Syntheses, structural and spectroscopic characterization of novel zinc(II)-bis(trithiocarbimato) complexes and bis(*N*-methylsulfonyldithiocarbimate)-sulfide

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ABSTRACT

Four zinc(II)-bis(trithiocarbimato) complexes with the general formula $A_2[Zn(RSO_2N=CS_3)_2]$ [$A = Ph_4P^+$; $R = CH_3$ (**1**), $4-CH_3C_6H_4$ (**2**); $A = Bu_4N^+$: $R = CH_3$ (**3**), $4-CH_3C_6H_4$ (**4**)] were obtained by the reaction of sulfur with the correspondent zinc(II)-bis(dithiocarbimato) complexes. Additionally, the compound $(Ph_4P)_2[(CH_3SO_2N=CS_2)_2S]$ (**5**) was prepared from the potassium methylsulfonyldithiocarbimate by oxidation with iodine. The compounds were characterized by elemental analyses and IR, 1H NMR and ^{13}C NMR spectroscopies. The compounds **4** and **5** were also characterized by X-ray diffraction techniques. The compound **4** crystallizes in the centrosymmetric space group $C2/c$ of the monoclinic system. The Zn(II) is in a distorted tetrahedral environment (ZnS_4) in compound **4**, and differ from the coordination mode observed in compound **1**, which involves one sulfur and one nitrogen atom of each trithiocarbimate ligand. Compound **5** is the first example of a compound containing a bis(*N*-alkylsulfonyldithiocarbimate)-sulfide dianion and crystallises in the non-centrosymmetric space group $P4_12_12$ of the tetragonal system. © 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Zinc(II) complexes with dithiocarbamate ligands (Scheme 1) are worldwide used in the vulcanization process [1–3]. Zinc(II)-polythiocarbamate complexes with one or more sulfur atoms inserted in the zinc-dithiocarbamate bond have been proposed as intermediates [3], but have never been isolated.

We have previously reported that zinc(II) complexes with dithiocarbimate ligands (Scheme 1) are also accelerators of the rubber vulcanization [4,5]. Furthermore, we have been able to isolate zinc(II)-bis(trithiocarbimato) species. At first, the $[Zn(CH_3SO_2N=CS_3)_2]^{2-}$ anion was obtained as a by-product of the synthesis of the related dithiocarbimate complex anion. It was the first example of a zinc(II)-bis(trithiocarbimato) complex derived from sulfonamide [6].

Now we have purposely synthesized the same zinc(II)-bis(trithiocarbimato) complex: $(Ph_4P)_2[Zn(CH_3SO_2N=CS_3)_2]$ (**1**) by the

reaction of sulfur with the corresponding dithiocarbimate complex, confirming the X-ray data previously reported [6]. We have proved that the same methodology applies to other dithiocarbimate complexes by the preparation of three other compounds of this class of substances: $(Ph_4P)_2[Zn(4-CH_3C_6H_4SO_2N=CS_3)_2]$ (**2**), $(Bu_4N)_2[Zn(CH_3SO_2N=CS_3)_2]$ (**3**) and $(Bu_4N)_2[Zn(4-CH_3C_6H_4SO_2N=CS_3)_2]$ (**4**).

Other important rubber vulcanization accelerators are the thiuram disulfides, $R_2NC(S)SS(S)CNR_2$ (R = organic groups) [3]. To our knowledge, only one crystal structure of a thiuram disulfide analog derived from a sulfonyldithiocarbimate has been described in the literature: $(Ph_4As)_2[(RN=C(S)SS(S)C=NR)]$ ($R = 4-ClC_6H_4SO_2$) [7]. The study of such substances is also important for the elucidation of the rubber vulcanization mechanisms. We have investigated the iodine-promoted oxidation of the potassium methylsulfonyldithiocarbimate in attempting to obtain the disulfide derivative. Surprisingly a mixture of products was obtained, from which the anion $[(CH_3SO_2N=C(S)SS(S)C=NSO_2CH_3)]^{2-}$ crystallized with tetraphenylphosphonium cations yielding (**5**), the first example of a bis(*N*-alkylsulfonyldithiocarbimate)-sulfide.

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Scheme 1. General formulae of the (a) dithiocarbamate and (b) dithiocarbamate anions.

Here we describe the preparation of compounds **1–5** and their characterization by elemental analyses, the IR, ^1H and ^{13}C NMR spectroscopies. The compounds **4** and **5** were also characterized by X-ray diffraction techniques. The environment of the Zn(II) in **4** will be compared with that observed for the complex **1** [6].

