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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	R_1 = 0.0685
	wR_2 = 0.1553	wR_2 = 0.1587
R_1 (all data)[a]	0.1047	0.1458
wR_2 (all data)[a]	0.1965	0.2195

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