



# Syntheses, crystal structure and spectroscopic characterization of novel *N*-*R*-sulfonyldithiocarbamate zinc(II) complexes

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## Abstract

Two new compounds of the general formula:  $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{RSO}_2\text{N}=\text{CS}_2)_2]$ , where  $\text{R} = \text{C}_6\text{H}_5$  (**1**) and  $4\text{-CH}_3\text{C}_6\text{H}_4$  (**2**) were obtained in crystalline form by the reaction of the appropriate potassium *N*-*R*-sulfonyldithiocarbamate ( $\text{RSO}_2\text{N}=\text{CS}_2\text{K}_2$ ) with zinc(II) acetate dihydrate in dimethylformamide. The compounds crystallise in the centrosymmetric space group of the triclinic system with  $Z = 2$ . The single crystal X-ray analysis showed a similarly distorted tetrahedral configuration around the zinc(II) cation due to the bidentate chelation by two sulfur atoms of the *N*-*R*-sulfonyldithiocarbamate ligands. Ionic interaction between oppositely charged moieties, i.e., the bis(*N*-*R*-sulfonyldithiocarbamate)zincate(II) dianion  $[\text{Zn}(\text{RSO}_2\text{N}=\text{CS}_2)_2]^{2-}$  and tetraphenylphosphonium cation  $\text{Ph}_4\text{P}^+$  and van der Waals interactions determine the crystal packing motif. The IR data are consistent with the formation of zinc–dithiocarbamate complexes. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra showed the expected signals for the tetraphenylphosphonium cation and the dithiocarbamate moieties.

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## 1. Introduction

Compounds containing zinc–sulfur-coordinated bonds have a wide range of application. For example, the Zn(II)–dithiocarbamate complexes are worldwide used in the rubber vulcanization process [1–7]. Several dithiocarbamate and *N*-substituted dithiocarbamate complexes and salts have been used as fungicides and pesticides mainly due to their high efficiency in controlling plant fungal diseases and relatively low toxicity [8–15]. 1,1-Dithiolates have been used for the removal of heavy metals cations from the mammalian systems [3,16]. Zinc dithiolates are used in metal organic chemical vapour deposition (MOCVD) processes for the growth of semiconductor ZnS films [17–21]. In all these applications, the use of anionic zinc–sulfur compounds

could be important. Vulcanization is greatly facilitated by the presence of anionic species. For example, vulcanizing mixtures containing  $[\text{Zn}(\text{Me}_2\text{NCS}_2)_3]^-$  are faster accelerators of vulcanization than mixtures containing  $[\text{Zn}(\text{Me}_2\text{NCS}_2)_2]$  [7]. The improvement of the anti-fungi activity is another interesting possibility either by the use of active counter ions or by the variation on the solubility of the salts of the complexes by the use of different cations. The variation on the solubility could also be important in the extraction of toxic metals, like cadmium, from biological systems [22]. In the MOCVD techniques, changing the counter ions could increase the salt volatility favouring an ideal film formation. As the zinc(II)–bisdithiocarbamate complexes are necessarily anionic species, it should be interesting to prepare and study this class of compounds.

Our interest in the syntheses and characterization of dithiocarbamate–metal complexes or salts is due to their similarities with the dithiocarbamate complexes. Earlier

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we have synthesized and characterized three novel nickel(II) complexes with *N*-*R*-sulfonyldithiocarbamate and triphenylphosphine ligands [23]. Here, we investigate two new zinc(II)-bis(*N*-*R*-sulfonyldithiocarbamate) anionic complexes that were isolated as tetraphenylphosphonium salts with the general formula of  $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{RSO}_2\text{N}=\text{CS}_2)_2]$ , where  $\text{R} = \text{C}_6\text{H}_5$  (**1**) and  $4\text{-CH}_3\text{C}_6\text{H}_4$  (**2**). These compounds were obtained in the crystalline form by the reaction of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  with dithiocarbamate anions derived from sulfonamides and tetraphenylphosphonium chloride. The complexes were characterized by the single crystal X-ray diffraction technique and by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

## 2. Experimental

### 2.1. Methods and materials

The solvents were purchased from Merck and used without further purification. The sulfonamides, zinc acetate dihydrate and tetraphenylphosphonium chloride were purchased from Aldrich. Carbon disulfide and potassium hydroxide were purchased from Vetec. The *N*-*R*-sulfonyldithiocarbamate-potassium salts dihydrate were prepared in dimethylformamide from sulfonamides analogously as described in the literature [24,25]. These salts, which are soluble in water and insoluble in most organic solvents, were recrystallized from hot ethanol/water solution. Melting points were determined with Mettler FP5 equipment. Microanalyses for C, H and N were obtained from a Perkin-Elmer 2400 CHN. Zinc was analysed by atomic absorption with a Hitachi Z-8200 Atomic Absorption Spectrophotometer. The elemental analyses of both Zn complexes have been also carried out on an energy dispersive spectrometer. The IR spectra were recorded with a Perkin-Elmer 283 B infrared spectrophotometer using CsI pellets. The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz) NMR spectra were recorded with a Bruker Advance RX-400 spectrophotometer in  $\text{CDCl}_3$  with TMS as internal standard.

