

Synthesis, structural and spectroscopic characterization of novel zinc(II) complexes with *N*-methylsulfonyldithiocarbimato and *N*-methylsulfonyltrithiocarbimato ligands

Marcelo R.L. Oliveira ^{a,*}, Genivaldo J. Perpétuo ^b, Jan Janczak ^c, Mayura M.M. Rubinger ^a

^a Departamento de Química, Universidade Federal de Viçosa, Viçosa, Minas Gerais, CEP 36571-000, Brazil

^b Departamento de Física, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, Ouro Preto MG, CEP 35400-000, Brazil

^c Institute of Low Temperature and Structure Research, Polish Academy of Science, P.O. Box 1410, 50-950 Wrocław, Poland

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Abstract

Two new zinc(II)-complexes, dithiocarbimato $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_2)_2]$ (**1**) and trithiocarbimato $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_3)_2]$ (**2**), were obtained in the crystalline form by the reaction of potassium *N*-methylsulfonyldithiocarbamate ($\text{RSO}_2\text{N}=\text{CS}_2\text{K}_2$) with zinc(II) acetate dihydrate and tetraphenylphosphonium chloride in dimethylformamide. Both complexes crystallize in the monoclinic system. The central Zn(II) ion has a distorted tetrahedral coordination in both compounds. In **1** the dithiocarbimato ligand coordinates via two S atoms while in **2** the trithiocarbimato ligand coordinates via S and N atoms. Both complexes were also characterized by IR, ¹H NMR and ¹³C NMR spectroscopies. Compound **2** is the first example of a zinc(II)-trithiocarbimato complex.

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1. Introduction

Compounds containing zinc–sulfur-coordinated ligands have a wide range of applications. For example, several dithiocarbamate complexes and salts have been used as fungicides mainly due to their high efficiency in controlling plant fungal diseases, showing relatively low toxicity [1–7]. Furthermore, zinc(II)–dithiocarbamate complexes are worldwide used in the vulcanization process [7–14]. Anionic zinc(II)–dithiocarbamate complexes are also active, and the $[\text{Zn}(\text{R}_2\text{NCS}_2)_3]^-$ ($\text{R} = \text{CH}_3\text{CH}_2$) was found to be a fast accelerator for rubber vulcanization [8]. Zinc(II)–polythiocarbamate complexes that have one or more sulfur atoms inserted in the zinc–dithiocarbamate bond such as $[\text{Zn}(\text{Me}_2\text{NCS}_3)_2]$ are very important intermediates in the vulcanization process [8]. It is also known that correlate

nickel(II)–bis(dithiocarbimato) complexes are anionic species, which can also react with sulfur [15,16]. Considering these facts we decided to prepare and study zinc(II) analogues. In a recent work we reported on the structures of compounds $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{C}_6\text{H}_5\text{SO}_2\text{N}=\text{CS}_2)_2]$ and $(\text{Ph}_4\text{P})_2[\text{Zn}(4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)_2]$ that contain dithiocarbamate anions from aromatic sulfonamides [17].

In the present work, we investigate two new tetraphenylphosphonium salts of anionic zinc(II) complexes with dithio and trithiocarbamate: $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_2)_2]$ (**1**) and $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_3)_2]$ (**2**). To our knowledge **2** is the first example of a zinc(II)-trithiocarbimato complex.

2. Experimental

2.1. Methods and materials

The solvents were purchased from Merck and used without further purification. The methanesulfonamide, zinc

* Corresponding author. Tel.: +55 31 3899 3059; fax: +55 31 3899 3065.
E-mail address: marcelor@ufv.br (M.R.L. Oliveira).