2. Experimental

2.1. Methods and materials

The solvents, potassium hydroxide and carbon disulfide were purchased from Vetec and used without further purification. The methanesulfonamide, 4-methylbenzenesulfonamide, zinc acetate dihydrate, tetraphenylphosphonium chloride and tetrabutylammonium bromide were purchased from Aldrich. The R-sulfonyldithiocarbamate potassium salts dihydrate were prepared in dimethylformamide from the sulfonamides analogously as described in the literature [9]. The zinc(II)-bis(dithiocarbamate) complexes: $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{RSO}_2\text{N}=\text{CS}_2)_2]$ ($\text{R} = \text{CH}_3$ and $4\text{-CH}_3\text{C}_6\text{H}_4$) [6,8] and $(\text{Bu}_4\text{N})_2[\text{Zn}(4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)_2]$ [4] were prepared as described in the literature. The compound $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_2)_2]$ is not described in the literature and was prepared analogously as similar compounds [4]. Melting points were determined with a MQAPF-302 equipment without correction. 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 ($4000\text{--}200\text{ cm}^{-1}$) were recorded with a Perkin–Elmer 283 B infrared spectrophotometer using CsI pellets. 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, except for compound **1** which was recorded in CD_2Cl_2 .

2.2. Syntheses of $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_2)_2]$

Zinc(II) acetate dihydrate (0.7 mmol) was added to a suspension of potassium 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 tetrabutylammonium bromide (1.5 mmol) were added to the solution obtained. The mixture was stirred for further 15 min and the white solid obtained was filtered, washed with distilled water and dried under reduced pressure for one day, yielding $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_2)_2]$ (ca. 80%).

Anal. Calc. for $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_2)_2]$: C, 48.65, 8.85, 6.30. Found: C, 48.94; 8.27; 6.33%. M.p. ($^\circ\text{C}$): 127.6–130.7. Selected IR data (cm^{-1}): 1383 $\nu(\text{C}=\text{N})$; 1287, 1266 $\nu_{\text{ass}}(\text{SO}_2)$; 1131 $\nu_{\text{sym}}(\text{SO}_2)$; 933 $\nu(\text{CS}_2)$; 329 $\nu(\text{ZnS})$. ^1H NMR (δ): 3.04 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ): 208.2 (N= CS_2); 39.4 (CH_3). The infrared and the NMR spectra present the expected bands and signals corresponding to the tetrabutylammonium cation.

2.3. Syntheses of the zinc(II)-bis(trithiocarbamate) complexes

The appropriate zinc(II)-dithiocarbamate complex (1.6 mmol) was dissolved in DMF (10 mL). Sulfur (0.4 mmol) was added to the solution obtained and reacted immediately. An intensely yellow solution was formed. The mixture was stirred for 1 h at room temperature. Water (30 mL) was added and the yellow solid product obtained was filtered, washed with distilled water and dried under reduced pressure for one day, yielding **1–4** (ca. 88%). The solid product was dissolved in dichloromethane:ethanol 2:1. After slow evaporation suitable crystals for X-ray diffraction analyses of **1** and **4** were obtained.

Anal. Calc. for $(\text{Ph}_4\text{P})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_3)_2]$ (**1**): C, 54.47; H 4.00; N 2.44; Zn, 5.71%. Found: C, 53.70; H 4.08; N, 2.44; Zn, 5.71%. Selected IR data (cm^{-1}): 1385, 1319 $\nu(\text{C}=\text{N})$; 1304, 1290 $\nu_{\text{ass}}(\text{SO}_2)$; 1143 $\nu_{\text{sym}}(\text{SO}_2)$; 984, 968, 937 $\nu(\text{CS}_3)$; 334 $\nu(\text{ZnS})$. ^1H NMR (δ): 3.28, 3.20*, 2.96 and 2.92* (four singlets, 6H, CH_3), (*low intensity). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ): 209.7 (broad, N= CS_3); 39.44 and 39.38 (equally intense, CH_3).

