PERGAMON

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 22 (2003) 1561–1566

POLYHEDRON

www.elsevier.com/locate/poly

Nickel(II) complexes of dithiocarbimates from sulfonamides: syntheses and crystal structures

Marcelo R.L. Oliveira [a,*], Renata Diniz [b], Vito M. De Bellis [b], Nelson G. Fernandes [b]

[a] *Departamento de Química, Universidade Federal de Viçosa, Viçosa MG, CEP 36571-000, Brazil*
[b] *Departamento de Química, ICEx, Universidade Federal de Minas Gerais, Belo Horizonte MG, CEP 31270-901, Brazil*

Received 6 October 2002; accepted 24 March 2003

Abstract

This work describes the syntheses of four compounds containing $[Ni(RSO_2N{=}CS_2)_2]^{2-}$ anions: $(Bu_4N)_2[Ni(C_6H_5SO_2N{=}CS_2)_2]$ (**1**), $(Bu_4N)_2[Ni(4\text{-}ClC_6H_4SO_2N{=}CS_2)_2]$ (**2**), $(Bu_4N)_2[Ni(2\text{-}CH_3C_6H_4SO_2N{=}CS_2)_2]$ (**3**) and $(Bu_4N)_2[Ni(4\text{-}BrC_6H_4SO_2N{=}CS_2)_2]$ (**4**). They were obtained in the crystalline form by the reaction of the appropriate potassium *N*-R-sulfonyldithiocarbimate ($RSO_2N{=}CS_2K_2$) with nickel(II) chloride hexahydrate in methanol/water. Elemental analyses were consistent with the proposed formulae. UV–Vis and IR data are consistent with the formation of nickel–sulfur diamagnetic planar complexes. The ^1H NMR and ^{13}C NMR spectra showed the expected signals for the tetra-*n*-butylammonium cation and the dithiocarbimate moieties. Single crystal structure analyses showed that $(Bu_4N)_2[Ni(2\text{-}CH_3C_6H_4SO_2N{=}CS_2)_2]$ crystallizes in the triclinic space group $P\bar{1}$, and $(Bu_4N)_2[Ni(4\text{-}BrC_6H_4SO_2N{=}CS_2)_2]$ crystallizes in the monoclinic space group $P2_1/c$. In these compounds the Ni atom is coordinated to four S atoms in a distorted square plane geometry. The Ni and S atoms form a plane and Ni–S bonds are different from each other. In both compounds the Ni atoms are in the crystallographic center of symmetry.

Keywords: Dithiocarbimate complexes; Nickel complexes; Sulfonamide; Crystal structure

1. Introduction

We have previously described the preparation and the structural studies of two salts of nickel complexes of dithiocarbimates derived from sulfonamides: $(Bu_4N)_2[Ni(CH_3SO_2N{=}CS_2)_2]$ [1] and $(Bu_4N)_2[Ni(4\text{-}CH_3C_6H_4SO_2N{=}CS_2)_2]$ [2]. The literature reports the syntheses and the structural characterization of $(Ph_4P)_2[Ni(C_6H_5SO_2N{=}CS_2)_2]$ and $(Ph_4P)_2[Ni(4\text{-}Cl\text{-}C_6H_4SO_2N{=}CS_2)_2]\cdot 2H_2O$ (Ph_4P = tetraphenylphosphonium cation) but spectroscopic data were not reported [3]. To the best of our knowledge, no other salts containing the *N*-R-sulphonyldithiocarbimatonickelate(II) anion have been structurally characterized.

We became interested in the syntheses and characterization of dithiocarbimates due to their similarities with the dithiocarbamates, which have a wide range of applications. Their metal complexes are used in the rubber vulcanization process and in the obtention of metal sulfides films (especially ZnS and CdS) [4]. Many dithiocarbamate salts and complexes have been used as fungicides [5]. As compounds containing dithiocarbimate anions are less studied and some sulfonamide complexes have also shown anti-fungi activity [6], we decided to prepare a series of complexes of dithiocarbimates from sulfonamides.