acetate dihydrate and tetraphenylphosphonium chloride were purchased from Aldrich. Carbon disulfide and potassium hydroxide were purchased from Vetec. The *N*-methylsulfonyldithiocarbamate potassium salt dihydrate was prepared in dimethylformamide from methanesulfonamide analogously as described in the literature [18,19]. Melting point was determined with a Mettler FP5 equipment. Microanalyses for C, H and N were obtained from a Perkin–Elmer 2400 CHN elemental analyzer. Zinc was analyzed by atomic absorption with a Hitachi Z-8200 Atomic Absorption Spectrophotometer. The IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded with a Perkin–Elmer 283 B infrared spectrophotometer using CsI pellets. Far-IR spectra ($550\text{--}100\text{ cm}^{-1}$) were recorded on a Bruker-IFS 113 V FT-IR spectrometer (polyethylene disks). The ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded with a Bruker Advance DRX-400 spectrophotometer in CDCl_3 with TMS as internal standard.

2.2. Syntheses

Zinc(II) acetate dihydrate (0.7 mmol) was added to a suspension of potassium *N*-methylsulfonyldithiocarbamate 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) was added to the solution obtained. The mixture was stirred for 15 min and the solid product was filtered, washed with distilled water and dried under reduced pressure for 1 day. The solid product was resolved in a mixture dichloromethane/methanol/water. After slowly evaporation of the solution two different crystals were obtained. The transparent colourless crystals are bis(tetraphenylphosphonium) bis(*N*-methylsulfonyldithiocarbamate)zincate(II): $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_2)_2]$ (**1**) (ca. 60%) while the other yellow crystals are bis(tetraphenylphosphonium) bis(*N*-methylsulfonyltrithiocarbamate)zincate(II): $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_3)_2]$ (**2**) (ca. 40%).

Elemental analysis for (**1**): found (calculated for $\text{C}_{52}\text{H}_{46}\text{N}_2\text{O}_4\text{P}_2\text{S}_6\text{Zn}$): C, 57.31 (57.69); H, 4.40 (4.28); N, 2.68 (2.59); O, 5.98 (5.91); P, 5.81 (5.72); S, 17.69 (17.77); Zn, 6.14 (6.04). Mp ($^\circ\text{C}$): 187.8–189.1 with decomposition. IR (most intense bands) (cm^{-1}): 1375 $\nu(\text{C}=\text{N})$; 1286, 1273 $\nu_{\text{ass}}(\text{SO}_2)$; 1131 $\nu_{\text{sym}}(\text{SO}_2)$; 957, 947, 936, 925 $\nu_{\text{ass}}(\text{CS}_2)$ and 328 $\nu(\text{ZnS})$; most intense tetraphenylphosphonium cation bands: 1437, 1108, 997, 763, 724, 692, 528. ^1H NMR (δ): 7.84–7.63 (m, 40H, Ph_4P^+); 2.96 (s, 6H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (δ): 208.71 ($\text{N}=\text{CS}_2$); 39.30 (CH_3); tetraphenylphosphonium cation signals (J (Hz)): 117.38 (d, $J = 88.9$, C1); 130.70 (d, $J = 12.8$, C2 and C6); 134.44 (d, $J = 10.3$, C3 and C5); 135.62 (d, $J = 3.0$, C4).

Elemental analysis for (**2**): found (calculated for $\text{C}_{52}\text{H}_{46}\text{N}_2\text{O}_4\text{P}_2\text{S}_8\text{Zn}$): C, 54.52 (54.47); H, 4.02 (4.00); N, 2.39 (2.44); O, 5.62 (5.58); P, 5.38 (5.42); S, 22.33 (22.37); Zn, 5.75 (5.71). Mp ($^\circ\text{C}$): 185.8–187.4 with decomposition. IR (most intense bands) (cm^{-1}): 1374 $\nu(\text{C}=\text{N})$; 1288, 1271 $\nu_{\text{ass}}(\text{SO}_2)$; 1132 $\nu_{\text{sym}}(\text{SO}_2)$; 959, 948, 924 $\nu(\text{CS}_3)$; 505 $\nu(\text{S}=\text{S})$;

431 $\nu(\text{ZnN})$ and 334 $\nu(\text{ZnS})$; most intense tetraphenylphosphonium cation bands: 1437, 1109, 998, 764, 723, 693, 527. ^1H NMR (δ): 7.84–7.63 (m, 40H, Ph_4P^+); 2.99 (s, 6H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (δ): 208.78 ($\text{N}=\text{CS}_2$); 39.10 (CH_3); tetraphenylphosphonium cation signals (J (Hz)): 117.38 (d, $J = 88.9$, C1); 130.70 (d, $J = 12.8$, C2 and C6); 134.44 (d, $J = 10.3$, C3 and C5); 135.62 (d, $J = 3.0$, C4).