### 2.2. Syntheses

The syntheses of the zinc(II)-*N*-*R*-sulfonyldithiocarbamate complexes were performed according to

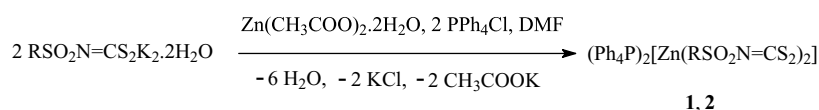
Scheme 1. Zinc(II) acetate dihydrate (0.7 mmol) was added to a suspension of the appropriate potassium *N*-*R*-sulfonyldithiocarbamate dihydrate (1.5 mmol) in DMF (15 mL). The mixture was stirred for 1.5 h at room temperature and filtered. Water (15 mL) and tetraphenylphosphonium chloride (1.5 mmol) were added to the solution obtained. The mixture was stirred for 15 min and the obtained yellowish solid product was filtered, washed with distilled water and dried under reduced pressure for three days, yielding  $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{RSO}_2\text{N}=\text{CS}_2)_2]$  (ca. 60%). Suitable colourless crystals for X-ray structure analysis were obtained after slow evaporation of the solutions of the compounds in dichloromethane/methanol/water.

#### 2.2.1. Bis(tetraphenylphosphonium)bis(*N*-phenylsulfonyldithiocarbamate)zincate(II), $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{S}_2\text{CNSO}_2\text{C}_6\text{H}_5)_2]$ (**1**)

*Elemental analysis*: Found (Calc. for  $\text{C}_{62}\text{H}_{50}\text{N}_2\text{O}_4\text{P}_2\text{S}_6\text{Zn}$ ): C, 61.55 (61.71); H, 4.31 (4.18); N, 2.24 (2.32); O, 5.42 (5.30); P, 5.10 (5.13); S, 15.98 (15.94) and Zn, 5.40 (5.42)%. *m.p.* (°C): 157.5–159.7. *IR* (most intense bands) ( $\text{cm}^{-1}$ ): 1368  $\nu(\text{C}=\text{N})$ ; 1278  $\nu_{\text{ass}}(\text{SO}_2)$ ; 1143  $\nu_{\text{sym}}(\text{SO}_2)$ ; 937  $\nu_{\text{ass}}(\text{CS}_2)$  and 339  $\nu(\text{ZnS})$ .  $^1\text{H}$  NMR ( $\delta$ ): 7.93–7.90 (m, 4H, H2 and H6 (R group)); 7.89–7.56 (m, 40H,  $\text{Ph}_4\text{P}^+$ ); 7.25–7.14 (m, 6H, H3, H4 and H5 (R group)).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ ): 209.76 (N= $\text{CS}_2$ ); 143.42 (C1); 127.52 (C2 and C6); 127.84 (C3 and C5); 130.42 (C4); tetraphenylphosphonium cation signals ( $J$  (Hz)): 117.41 (d,  $J = 88.9$ , C1'); 130.65 (d,  $J = 12.8$ , C2' and C6'); 134.50 (d,  $J = 10.3$ , C3' and C5'); 135.51 (d,  $J = 3.0$ , C4').

#### 2.2.2. Bis(tetraphenylphosphonium)bis(*N*-4-methylphenylsulfonyldithiocarbamate)zincate(II), $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{S}_2\text{CNSO}_2\text{C}_6\text{H}_4\text{CH}_3)_2]$ : (**2**)

*Elemental analysis*: Found (Calc. for  $\text{C}_{64}\text{H}_{54}\text{N}_2\text{O}_4\text{P}_2\text{S}_6\text{Zn}$ ): C, 62.08 (62.25); H, 4.56 (4.41); N, 2.29 (2.27); O, 5.31 (5.18); P, 4.98 (5.02); S, 15.52 (15.58) and Zn, 5.26 (5.29)%. *m.p.* (°C): 167.3–168.7. *IR* (most intense bands) ( $\text{cm}^{-1}$ ): 1383  $\nu(\text{C}=\text{N})$ ; 1277  $\nu_{\text{ass}}(\text{SO}_2)$ ; 1141  $\nu_{\text{sym}}(\text{SO}_2)$ ; 930  $\nu_{\text{ass}}(\text{CS}_2)$  and 330  $\nu(\text{ZnS})$ .  $^1\text{H}$  NMR ( $\delta$ ): 7.83–7.55 (m, 44H, H2, H6 (R group) and  $\text{Ph}_4\text{P}^+$ ), 6.98 (d ( $J = 8.2$  Hz), 4H, H3 and, H5 (R group)) and 2.20 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\delta$ ): 209.29 (N= $\text{CS}_2$ ); 140.46 (C1 and C4); 127.85 (C2 and



**1** (R =  $\text{C}_6\text{H}_5$ )  
**2** (R =  $4\text{-CH}_3\text{C}_6\text{H}_4$ )

Scheme 1.