Anal. Calc. for $(\text{Ph}_4\text{P})_2[\text{Zn}(4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_3)_2]$ (**2**): C, 59.18; H, 4.19; N, 2.16; Zn, 5.03. Found: C, 57.73; H, 4.08; N, 2.85; Zn, 5.08%. Selected IR data (cm^{-1}): 1373 $\nu(\text{C}=\text{N})$; 1283 $\nu_{\text{ass}}(\text{SO}_2)$; 1143 $\nu_{\text{sym}}(\text{SO}_2)$; 985, 940 $\nu(\text{CS}_3)$; 326 $\nu(\text{ZnS})$. ^1H NMR (δ): 7.79–7.63 (m, 44H, $\text{H}_2 + \text{H}_6 + \text{Ph}_4\text{P}^+$); 7.00–6.98 (m, 4H, $\text{H}_3 + \text{H}_5$); 2.23 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ): 210.3 (N= CS_3); 141.2 (C4); 140.2 (C1); 128.6 (C3 and C5); 128.2 (C2 and C5); 21.7 (CH_3).

Anal. Calc. $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_3)_2]$ (**3**): C, 45.37; H 8.25; N, 5.88; Zn, 6.86. Found: C, 44.79; H, 8.20; N, 6.18; Zn, 7.06%. Selected IR data (cm^{-1}): 1383, 1321 $\nu(\text{C}=\text{N})$; 1305, 1293 $\nu_{\text{ass}}(\text{SO}_2)$; 1141 $\nu_{\text{sym}}(\text{SO}_2)$; 981, 971, 935 $\nu(\text{CS}_3)$; 334 $\nu(\text{ZnS})$. ^1H NMR (δ): 3.39, 3.34*, 3.08 and 3.06* (four singlets, 6H, CH_3), (*low intensity). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ): 209.5 and 209.2 (equally intense, N= CS_3); 40.0, 39.5 (equally intense) and 40.1, 39.9 (very low intensity) (CH_3).

Anal. Calc. $(\text{Bu}_4\text{N})_2[\text{Zn}(4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_3)_2]$ (**4**): C, 52.17; H, 7.84; N, 5.07; Zn, 5.92. Found: C, 51.38; H, 7.54; N, 5.05; Zn, 5.81%. Selected IR data (cm^{-1}): 1377 $\nu(\text{C}=\text{N})$; 1269 $\nu_{\text{ass}}(\text{SO}_2)$;

Table 1
Crystallographic data for **4**, and **5**.

Compound	4	5
Formula	$2(\text{C}_{16}\text{H}_{36}\text{N})\cdot\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{S}_8\text{Zn}$	$2(\text{C}_{24}\text{H}_{20}\text{P})\cdot\text{C}_4\text{H}_6\text{N}_2\text{O}_4\text{S}_7$
Molecular weight	1105	1049.27
Temperature	295(2)	295(2)
Crystal system	monoclinic	tetragonal
Space group	$\text{C}2/c$ (No. 15)	$\text{P}4_12_12$ (No. 92)
<i>a</i> (Å)	22.478(5)	10.1081(14)
<i>b</i> (Å)	14.819(3)	10.1081(14)
<i>c</i> (Å)	19.159(4)	50.953(10)
β ($^\circ$)	106.75(1)	
<i>V</i> (Å ³)	6111(2)	5206.1(14)
<i>Z</i>	4	4
<i>D</i> _{calc} / <i>D</i> _{exp} (g cm ^{−3})	1.201/1.20	1.339/1.40
μ (mm ^{−1})	0.715	0.41
Crystal size (mm ³)	$0.44 \times 0.21 \times 0.18$	$0.28 \times 0.14 \times 0.14$
<i>T</i> _{min} / <i>T</i> _{max}	0.837/0.876	0.8693/0.8963
Total/unique/ Observed reflections	39074/7587/4484	36831/6679/3780
<i>R</i> _{int}	0.0584	0.0624
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] ^a	0.0684	0.0669
<i>wR</i> [<i>F</i> ² all reflections] ^b	0.1808	0.1228
<i>S</i>	1.065	1.088
Residual electron density, Δρ _{max} , Δρ _{min} (e Å ^{−3})	+0.543, −0.389	+0.448, −0.449

^a $R = \sum ||F_o| - |F_c|| / \sum F_o$.

^b $wR = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4 \}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$. The *a* and *b* parameters are 0.054 and 2.25 for **4** and 0.04 and 0.22 for **5**.

1140 $\nu_{\text{sym}}(\text{SO}_2)$; 986, 935 $\nu(\text{CS}_3)$; 321 $\nu(\text{ZnS})$. ^1H NMR (δ): 7.87–7.77 (m, 4H, H2 and H6); 7.13–7.09 (m, 4H, H3 and H5); 2.34 (s, 6H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ): 209.4 (N=CS₃); 141.7 (C4); 140.0 (C1); 128.8 (C3 and C5); 127.9 (C2 and C6); 21.7 (CH_3).

