K1–O3	2.822(2)	K2–O1 <sup>iv</sup>	2.680(2)	S1–C1	1.731(2)
K1–O3 <sup>i</sup>	2.902(2)	K2–O2	2.725(2)	S2–C1	1.706(2)
K1–O4 <sup>i</sup>	2.759(2)	K2–O3	3.130(2)	C1–N1	1.351(2)
K1–O4 <sup>ii</sup>	3.056(2)	K2–O4 <sup>i</sup>	2.947(2)	N1–S3	1.610(2)
K1–N1	3.051(2)	K2–S2 <sup>iv</sup>	3.206(2)	S3–O1	1.443(2)
K1–O2	3.051(2)	K2–F1 <sup>v</sup>	2.785(2)	S3–O2	1.445(2)
K1–S1 <sup>iii</sup>	3.371(2)	K2–S1 <sup>vi</sup>	3.375(2)	S3–C2	1.768(2)
K1–K2	3.974(2)	K2–S2 <sup>vi</sup>	3.195(2)	C5–F1	1.362(2)
Compound <b>3</b>		Compound <b>4</b>		Compound <b>3</b>	
Pt–S1	2.325(2)	Pt–S2	2.316(3)	S3–O1	1.432(3)
Pt–S2	2.314(1)	S1–C1	1.735(4)	S3–O2	1.436(3)
S1–C1	1.735(4)	S2–C1	1.732(4)	S3–C2	1.770(4)
S2–C1	1.732(4)	C1–N1	1.302(4)	C5–I1	2.094(4)
C1–N1	1.302(4)	N1–S3	1.619(3)	C5–F1	1.364(5)
N1–S3	1.619(3)	S1–Pt–S2	1.615(3)		
S1–Pt–S2	74.39(4)		73.88(5)	S1–Pt–S2 <sup>i</sup>	105.61(4)
Torsion angles	<b>3</b>	4-BrC <sub>6</sub> H <sub>4</sub> -derivative <sup>a</sup>	<b>4</b>	Ph-derivative <sup>a</sup>	
C11–C12–C13–C14	–179.6(1)	–178.3(1)	172.3(1)	175.3(1)	
C21–C22–C23–C24	175.9(1)	174.8(1)	174.5(1)	174.4(1)	
C31–C32–C33–C34	176.1(1)	178.6(1)	–177.3(1)	–178.3(1)	
C41–C42–C43–C44	164.2(1)	160.8(1)	–92.9(1)	–173.2(1)	

Symmetry code compound **2**: (i)  $-x+1, -y+1, -z$ ; (ii)  $x-1, y, z$ ; (iii)  $-x, -y, -z$ ; (iv)  $x, y+1, z$ ; (v)  $-x, y+0.5, -z+0.5$ ; (vi)  $x+1, y+1, z$ .

Symmetry code compounds **3** and **4**: (i)  $-x, -y, -z$ .

<sup>a</sup> Data from Ref. [10].

**Table 1**

Crystallographic data and structure refinement parameters

	<b>2</b>	<b>3</b>	<b>4</b>
<b>Crystal data</b>			
Formula	C <sub>7</sub> H <sub>8</sub> FNO <sub>4</sub> S <sub>3</sub> K <sub>2</sub>	C <sub>46</sub> H <sub>80</sub> I <sub>2</sub> N <sub>4</sub> O <sub>4</sub> S <sub>6</sub> Pt	C <sub>46</sub> H <sub>80</sub> F <sub>2</sub> N <sub>4</sub> O <sub>4</sub> S <sub>6</sub> Pt
Molecular weight	363.52	1394.39	1178.59
(g mol <sup>−1</sup> )			
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2 <sub>1</sub> /c (No. 14)	P2 <sub>1</sub> /c (No. 14)	P1̄ (No. 2)
a (Å)	6.251(1)	9.099(2)	9.837(2)
b (Å)	7.178(1)	12.6451(3)	9.969(2)
c (Å)	30.105(5)	24.716(4)	15.435(3)
α (°)			89.79(2)
β (°)	90.34(2)	94.23(2)	74.50(2)
γ (°)			69.55(2)
Volume, V (Å <sup>3</sup> )	1350.8(4)	2837.3(11)	1359.9(5)
Z	4	2	1
D <sub>calc</sub> ; D <sub>obs</sub> (floatation)	1.788; 1.78	1.632; 1.63	1.439; 1.43
(g cm <sup>−3</sup> )			
Radiation, λ (Å)		Mo Kα (0.71073)	
Absorption coefficient μ	1.18	3.82	2.86
(mm <sup>−1</sup> )			
Transmission factor, T <sub>max</sub> ; T <sub>min</sub>	0.855; 0.736	0.681; 0.362	0.588; 0.350
<b>Data collection</b>			
2θ <sub>max</sub> (°)	59.2	59.4	58.2
Collected/unique reflections	16650/3501	36868/7392	17388/6619
Observed reflections (I > 2σ(I))	3029	4698	4722
R <sub>int</sub>	0.019	0.045	0.041
<b>Refinement</b>			
R(F <sub>o</sub> <sup>2</sup> > 2σ(F <sub>o</sub> <sup>2</sup> ))	0.033	0.037	0.039
wR(F <sub>o</sub> <sup>2</sup> , all reflections)	0.070	0.081	0.081
Δρ <sub>min</sub> ; Δρ <sub>max</sub> (e Å <sup>−3</sup> )	−0.309; +0.401	−1.139; +1.769	−1.119; +0.668
Goodness-of-fit	1.001	1.010	1.010