In a previous paper the syntheses of the complexes $[Ni(PPh_3)_2(RSO_2N{=}CS_2)]$ (PPh_3 = triphenylphosphine; R = $4\text{-}CH_3C_6H_4$, $2\text{-}CH_3C_6H_4$ and $4\text{-}BrC_6H_4$) were reported [7]. The first complex showed interesting relations between the spectroscopic data and the X-ray diffraction experiment data when compared with the anionic complex $[Ni(4\text{-}CH_3C_6H_4SO_2N{=}CS_2)_2]^{2-}$ [2]. Here we describe the syntheses of the compounds $(Bu_4N)_2[Ni(N\text{-}R\text{-}SO_2N{=}CS_2)_2]$ (R = C_6H_5 (**1**), $4\text{-}ClC_6H_4$ (**2**), $2\text{-}CH_3C_6H_4$ (**3**), $4\text{-}BrC_6H_4$ (**4**)), which were characterized by IR, UV–Vis, ^1H NMR and ^{13}C

---

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

0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00265-1

NMR. Although the anionic complexes of **1** and **2** are not new, their tetra-*n*-butylammonium salts were not described in the literature. The anionic complexes of **3** and **4** are new and were also analyzed by single crystal X-ray diffraction.

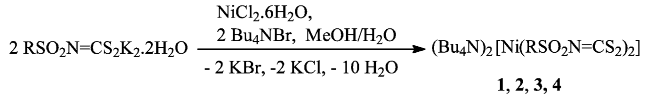
2. Experimental

2.1. Methods and materials

The solvents were purchased from Merck and used without further purification. The sulfonamides, bromobenzenesulphonyl chloride and nickel(II) chloride hexahydrate were purchased from Aldrich. Carbon disulfide and potassium hydroxide were purchased from Vetec and Merck, respectively. Tetra-*n*-butylammonium bromide was purchased from Carlo Erba. The 4-bromobenzenesulfonamide [8] and *N*-R-sulfonyldithiocarbimate potassium salts were prepared according to the literature [9,10]. Melting points (m.p.) were determined with a Mettler FPS equipment. The IR spectra were recorded with a Perkin–Elmer 283 B infrared spectrophotometer using CsI pallets. The UV–Vis spectra were recorded with a Beckman DU 640 spectrometer using a quartz cell of 1 cm path length in EtOH. The ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded with a Varian Mercury 300 spectrophotometer in $CDCl_3$ with TMS as internal standard. Microanalyses of C, H and N were obtained from a Perkin–Elmer 2400 CHN Elemental Analyzer. Nickel was analyzed by atomic absorption on a Hitachi Z-8200 Atomic Absorption Spectrophotometer.

2.2. Syntheses

The compounds were prepared according to the methodology applied for the syntheses of similar compounds [1–3] (see Scheme 1). A solution of nickel(II) chloride hexahydrate (1.0 mmol) and tetra-*n*-butylammonium bromide (2.0 mmol) in methanol (10 ml) was added to a solution of potassium *N*-R-sulfonyldithiocarbimate (2.0 mmol) in methanol:water 1:1 (10 ml) and the mixture was stirred for 1 h at room temperature. The green solid produced was filtered, washed with distilled water and dried under reduced pressure for 1 day, yielding $(Bu_4N)_2[Ni(RSO_2N{=}CS_2)_2]$ ($\approx$80%, based on nickel(II) chloride hexahydrate). Dark green crystals suitable for X-ray structure analyses of **3** and **4** were obtained by slow evaporation of their solutions in methanol:water (1:3) at room temperature.



$$2\ RSO_2N{=}CS_2K_2.2H_2O \xrightarrow[-\ 2\ KBr,\ -2\ KCl,\ -\ 10\ H_2O]{NiCl_2.6H_2O,\ 2\ Bu_4NBr,\ MeOH/H_2O} (Bu_4N)_2[Ni(RSO_2N{=}CS_2)_2]$$

1, 2, 3, 4

1 (R = C_6H_5), **2** (R = 4-ClC_6H_4), **3** (R = 2-$CH_3C_6H_4$), **4** (R = 4-BrC_6H_4)

Scheme 1.