The infrared and NMR spectra present the bands and signals expected for the tetraphenylphosphonium cation (compounds **1** and **2**) or the tetrabutylammonium cation (compounds **3** and **4**).

2.4. Attempt of synthesis of $(\text{Ph}_4\text{P})_2[(\text{CH}_3\text{SO}_2\text{N}=\text{C}(\text{S})\text{SS}(\text{S})\text{C}=\text{NSO}_2\text{CH}_3)]$

Iodine (5.0 mmol) solution in ethyl acetate (10 mL) was added to a suspension of potassium methylsulfonyldithiocarbamate dihydrate (10.0 mmol) in ethyl acetate (10 mL). The mixture was stirred at room temperature for 20 min. Tetraphenylphosphonium chloride (10.5 mmol) was slowly added. The mixture was placed in a cold bath and stirred for further 20 min. The yellow solid was filtered, washed with distilled water, ethanol, diethyl ether and dried under reduced pressure. Appropriate crystals for X-ray diffraction experiments were obtained by recrystallization in acetone:water 1:1 mixture yielding $(\text{Ph}_4\text{P})_2[(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_2)_2\text{S}]$ (**5**) (20% from the dithiocarbamate potassium salt).

Anal. Calc. for $(\text{Ph}_4\text{P})_2[(\text{CH}_3\text{SO}_2\text{N}=\text{C}(\text{S})\text{SSS}(\text{S})\text{C}=\text{NSO}_2\text{CH}_3)]$ (**5**): C, 59.52; H, 4.42; N, 2.67. Found: C, 58.42; H, 4.35; N, 2.48%. Selected IR data (cm^{-1}): 1407 $\nu(\text{C}=\text{N})$; 1286 $\nu_{\text{ass}}(\text{SO}_2)$; 1128 $\nu_{\text{sym}}(-\text{SO}_2)$; 955, 905 $\nu(\text{CS}_3)$. ^1H NMR (δ): 3.11 (s, 6H, H1). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ): 198.9 (N=C), 39.6 (CH_3).

The infrared and the NMR spectra of **5** present the expected bands and signals corresponding to the tetraphenylphosphonium cation.

2.5. X-ray crystallography

The yellow single crystals of **1**, **4** and **5** were used for data collected using graphite monochromatic MoK α 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. One image was used as a standard for monitoring the crystal stability as well as for monitoring the data collection after every 40 images. No correction on the relative intensity variation was necessary. Data collections were made using the CrysAlis CCD program [10]. Integration, scaling of the reflections, correction for Lorentz and polarization effects and absorption corrections were performed using the CrysAlis Red program [10]. The structures were solved by direct methods using the SHELXS of the SHELXL97 program [11]. 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 and HFIX 23 for CH_2 with isotropic thermal parameters of $1.5U_{\text{eq}}$ of carbon atoms of CH_3 or CH_2 groups). Final difference Fourier maps showed no peaks of chemical significance. Details of the data collection parameters and final agreement factors for compounds **4** and **5** are collected in Table 1. Selected bond lengths and angles and torsion angles are listed in Table 2. Visualization of the structures was made with the DIAMOND 3.0 program [12]. The lattice parameters, the bond lengths and angles observed for compound **1** did not differ from the previously published data [6].

3. Results and discussion

The compounds **1–4** were synthesized as shown in Scheme 2. The zinc(II)-bis(dithiocarbamate) complexes precursors are described in the literature [4,8], except for $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_2)_2]$ which preparation is described in this work.

As said before, the compound **5** was obtained accidentally during the attempt to obtain the disulfide derivative of potassium methylsulfonyldithiocarbamate.