stable at room temperature. Compound **4** is soluble in polar organic solvents such as DMF, DMSO, ethanol, methanol, dichloromethane and chloroform. Compound **3** is soluble in DMF, DMSO, and differently from compound **4** and the analogues with R = C<sub>6</sub>H<sub>5</sub> and 4-BrC<sub>6</sub>H<sub>4</sub> [10], only slightly soluble in the other organic solvents mentioned above. The molar conductances of **3** and **4** at 10<sup>−3</sup> mol L<sup>−1</sup> in acetonitrile are in the range of 220–300 Ω<sup>−1</sup> cm<sup>2</sup> mol<sup>−1</sup>, commonly attributed to 1:2 electrolytes [19].

The spectroscopic properties of compounds **3** and **4** are similar to those presented by other platinum(II) complexes of dithiocarbamate from sulfonamides described in the literature [10] (Tables 3 and 4). In the IR spectra of the potassium dithiocarbimates **1** and **2**, there are no strong bands in the 1450–1550 cm<sup>−1</sup> spectral region, the νCN band being observed at 1280 and 1259 cm<sup>−1</sup>, respectively. A strong band observed at 1384 cm<sup>−1</sup> in the spectrum of compound **3** and at 1376 cm<sup>−1</sup> in the spectrum of compound **4** was assigned to the νCN. The CN bond is formally a double bond. However, because of the SO<sub>2</sub> neighbour group, the canonical forms (a) and (b) (Scheme 2) contribute appreciably to the resonance hybrid. This fact explains the low values observed for the νCN band wavenumbers. The νCS<sub>2asym</sub> were observed at higher wavenumbers in the spectra of the potassium salts of dithiocarbimates (971 and 977 cm<sup>−1</sup> for **1** and **2**, respectively) than in the spectra of compounds **3** and **4** (936 and 934 cm<sup>−1</sup>, respectively). The shifts observed in the νCS<sub>2asym</sub> and νCN bands in the vibrational spectra of the complexes when compared to the spectra of the free ligands, are consistent with the increased importance of the canonical form (c) after complexation (Scheme 2). The spectra of compounds **3** and **4** also show the expected medium/strong band in the 300–400 cm<sup>−1</sup> range assigned to the νPtS.

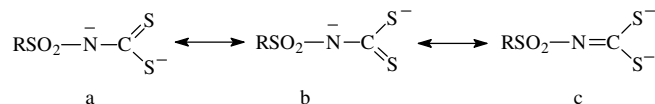
The NMR spectra were typical for diamagnetic species and were consistent with the proposed structures. The integration curves on the <sup>1</sup>H NMR spectra of **3** and **4** were consistent with a 2:1 proportion between the tetrabutylammonium cation and the Pt-bis(dithiocarbimate) complex anion. In the <sup>13</sup>C NMR spectra of compounds **3** and **4** the signal of the quaternary carbon of the dithiocarbimate

**Table 3**Comparison between the  $\nu\text{CS}_2$  and the  $\text{CS}_2$  bond lengths and angles in dithiocarbamate potassium salts and complexes