C6); 128.04 (C3 and C5); 21.31 (CH<sub>3</sub>); tetraphenylphosphonium cation signals ( $J$  (Hz)): 129.33 (d,  $J = 54$ , C1'); 134.29 (t,  $J = 6$ , C2' and C6'); 128.33 (t,  $J = 5$ , C3' and C5'); 130.75 (s, C4').

### 2.3. X-ray crystallography

X-ray intensity data for both crystals were collected using graphite monochromatic Mo K $\alpha$  radiation on a four-circle  $\kappa$ -geometry KUMA KM-4 diffractometer with a two-dimensional area CCD detector (in Department of Crystallography, Institute of Low Temperature and Structural Research, Polish Academy of Science, Wrocław, Poland). The  $\omega$ -scan technique with  $\Delta\omega = 0.75^\circ$  for each image was used for data collection. The 960 images for six different runs covered about 95% of the Ewald sphere. Initially the lattice parameters were refined on about 150 reflections obtained from 40 images for eight runs with different orientation in the reciprocal space. Finally the lattice parameters were refined by least-squares methods based on all the reflections with  $I > 2\sigma(F^2)$ . One image was used as a standard for monitoring the stability of the crystals as well as for monitoring the data collection after every 40 images, and no correction on the relative intensity variation was necessary. Integration of the intensities, correction for Lorenz and polarization effects were performed using a KUMA KM-4 CCD program system [26]. The face-indexed analytical absorption was calculated using the SHELXTL

program [27]. The structures were solved by direct methods using SHELXS of the SHELXL97 program [28]. The calculated E map revealed the Zn, S, P, 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. Difference Fourier maps gave electron density concentrations approximately located for all hydrogen atom positions; these positions were idealised (HFIX 43 for all H atoms of the phenyl rings with isotropic thermal parameters of  $1.2U_{eq}$  of the carbon atoms joined directly to the hydrogen atoms, and HFIX 137 for the CH<sub>3</sub> group in the compound **2** with isotropic thermal parameters of  $1.5U_{eq}$  of the methyl 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 are listed in Table 2.

### 3. Results and discussion

Both compounds in solid state are quite stable at the ambient conditions. They are slightly soluble in water, methanol and ethanol, and are soluble in chloroform and dichloromethane. The ideal mixture of solvents used for crystallization of the compounds is methanol/water with some drops of dichloromethane. The low melting

Table 1  
Crystal data, data collection and refinement details for **1** and **2**

Formula	C <sub>62</sub> H <sub>50</sub> N <sub>2</sub> O <sub>4</sub> P <sub>2</sub> S <sub>6</sub> Zn	C <sub>64</sub> H <sub>54</sub> N <sub>2</sub> O <sub>4</sub> P <sub>2</sub> S <sub>6</sub> Zn
Molecular weight	1206.71	1234.76
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions:		
$a, b, c$ (Å)	11.136(2), 16.273(3), 17.649(4)	9.422(2), 17.582(4), 20.081(4)
$\alpha, \beta, \gamma$ (°)	89.50(3), 79.49(3), 72.20(3)	73.66(3), 82.79(3), 84.60(3)
Volume, $V$ (Å <sup>3</sup> )	2990.3(10)	3160.9(12)
$Z$	2	2
$D_{calc}$ (g/cm <sup>3</sup> )	1.340	1.297
$D_{obs}$ (floatation) (g/cm <sup>3</sup> )	1.34	1.29
Radiation, Mo K $\alpha$ (Å)	0.71073	0.71073
Index range:		
$h$	-14 → 10	-13 → 9
$k$	-20 → 20	-23 → 24
$l$	-22 → 22	-27 → 27
Reflections collected	25,635	29,512
Independent reflections	12,671 ( $R_{int} = 0.0214$ )	15,474 ( $R_{int} = 0.0609$ )
Absorption coefficient, $\mu$ (mm <sup>-1</sup> )	0.721	0.684
Correction:	Lorenz and polarization, absorption, $T_{min} = 0.7515$ , $T_{max} = 0.9058$	Lorenz and polarization, absorption, $T_{min} = 0.832$ , $T_{max} = 0.947$
Refinement on $F^2$		
$R(F^2 > \sigma)$	0.0475	0.0688
$wR(F^2$ all reflections)	0.1107	0.0796
Residual electron density (eÅ <sup>-3</sup> )	-0.513 and +0.762	-0.755 and +1.001

