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Syntheses, crystal structure and spectroscopic characterization of bis(dithiocarbimato)-nickel(II)-complexes: A new class of vulcanization accelerators

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ABSTRACT

The compounds $(Ph_4P)_2[Ni(RSO_2N{=}CS_2)_2]$ [Ph_4P^+ = tetraphenylphosphonium cation; R = CH_3 (**1b**), CH_3CH_2 (**2b**), $CH_3(CH_2)_3$ (**3b**) and $CH_3(CH_2)_7$ (**4b**)] were synthesized by the reaction of $RSO_2N{=}CS_2K_2{\cdot}2H_2O$ (**1a**–**4a**) with $NiCl_2{\cdot}6H_2O$ and Ph_4PBr. The elemental analyses of C, H, N and Ni were consistent with the proposed formula for **1b**–**4b**. The IR data were consistent with the formation of bis(dithiocarbimato)-nickel(II)-complexes. The NMR spectra showed the expected signals for the cation and the dithiocarbimate anionic complex in a 2:1 proportion. The compounds **2b** and **3b** were also characterized by X-ray diffraction techniques. Compounds **2b** and **3b** crystallize in the $P2_1/c$ and $P\bar{1}$ space groups, respectively. The nickel(II) ions are positioned in special positions being coordinated by four sulfur atoms of the dithiocarbimate moieties in a square planar environment. The Ph_4P^+ counter-ions enter the structure interstice performing weak C–H···O and C–H···S intermolecular interactions. The activity of compounds **1b**–**4b** in the vulcanization of the natural rubber was evaluated. These studies confirm that the bis(dithiocarbimato)-nickel(II)-complexes are new vulcanization accelerators worth of further investigation.

1. Introduction

Several dithiocarbamate and *N*-substituted dithiocarbamate complexes and salts have been used as agrochemicals mainly due to their high efficiency in controlling plant fungal diseases, and relatively low toxicity [1–6]. It is interesting to note that many dithiocarbamato-zinc(II)-complexes are simultaneously fungicides and vulcanization accelerators. A classical example is the bis(dimethyldithiocarbamato)zinc(II) (Ziran) [2]. Bis(dithiocarbamato)-zinc(II)-complexes are worldwide used in the rubber vulcanization process and are known as ultra-accelerators due to their extremely rapid vulcanization properties [1,2,7–10]. Nevertheless, despite their widespread application in the rubber industries, these accelerators are frequently criticized due to the potential production of nitrosamines during the vulcanization processes [11]. Derivatives of the dithiocarbamate class suitable for industrial application have been prepared from "safe" amines in order to avoid the formation of the carcinogenic nitrosamines [12]. Furthermore, dithiocarbamates such as bis(dimethyldithiocarbamato)zinc(II) show very low scorch safety [13], what may represent a processing problem.

Metal(II)-dithiocarbamato-complexes are neutral substances while the analogous dithiocarbimato-complexes are anionic species. The improvement and/or modulation of the vulcanization activity is an interesting possibility for anionic metal-sulfur compounds, which can be accomplished either by modifying the solubility of the complexes salts with the use of different cations or different R groups on the dithiocarbimate structures, or by using active counter ions. Besides, the right choice of R groups and counter-ions can avoid the formation of nitrosamines.

Here, we describe the syntheses and the rubber vulcanization activity of related compounds containing dithiocarbimate anions derived from sulfonamides with the formula $(Ph_4P)_2[Ni(R{-}SO_2N{=}CS_2)_2]$ [Ph_4P^+ = tetraphenylphosphonium cation; R = CH_3 (**1b**), CH_3CH_2 (**2b**), $CH_3(CH_2)_3$ (**3b**) and $CH_3(CH_2)_7$ (**4b**)]. The presence of the R-sulphonyl group linked to the nitrogen atom of the dithiocarbimate moiety is important and may avoid the production of nitrosamines. The compounds **1b**–**4b** were characterized by IR, ^1H and ^{13}C NMR spectroscopies, and by C, H, N and Ni elemental analyses. The compounds **2b** and **3b** were also characterized by X-ray diffraction techniques.