Substances	$\nu\text{CS}_2$ ( $\text{cm}^{-1}$ )	C(1)–S(1) (Å)	C(1)–S(2) (Å)	S(1)–C(1)–S(2) ( $^\circ$ )
$\text{K}_2(\text{C}_6\text{H}_5\text{SO}_2\text{C}=\text{NS}_2)^{\text{a}}$	971			
$\text{K}_2(4\text{-BrC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)^{\text{a}}$	973			
$\text{K}_2(4\text{-IC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)$ ( <b>1</b> )	971			
$\text{K}_2(4\text{-FC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)$ ( <b>2</b> )	977	1.731(2)	1.706(2)	119.5(1)
$[\text{Pt}(\text{C}_6\text{H}_5\text{SO}_2\text{C}=\text{NS}_2)_2]^{2-}$	934	1.733(2)	1.750(2)	107.87(11)
$[\text{Pt}(4\text{-BrC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)_2]^{2-}$	930	1.732(4)	1.737(4)	108.5(2)
$[\text{Pt}(4\text{-IC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)_2]^{2-}$ ( <b>3</b> )	936	1.735(2)	1.732(2)	108.0(2)
$[\text{Pt}(4\text{-FC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)_2]^{2-}$ ( <b>4</b> )	934	1.732(4)	1.739(4)	106.9(2)

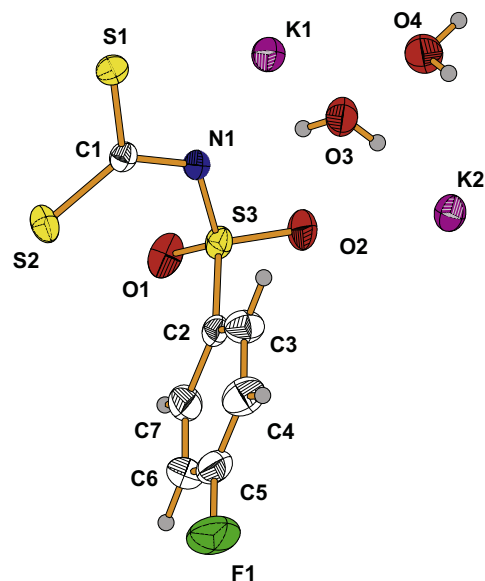
<sup>a</sup> Data from Ref. [10].**Table 4**Comparison between the crystallographic and spectroscopic data for the CN bond in the  $\text{NCS}_2$  moiety of the dithiocarbamate anions

Substances	$\nu\text{CN}$ ( $\text{cm}^{-1}$ )	$^{13}\text{C}$ NMR ( $\text{NCS}_2$ ) (ppm)	CN length (Å)
$\text{K}_2(\text{C}_6\text{H}_5\text{SO}_2\text{C}=\text{NS}_2)^{\text{a}}$	1267	223.19	
$\text{K}_2(4\text{-BrC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)^{\text{a}}$	1258	225.74	
$\text{K}_2(4\text{-IC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)$ ( <b>1</b> )	1280	225.62	
$\text{K}_2(4\text{-FC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)$ ( <b>2</b> )	1259	225.29	1.351(2)
$[\text{Pt}(\text{C}_6\text{H}_5\text{SO}_2\text{C}=\text{NS}_2)_2]^{2-}$	1395	212.74	1.293(3)
$[\text{Pt}(4\text{-BrC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)_2]^{2-}$	1380	213.29	1.313(4)
$[\text{Pt}(4\text{-IC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)_2]^{2-}$ ( <b>3</b> )	1384	212.37	1.302(4)
$[\text{Pt}(4\text{-FC}_6\text{H}_4\text{SO}_2\text{C}=\text{NS}_2)_2]^{2-}$ ( <b>4</b> )	1376	212.96	1.299(4)