2.2.1. Tetra-n-butylammonium bis(phenylsulphonyldithiocarbimato)nickelate(II) (1)

Elemental analysis: Found (Calc.): C, 55.09 (54.91); H, 8.05 (8.21); N, 5.62 (5.57); Ni, 5.90 (5.83)%. M.p. (°C): 132.5–134.5. IR (most important bands) (cm^{-1}): 1380 (νCN), 1275 (νSO_{2ass}), 1135 (νSO_{2sym}), 925 (νCS_{2ass}), 365 (νNiS). UV–Vis [λ (nm), ε (l mol^{-1} cm^{-1})]: 217 (28 183) ($\pi \to \pi^*$ (NCS)), 254 (30 903) ($\pi \to \pi^*$ (SCS)), 330 (35 481) ($n \to \pi^*$ (S)), 427 (7586) (CT). ^{1}H NMR (dithiocarbimate anion signals) (δ), J (Hz): 7.93 (d, $J = 8.7$, 4H, H2 and H6), 7.40–7.33 (m, 6H, H3, H4 and H5). ^{13}C NMR (δ): 210.63 ($N = CS_2$), 143.60 (C1), 131.03 (C4), 127.91 (C3 and C5), 127.79 (C2 and C6).

2.2.2. Tetra-n-butylammonium bis(4-chlorophenylsulphonyldithiocarbimato)nickelate(II) (2)

Elemental analysis: Found (Calc.): C, 51.32 (51.39); H, 7.72 (7.50); N, 5.26 (5.21); Ni, 5.57 (5.46)%. M.p. (°C): 132.5–134.5. IR (most important bands) (cm^{-1}): 1375 (νCN), 1280, 1265 (νSO_{2ass}), 1130 (νSO_{2sym}), 925 (νCS_{2ass}), 350 (νNiS). UV–Vis [λ (nm), ε (l mol^{-1} cm^{-1})]: 226 (38 760) ($\pi \to \pi^*$ (NCS)), 258 (44 248) ($\pi \to \pi^*$ (SCS)), 322 (30 120) ($n \to \pi^*$ (S)), 432 (7008) (CT); ^{1}H NMR (dithiocarbimate anion signals) (δ), J (Hz): 7.84 (d, $J = 8.4$, 4H, H2 and H6), 7.44 (d, $J = 8.4$, 4H, H3 and H5). ^{13}C NMR (dithiocarbimate anion signals) (δ): 212.73 ($N = CS_2$), 144.54 (C1), 136.89 (C4), 130.13 (C3 and C5), 128.64 (C2 and C6).

2.2.3. Tetra-n-butylammonium bis(2-methylphenylsulphonyldithiocarbimato)nickelate(II) (3)

Elemental analysis: Found (Calc.): C, 55.86 (55.74); H, 8.55 (8.38); N, 5.38 (5.42); Ni, 5.81 (5.67)%. M.p. (°C): 131.0–133.0. IR (most important bands) (cm^{-1}): 1365 (νCN), 1265 (νSO_{2ass}), 1105 (νSO_{2sym}), 930 (νCS_{2ass}), 360 (νNiS). UV–Vis [λ (nm), ε (l mol^{-1} cm^{-1})]: 218 (38 019) ($\pi \to \pi^*$ (NCS)), 254 (41 686) ($\pi \to \pi^*$ (SCS)), 331 (43 652) ($n \to \pi^*$ (S)), 426 (9550) (CT). ^{1}H NMR (dithiocarbimate anion signals) (δ), J (Hz): 7.97 (d, $J = 7.8$, 2H, H6), 7.27–7.24 (m, 2H, H5), 7.15–7.13 (m, 4H, H3, H4), 2.83 (s, 6H, CH_3). ^{13}C NMR (dithiocarbimate anion signals) (δ): 209.35 ($N = CS_2$), 141.82 (C1), 137.27 (C2), 131.03 (C4), 130.67 (C3), 128.89 (C5), 124.62 (C6), 21.03 (CH_3).