The compounds **1–5** and $(\text{Bu}_4\text{N})_2[\text{Zn}(\text{CH}_3\text{SO}_2\text{N}=\text{CS}_2)_2]$ are stable in the solid state at the ambient conditions, but decomposition is observed above ca. 120 °C for the complexes **1–4**, and ca. 220 °C for the compound **5**. Compounds **1–5** are insoluble in water, slightly soluble in ethanol and soluble dichloromethane. All intense bands of the counter-ions (Ph_4P^+ or Bu_4N^+) vibrations are present in the infrared spectra of the compounds. The spectra of **2** and **4** are similar to those presented by the zinc-dithiocarbamate precursors [4,8] with a strong band in the region of 1380–1370 cm^{-1} , due to the νCN vibration of the RSO_2NC group. The spectra of **1** and **3** are more complex, showing two intense bands at 1385–1310 cm^{-1} . This fact points to a similar coordination of the trithiocarbamate ligands in **2** and **4** but different from **1** and **3** (see the X-ray diffraction discussion). The spectrum of **5** shows an intense band in 1407 cm^{-1} assigned to the νCN vibration. This band is shifted to an even higher wavenumber with respect to the corresponding dithiocarbamate potassium salt (1260 cm^{-1}) [13]. A multiple band between 990 and 905 cm^{-1} observed in the spectra of **1–5** was assigned to νCS_3 . The expected νSS band at ca. 500 cm^{-1} [14,15] was obscured by other bands of the ligands and counter ions. The spectra of **1–4** show the expected band at 340–325 cm^{-1} assigned to the ZnS stretching vibration [16].

The ^1H NMR spectra of the compounds **1–5** showed the signals for the hydrogen atoms of the cations and the anions, the

Table 2
Selected geometrical parameters ($\text{\AA}$, $^\circ$).

Compound 4 ^a			
Zn1–S1	2.329(2)	Zn1–S3	2.335(2)
S1–S2	2.014(2)	S2–C1	1.788(5)
S3–C1	1.696(5)	C1–N1	1.277(5)
N1–S4	1.631(4)	S4–O1	1.428(3)
S4–O2	1.417(5)	S4–C2	1.853(11)
S1–Zn1–S3	98.10(5)	S1–Zn1–S1 ⁱ	107.44(8)
S1–Zn1–S3 ⁱ	118.61(5)	S3–Zn1–S3 ⁱ	116.85(9)
C1–S2–S1	111.7(2)	S3–C1–S2	124.4(3)
C1–N1–S4	123.1(4)	N1–C1–S2	106.0(3)
N1–C1–S3	129.6(4)	O2–S4–O1	117.1(3)
O2–S4–N1	112.6(3)	O1–S4–N1	113.3(2)
N1–S4–C2	98.0(3)	O1–S4–C2	103.9(4)
O2–S4–C2	109.5(4)		
Zn1–S1–S2–C1	3.3(2)	S1–S2–C1–S3	1.0(4)
Zn1–S3–C1–N1	174.5(5)	Zn1–S3–C1–S2	−4.7(4)
S1–S2–C1–N1	−178.4(3)		
Compound 5 ^b			
C1–S1	1.776(8)	S1–O1	1.428(6)
S1–O2	1.441(6)	S1–N1	1.643(6)
N1–C2	1.291(9)	C2–S2	1.688(8)
C2–S3	1.817(7)	S3–S4	2.061(3)
S4–S3 ⁱ	2.061(3)		
O1–S1–O2	116.6(4)	O1–S1–N1	112.0(3)
O2–S1–N1	104.7(3)	O1–S1–C1	108.4(4)
O2–S1–C1	107.6(4)	N1–S1–C1	107.0(4)
C2–N1–S1	120.6(5)	N1–C2–S2	136.1(5)
N1–C2–S3	116.2(5)	S2–C2–S3	107.7(4)
C2–S3–S4	107.8(3)	S3–S4–S3 ⁱ	105.4(2)
S1–N1–C2–S3	−170.8(4)	S2–C2–S3–S4	177.1(3)
N1–C2–S3–S4	−3.0(6)	C2–S3–S4–S3 ⁱ	−94.9(3)

^a Symmetry code: (i) $-x, y, -z + 3/2$.

^b Symmetry code: (i) $y - 1, x + 1, -z$.

Scheme 2. Syntheses of the compounds 1–4.

integration curves being consistent with a 2:1 proportion between cations and bis(*R*-sulfonyltrithiocarbimate)zincate(II) anions (1–4) or the bis(*N*-methylsulfonyldithiocarbimate)-sulfide anion (5). The new compounds are very soluble in chloroform, except from 1, which NMR spectra were best obtained in CD₂Cl₂. In the spectra of 5 the signal of the N=C group was observed at δ 198.9, while the same signal in the parent potassium dithiocarbimate is observed down field at δ 224.3 (in D₂O). The signal of the CH₃ groups was observed in the ¹³C and ¹H NMR spectra of 5 at δ 39.6 and 3.11, respectively.