2.3. X-ray crystallography

X-ray intensity data for both crystals were collected using graphite monochromatic $\text{Mo K}\alpha$ radiation on a four-circle κ -geometry KUMA KM-4 diffractometer with a two-dimensional area CCD detector at room temperature. The ω -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 were performed. 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 $I > 2\sigma(I^2)$. 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 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 [20]. The face-indexed analytical absorption was calculated using the SHELXTL program [21]. The structures were solved by direct methods using the SHELXS of the SHELXL97 program [22]. 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 atoms positions; these positions were idealized (HFIX 43 for all H atoms of the phenyl rings with isotropic thermal parameters of $1.2U_{\text{eq}}$ of the carbon atoms joined directly to the hydrogen atoms, and HFIX 137 for the CH_3 group in the compound **2** with isotropic thermal parameters of $1.5U_{\text{eq}}$ 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 and torsion angles are listed in Table 2.

3. Results and discussion

Compounds **1** and **2** are quite stable in the solid state at the ambient conditions. They are insoluble in water, slightly soluble in ethanol and are soluble in methanol, chloroform and dichloromethane. Compounds **1** and **2** were obtained by recrystallization of the crude product. The obtained crystals have different colours (colourless

Table 1
Crystallographic data and structure refinement parameters

Crystal data	1	2
Formula	C ₅₂ H ₄₆ N ₂ O ₄ P ₂ S ₆ Zn	C ₅₂ H ₄₆ N ₂ O ₄ P ₂ S ₈ Zn
Molecular weight (g mol ^{−1})	1082.58	1146.70
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)
Lattice parameters		
<i>a</i> , <i>b</i> , <i>c</i> (Å)	28.344(6), 7.623(2), 24.506(5)	24.934(5), 11.648(2), 19.351(4)
β (°)	106.40(3)	110.60(3)
Volume, <i>V</i> (Å ³)	5080(2)	5261(2)
<i>Z</i>	4	4
<i>D</i> _{Calc.} ; <i>D</i> _{Obs.} (flotation) (g cm ^{−3})	1.416; 1.41	1.448; 1.44
Radiation, λ (Å)	Mo K α (0.71073)	
Absorption coefficients μ (mm ^{−1})	0.840	0.892
Transmission factor, <i>T</i> _{max} ; <i>T</i> _{min}	0.901; 0.792	0.942; 0.825
Data collection		
<i>h</i> , <i>k</i> , <i>l</i> Range	−38 to 39, −10 to 7, −32 to 33	−34 to 32, −15 to 15, −24 to 26
Collected reflections	46801	25033
Unique reflections	13081	6873
Observed reflections (>2 σ (<i>I</i>))	5826	2778
Refinement		
<i>R</i> (<i>F</i> _o ² > 2 σ (<i>F</i> _o ²))	0.0479	0.0464
<i>wR</i> (<i>F</i> _o ² , all reflections) ^{a,b}	0.0851	0.0648
$\Delta\rho_{\min}$; $\Delta\rho_{\max}$ (e Å ^{−3})	−0.573; +0.785	−0.924; +0.406
Goodness-of-fit(<i>S</i>)	1.012	1.003

^a $w = 1/[\sigma^2(F_o^2) + (0.0150P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$.

^b $w = 1/[\sigma^2(F_o^2) + (0.0063P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$.