2. Experimental

2.1. Materials and methods

The solvents were purchased from Merck and used without further purification. Carbon disulfide and potassium hydroxide were

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purchased from Vetec. The tetraphenylphosphonium bromide, ethanesulfonyl chloride, butanesulfonyl chloride, octanesulfonyl chloride and methanesulfonamide were purchased from Aldrich. The other sulfonamides were prepared from the corresponding alkylsulfonyl chlorides, in reaction with concentrated ammonia aqueous solution (Vetec), under reflux. The sulfonamides were isolated after extraction with ethyl acetate and solvent evaporation. Melting points (m.p.) were determined with a Mettler FPS equipment. Microanalyses for C, H and N were obtained from a Perkin Elmer Elemental Analyzer 2400 CHN. Nickel was analyzed by atomic absorption with a Varian Spectra AA200 Atomic Absorption Spectrophotometer. The IR spectra were recorded with a Perkin Elmer 283 B infrared spectrophotometer using CsI pellets. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Advance DRX-400 spectrophotometer in D_2O for the dithiocarbimate potassium salts and $CDCl_3$ for the other compounds.

2.2. Syntheses of the dithiocarbimate potassium salts

The syntheses of **1a** and **2a** are described in literature [14,15].

All the procedure was carried out in ice bath. Carbon disulfide (0.2 mol) and potassium hydroxide (0.1 mol) were added to a solution of the corresponding sulfonamide (0.2 mol) in DMF (100 mL). The mixture was stirred for 2 h previous to the addition of a second portion of potassium hydroxide (0.1 mol). After stirring for further 2 h, 30 mL of ice cold ethanol was added. The yellowish solid obtained was separated by filtration, washed with ice ethanol, ethyl acetate, diethyl ether, and dried under reduced pressure yielding $RSO_2N{=}CS_2K_2{\cdot}2H_2O$ (*ca.* 65% based on the sulfonamide).

*2.2.1. Potassium N-butylsulfonyldithiocarbimate dihydrate, (**3a**)*

IR (CsI) (most important bands) (cm^{-1}): 1283 (νCN), 1255 (νSO_{2as}), 1106 (νSO_{2s}), 966 (νCS_{2as}). ^{1}H NMR (δ), *J* (Hz): 0.89 (t, *J* = 7.4, 3H, H4); 1.41 (m, 2H, H3); 1.66 (m, 2H, H2); 3.49 (t, *J* = 8,0, 2H, H1). ^{13}C NMR (δ): 13.0(C4); 21.1(C3); 25.0(C2); 50.2(C1); 223.6($N{=}CS_2$).

*2.2.2. Potassium N-octylsulfonyldithiocarbimate dehydrate, (**4a**)*

IR (CsI) (most important bands) (cm^{-1}): 1285 (νCN), 1255 (νSO_{2as}), 1112 (νSO_{2s}), 979 (νCS_{2as}). ^{1}H NMR (δ), *J* (Hz): 0.73–0.78 (m, 3H, H8), 1.1–1.4 (m, 10H, H7 to H3); 1.5–1.7 (m, 2H, H2); 3.42 (t, *J* = 8.1, 2H, H1). ^{13}C NMR (δ): 13.5(C8); 22.0(C7); 22.8(C6); 27.7(C5); 28.3(C3 and C4); 31.1(C2); 50.4(C1); 223.6($N{=}CS_2$).

2.3. Syntheses of the nickel complexes

The synthesis of **4b** is described in literature. In this work, the preparation of **4b** was confirmed by IR and comparison with the published data [16]. The compounds **1b**–**4b** were prepared as described below.

Nickel(II) chloride hexahydrate (20.0 mmol) and tetraphenylphosphonium bromide (40.0 mmol) were added to a solution of the appropriate potassium N-R-sulfonyldithiocarbimato (40.0 mmol) in 1:1 (100 mL) methanol:water. The mixture was stirred at room temperature for 1 h and the green solid obtained was filtered, washed with distilled water and dried under reduced pressure for 1 day, yielding $(Ph_4P)_2[Ni(RSO_2N{=}CS_2)_2]$ (*ca.* 90%, based on nickel (II) chloride hexahydrate). Compounds **2b** and **3b** were obtained as dark green/brown single crystals suitable for X-ray diffraction experiments by slow evaporation of their solutions in methanol:water (2:1) at room temperature.