2.2.4. Tetra-n-butylammonium bis(4-bromophenylsulphonyldithiocarbimato)nickelate(II) (4)

Elemental analysis: Found (Calc.): C, 47.40 (47.46); H, 6.62 (6.93); N, 4.66 (4.81); Ni, 5.18 (5.04)%. M.p. (°C): 152.0–154.0. IR (most important bands) (cm^{-1}): 1370 (νCN), 1275,1265 (νSO_{2ass}), 1125 (νSO_{2sym}), 930 (νCS_{2ass}), 355 (νNiS). UV–Vis [λ (nm), ε (l mol^{-1} cm^{-1})]: 227 (49 290) ($\pi \to \pi^*$ (NCS)), 256 (36 963) ($\pi \to$

π* (SCS)), 330 (35 999) (n → π* (S)), 431 (8272) (CT), 610 (106) (d → d). ^{1}H NMR (dithiocarbimate anion signals) (δ), J (Hz): 7.81 (d, $J = 8.4$, 4H, H2 and H6), 7.47 (d, 4H, H3 and H5). ^{13}C NMR (dithiocarbimate anion signals) (δ): 210.97 ($N=CS_2$), 142.26 (C1), 130.61 (C3 and C5), 129.35 (C2 and C6), 125.22 (C4).

2.3. X-ray diffraction experiments

Data for single crystals were collected on an automated SIEMENS P4 four-circle diffractometer using graphite-monochromatized Mo Kα radiation (λMo Kα = 0.71073 Å). Data collection, cell refinement and data reduction were performed by XSCANS program [11]. Unit-cell parameters were determined from 20 reflections in the range $22.0° \le 2\theta \le 25°$ for **3** and 42 reflections in the range $18.0° \le 2\theta \le 25°$ for **4**. Intensity measurements were made in the $\theta - 2\theta$ scan mode with $2\theta_{max} = 60°$ and 50° for **3** and **4**, respectively, and three standard reflections monitored at intervals of 300 reflections showed no systematic intensity variation for both data set. The data were corrected for Lorentz, polarization and analytical absorption. The structures were solved by SHELXTL-86 program [12] and refined using the crystallographic program package SHELXTL-97 [13]. Absorption corrections were performed using JANA-98 program [14]. Details of data collection and refinement from X-ray crystallography are shown on Table 1.

3. Results and discussion

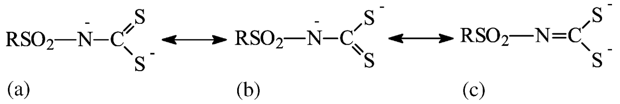
The compounds are stable at the ambient conditions. They are soluble in most of organic solvents and insoluble in water.

The electronic spectra of the nickel complexes in ethanol showed four or five bands. The band V (610 nm), when observed, appeared in the same region of the d–d transition of the spectrum of $[Ni(S_2CNEt_2)_2]$ [15]. The band around 400 nm was assigned to the charge transfer transition. These bands are also observed in the spectra of many other diamagnetic planar nickel(II) complexes that contain the NiS_4^{2-} chromophore [16]. The three other bands were assigned to the internal transitions of the ligands [15–17].

Table 1
Crystal data

Compound	3	4
Formula	$C_{48}H_{86}N_4O_4S_6Ni$	$C_{46}H_{80}Br_2N_4O_4S_6Ni$
Formula weight	1034.29	1164.03
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.522(1)	9.0895(8)
b (Å)	10.742(1)	12.685(1)
c (Å)	13.874(1)	24.454(3)
α (°)	111.420(8)	90.00
β (°)	104.687(7)	95.09(6)
γ (°)	90.560(8)	90.00
V (Å^3)	1403.0(3)	2808.4(6)
Z	1	2
Crystal size (mm)	0.26 × 0.25 × 0.10	0.22 × 0.20 × 0.10
ρ_{calc} (g cm^{-3})	1.224	1.377
μ(Mo Kα) (cm^{-1})	0.61	2.03
Min/max transmission factors	0.8515/0.9466	0.6361/0.8575
No of unique reflexions	7784	4877
No. of observed reflexions, $F_o^2 > 2\sigma(F_o^2)$	5604	3146
No. of parameters refined	290	289
R [a], R_w [b], S [c]	0.0708, 0.1454, 1.069	0.1029, 0.2005, 1.521
RMS peak (e Å^{-3})	0.060	0.089