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

Compound 1		Compound 2	
Zn1–S1	2.360(1)	Zn1–S4	2.285(1)
Zn1–S2	2.321(1)	Zn1–S5	2.021(2)
S1–C1	1.725(3)	S4–C3	1.726(3)
S2–C1	1.722(3)	S5–C3	1.750(4)
C1–N1	1.319(4)	C3–N2	1.295(4)
N1–S3	1.621(3)	N2–S6	1.626(3)
S3–O1	1.428(2)	S6–O3	1.429(2)
S3–O2	1.442(2)	S6–O4	1.446(2)
S3–C2	1.758(3)	S6–C4	1.760(3)
S1–Zn1–S2	76.81(4)	S4–Zn1–S5	76.44(4)
S1–C1–S2	115.0(2)	S4–C3–S5	114.1(2)
S1–C1–N1	127.8(2)	S5–C3–N2	127.0(3)
S2–C1–N1	117.1(2)	S4–C3–N2	118.9(3)
C1–N1–S3	123.1(2)	C3–N2–S6	124.9(2)
O1–S3–O2	115.9(1)	O3–S6–O4	115.9(2)
O1–S3–N1	114.2(1)	O3–S6–N2	109.5(2)
O1–S3–N1–C1	51.3(2)	O3–S6–N2–C3	−86.3(2)
O2–S3–N1	105.9(2)	O4–S6–N2	115.1(1)
O2–S3–N1–C1	180.0(2)	O4–S6–N2–C3	46.3(2)
C2–S3–N1	106.1(2)	C4–S6–N2	98.8(2)
C2–S3–N1–C1	−67.1(2)	C4–S6–N2–C3	159.6(2)
		S4–Zn1–N1	92.9(1)
		S4–Zn1–S4 ⁱ	117.7(1)
		N1–Zn1–N1 ⁱ	125.2(1)
		S3–C2–S2	112.0(2)
		S3–C2–N1	131.7(3)
		O1–S1–O2	117.9(1)
		O1–S1–N1	112.7(1)
		O1–S1–N1–C2	56.4(2)
		O2–S1–N1	104.3(1)
		O2–S1–N1–C2	−174.6(2)
		C1–S1–N1	106.3(2)
		C1–S1–N1–C2	−61.9(2)

Symmetry operation code i: $-x, y, 1/2 - z$.

and yellow) and morphologies, therefore it was possible to separate and characterize them. All intense bands of the Ph₄P⁺ ion vibrations are present in the infrared spectrum of both **1** and **2** compounds. In the spectrum of **1** a strong

band at 1375 cm^{−1} was assigned to the ν CN vibration of the RSO₂NC group. Some vibrational bands due to the SO₂ group are observed between 1300 and 1100 cm^{−1}. A multiple band centred at 936 cm^{−1} observed in the

spectrum of **1** was assigned to $\nu_{\text{ass}}\text{CS}_2$. The spectrum also shows the expected band at 328 cm^{-1} assigned to the ZnS stretching vibration [23]. The IR spectrum of the complex **2** is similar to the spectrum of the compound **1** and shows some additional bands. The band at 505 cm^{-1} was assigned to $\nu(\text{S}-\text{S})$. Due to N and S coordination of the trithiocarbamate ligand to Zn in **2** the band at 431 was assigned to $\nu(\text{ZnN})$.

The ^1H NMR spectra of the compounds **1** and **2** showed the expected signals for the hydrogen atoms of the tetra-

phenylphosphonium cation, and the hydrogen atoms of the CH_3 group. The integration curves were consistent with a 2:1 proportion between the tetraphenylphosphonium cation and the bis(*N*-methylsulfonyldithiocarbamate)zincate(II) or bis(*N*-methylsulfonyltrithiocarbamate)zincate(II) anions.

The ^{13}C NMR spectra of the compounds **1** and **2** showed the expected doublets for the signals of the tetraphenylphosphonium cation in the aromatic region. The signal at $208.71\text{ }\delta$ in the spectrum of **1**, assigned to the dithiocarbamate group (NCS_2), was observed in the same region of other zinc(II)-*R*-sulfonyldithiocarbamate complexes [17]. The methyl group signal of compound **1** was observed at $39.30\text{ }\delta$. The ^{13}C NMR spectrum of the compound **2** shows signals at 208.78 and $39.10\text{ }\delta$, which were assigned to the carbons of the NCS_3 and CH_3 groups.