*2.3.1. Tetraphenylphosphonium bis(methylsulphonyldithiocarbimato)nickelate(II), (**1b**)*

Found (Calcd for $C_{52}H_{46}N_2O_4P_2S_6Ni$): C, 57.72 (58.05); H, 4.15 (4.31); N, 2.72 (2.60); Ni, 5.22 (5.45). M.p. (°C): 211.8–213.4. IR (CsI) (most important bands) (cm^{-1}): 1403 (νCN), 1285 (νSO_{2as}), 1129 (νSO_{2s}), 926 (νCS_{2as}), 396 (νNiS). ^{1}H NMR (dithiocarbimate anion signals) (δ): 3.1 (s, H1). ^{13}C NMR (dithiocarbimate anion signals) (δ): 40.1 (C1), 210.3 ($N{=}CS_2$).

*2.3.2. Tetraphenylphosphonium bis(4-ethylsulphonyldithiocarbimato)nickelate(II), (**2b**)*

Found (Calcd for $C_{54}H_{50}N_2O_4P_2S_6Ni$): C, 58.62 (58.75); H, 4.54 (4.56); N, 2.84 (2.54); Ni, 5.43 (5.32). M.p. (°C): 192.7–193.9. IR (CsI) (most important bands) (cm^{-1}): 1429 (νCN), 1280 (νSO_{2as}), 1115 (νSO_{2s}), 936 (νCS_{2as}), 394 (νNiS). ^{1}H NMR (dithiocarbimate anion signals) (δ), *J* (Hz): 1.21 (t, *J* = 7.4, 6H, H2); 3.13 (q, *J* = 7.4, 4H, H1). ^{13}C NMR (dithiocarbimate anion signals) (δ): 8.4 (C2); 46.7 (C1); 212.0 ($N{=}CS_2$).

*2.3.3. Tetraphenylphosphonium bis(butylsulphonyldithiocarbimato)nickelate(II), (**3b**)*

Found (Calcd for $C_{58}H_{58}N_2O_4P_2S_6Ni$): C, 59.45 (60.05); H, 4.86 (5.04); N, 2.56 (2.41); Ni, 4.87 (5.06). M.p. (°C): 184.4–185.9. IR (CsI) (most important bands) (cm^{-1}): 1425 (νCN), 1267 (νSO_{2as}), 1109 (νSO_{2s}), 935 (νCS_{2as}), 393 (νNiS). ^{1}H NMR (dithiocarbimate anion signals) (δ), *J* (Hz): 0.84 (t, *J* = 7.3, 6H, H4); 1.33 (m, 4H, H3); 1.75 (m, 4H, H2); 3.16 (t, *J* = 8.0, 4H, H1). ^{13}C NMR (dithiocarbimate anion signals) (δ): 13.7 (C4); 21.9 (C3); 25.6 (C2); 52.4 (C1); 211.8 ($N{=}CS_2$).

2.4. X-ray diffraction experiments

Crystallographic and structural refinements data of **2b** and **3b** are summarized in Table 1. Compounds **2b** and **3b** samples of prismatic shape were used for data collections performed using a KappaCCD diffractometer [17]. Unit cell refinement and data reduction were performed with Denzo and Scalepack packages [18]. All data collections were carried out with Co Kα radiation at room temperature. All data were corrected for absorption effects by the Gaussian method using indexed faces [19]. The structures were solved by

Table 1
Crystal data and structure refinement for compounds **2b** and **3b.**

Compound	**2b**	**3b**
Empirical formula	$C_{54}\,H_{50}\,N_2\,NiO_4\,P_2\,S_6$	$C_{58}H_{58}N_2NiO_4P_2S_6$
M	1104.01	1160.11
T (K)	298(2)	299(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	12.1911(3)	10.1209(3)
b (Å)	14.2762(3)	10.4710(3)
c (Å)	16.2390(3)	14.3200(4)
α (°)	-	71.275(1)
β (°)	109.887(1)	80.178(2)
γ (°)	-	86.531(2)
V ($Å^3$)	2657.73(10)	1416.16(7)
Z	2	1
D_c ($g\,cm^{-3}$)	1.380	1.360
μ (mm^{-1})	0.708	0.668
Reflections collected	10527	26353
Independent reflections	6029	6417
(R_{int})	0.0201	0.0843
Goodness-of-fit (GOF) on F^2	1.074	1.050
Final *R* indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0603$ $wR_2 = 0.1553$	$R_1 = 0.0685$ $wR_2 = 0.1587$
R_1 (all data)[a]	0.1047	0.1458
wR_2 (all data)[a]	0.1965	0.2195

[a] $R_1 = \Sigma(||F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.

direct methods and refined by the full matrix least squares method, both using SHELX package [20]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined with riding constraints to their parent atoms.