$R = \sum ||F_o| - |F_c|| / \sum F_o$ ,  $wR(F^2) = \{[\sum w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{1/2}$ ,  $w^{-1} = [\sigma^2(F_o^2) + (0.0330P)^2 + 0.9700P]$  for compound **1** and  $w^{-1} = [\sigma^2(F_o^2) + (0.000P)^2 + 0.0000P]$  for compound **2**, where  $P = (F_o^2 + 2F_c^2)/3$ .

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

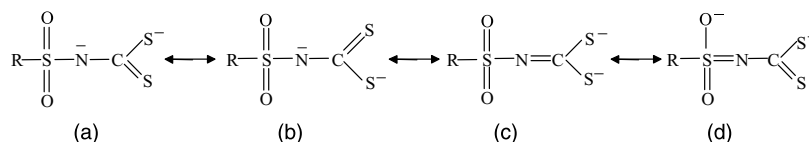
	1	2
<i>Bond lengths</i>		
Zn1–S1	2.344(2)	2.321(2)
Zn1–S2	2.336(2)	2.365(2)
Zn1–S11	2.363(2)	2.321(2)
Zn1–S12	2.320(2)	2.379(2)
S1–C1	1.742(3)	1.758(6)
S2–C1	1.749(4)	1.716(6)
C1–N1	1.297(4)	1.333(6)
N1–S3	1.632(3)	1.621(5)
S3–O1	1.448(3)	1.420(4)
S3–O2	1.432(3)	1.444(4)
S3–C2	1.763(4)	1.773(6)
S11–C11	1.849(5)	1.740(7)
S12–C11	1.714(4)	1.791(6)
C11–N11	1.252(4)	1.313(7)
N11–S13	1.642(4)	1.601(5)
S13–O11	1.381(3)	1.437(4)
S13–O12	1.472(3)	1.478(4)
S13–C12	1.779(4)	1.750(7)
<i>Bond angles</i>		
S1–Zn1–S2	77.73(4)	76.91(6)
S11–Zn1–S12	78.33(5)	77.56(6)
S1–Zn1–S11	134.38(5)	128.45(7)
S2–Zn1–S12	126.78(5)	134.87(7)
S1–Zn1–S12	122.90(5)	121.51(7)
S2–Zn1–S11	124.47(5)	125.77(7)
S1–C1–N1	128.9(3)	128.6(5)
S2–C1–N1	116.5(2)	117.4(5)
S1–C1–S2	114.6(2)	114.0(4)
C1–N1–S3	123.0(2)	119.9(4)
N1–S3–C2	105.2(2)	110.7(3)
N1–S3–O1	113.6(2)	114.6(3)
N1–S3–O2	104.4(2)	102.8(3)
C11–N11–S13	127.0(3)	121.5(5)
S11–C11–N11	124.8(4)	119.2(5)
S12–C11–N11	122.3(4)	127.9(5)
S11–C11–S12	112.2(2)	113.0(4)
N11–S13–C12	102.5(2)	109.0(3)
N11–S13–O11	106.2(2)	101.5(3)
N11–S13–O12	113.2(2)	116.0(3)
O11–S13–O12	116.0(2)	116.7(3)

points are desirable for liquid precursors in the MOCVD techniques. As compounds **1** and **2** have lower melting points (157.5–159.7 and 167.3–168.7 °C, respectively) than either [Zn(Et<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>] (178 °C) or [Zn(Me<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>] (ca. 250 °C) [17], they are potential precursors for ZnS film deposition. Furthermore, lower melting points might be obtained by replacing the Ph<sub>4</sub>P<sup>+</sup> cation by other counter ion.

There are no strong or medium bands in the 1400–1600 cm<sup>-1</sup> region in the IR spectra of the compounds **1**