[a] $R = \Sigma||I_o| - |I_c||/\Sigma|I_o|$.
[b] $R_w = [\Sigma w(|I_o^2| - |I_c^2|)^2/\Sigma w|I_o^2|^2]^{1/2}$; $w = 1/\sigma^2(|I_o^2|)$.
[c] $S = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.



Scheme 2.

There are no strong or medium bands in the 1450–1550 cm^{-1} region in the IR spectra of the potassium dithiocarbimates related to the complexes here prepared, the νCN band being observed at approximately 1260 cm^{-1} [18]. A strong band observed around 1390 cm^{-1} in the spectra of the complexes was assigned to the νCN. In the case of the dithiocarbimates here studied, the CN bond is formally a double bond. However, because of the SO_2 neighbor group, the canonical forms (a) and (b) (Scheme 2) contribute appreciably to the resonance hybrid. This fact explain the low value for de νCN band wavenumbers. The $\nu_{ass}CS_2$ were observed at higher frequencies in the spectra of the potassium salts of dithiocarbimates (≈955 cm^{-1}) [18] than in the spectra of the complexes (≈925 cm^{-1}). The shifts observed in the $\nu_{ass}CS_2$ and νCN bands of the complexes when compared to the spectra of the free ligands, are consistent with the increased importance of the canonical form (c) after complexation (Scheme 2). The spectra of the complexes also show the expected medium/strong band in the 300–400 cm^{-1} range assigned to the NiS vibrations.

The NMR spectra were typical for diamagnetic species and were consistent with the proposed structures. The integration curves on the ^{1}H NMR spectra were consistent with a 2:1 proportion between the tetra-n-butylammonium cation and the dithiocarbimate anion. In the ^{13}C NMR spectra of the complexes the signal of the quaternary carbon of the dithiocarbimate moiety is shifted upfield when compared to the correspondent signal in the potassium dithiocarbimate spectra [18].

This fact is also consistent with the increase in the contribution of canonical form (c) after the complexation (Scheme 2).

The results of the X-ray diffraction for the compounds **3** and **4** show that the Ni atom lies at a crystallographic center of symmetry and the four S atoms around it form a planar environment, once all five atoms are exactly in a plane (Figs. 1 and 2). However, they form a distorted square, once the NiS bond lengths are different from each other. Some selected interatomic distances and bond angles are shown in Table 2. They are in agreement with earlier results obtained for nickel(II) dithiocarbamates [19] and nickel(II) dithiocarbimates [1–3]. Figs. 1 and 2 display the molecular structure for the anions of **3** and **4**. In compound **4**, the tetra-*n*-butylammonium cation is disordered. The disorder is pronounced at the ending of the carbon chains.

The N=CS$_2$ fragments of the complexes show interesting features. As with our compounds **3** and **4**, the CS bond lengths in (Ph$_4$P)$_2$[Ni(C$_6$H$_5$SO$_2$N=CS$_2$)$_2$] and (Ph$_4$P)$_2$[Ni(4-ClC$_6$H$_4$SO$_2$N=CS$_2$)$_2$]·2H$_2$O are nearly equal [3]. However, in the parent ligands they are quite different [10] (Table 3). Their differences can be explained by the greater repulsive interaction between S(2) and the lone-pair located on the nitrogen [10] than the repulsion between S(1) and the RSO$_2$ group. When the complexation occurs two factors must be considered. First, the S(1)–C(1)–S(2) angle decreases. This fact weakens the interaction between S(2) and the nitrogen lone-pair favoring the C(1)–S(2) bond length reduction. On the other hand, the approximation between S(1) and S(2), favors an increase in the C(1)–S(2) and C(1)–S(1) bond lengths. Second, the contribution of the canonical form (c) to the resonance hybrid increases. These factors acting simultaneously can explain the data displayed in Table 3.