2.5. Vulcanization

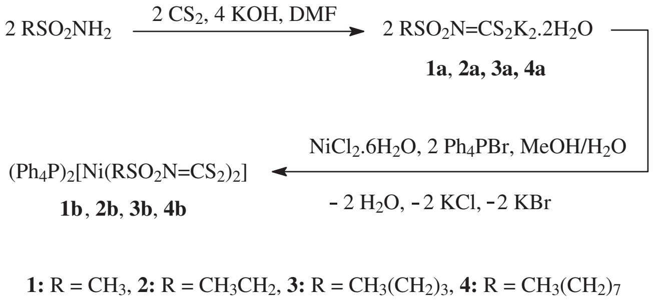
Natural rubber was compounded following the addition order in which each additive appears in the formulation (in phr): natural rubber, NR (100), stearic acid (2.5), zinc oxide (3.5), sulfur (2.5), carbon black (0 or 20), aminox (2.0), accelerator (1.2). Natural rubber, Mooney viscosity ML 1 + 4(100 °C) = 74.8, was supplied by Sociedade Michelin de Participações, Indústria e Comércio Ltda; the other ingredients were of grades commonly used in the industry. The mixture was carried out in a roll mill with 1:1.25 friction rate, at room temperature. Rheometric parameters were determined in an oscillating disk rheometer from Tecnologia Industrial, at 150 °C and 1° arc, according to ASTM D 2084.

3. Results and discussion

Scheme 1 illustrates the protocol used in the preparation of the complexes. The procedure involves the reaction of the appropriate sulphonamides with carbon disulfide in alkaline medium, followed by the reaction with a nickel(II) salt.

The potassium dithiocarbimates **1a**–**4a** are soluble in water and insoluble in most organic solvents. These compounds are not very stable and a white solid is obtained from their aqueous solutions after some days at room temperature. When kept in the solid state at the ambient temperature, these potassium salts were also converted into white solids after several months. On the other hand, the compounds **1b**–**4b** are stable at the ambient conditions. They are insoluble in water, and soluble in methanol, ethanol, chloroform and dichloromethane.

A strong band at 1400–1425 cm^{-1} observed in the vibrational spectra of **1b**–**4b** was assigned to the $\nu C{=}N$ vibration. The $\nu_{as}CS_2$ was observed at higher frequency in the spectra of the parent dithiocarbimate potassium salts (940–970 cm^{-1}) than in the spectra of the complexes (939 cm^{-1}), confirming the complexation. The spectra of compounds **1b**–**4b** also show the expected medium band at *ca.* 390 cm^{-1} range, assigned to the Ni–S stretching vibration, indicating a didentade coordination by two sulfur atoms of the dithiocarbimato ligand. The ^1H NMR spectra of the complexes showed all the signals for the hydrogen atoms of the tetraphenylphosphonium cation. The remaining signals could be assigned to the alkyl groups of the dithiocarbimate moiety. The integration curves were consistent with a 2:1 proportion between the tetraphenylphosphonium cation and the complexes anions. The ^{13}C NMR spectra of compounds **1b**–**4b** showed the expected signals due to the dithiocarbimate moiety. The $N{=}CS_2$ signal is shifted in the spectra of the compounds **1b**–**4b** to higher field (*ca.* 210 δ) if compared to the spectra of the ligands **1a**–**4a** (*ca.* 225 δ) due to the complexation by two sulfur atoms [21].



Scheme 1. The synthetic route for the preparation of the nickel(II) dithiocarbimate complexes.

Compounds **2b** and **3b** yielded dark green crystals by slow evaporation of their solutions in methanol:water (2:1) at room temperature. The crystal structure of the compound **4b** is already published by our group [16]. A number of attempts to recrystallise **1b** yielded crystals not suitable for X-ray experiments, but the crystal structure of the analogue $(Bu_4N)_2[Ni(CH_3SO_2N{=}CS_2)_2]$ containing the same anionic dithiocarbimato-nickel(II)-complex of **1b** is already published [22]. The infrared and NMR data for **1b** and $(Bu_4N)_2[Ni(CH_3SO_2N{=}CS_2)_2]$ are very similar, except for the cations signals.