and **2** as well as in the spectra of the potassium dithiocarbimates related to the compounds. The ν CN band in the spectra of the potassium dithiocarbimates is observed at around 1260 cm<sup>-1</sup> [29]. This low value indicates a great contribution of the canonical form (a) and (b) for the resonance hybrid in the dithiocarbamate potassium salts (Scheme 2). A strong band at 1368 and 1383 cm<sup>-1</sup> observed in the spectra of the compounds **1** and **2**, respectively, is assigned to the νC=N vibration of the RSO<sub>2</sub>N=CS<sub>2</sub> group. In the spectral region of 1300–1100 cm<sup>-1</sup> two vibrational bands are observed. They are assigned to the sulfonyl SO<sub>2</sub> group: one band at lower frequency is assigned to the symmetric vibration mode of the sulfonyl group – ν<sub>sym</sub>(SO<sub>2</sub>) (1143 and 1141 cm<sup>-1</sup> in the spectrum of **1** and **2**, respectively) and one at higher frequency (1278 and 1277 cm<sup>-1</sup> in **1** and **2**, respectively) is assigned to the asymmetric ν<sub>ass</sub>(SO<sub>2</sub>). The spectral region of 1000–900 cm<sup>-1</sup> is characteristic for the disulfuric chelation [30]. The ν<sub>ass</sub>CS<sub>2</sub> was observed at higher frequency in the spectra of the potassium salts of dithiocarbimates (ca. 955 cm<sup>-1</sup>) [29] than that in the spectra of the compounds here studied (937 and 930 cm<sup>-1</sup> for **1** and **2**, respectively). The shifts observed in the ν<sub>ass</sub>CS<sub>2</sub> and νCN in the spectra of the compounds here studied, when compared with the spectra of the ligands, are consistent with the increased importance of the canonical form (c) in both Zn complexes (Scheme 2). The spectra of the compounds also show the expected medium band in the 300–400 cm<sup>-1</sup> range assigned to the Zn–S stretching vibration indicating the *gem*-disulfur ligand [31]. Only one band being observed in the spectral region of Zn–S stretching vibration may be explained by the fact that the differences between the Zn–S bond lengths are relatively small, as shown by the X-ray single crystal analysis.

The NMR spectra showed the expected signals for the compounds. The <sup>1</sup>H NMR spectra showed the signals for the hydrogen atoms of the tetraphenylphosphonium cation. The remaining signals could be assigned to the CH<sub>3</sub> group of the aromatic moiety and the other aromatic hydrogen atoms. The integration curves on the <sup>1</sup>H NMR spectra were consistent with a 2:1 proportion between the tetraphenylphosphonium cation and the bis(*N*-R-sulfonyldithiocarbimate)zincate(II) dianions. The signals of the free *N*-R-sulfonyldithiocarbimates [29] and those of the *N*-R-sulfonyldithiocarbimate moieties of the compounds here studied show approximately the same chemical shifts. The <sup>13</sup>C NMR spectra showed, for both compounds, only five signals assigned to the dithiocarbimate moiety (the signals of C1 and C4 of compound **2**



Scheme 2.

were superimposed). This fact points to a magnetic equivalence of the corresponding atoms in both dithiocarbamate ligands in each compound in solution. The chemical shifts of the aromatic carbon atoms of the dithiocarbamate anions in the compounds are similar to those of the corresponding sulfonamides [32]. The  $\text{N}=\text{CS}_2$  (C1) signal is shifted in the spectra of the complexes to higher field if compared to the spectra of the ligands. Although the solvents are necessarily different, this shift is expected. If the canonical form (c) (Scheme 2) is more important for the complexes than for the ligands, then the C1 carbon atom is expected to be more shielded in the complexes.

The X-ray single crystal analysis of the two ionic complexes here studied are the first examples of this type of dithiocarbamate structures. The molecular structures of  $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{S}_2\text{CNSO}_2\text{C}_6\text{H}_5)_2]$  (**1**) and  $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{S}_2\text{CNSO}_2\text{C}_6\text{H}_4\text{CH}_3)_2]$  (**2**) are shown in Figs. 1(a) and (b), respectively. In both compounds the zinc atom is coordinated by four sulfur atoms of two *N*-*R*-sulfonyldithiocarbamate ligands into a similarly distorted tetrahedral configuration due to the chelating effect of the ligands, which is clearly manifested in the S—Zn—S angles. The two S—Zn—S angles containing both sulfur atoms of the same *N*-*R*-sulfonyldithiocarbamate chelating ligand (S1 and S2 or S11 and S12) are significantly

smaller, while the remaining four S—Zn—S angles containing the sulfur atoms of two *N*-*R*-sulfonyldithiocarbamate chelating ligands are significantly greater than the angles observed for ideal  $\text{ZnS}_4$  tetrahedral geometry ( $\sim 109.3^\circ$ ). The  $\text{ZnS}_4$  coordination polyhedron is additionally distorted due to the interaction with the large tetraphenylphosphonium cations that can be illustrated by the deviation from  $90^\circ$  (in an ideal tetrahedral) of the dihedral angle between the Zn1, S1, S2 and Zn1, S11, S12 planes. This angle is equal to  $83.4(3)$  and  $82.0(3)$  in compound **1** and **2**, respectively. The slightly greater deviation of the dihedral angle from  $90^\circ$  for the compound **2** can be explained by the stereochemistry affecting the large  $\text{Ph}_4\text{P}^+$  cations that interact with the *p*- $\text{CH}_3$  group of the *N*-*R*-sulfonyldithiocarbamate chelating ligands coordinated to the Zn atom. The *N*-*R*-sulfonyldithiocarbamate dianion  $(\text{RSO}_2\text{N}=\text{CS}_2)^{2-}$  as bidentate ligands form stable four membered rings by chelation through the two sulfur atoms ( $\text{ZnS}_2\text{C}$ ).