The molecular structures of **1** and **2** are shown in Figs. 1 and 2, respectively. In both compounds the central Zn(II) atom has a distorted tetrahedral coordination. The asymmetric unit of **1** consists of two chemical equivalents but crystallographically independent *N*-methylsulfonyldithiocarbamate ligands coordinated to the Zn atom, and two tetraphenylphosphonium cations. The *N*-methylsulfonyldithiocarbamate ligands have similar bond lengths but different bond angles and torsion angles (Table 2) due to the interactions with the adjacent cations (Fig. 1). The distortion from the ideal tetrahedral geometry around Zn(II) in **1** is due to the coordination by the two sulfur atoms of each chelating ligand leading to the considerably smaller $\text{S1}-\text{Zn1}-\text{S2}$ and $\text{S4}-\text{Zn1}-\text{S5}$ bond angles when compared to the other $\text{S}-\text{Zn}-\text{S}$ bond angles. The two $\text{Zn}-\text{S}_2-\text{C}$ four membered rings are almost planar with a dihedral angle of $79.1(1)^\circ$. The average value of $1.731\text{ }\text{\AA}$ for the C–S bonds within the rings is similar to those observed for other Ni(II) and Zn(II) *N*-*R*-sulfonyldithiocarbamate complexes [17,24]. The average length of $2.349\text{ }\text{\AA}$ for the Zn–S bonds are also in the range of analogous Zn(II) complexes [17]. The chemical equivalent and crystallographic independent C1–N1 and C3–N3 bond lengths are equal within three e.s.d. and

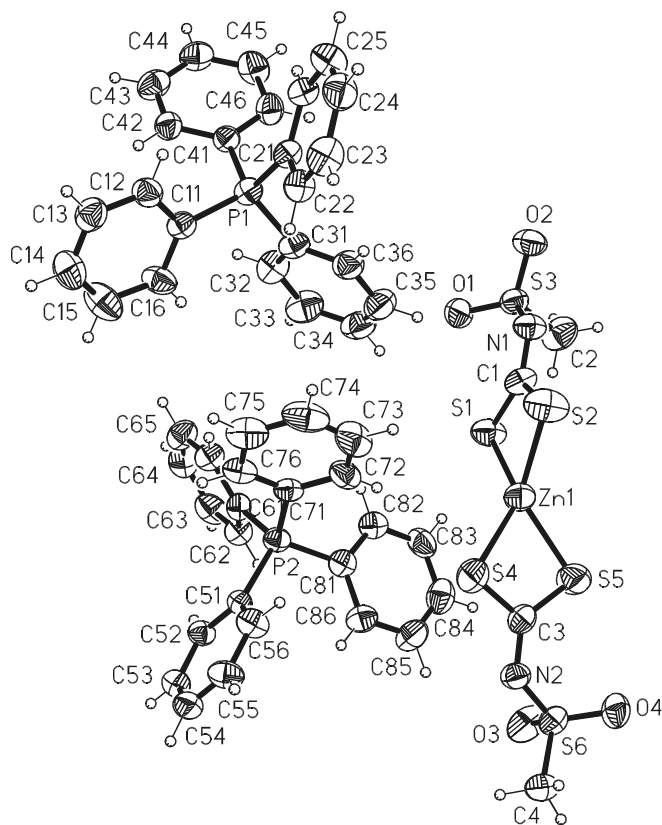


Fig. 1. X-ray molecular structure of tetraphenylphosphonium bis-(*N*-methylsulfonyldithiocarbamate)zincate(II).