The ortep diagrams [23] for compounds **2b** and **3b** are shown in Figs. 1 and 2, respectively.

All nickel(II) ions lie in a special position, the coordination environment is perfectly planar. The S–Ni bond lengths are 2.2011(11) and 2.1940(10) for **2b,** and 2.1925(11) and 2.1982(11) for **3b**. They are very similar to the S–Ni bond lengths for **4b** and $(Bu_4N)_2$-$[Ni(CH_3SO_2N{=}CS_2)_2]$ [16,22]. The S1–C–N1 angle (α) is larger than the S2–C–N1 angle (β) in the $(Bu_4N)_2[Ni(CH_3SO_2N{=}CS_2)_2]$ [$\alpha = 127(1)°$ and $\beta = 124(1)°$] (Fig. 3) [22]. This is reversed in the structures of **2b**–**4b**, where β (131°) is larger than α (121°) [16]. This fact is consistent with the increase in the size of the alkyl group and can be interpreted on the basis of repulsive interactions between S1 and the lone-pair located on N1 versus the repulsive interactions between S2 and the R group. If the R group is large, the steric effect between S2 and the R group is more important than that between S1 and the lone-pair [22].

The S1-C1 and S2-C1 bonds show the same length for **3b** (1.741 Å) and are nearly equal for **2b** (1.722 and 1.737 Å). They are slightly shorter than the typical C–S single bond length (*ca.* 1.81 Å) due to partial π-delocalization in the NCS_2 groups [24]. The literature reports that the CN bond in potassium dithiocarbimates are approximately equal to 1.35 Å [25,26]. The compounds **2b** and **3b** show slightly shorter CN bonds (1.299 and 1.290 Å) confirming the complexation. These facts can be explained by the increased importance of the canonical form (c) upon complexation (Scheme 2). This leads not only to shorter CN bond lengths in the complexes, but also to lower wavenumbers for the νCS_2 in the spectra of the complexes when compared with the spectra of the ligands, the higher wavenumbers for the νCN in the spectra of the complexes, and the variation on the chemical shift of the dithiocarbimate group carbon atom signal in the ^{13}C NMR spectra after the complexation (see Section 2).

The crystal packing in **2b** and **3b** is formed by alternated layers of the anionic complex and of the counter-ion. Due to the lack of intermolecular interactions involving the terminal atoms of the alkyl groups, structural disorder was observed for compound **3b**, caused by static disorder due to the butyl groups' flexibility and thermal motion. Weak intermolecular interactions of the type C–H···O and C–H···S were observed as detailed in the supplementary material.

The compounds **1a**–**4a** were not very active as vulcanization accelerators, showing very low maximum torque values (*ca.* 10 dN m), indicating a low number of crosslinks, after t_{90} of *ca.* 60 min. As it was said before, the potassium dithiocarbimates are soluble in water and insoluble in most organic solvents, thus presenting low solubility in the natural rubber medium, making it difficult to achieve a good dispersion of the compounds throughout the polymer matrix, thus leading to poor vulcanization.

The efficiency of the **1b–4b** as accelerators for natural rubber vulcanization was investigated by rheometry. Table 2 shows the data obtained from the rheometric curves for **1b–4b**. These results were compared to published data for three commercial accelerators, CBS, MBTS and TMTD, as well as to $(Bu_4N)_2$[Zn(4-

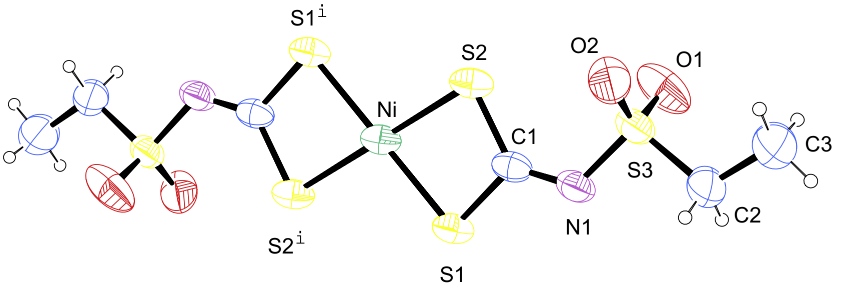


Fig. 1. Ortep [23] diagram of **2b** drawn at 30% of atomic displacement probability and the labelling scheme. Symmetry code: (i) $-x$, $2-x$, $-x$.