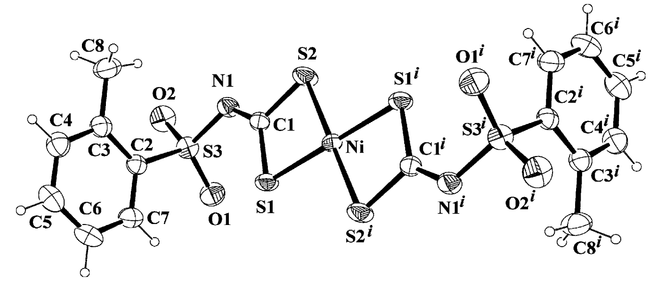


Fig. 1. ORTEPIII drawing of the anion of compound **3**. Displacement ellipsoids are drawn to include 25% probability. Symmetry code *i* (−*x*, −*y*, −*z*).

The CN double bonds in (Ph$_4$P)$_2$[Ni(C$_6$H$_5$SO$_2$N=CS$_2$)$_2$] and (Ph$_4$P)$_2$[Ni(4-ClC$_6$H$_4$SO$_2$N=CS$_2$)$_2$]·2H$_2$O [3] have approximately the same lengths of the CN bonds in **3** and **4**, and are shorter than the CN bonds in the (C$_6$H$_5$SO$_2$N=CS$_2$)$^{2-}$ and (4-ClC$_6$H$_4$SO$_2$N=CS$_2$)$^{2-}$ anions [10] (Table 4). On the other hand, the CN bonds in these anionic complexes are longer than in the neutral complexes [Ni(PPh$_3$)$_2$(RSO$_2$N=CS$_2$)] (PPh$_3$ = triphenylphosphine, R = 2-CH$_3$C$_6$H$_4$ and 4-BrC$_6$H$_4$) [7]. This fact is probably due to a major negative charge on the Ni atom in the anionic complexes of **3** and **4** in comparison to the neutral complexes. The substitution of one dithiocarbimate ion by two triphenylphosphine molecules is expected to result in a greater drift of electrons from the remainder dithiocarbimate ion to the metal, favoring the canonical form (c) (Fig. 1).

4. Conclusion

Four novel tetra-*n*-butylammonium salts of nickel(II) dithiocarbimates complexes from sulfonamides were described. The novel anionic complexes of **3** and **4** were also characterized by X-ray diffraction.

There is an interesting relationship between the spectroscopic data and the X-ray experiments results (Table 4) that pointed to an increase of the contribution of the canonical form (c) to the resonance hybrid from the ligands to the complexes, with a consequent increase of the CN double bond character. Thus, in the IR spectra the wavenumbers of the *ν*CN are smaller for the ligands than for the complexes, the NMR spectra show that the carbon atom of the dithiocarbimate moiety are more shielded in the complexes than in the parent ligands, and the crystallographic data show that the CN bond are shorter in the complexes than in the ligands. When the data for the compounds **3** and **4** are compared with the data for [Ni(PPh$_3$)$_2$(RSO$_2$N=CS$_2$)]

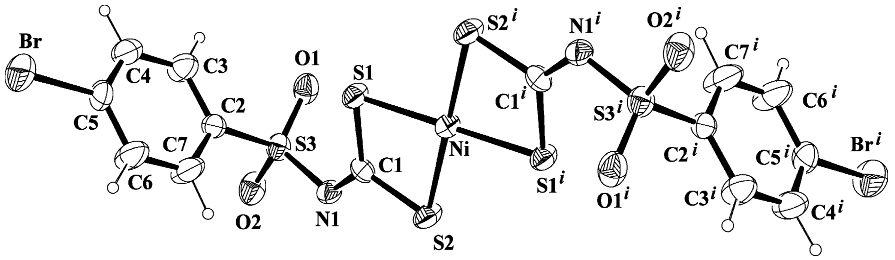


Fig. 2. ORTEPIII drawing of the anion of compound **4**. Displacement ellipsoids are drawn to include 25% probability. Symmetry code *i* (1−*x*, 1−*y*, −*z*).