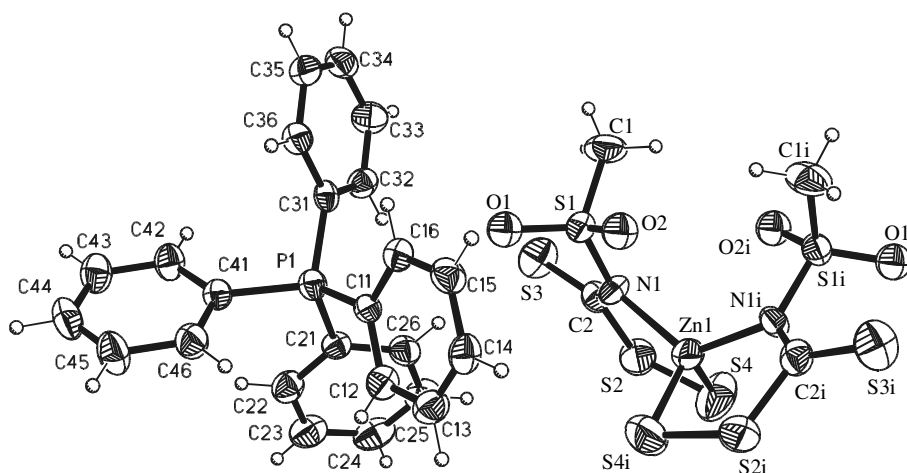
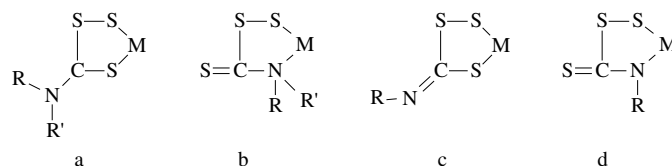


Fig. 2. X-ray molecular structure of tetraphenylphosphonium bis(*N*-methylsulfonyltrithiocarbamate)zincate(II), symmetry code: $i = -x, y, 1/2 - z$.

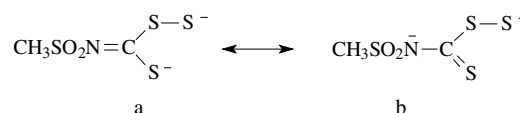
indicate a $C(sp^2)-N(sp^2)$ double-bond character [25]. The $S1-C1-N1$ and $S5-C3-N2$ angles are about 10° greater than $S2-C1-N1$ and $S4-C3-N2$ due to the interaction between the two CH_3SO_2 groups and $S1$ and $S5$ atoms, respectively, which are in *cis* positions in relation to the $C1-N1$ and $C3-N2$ bonds. The steric effects of the two CH_3SO_2 groups are greater than the effects of non-bonding lone-pair of electrons at the $N1$ and $N2$ atoms, since the $C1-N1-S3$ and $C3-N2-S6$ angles are greater than 120° , differently than it would be predicted by the VSEPR theory [26,27].

The asymmetric unit of **2** consists of a half *N*-methylsulfonyltrithiocarbamate zincate(II) anion and a tetraphenylphosphonium cation (Fig. 2). The central zinc lies on a twofold axis and is coordinated by two nitrogen $N1$ and two sulfur $S4$ atoms of the anions $CH_3SO_2N=CS_3^{2-}$, in a considerably distorted tetrahedral geometry, with very distinct bond angles $S-Zn-S$, $N-Zn-N$ and $N-Zn-S$ (Table 2). However, the five-membered ring defined by $Zn1-N1-C2-S2-S4$ atoms is almost planar (maximum deviation atom to mean plane 0.11 \AA) and forms a dihedral angle of 87.5° with its crystallographic equivalent plane $Zn1-N1^i-C2^i-S2^i-S4^i$. The $Zn1-S4$ bond length is slightly smaller than the $Zn-S$ bond lengths in compound **1**, whereas the $S2-C2$ bond length is similar to the corresponding values observed in **1**. The bond length of $S2-S4$ is typical for single bond values observed in several organic compounds (2.03 \AA) and the $S3-C2$ bond length is similar to those observed for thioureas $S=C$ bonds [25]. The $Zn1-N1$ bond length of $2.021(2) \text{ \AA}$ is in the usual range for $Zn-N$ coordination bonds [28]. The bond lengths and bond angles within the *N*-methylsulfonyl group are very similar to those in the structure of **1**. Different contributing forces count to the stabilization of the molecular structure of **2**: the oxygen atom $O2$ is approximately on the mean plane minimizing the stereo repulsion to $S3$; further repulsion between the sulfur and $C1$ and $O1$ can be seen in the bond angles on the C_{ring} carbon, namely, an enhancement of the $S3-C2-N1$ bond angle in comparison to $S3-C2-S2$; on the other hand, two equivalent $H1c \cdots O2 \cdots H1c^i$ intermolecular contacts ($2.72(1) \text{ \AA}$) indicate an attractive interaction between the oxygen $O2$ and two methyl hydrogen atoms.