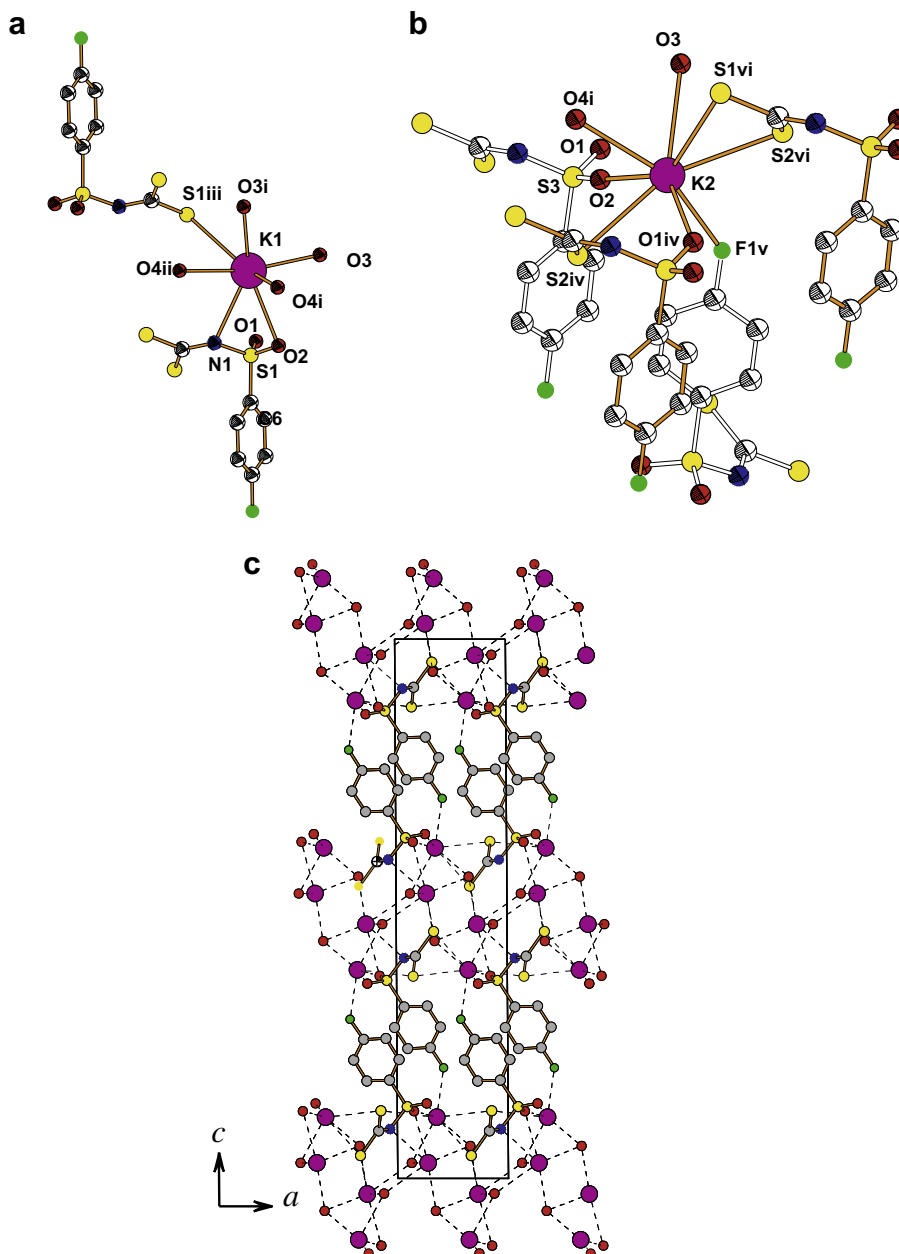
<sup>a</sup> Data from Ref. [10].**Scheme 2.** Three canonical forms for *N*-R-sulfonyldithiocarbamate anion.

moiety is shifted upfield when compared to the corresponding signal in the potassium dithiocarbamates spectra. This fact is also consistent with the increase in the contribution of canonical form (c) after the complexation (Scheme 2). The coupling constants between the fluorine and the carbon atoms in the spectra of compounds **2** and **4** were observed in the normal range for other fluorinated aromatic compounds ( $^1J_{\text{C},\text{F}} \approx 249$  Hz and  $^2J_{\text{C},\text{F}} \approx 22.5$  Hz), and it was also possible to observe the coupling with C-2 ( $^3J_{\text{C},\text{F}} \approx 9$  Hz).