The NMR spectra of the compounds 2 and 4 are similar to those presented by the corresponding zinc(II)-bis(dithiocarbimate) complexes [4,6,8], with small differences in all chemical shifts. The ¹H NMR spectrum of a mixture of compound 2 and the precursor tetraphenylphosphonium zinc(II)-bis(4-methylphenyldithiocarbimate) showed two singlets at δ 2.20 and 2.22 due to the CH₃ hydrogens of each anion, with integration curves consistent with a 2:1 proportion between the cation and the anions, confirming that (Ph₄P)₂[Zn(4-CH₃C₆H₄SO₂N=CS₂)₂] reacts with sulfur, forming the compound 2.

An interesting situation was observed in the NMR of compounds 1 and 3. In their ¹H NMR spectra two singlets were observed in the CH₃ region, accompanied by two other signals of much less intensity. The area of the four signals was consistent with a total of 6 hydrogens atoms when compared to the cations signals areas. While the N=C signal of the precursor (Bu₄N)₂[Zn(CH₃SO₂N=CS₂)₂] was observed at δ 208.2, in the ¹³C NMR spectrum of 3 two equally intense signals were observed at δ 209.2 and 209.4, followed by two other signals of much smaller intensities at ca. δ 210. Also, two signals were observed at δ 39.5 and 40.0 in the spectrum of 3, together with two signals of very low intensities at δ 39.9 and 40.1. Similar results were observed in the ¹³C NMR spectrum of 1, being more difficult to identify the less intense signals. Those results were indicative of an equilibrium between isomers in solution.

The ¹H NMR spectra of a mixture of 2 and 4 showed only one signal for the CH₃ hydrogen atoms, confirming that both compounds present the same complex anion. The same experiment for compounds 1 and 3 (in CDCl₃) showed the four signals with the same chemical shifts observed in the spectrum of 3. Their integration curves in comparison with the Bu₄N⁺ and Ph₄P⁺ cations signals were consistent with the 6 hydrogen atoms of the CH₃ groups, indicating that the same isomers were present in the solutions of 1 and 3. Whether they represent different coordination modes (S,S or N,S) or only geometrical isomers (Scheme 3) it could not be established.

The X-ray studies of compound 1 showed that each trithiocarbimate ligand coordinates to the Zn(II) via S and N atoms in the solid state (Fig. 1). The lattice parameters, the bond lengths and angles observed for compound 1 did not differ from the previously published data [6]. Therefore, they confirmed that we could purposely prepare exactly the same compound unintentionally obtained as a

byproduct of the corresponding dithiocarbimate zinc complex synthesis. Nevertheless, the infrared spectrum of compound 1 showed some differences from the data early published, probably due to the presence of some dithiocarbimate-zinc-complex in the first sample, as the purification process used at that time consisted in the visual separation of yellow and white crystals under the microscope [6].

The X-ray experiments showed that the asymmetric unit of compound 4 consists of a half *N*-(4-methylphenylsulfonyl)trithiocarbimate zincate(II) anion and a tetrabutylammonium cation (Fig. 2). The central zinc(II) lies on a twofold axis and is coordinated by four sulfur atoms of two trithiocarbimate anions, CH₃C₆H₄SO₂NCS₃²⁻, in a considerably distorted tetrahedral geometry, with very distinct bond angles S–Zn–S (Table 2). The distortion from the ideal tetrahedral environment around the Zn(II) is due to the coordination by two sulfur atoms of each chelating ligand leading to the considerably smaller S1–Zn–S3 or its equivalent S1ⁱ–Zn–S3ⁱ bond angles when compared with the other S–Zn–S angles involving the S atoms of both trithiocarbimate ligands. The five-membered rings involving the central Zn atom (Zn,S1,S2,C1,C3 or its equivalent) are almost planar (the greatest deviation of the atoms from the mean plane is equal to 0.047(2) Å) and form a dihedral angle of 96.1(2)°.

The coordination environment around the Zn(II) in 4 (Fig. 2) is different to that found in the complex 1 described previously [6], in which the Zn cation is coordinated by the sulfur and nitrogen atoms of the sulfur-rich trithiocarbimate ligands (Fig. 1). The *N,S*-coordinating mode of the trithiocarbimate ligands results in greater distortion of the *N*₂S₂-tetrahedral environment of Zn than the *S*₄-environment of Zn as in the structure of 4. The average Zn–S bond length of 2.332 Å in 4 is slightly longer than that in 1 (2.285 Å), whereas the opposite relation in the distance of C1–N1 is observed [1.277(5) Å in 4 and 1.328(3) Å in 1]. The bond length of S1–S2 in both complexes is typical for the single bond value 2.03 Å observed in several organic compounds containing the disulfide S–S group [17].