The four Zn—S bond lengths are ranging from  $2.320(2)$  to  $2.363(2)$  Å for compound **1** and they are compared with those observed in compound **2** ( $2.337(2)$ – $2.377(2)$  Å). The C1—N1 and C11—N11 bond lengths of  $1.297(4)$  and  $1.252(4)$  Å, respectively, in compound **1** are shorter than in the *N*-phenylsulfonyldithiocarbamate potassium salt ( $\text{C}_6\text{H}_5\text{SO}_2\text{N}=\text{CS}_2\text{K}_2$ ) ( $1.342(9)$  Å) [25] and than those found in compound **2** ( $1.333(6)$  and  $1.313(7)$  Å, respectively). These values are shorter than the normal single  $\text{C}(\text{sp}^2)$ — $\text{N}(\text{sp}^2)$  bond length (ca.  $1.35$  Å). In compound **1** the C—N bond lengths are similar to that of the double bond  $\text{C}(\text{sp}^2)=\text{N}(\text{sp}^2)$  ( $1.273$ – $1.295$  Å) [33,34], while in compound **2** the double character of this C—N bond decreases. The C—S bond lengths of both dithio  $\text{CS}_2$  chelating groups are very similar (average value of  $1.748^\circ$ ) and are slightly shorter than the typical C—S single bond length (ca.  $1.81$  Å) due to partial  $\pi$ -delocalization in the S—C—S groups. The S1—C1—N1 and S11—C11—N11 angles are significantly greater than S2—C1—N1 and S12—C11—N11 due to the interaction between the  $\text{SO}_2\text{R}$  groups and S1 and S11 atoms, which are joined in *cis* positions in relation to the C1—N1 and C11—N11 bonds. The steric effect of the phenylsulfonyl or 4-methyl-phenylsulfonyl ( $\text{RSO}_2$ ) groups are greater than the effect of the non-bonding lone-pair of electrons at the N1 and N11 atoms, since the C1—N1—S3 and C11—N11—S13 angles are greater than  $120^\circ$  in both complexes. If the group linked to the N atom is small such as  $-\text{SO}_2\text{CH}_3$  [35] or  $-\text{C}\equiv\text{N}$  [36] groups the non-bonding effect of the lone-pair of electrons predicted by the valence-shell electron pair repulsion theory (VSEPR) [37,38] is greater than the steric effect of these groups.

The Zn1, S1, S2, C1, N1, S3 (plane 1) and Zn1, S11, S12, C11, N11, C13 (plane 2) fragments of the bis(*N*-*R*-sulfonyldithiocarbamato)zincate(II) dianion are almost planar, the greatest deviations of atoms from the

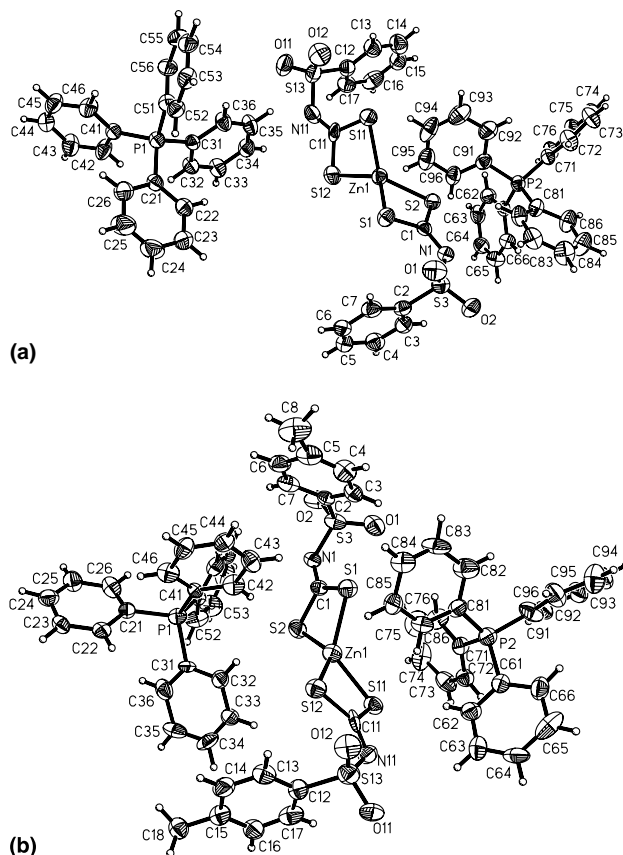


Fig. 1. View of the molecular structure of compounds **1** (a) and **2** (b).