The asymmetric unit of compound **2** is illustrated in Fig. 1. The dithiocarbamate(2-) group together with the sulfur atom of sulfonyl group of the 4-fluorophenyl-sulfonyldithiocarbamate(2-) anion (the S1S2C1N1S3 fragment) is planar and almost perpendicular to the phenyl ring. The dihedral angle between the planes defined by the S1S2C1N1S3 atoms and by the C atoms of the phenyl ring is equal to  $98.9(1)^\circ$ . The potassium cations, K1 and K2, have different coordination environments. The K1 cation is surrounded by two 4-fluorophenylsulfonyldithiocarbamate(2-) anions and three water molecules (Fig. 2a). One of the 4-fluorophenylsulfonyldithiocarbamate(2-) ligands is joined to K1 by the S1 atom of dithiocarbamate group, while the other ligand by O2 of sulfonyl group and by the N1 atom. The K2 cation interacts with four neighbouring 4-fluorophenylsulfonyldithiocarbamate(2-) ligands and with two water molecules (Fig. 2b). Each of these 4-fluorophenylsulfonyldithiocarbamate(2-) ligands interacts differently with the K2 cation. One of them interacts by both S atoms of  $\text{CS}_2$  group, the other by

**Fig. 1.** The atomic numbering scheme of  $\text{K}_2(4\text{-FC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2) \cdot 2(\text{H}_2\text{O})$ . Displacement ellipsoids are drawn at the 50% probability level.

the O atom of sulfonyl group and by one S atom of  $\text{CS}_2$  group. The third 4-fluorophenylsulfonyldithiocarbamate(2-) ligand is directed towards the K2 cation by the F atom (K2–F1, 2.785(2) Å), and the fourth ligand is oriented to the K2 cation by the O atom of sulfonyl group (K2–O2, 2.725(2) Å). Thus the potassium cations, K1 and K2, have not only different environments, but also different coordination numbers. Ab initio molecular orbital calculations performed for an isolated 4-fluorophenylsulfonyldithiocarbamate(2-) ligand have shown a quite similar conformation of the anion as found in the crystal of the potassium salt (Table 5). Thus the interaction between the potassium cations and the 4-fluorophenylsulfonyldithiocarbamate(2-) anions is mainly ionic which does not disturb significantly the geometric conformation of the ligand. The bond lengths and angles, as well as the orientation of the almost planar dithiocarbamate group ( $\text{CS}_2$ ), together with the sulfur atom of the sulfonyl group (S1S2C1N1S3 fragment) in relation to the phenyl ring in the potassium salt preserve almost the same values as in the gas-phase which describes the most stable conformation of the ligand. The arrangement of the molecules in the crystal **2** (Fig. 2c) is mainly determined by the ionic interaction of the oppositely charged moieties, i.e. the 4-fluorophenylsulfonyldithiocarbamate(2-) ligand and the potassium cations surrounded by the water molecules. The water molecules interact with the potassium cations forming infinite 2D-layers parallel to the (001) plane at  $z=0$  and  $z=1/2$ , while the 4-fluorophenylsulfonyldithiocarbamate(2-) ligands are alternatively oriented and located almost per-



**Fig. 2.** Coordination environment of K1 (a) and K2 (b) and the molecular arrangement of compound **2** in the unit cell showing the 2D-layers of K1 and K2 surrounded by water at  $z = 0$  and  $1/2$  and the layers of 4-fluorophenylsulfonylethioldithiocarbamate(2-) anions at  $z = 1/4$  and  $3/4$  (c). H atoms are omitted for clarity. Symmetry code: (i)  $-x + 1, -y + 1, -z$ ; (ii)  $x - 1, y, z$ ; (iii)  $-x, -y, -z$ ; (iv)  $x, y + 1, z$ ; (v)  $-x, y + 0.5, -z + 0.5$ ; (vi)  $x + 1, y + 1, z$ .

pendicularly to the (001) plane by their phenyl ring, and also form layers parallel to the (001) plane at  $z = 1/4$  and  $z = 3/4$ . Besides, due to the ionic attraction between the oppositely charged layers, the hydrogen bond between the water molecule (O3) as a donor and the nitrogen atom (N1) as an acceptor is formed (O3–H31...N1, the distance between donor and acceptor and the D–H...A angle are 2.970(3) Å, and 171.5°). This hydrogen bond slightly diminishes the steric effect of the lone pair of electrons at the N atom and leads to a decreased C1–N1–S3 angle by about 3° compared to the gas-phase structure.