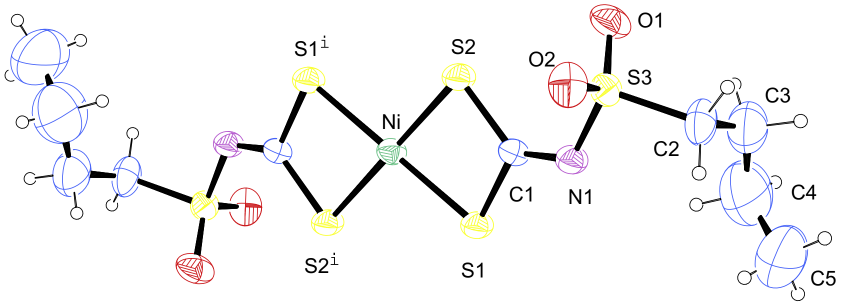


Fig. 2. Ortep [23] diagram of **3b** drawn at 30% of atomic displacement probability and the labelling scheme. The large displacement ellipsoids are caused by static disorder and thermal motion. Symmetry code: (i) $-x$, $1-x$, $2-x$.

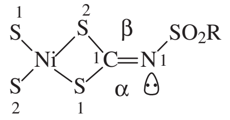
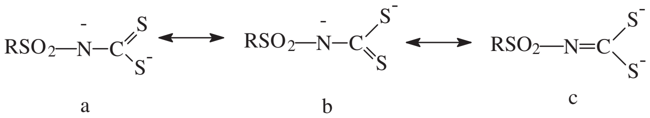


Fig. 3. Comparison between S2–C1–N1 and S1–C1–N1 angles.



Scheme 2. Three canonical forms for *N*-R-sulfonyldithiocarbimate anion.

$CH_3C_6H_4SO_2N{=}CS_2)_2]$, ZNIBU, a bis(dithiocarbimato)-metal(II)-complex previously described [21,27].

Trithiocarbamato-zinc(II)-complexes are inferred to be important intermediates when dithiocarbamates are used in the rubber vulcanization. It has been suggested that they are formed when the zinc complex incorporate extra sulfur atoms from the vulcanization mixture into the dithiocarbamate ring (Scheme 3) [9,10].

From the t_{90} shown in Table 2 it can be seen that vulcanization with **1b–4b** proceeds at lower rates than with ZNIBU [21]. This fact is probably due to the higher lability of the zinc(II) complexes when compared with the nickel(II) complexes in the formation of sulfur-rich compounds [9]. The vulcanization with **1b–4b** also proceeds at lower rates than the commercial compounds in the tested conditions.

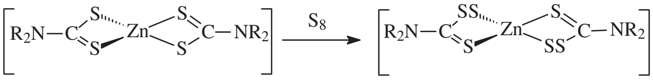
Scorch safety is often a major factor limiting mixing and processing rates. The data in Table 1 shows an increment in the scorch

Table 2
Rheometric parameters for NR mixes compounded with **1b–4b**, ZNIBU, CBS, MBTS or TMTD as the accelerator at 1.2 phr (1.2 g accelerator/100 g NR).

Accelerator	Carbon black (phr)	t_{90} (min)	ts_1 (min)	Ml (dN m)	Mh (dN m)	(Mh − Ml) (dN m)
1b	0	44.4	6.0	2.03	21.56	19.53
	20	32.4	4.2	2.94	28.11	25.18
2b	0	46.2	6.0	2.14	21.90	19.76
	20	36.0	5.4	2.60	26.76	24.16
3b	0	34.2	3.0	1.47	20.89	19.42
	20	25.2	2.4	2.94	29.01	26.08
4b	0	36.6	3.0	3.39	22.80	19.42
	20	25.8	1.8	4.40	27.77	23.37
ZNIBU[a]	0	30. 0	2.4	5.53	25.06	19.53
	20	21.0	1.8	5.31	32.06	26.75
CBS[a]	0	8.73	4.6	2.93	27.09	24.16
	20	8.27	4.4	6.21	34.00	27.79
MBTS[a]	0	7.59	4.0	6.10	23.03	17.03
	20	10.18	3.3	6.32	27.54	21.22
TMTD[a]	0	3.61	1.5	4.63	27.55	22.92
	20	3.81	1.9	6.55	34.40	27.85

phr: parts per hundred parts of the resin; t_{90}: optimim vulcanization time; ts_1: scorch time; Ml: minimum torque; Mh: maximum torque; CBS (N-cyclohexylbenzothiazole sulfenamide), MBTS (dibenzothiazole disulfide), TMTD (tetramethylthiuram disulfide).