Scheme 3. Some possible isomeric structures for the anions of the compounds 1 and 3 in solution.

Since the nitrogen atom N1 in compound **4** is co-planar with the five-membered ring Zn,S1,S2,C1,S3, therefore the partial delocalisation of the π -bond electrons of the N=C in the ring is possible

Fig. 1. View of the molecular structure of **1** with the labeling scheme. Symmetry code: (i) $-x, y, 0.5 - z$.

Fig. 2. View of the molecular structure of **4** with the labeling scheme. Symmetry code: (i) $-x, y, -z + 3/2$.

Fig. 3. View along *b* of the arrangement of tetrabutylammonium cations and bis(*N*-(4-methylphenyl)sulfonyl)trithiocarbamatezincate(II) dianions in **4**. H atoms are omitted for clarity.

Scheme 4. Possible ways of coordination of the sulfur-rich-dithiocarbamato (a, b) and sulfur-rich-dithiocarbimato (c, d) ligands.

Scheme 5. Two canonical forms for *N*-methylsulfonyltrithiocarbamate anion.

and leads to the elongation of the N=C bond and to the shortening of the bonds within the ring. The C1–N1–S4 as well as the N1–S4–C2 angles are significantly different than the expected values due to the steric hindrance effect of the sulfonyl and phenyl groups.

Fig. 3 shows the crystal-packing of **4** viewed along the *b* axis. The molecular arrangement is mainly determined by the ionic attraction between the oppositely charged *N*-(4-methylphenylsulfonyl)trithiocarbimatezincate(II) anions and the

tetrabutylammonium cations and by the van der Waals forces, since in the crystal there are no observed directional forces like hydrogen bonds.

Some trithiocarbamate complexes of transition metals are known [20,21]. In general the trithiocarbamate ion is coordinated to the metal by two sulfur atoms as shown in the Scheme 4(a). The same coordination mode was proposed for the structures of the still not isolated zinc(II)-bis(trithiocarbamate) complexes [22]. Examples of sulfur-rich-nickel(II)-dithiocarbamate complexes have been synthesized and in these cases the coordination of the trithiocarbamate anion can be represented by the structure (c) in Scheme 4 [14,15]. Compound **1** was 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 the nitrogen atoms (Scheme 4d) [6].

The strong electron withdrawing property of the SO₂ group might be important for the coordination fashion observed in compound **1** (Scheme 4d). The SO₂ neighboring group stabilises the negative charge in the nitrogen atom, and the canonical form (II) (Scheme 5) contributes appreciably to the resonance hybrid. On the other hand, in the compound **4**, the coordination feature is best represented as shown in the scheme 4(c). It seems that the repulsion between the larger aromatic groups in **4** is the key to the adopted coordination.

The molecular structure of compound **5** is shown in Fig. 4. The asymmetric unit of **5** consists of the tetraphenylphosphonium cation, PPh₄⁺, and a half of the bis(*N*-methylsulfonyldithiocarbimate)-sulfide dianion, [(CH₃SO₂N=C(S)SS(S)C=NSO₂CH₃)]²⁻, having a twofold symmetry axis. The conformation of the bis(*N*-methylsulfonyldithiocarbimate)-sulfide dianion is non-planar. However

Fig. 4. View of the molecular structure of **5** with the labeling scheme. Symmetry code: (i) $y - 1, x + 1, -z$.

Scheme 6. Two canonical forms for the bis(*N*-methylsulfonyldithiocarbimate)-sulfide dianion.

Fig. 5. View along *a* of the arrangement of tetraphenylphosphonium cations and bis(*N*-methylsulfonyldithiocarbimate)-sulfide dianions in **5**. H atoms are omitted for clarity.