The molecular structures of compounds **3** and **4** are shown in Fig. 3a and b, respectively. The crystals are built up from the  $[\text{Pt}(\text{R-SO}_2\text{N}=\text{CS}_2)_2]^{2-}$  anions (R = 4-IC<sub>6</sub>H<sub>4</sub> (**3**) and 4-FC<sub>6</sub>H<sub>4</sub> (**4**)) and two univalent Bu<sub>4</sub>N<sup>+</sup> cations related by the inversion centre at the Pt atom. In both complexes the Pt cation is coordinated by

two symmetrically equivalent dithiocarbamate(2-) ligands into a distorted square-planar configuration. However, in compound **3**, due to mutual orientation of the  $[\text{Pt}(4\text{-IC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)_2]^{2-}$  anions, the iodine atoms of two neighbouring complex anions interact with the central Pt cation forming chains along the  $b$ -axis (Fig. 4a) with the elongated square bipyramid around the Pt cations (average Pt–S distance is 2.319(3) Å, Pt–I, 4.253(1) Å). For a comparison the axial Pt...Br distance in the isostructural 4-BrC<sub>6</sub>H<sub>4</sub>-derivative with a value of 4.249(3) Å [10] indicates significantly weaker interaction between the neighbouring complex anions than in the 4-IC<sub>6</sub>H<sub>5</sub>-derivative due to their ionic radii ( $r_{\text{I}} = 2.20$  Å and  $r_{\text{Br}} = 1.81$  Å) [20]. The bidentate chelation by two sulfur atoms of the dithiocarbamate(2-) ligands to Pt in both complexes makes the S1–C1–S2 angle significantly smaller (~108°) than those found in the parent dipotassium salt (119.5(1)°) in



**Table 5**

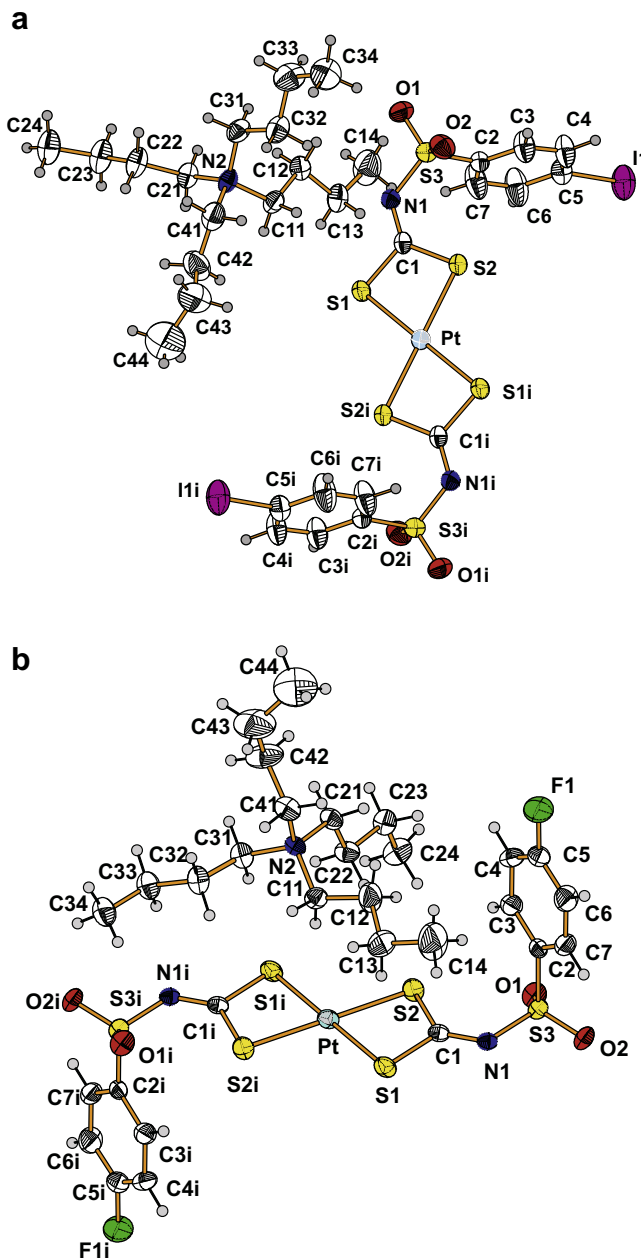
Comparison of the X-ray and gas-phase geometry of the 4-fluorophenylsulfonyldithiocarbamate(2-) anion (in Å, °)