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

	3	**4**		**3**	**4**
Bond lengths					
Ni–S(1)	2.198(1)	2.201(3)	N(1)–S(3)	1.630(2)	1.620(9)
Ni–S(2)	2.187(1)	2.211(2)	O(1)–S(3)	1.437(2)	1.426(8)
C(1)–S(1)	1.731(3)	1.722(10)	O(2)–S(3)	1.440(2)	1.437(8)
C(1)–S(2)	1.731(3)	1.722(11)	C(2)–S(3)	1.781(3)	1.767(11)
C(1)–N(1)	1.311(3)	1.321(12)			
Bond angles					
S(1)–Ni–S(2)	78.84(3)	78.56(10)	O(1)–S(3)–N(1)	112.9(14)	112.1(5)
C(1)–S(1)–Ni	86.86(10)	86.5(4)	O(2)–S(3)–N(1)	104.98(13)	105.8(5)
C(1)–S(2)–Ni	87.20(9)	86.1(4)	O(1)–S(3)–C(2)	107.38(14)	107.8(5)
S(1)–C(1)–S(2)	107.09(15)	108.4(6)	O(2)–S(3)–C(2)	106.2(13)	105.6(5)
S(1)–C(1)–N(1)	131.8(2)	130.2(8)	N(1)–S(3)–C(2)	107.30(12)	109.0(5)
S(2)–C(1)–N(1)	121.1(2)	121.4(8)	S(3)–N(1)–C(1)	121.1(2)	122.6(7)
O(1)–S(3)–O(2)	116.15(14)	116.2(5)			

Table 3
Comparison between the CS_2 bonds in the dithiocarbimate anions

Substances	C(1)–S(1) (Å)	C(1)–S(2) (Å)	S(1)–C(1)–S(2) (°)
$K_2(C_6H_5SO_2N = CS_2) \cdot 2H_2O$ [a]	1.701(7)	1.745(7)	119.4(4)
$(PPh_4)_2[Ni(C_6H_5SO_2N{=}CS_2)_2]$ [b]	1.70(1)	1.72(1)	109.2(7)
$K_2(4\text{-}ClC_6H_4SO_2N{=}CS_2) \cdot 2H_2O$ [a]	1.704(4)	1.741(3)	119.4(2)
$(PPh_4)_2[Ni(4\text{-}ClC_6H_4SO_2N{=}CS_2)_2] \cdot 2H_2O$ [b]	1.724(5)	1.724(4)	108.3(3)
3	1.731(3)	1.731(3)	107.09(15)
4	1.722(10)	1.722(11)	108.4(6)

[a] Ref. [10].
[b] Ref. [3].

Table 4
Comparison between crystallographic and spectroscopic data for the CN bond in the dithiocarbimate anions

Substances	νCN (cm^{-1})	^{13}C chemical shift (NCS_2) (ppm)	CN length (Å)
$K_2(C_6H_5SO_2N{=}CS_2) \cdot 2H_2O$ [a,b]	1255	223.19	1.342(9)
1 [c]	1380	210.63	1.32(2)
$K_2(4\text{-}ClC_6H_4SO_2N{=}CS_2) \cdot 2H_2O$ [a,b]	obscured	225.72	1.354(5)
2 [c]	1375	212.73	1.320(7)
$K_2(2\text{-}CH_3C_6H_4SO_2N{=}CS_2) \cdot 2H_2O$ [a]	1280	222.74	
3	1365	209.35	1.311(3)
$[Ni(PPh_3)_2(2\text{-}CH_3C_6H_5N{=}CS_2)]$ [d]	1440	197.35	1.279(3)
$K_2(4\text{-}BrC_6H_4SO_2N{=}CS_2) \cdot 2H_2O$ [a]	obscured	225.74	
4	1370	210.97	1.321(12)
$[Ni(PPh_3)_2(4\text{-}BrC_6H_5N{=}CS_2)]$ [d]	1435	*	1.296(4)
$K_2(4\text{-}CH_3C_6H_4SO_2N{=}CS_2) \cdot 2H_2O$ [a]	1260	225.19	
$[Ni(4\text{-}CH_3C_6H_4SO_2N{=}CS_2)]$ [e]	1390	210.07	1.35(2)
$[Ni(PPh_3)_2(4\text{-}CH_3C_6H_5N{=}CS_2)]$ [d]	1445	197.37	1.288(5)