both arms containing the S1,N1,C2,S2,S3,S4 atoms or their equivalents are planar (the largest deviation of an atom from the mean plane is smaller than 0.04 Å) and form a dihedral angle of 79.1(2)°. The central S4 atom lies on the twofold symmetry axis and links both *N*-methylsulfonyldithiocarbimate units by two S4–S3 and S4–S3ⁱ equivalent bonds with a distance of 2.061(3) Å forming the bis(*N*-methylsulfonyldithiocarbimate)-sulfide dianion. The value of the S–S bond distance is typical for a single S–S bond and is comparable to that found in (Ph₄As)₂[(RN=C(S)SS(S)C=NR] (R = 4-ClC₆H₄SO₂) (2.047 Å) [7,23]. The N1–C2 bond length of 1.291(9) Å is slightly longer than the value of 1.279 Å for a typical double N(sp²)=C(sp²) bond [24]. In the *N*-methylsulfonyldithiocarbimate unit the C2–S2 bond with a distance of 1.688(8) Å is significantly shorter than the C2–S3 bond with a distance of 1.817(7) Å. This fact is also observed for (Ph₄As)₂[(RN=C(S)SS(S)C=NR] (R = 4-ClC₆H₄SO₂) (CS bonds: 1.68 and 1.80 Å) [7]. The first bond length is between a typical C=S double bond and a C–S single bond, while the C2–S3 bond represents a typical single bond. Thus, the observed bond lengths in the bis(*N*-methylsulfonyldithiocarbimate)-sulfide dianion can be illustrated by the canonical forms (a) and (b) as shown in the Scheme 6.

However, the planarity of the arms (S1,N1,C2,S2,S3,S4 and its equivalent) of the dianion 5 points to the sp² hybridisation of the orbitals on the C, N and S atoms. Thus the partial delocalisation of the π bond over N1, C2 and S2 atoms due to the symmetry of the p orbitals is possible and leads to the elongation of the C2=N1 double bond and to the shortening of the C2–S2 single bond (Table 2). Fig. 5 shows the crystal-packing of compound **5** viewed along the *a* axis. The arrangement of tetraphenylphosphonium cations and bis(*N*-methylsulfonyldithiocarbimate)-sulfide dianions in the crystal is mainly determined by the ionic attraction forces and by the van der Waals forces. No hydrogen bonds between the oppositely charged units are observed. The bis(*N*-methylsulfonyldithiocarbimate)-sulfide dianions are located along the *c* axis with the planar arms (S1,N1,C2,S2,S3,S4 and its equivalent) almost parallel to the (100) and (010) plane, since both arms of the dianion are related by a twofold symmetry axis.

The compound **5** was unexpectedly obtained. The oxidation of analogous salts, for example, potassium 4-chlorophenylsulfonyldithiocarbimate, involves dimerization of the anion by the formation of an S–S bond, followed by an intramolecular cyclization with elimination of sulfur [7]. This is a possible source of the third sulfur atom that gave rise to the bis(*N*-methylsulfonyldithiocarbimate)-sulfide dianion. To our knowledge, compound **5** is the first example of a bis(*N*-alkylsulfonyldithiocarbimate)-sulfide.

4. Conclusion

Four zinc(II) complexes with trithiocarbamate ligands (**1–4**) were obtained. The compound **1** was already described in the literature [6]. In that case it was accidentally obtained. In this work it was intentionally prepared by the reaction of the correspondent zinc(II)-dithiocarbamate complex with sulfur.

The νCN region in their vibrational spectra of the new compounds, pointed to different coordination modes of the methylsulfonyltrithiocarbamate ligands (**1** and **3**) and the methylphenylsulfonyltrithiocarbamate ligands (**2** and **4**) in the solid state. The X-ray diffraction studies confirmed that the zinc cation in compounds **1** and **4** present different coordination environments. In **1** the trithiocarbamate ligand coordinates via S and N atoms while in **4** the coordination occurs via two S atoms of each ligand.

The NMR spectra of **2** and **4** are similar as they present the same complex anion. The ¹H and ¹³C NMR spectra of **1** and **3** indicated the presence of isomers solution. The ¹H NMR spectrum of a mixture of **1** and **3** confirmed that the two solutions contain the same complex anions, in similar proportions.

The influence of the R groups in the coordination features of the zinc complexes as well as the formation of the bis(tetraphenylphosphonium) bis(*N*-methylsulfonyldithiocarbimate)-sulfide **5** are under investigation. The structure determination of such compounds were very important since it has been proposed that polythiocarbamate ligands are key intermediates in the rubber vulcanization accelerated by zinc-dithiocarbamate compounds and by thiuram disulfides. The compound **5** is the first example of a bis(*N*-alkylsulfonyldithiocarbimate)-sulfide dianion.

We have proved that the zinc-dithiocarbimates and the bis-dithiocarbimate anions readily react with sulfur, forming stable products. These results shall be important for the understanding of the vulcanization process under dithiocarbamate derivatives acceleration.

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Appendix A. Supplementary data

CCDC 832015 and 832014 contains the supplementary crystallographic data for **4** and **5**. 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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