Bonds	X-ray (in <b>2</b> )	X-ray (in <b>4</b> )	Ab initio
C1–S1	1.731(2)	1.732(4)	1.747
C1–S2	1.706(2)	1.739(4)	1.743
C1–N1	1.351(2)	1.299(4)	1.368
N1–S3	1.610(2)	1.615(3)	1.613
S3–O1	1.443(2)	1.435(3)	1.491
S3–O2	1.445(2)	1.434(3)	1.494
S3–C2	1.768(2)	1.764(4)	1.839
C5–F1	1.362(3)	1.364(5)	1.385
S1–C1–S2	119.5(1)	106.9(2)	121.8
S1–C1–N1	114.9(1)	121.6(3)	114.3
S2–C1–N1	125.6(2)	131.5(3)	123.9
C1–N1–S3	122.0(1)	123.2(3)	125.0
N1–S3–O1	114.7(1)	114.4(2)	117.7
N1–S3–O2	104.1(1)	106.2(2)	106.6
N1–S3–C2	108.1(1)	104.9(2)	110.2
O1–S3–O2	114.4(1)	117.5(2)	114.2
O2–S3–C2	107.1(1)	106.4(2)	102.0
S1–C1–N1–S3	178.5(1)	177.7(2)	175.2
Dihedral angle between the S3N1=C1S1S2	98.9(1)	103.2(2)	98.3

which the interaction between the  $K^+$  cations and the dithiocarbamate(2-) ligands is mainly ionic (Table 5). The arrangement of the molecules in the crystal of compound **4** is shown in Fig. 4b, as a packing diagram of the unit cell on the *bc* plane. The square plane of the Pt coordination in the  $[Pt(4-FC_6H_4SO_2N=CS_2)_2]^{2-}$  entities is perpendicular to the (1 0 0) plane and the  $Bu_4N^+$  cations are located on both sides of the anions.

In compounds **3** and **4**, the CS bond lengths are nearly equal and are slightly shorter than typical C–S single bond lengths (ca. 1.815 Å) but longer than typical C=S double bonds (ca. 1.671 Å) [21] due to the partial  $\pi$ -delocalization in the S–C–S group (Scheme 2). Quite similar behaviour is observed in the square-planar palladium(II) and nickel(II) complexes of dithiocarbamates [10,12,22,23]. However, in compound **2** they are slightly different [C1–S1 is 1.731(2) Å and C1–S2 is 1.706(2) Å] (Table 3). This difference can be explained by a balance between the repulsive interactions of the lone-pair of electrons on the nitrogen atom and the S2, as well as between the S1 and the  $RSO_2$  group. When the complexation occurs two factors must be considered. First, the S1–C1–S2 angle decreases, weakening the interactions mentioned above, and diminishing the difference between the C1–S1 and the C1–S2 bond lengths. Another factor is the increasing importance of the canonical form (c) upon complexation, explaining not only a shorter CN bond length in **3** and **4** than in **2**, but also the lower wavenumbers for the  $\nu_{CS_2}$  in the spectra of the complexes when compared with the spectra of the ligands, the higher wavenumbers for the  $\nu_{CN}$  in the spectra of the complexes, and the variation on the chemical shift of the dithiocarbamate group carbon atom signal in the  $^{13}C$  NMR spectra after the complexation (Tables 3 and 4).