Some sulfur-rich dithiocarbamate complexes are known [29–31]. The osmium(II) dithiocarbamate complex $[Os_2-(S_3CNMe_2)_2(S_2CNMe_2)_3]^+$ is an example of such compounds [30]. The single-crystal X-ray analysis of this cation showed that the trithiocarbamate ion is coordinated to de osmium cation by two sulfur atoms as shown in Scheme 1a. The same coordination mode was proposed for the structures of zinc(II)–trithiocarbamate complexes [31]. Examples of sulfur-rich-nickel(II)–dithiocarbamate complexes have been synthesized and in these cases the coordination of the trithiocarbamate anion can be as represented by the structure in Scheme 1c [15,16]. So, to our knowledge, compound **2** is the first example of a sulfur-rich-zinc(II)–dithiocarbamate, and also the first example of a sulfur-rich-trithio-complex where the metal is coordinated by the sulfur and nitrogen atoms (Scheme 1d).



Scheme 1. Possible ways of coordination of the sulfur-rich-dithiocarbamate (a, b) and sulfur-rich-dithiocarbamate (c, d) ligands.



Scheme 2. Two canonical forms for *N*-methylsulfonyltrithiocarbamate anion.

The strong electron withdrawing property of the SO_2 group might be important for this coordination fashion. The SO_2 neighbouring group stabilizes the negative charge in the nitrogen atom, and the canonical form (b) (Scheme 2) contributes appreciably to the resonance hybrid.

The structure determination of the compound **2** is very important since it has been proposed that correlated trithiocarbamate ligands ($R_2NCS_3^-$) are key intermediates in rubber vulcanization accelerated by zinc dithiolate compounds [8,31]. The formation of the compound **2** is under investigation. The potassium *N*-methylsulfonyldithiocarbamate precursor is not very stable. The oxidation of analogous salts, for example, potassium phenylsulfonyldithiocarbamate, involves dimerization of the anion by the formation of a $S-S$ bond, followed by an intramolecular cyclization with elimination of sulfur [32]. This is a possible source of the third sulfur atom that gives rise to the trithiocarbamate ligand in compound **2**.

4. Conclusion

Two new zinc(II) complexes with dithiocarbamate (**1**) and trithiocarbamate (**2**) ligands as tetraphenylphosphonium salts were obtained in crystalline form and their structures were determined by single crystal X-ray diffraction technique. The compound **2** is the first example of a zinc–trithiocarbamate complex. Furthermore, it is the first example of a sulfur-rich-dithiolate in which the ligand coordinates to the metal cation by sulfur and nitrogen atoms, and not only by the sulfur atoms. The structure determination of **2** is very important since it has been proposed that trithiocarbamate ligands ($R_2NCS_3^-$) are key intermediates in rubber vulcanization accelerated by zinc dithiocarbamate compounds.

Acknowledgements

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Appendix A. Supplementary material

CCDC Nos. 605156 and 605157 contain the supplementary crystallographic data for **1** and **2**, respectively. 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. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2006.08.002](https://doi.org/10.1016/j.poly.2006.08.002).

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