weighted mean plane through the fragments are smaller than  $\pm 0.1$  Å. The dihedral angle between the above-mentioned planes (1 and 2) is equal to  $81.5(3)^\circ$  and  $84.6(3)^\circ$  in compounds **1** and **2**, respectively. The planar C2–C7 phenyl ring is inclined by about  $91.5(3)^\circ$  to plane 1 and the second C12–C17 phenyl ring is inclined by  $87.4(3)^\circ$  to plane 2 in compound **1**, and the equivalent angles in compound **2** are  $79.9(3)^\circ$  and  $87.5(3)^\circ$ , respectively. The C1–N1–S3–C2 and N1–S3–C2–C3 torsion angles for one *N*-*R*-sulfonyldithiocarbamate ligand and the torsion angles of C11–N11–S13–C12 and N11–S13–C12–C13 for the second ligand describe the conformation of the ligands along the N1–S3 or N11–S13 bonds (see Fig. 1a) and the orientation of the planar phenyl rings (the second torsion angles). These angles are equal to  $68.1(3)^\circ$  and  $61.7(3)^\circ$  for the first ligand and  $66.7(3)^\circ$  and  $-124.1(3)^\circ$  for the second ligand in compound **1**. The corresponding torsion angles in compound **2** (see Fig. 1(b)) are equal to  $-63.4(3)^\circ$  and  $113.2(3)^\circ$  for one ligand and  $67.7(3)^\circ$  and  $-129.5(3)^\circ$  for the second ligand, respectively. Thus the conformation of the ligands along N1–S3 and N11–S13 in the compound **1** is similar [ $68.1(3)^\circ$  and  $66.7(3)^\circ$ ] and in compound **2** the conformation of one ligand [along N1–S3,  $-63.4(3)^\circ$ ] is opposite to the other ligand [along N11–S13,  $113.2(3)^\circ$ ].

The sulfonyl S3 and S13 atoms of both *N*-*R*-dithiocarbamate ligands have an expected distorted tetrahedral geometry. The O1–S3–O2 and O11–S13–O12 angles are significantly greater than the value for ideal tetrahedral geometry due to the steric effect of lone-pairs of electrons on both oxygen atoms. The S3–O1 and S3–O2 bond lengths indicate their double bond character (S=O); a typical distance of the double S=O bond ranges from 1.418 to 1.442 Å [34,36]. The difference between the S13–O11 and S13–O12 bonds in compound **1** [1.381(3) and 1.472(3) Å] is more obvious than in compound **2** in which all S–O distances in the sulfonyl –SO<sub>2</sub>R groups are as expected. The chemically equivalent S–O bond lengths of both *N*-*R*-sulfonyldithiocarbamate ligands in the compound **2** are very similar, however in the compound **1** the differences between the corresponding bonds of both *N*-*R*-sulfonyldithiocarbamate ligands, especially the above-mentioned S13–O11 and S13–O12 bonds are greater. These differences can be explained by the slightly single character of the S13–O12 bond (1.472(3) Å, this value is slightly longer than the normal double S=O bond) with shortening the other S13–O11 bond in the sulfonyl SO<sub>2</sub> group. These S–O distances indicate a contribution of the canonical form (d) (Scheme 2) in one of the *N*-*R*-sulfonyldithiocarbamate ligands in compound **1**. The observed differences between the S–O bonds of the *N*-*R*-sulfonyldithiocarbamate ligand in the X-ray experiment might be due to the greater anisotropic thermal parameters of S13, O11 and O12 in comparison to the

other sulfonyl group (S3, O1, O2) indicating the possibility of disorder. However, when used for the sulfonyl group (atoms S13, O11, S12) some disorder models were not successful, thus the greater anisotropic thermal parameters (in relation to the other SO<sub>2</sub> group) indicate rather on the greater molecular motion. The calculated corrections of the S13–O11 and S13–O12 bond lengths using the Schomaker and Trueblood [39] procedure for the librations indicate that the corrections of the S–O bond lengths are not greater than  $\pm 0.02$  Å. Thus, most probably, as suggested before, the difference between the S–O distances could be explained by the slightly single character of the S13–O12 bond as shows the resonance hybrid (d) (Scheme 2). The S3–C2 and S13–C12 bonds with distances of 1.763(4) and 1.779(4) Å in compound **1** and 1.773(6) and 1.750(7) Å in compound **2**, respectively, correlate well with the distances of 1.749–1.798 Å for C<sub>ar</sub>–S bonds in related complexes which comprise the C<sub>ar</sub>–SO<sub>2</sub>–N fragment [34]. The S3–N1 and S13–N11 bond lengths with the average distance of 1.624 Å indicate a single bond nature; the typical value of the N(sp<sup>2</sup>)–S bond distance is 1.623–1.659 Å [34].