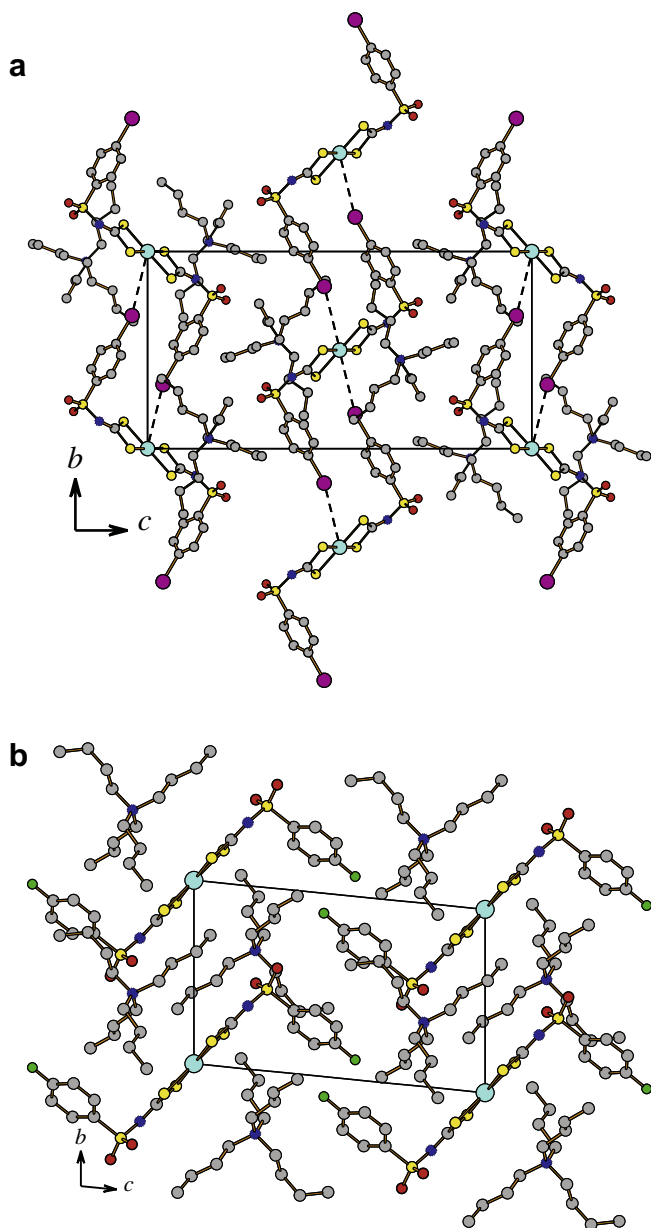
The bond lengths and angles of the tetrabutylammonium cations are in agreement with the expected values (Table 2). However, the torsion angle C41–C42–C43–C44 in the compound **4** is deviated significantly from 180° due to repulsive interaction between the hydrogen atoms of the symmetrically equivalent  $Bu_4N^+$  cations, which are oriented by the terminal methyl group of C44 atom, as well as due to attractive interaction of the H atom of the methyl group with the phenyl ring (C44–H44A  $\cdots \pi$ (phenyl ring)  $\sim 3.2$ ). The conformation of the tetrabutylammonium cation is different from that found in the isostructural Pt-phenyl-derivative dithiocarbamate complex [10] in which all torsion angles of the carbonic chains of the tetrabutylammonium cation are only slightly distorted from the expected value of 180° (Table 2).



**Fig. 3.** View of the molecular structure of compounds **3** (a) and **4** (b) with the labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

#### 4. Conclusion

A new dithiocarbamate anion (4-fluorophenylsulfonyldithiocarbamate) was obtained and its potassium salt was characterized by X-ray diffraction techniques. Besides, two new platinum(II)-bis(dithiocarbamate) complexes were obtained as tetrabutylammonium salts in the crystalline form and their structures were characterized by single crystal X-ray diffraction. The  $Pt^{2+}$  in both complexes is located at the inversion centre and the  $PtS_4$  moiety has a square-planar configuration. Spectroscopic data are consistent with the X-ray experimental results and point to an increase of the contribution of the canonical form (c) to the resonance hybrid upon complexation with a consequent increase of the CN double bond character. Thus, in the IR spectra the wavenumbers of the  $\nu_{CN}$  are smaller for the ligands than for the complexes, and the  $^{13}C$  NMR spectra show that the carbon atom of the dithiocarbamate



**Fig. 4.** Molecular arrangement of the complexes **3** (a) and **4** (b) in the unit cell. H atoms are omitted for clarity.

moiety is more shielded in the complexes than in free ligands. The ionic interaction between the potassium cations and the 4-fluorophenylsulfonyldithiocarbamate dianions does not disturb significantly the conformation of the anionic ligand, while the bidentate chelation by two S atoms of dithiocarbamate group to

Pt cation is more covalent and leads to a decrease on the S1–C1–S2 angle in the ligand.

### Acknowledgement

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### Appendix A. Supplementary data

CCDC 671481, 671482 and 671483 contain the supplementary crystallographic data for **2**, **3** and **4**. 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](mailto:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2008.02.030](https://doi.org/10.1016/j.poly.2008.02.030).

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