[a] Ref. [21].



Scheme 3. Trithiocarbamato-zinc(II) formation.

time with the nickel compounds when compared to the zinc analog. This is possibly due to the same reason influencing the optimum vulcanization time: the less labile Ni–S bond. The ts_1 values observed for **1b**–**2b** are even higher than those presented by the commercial accelerators tested, the four new compounds presenting better scorch safety than TMTD. These results indicate that the new accelerators shall enhance the processing safety of industrial formulations.

The values of (Mh–Ml) are of the same magnitude as those obtained with the commercial accelerators. This indicates that the obtained vulcanizates show similar degrees of crosslinking. Furthermore, the lower minimum torques (Ml) observed suggest that the use of the new nickel complexes shall improve the processibility of the formulations.

Carbon black is commonly used in the rubber industry as a pigment and a reinforcing filler, especially for tires. As expected, the use of carbon black increases the (Mh − Ml) values of the mixes vulcanized with the Ni-derivatives in similar proportions as it does to the compositions obtained from the commercial accelerators. The increase in Ml is related to the well known effect on the viscosity caused by carbon black reinforcing character and the increase in ΔM to the total crosslink density. Carbon black usually has an accelerating effect on the cure behavior of rubber [28]. Table 1 shows that the use of carbon black reduced t_{90} for the new compositions, although at the expenses of the scorch safety.

The effect of the chain length of the dithiocarbimate ligands on the activity of the complexes **1b**–**4b** is not straight forward, but it seems to be governed by two antagonist factors: the solubility on the composition medium, and the mobility on the polymeric matrix. The two larger anions **3b**-**4b** presented lower optimum vulcanization times than the less soluble complexes **1b**–**2b**. Nevertheless, in both groups, the increase in the chain size slightly increases t_{90}, possibly due to a decreased mobility of the larger anion. These aspects shall be further investigated.

4. Conclusions

Four potassium dithiocarbimate were prepared (**1a**–**4a**). The spectroscopic data for **3a** and **4a** were presented here for the first time. Four nickel(II) complexes with *N*-R-sulfonyldithiocarbimate anions were prepared (**1b**–**4b**). The tetraphenylphosphonium salts of the complexes were isolated and characterized by IR, ^{1}H, and ^{13}C NMR and by elemental analyses. The structure of compound **4b** was previously described [16]. The compounds **2b** and **3b** had their structures resolved by X-ray diffraction techniques, showing a perfect square planar coordination of the nickel(II) ion, which is positioned in an inversion center, and the molecular geometries are in good agreement with reported values for similar compounds.

The compounds **1a**–**4a** were not active as vulcanization accelerators, probably due to their low solubility in the natural rubber formulation. On the other hand, the addition of the complexes **1b**–**4b** to a standard natural rubber formulation showed that they behave as accelerators for the vulcanization, being slower than the commercial products CBS, MBTS and TMTD, and slightly slower than the analogous bis(dithiocarbimato)-zinc(II)-complex recently reported [21]. The zinc complex is a faster accelerator probably due the higher inertness of the nickel complexes. But, the new nickel complexes lead to similar degrees of crosslinking and showed higher ts_1 than the compositions with the zinc-analog or with the commercial accelerators.

In the light of the aforementioned results it might be concluded that the new nickel-complexes are active and have facilitated processing by increasing the scorch time. These compounds are the first examples of active nickel-dithiocarbimates, being part of a promising novel class of rubber vulcanization accelerators. Analogous compounds are being prepared to extend the studies on their vulcanization activities and on the rubber properties thus obtained.

5. Supplementary material

CCDC 763755 and 763756 contain the supplementary crystallographic data for 2b and 3b, 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.

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