The arrangement of the molecules in the crystal **1** and **2** (see Figs. 2(a) and (b)) is mainly determined by the ionic interaction of the oppositely charged moieties, i.e., bis(*N*-*R*-sulfonyldithiocarbamate)zincate(II) dianion and tetraphenylphosphonium cations and by the van der

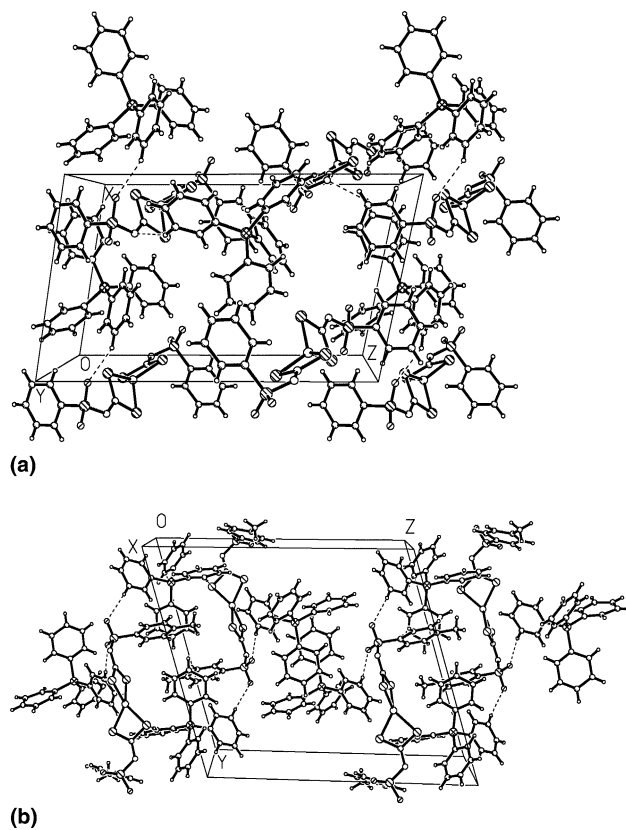


Fig. 2. Molecular arrangements of compounds **1** (a) and **2** (b) in the unit cells.

Waals forces. The structures are slightly stabilized by the weak C—H···O and C—H···N interactions with the C···O and C···N distances of approximately 3.33 and 3.45 Å in the crystal of **1** and 3.44 and 3.30 Å in the crystal of **2**, respectively. Although in both crystals the C—H···O and C—H···N interactions are weak, we suppose that they are important for the crystal packing. The usually weak C—H···N and C—H···O hydrogen bonds play a significant role in the formation and stabilisation of supramolecular architectures, especially in biological systems. The formation of a non-covalent association of proteins and ligands, formation of a phospholipid bilayer, interaction of a transcription factor with DNA, and folding of a tRNA into its three-dimensional conformation are examples of processes that depend on noncovalent weak C—H···O and C—H···N interactions [40]. As can be seen from the crystal packing (Fig. 2) the hydrophobic phenyl rings of the Ph<sub>4</sub>P<sup>+</sup> cations are located close on both sides of the polar (hydrophilic) sulfonyl groups. This arrangement together with the weak C—H···O and C—H···N interactions are responsible for the observed only slightly solubility of these complexes in polar solvents like water, methanol or ethanol, as well as for the relatively low melting point.

#### 4. Conclusion

Two novel anionic zinc(II) complexes with dithiocarbimates were obtained. Their tetraphenylphosphonium salts were isolated in crystalline form and characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR and by single crystal X-ray diffraction techniques. The single crystal X-ray analysis and spectroscopic data show interesting correlations. The frequency value of the IR νC=N vibration observed in the spectrum of compound **1** is greater than that observed for the free ligand (around 1260 cm<sup>-1</sup>) [29]. This observation is in agreement with the suggestion that the C—N bond in the free ligand is more single (C—N, 1.342(9) Å [25]) and after complexation the double character of this C—N bond increases. The NMR spectra show that carbon atoms C1 and C11 of the *N*-R-sulfonyldithiocarbimate ligand of compound **1** are more shielded than that of the parent ligands [29]. This fact is in accordance with an increase of the contribution of the canonical form (c) (Scheme 2) to the resonance hybrid from the free ligand to the Zn-complexes, and consequently with the increase of the C—N double bond character.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC Nos. 201751 and 201752 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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