*Not observed.
[a] IR and NMR data from Ref. [18].
[b] Crystallographic data from Ref. [10].
[c] Crystallographic data for tetraphenylphosphonium salts (dihydrate for **2**) from Ref. [3].
[d] Data from Ref. [7].
[e] Data from Ref. [2].

(PPh_3 = triphenylphosphine, R = 2-$CH_3C_6H_4$ and 4-BrC_6H_4) [7] the same tendency is observed. Thus, the chemical shifts of the signal for the carbon atom of the $N{=}CS_2$ fragment is observed at lower field in the ^{13}C NMR spectra of compounds **3** and **4** if compared to these neutral complexes. The CN bonds are longer in the anionic complexes and the correspondent *v*CN bands appears at lower wavenumbers in the IR spectra of **3** and **4**.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 168707 and 168708 for the **3** and **4**, respectively. Copies of this information may be obtained free of charge from The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work has been supported by FAPEMIG (Grant CEX 1123/90), FINEP, CNPq and CAPES (Brazil).

References

[1] M.R.L. Oliveira, V.M. De Bellis, N.G. Fernandes, Struct. Chem. 8 (3) (1997) 205.

[2] M.R.L. Oliveira, J.E.J.C. Graúdo, V.M. De Bellis, N.L. Speziali, Struct. Chem. 10 (1) (1999) 41.

[3] H.U. Hummel, U.Z. Korn, Naturforsch 44B (1989) 29.

[4] M.J. Cox, E.R.T. Tienkink, Z. Kristallogr. 214 (1999) 630.

[5] D. Coucouvanis, Prog. Inorg. Chem. 11 (1969) 233.

[6] A. Mastrolorenzo, A. Scozzafava, C.T. Supuran, Eur. J. Pharm. Sci. 11 (2000) 99.

[7] M.R.L. Oliveira, H.P. Vieira, G.J. Perpétuo, J. Janczak, V.M. De Bellis, Polyhedron 21 (22) (2002) 2243.

[8] A.I. Vogel, A Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis, third ed., Longmans, London, 1956, p. 543.

[9] K. Hartke, Archiv der Pharmazie 299 (1966) 174.

[10] H.U. Hummel, U.Z. Korn, Naturforsch 44B (1989) 24.

[11] Siemens. XSCANS User's Manual, Analytical X-ray Instruments Inc. Madison, WI, 1991.

[12] G.M. Sheldrick, SHELXTL-PC. Structure Determination Software Programs, Siemens Alnalytical X-ray Intruments Inc, Madison, WI, 1990.

[13] G.M. Sheldrick, SHELXL-97. Program for the refinement of crystal Structures. University of Göttingen, Germany, 1997, Release 97-2.

[14] V. Petricek, M. Dusek, M. JANA'98. A Crystallographic Computing System. Institute of Physics. Academy of Science of Czech Republic, Prague, Czech Republic, 1998.

[15] R. Dingle, Inorg. Chem. 10 (1971) 1141.

[16] C.A. Tsipis, I.J. Meleziadis, D.P. Kessissoglou, G.A. Katsoulos, Inorg. Chim. Acta 90 (1984) L19.

[17] C.C. Hadjikostas, G.A. Katsoulos, M.P. Sigalas, C.A. Tsipis, Inorg. Chim. Acta 163 (1989) 173.

[18] M.R.L. Oliveira, V.M. De Bellis, Trans. Met. Chem. 24 (2) (1999) 127.

[19] M. Bonamico, G. Dessy, C. Mariani, A. Valiago, L. Zabonelli, Acta Cryst. 19 (1965) 619.