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# Syntheses, crystal structure and spectroscopic characterization of novel *N*-R-sulfonyldithiocarbimate and triphenylphosphine nickel(II) complexes

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## Abstract

Three new complexes of the general formula: $[Ni(PPh_3)_2(RSO_2N{=}CS_2)]$ where R = $2\text{-}CH_3C_6H_4$ (**1**), $4\text{-}CH_3C_6H_4$ (**2**) and $4\text{-}BrC_6H_4$ (**3**) were obtained in crystalline form by the reaction of the appropriate potassium *N*-R-sulfonyldithiocarbimates ($K_2(RSO_2N{=}CS_2)$) and triphenylphosphine with nickel(II) chloride in ethanol–water. The **1** complex crystallizes in the centrosymmetric space group of the triclinic system with two molecules per unit cell, while **2** and **3** complexes crystallize in the *Pbca* space group of the orthorhombic system with eight molecules per unit cell. The X-ray single-crystal analysis showed that all complexes present a similarly distorted square-planar configuration around the nickel atom due to the steric effect of the triphenylphosphine ligands and the didendate chelation by the two sulfur atoms of the dithiocarbimate ligand. The IR and UV–Vis spectral data are consistent with the formation of almost square-planar nickel complexes. The $^1H$ NMR, $^{13}C$ NMR, $^{31}P$ NMR spectra showed the expected signals for the triphenylphosphine and the dithiocarbimate moieties.

*Keywords:* Dithiocarbimates; Triphenylphosphine; Nickel complexes; Crystal structures

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## 1. Introduction

We became interested in the syntheses and characterization of dithiocarbimate metal complexes due to their similarities with the dithiocarbamate compounds, which have a wide range of applications. For example, they are used in the rubber vulcanization process [1] as well as several dithiocarbamates salts and complexes have been used as fungicides [2]. Nickel(II) dithiocarbamates normally react with phosphines to form complexes with the $NiS_2P_2$ chromophore [3]. Complexes containing the $NiXS_2P$ chromophore (X = halide) are usually obtained by reacting $NiX_2$ with dithiocarbamates and $PR_3$ (R = alkyl/aryl) [4]. Complexes containing the $NiXS_2P$ chromophore have shown catalytic activity, especially for oligomerization of olefins [5–7]. Many complexes that involve nickel(II), phosphine and dithiocarbamate ligands, as $[Ni(L)(PR_3)_2]^+$, $[Ni(L)(P{-}P)]^+$, $[NiX(L)(PR_3)_2]$ and $[NiX(L)(P{-}P)]$ (L = several dithiocarbamates, R = many different groups, X = halides and pseudohalides and P–P = diphosphines) have been characterized [8,9].

Some complexes of palladium and platinum with dithiocarbimates and phosphines have been structurally characterized and using the quantum chemical calculations (CNDO/2) the mechanism of the formation of the complexes has been investigated [10,11]. Additionally, dimeric nickel complexes $[Ni(PR_3)_2(R'N{=}CS_2)]$ (R and R′ = alkyl/aryl) have been obtained by the reaction of

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$[Ni(NO_2)(R'NHCS_2)(PR_3)]$ or $[NiBr(R'NHCS_2)(PR_3)]$ with Lewis bases such as $(CH_3)_3N$ and $NH_3$ [12]. However, their structures were not determined by X-ray diffraction techniques.

Herein we investigate the three new bis(triphenylphosphine)*N*-R-sulfonyldithio-carbimatenickel(II) complexes ($R = 2\text{-}CH_3C_6H_4$, $4\text{-}CH_3C_6H_4$, $4\text{-}BrC_6H_4$) that were obtained in the crystalline form by the reaction of $NiCl_2 \cdot 6H_2O$ with triphenylphosphine and dithiocarbimate anions derived from sulfonamides. These complexes were characterized by UV–Vis, IR, $^1H$, $^{13}C$ and $^{31}P$ NMR, elemental analyses for C, H, N, Ni and by single crystal X-ray diffraction techniques.

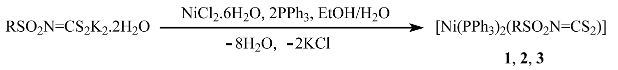
## 2. Experimental

### *2.1. Methods and materials*

The solvents were purchased from Merck and used without further purification. The sulfonamides, 4-bromophenylsulphonyl chloride, nickel(II) chloride hexahydrate and triphenylphosphine were purchased from Aldrich. Carbon disulfide and potassium hydroxide were purchased from Vetec. The 4-bromobenzenesulphonamide was prepared from the 4-bromobenzenesulphonyl chloride as described elsewhere [13]. The *N*-R-sulfonyldithiocarbimate potassium salts dihydrate were prepared in dimethylformamide from sulfonamides analogously as described in the literature [14,15]. These salts, which are soluble in water and insoluble in most of the organic solvents, were re-crystallized from hot ethanol–water. Melting points (m.p.) were determined with a Mettler FP5 equipment. Microanalyses for C, H and N were obtained from a Perkin–Elmer 2400 CHN. Nickel was analyzed by atomic absorption with a Hitachi Z-8200 Atomic Absorption Spectrophotometer. The IR spectra were recorded with a Perkin–Elmer 283 B infrared spectrophotometer using CsI pellets. The UV–Vis spectra were recorded with a Beckman DU 640 spectrometer using nujol mull suspension. The $^1H$ (400 MHz), $^{13}C$ (100 MHz) and $^{31}P$ (162 MHz) NMR spectra of the complexes were recorded on a Bruker Advance RX-400 spectrophotometer in $CDCl_3$ with TMS ($H_3PO_4$ for $^{31}P$ NMR spectra) as internal standard.

### *2.2. Syntheses*

The syntheses of the nickel(II) complexes were performed according to the Scheme 1. A solution of *N*-R-sulfonyldithiocarbimate dihydrate (1.0 mmol) in water (10 ml) was added to a solution of triphenylphosphine (2.0 mmol) in ethanol (40 ml). Nickel(II) chloride hexahydrate (1.0 mmol) was added to the suspension and the reaction mixture was stirred for 6 h at room temperature (r.t.). The color of the suspension changed from green to pink/red. The solid product of the reaction was filtered, washed with distilled water and ethanol, and dried under reduced pressure for 1 day yielding $[Ni(PPh_3)_2(RSO_2N{=}CS_2)]$ (ca. 70%). Suitable crystals for X-ray structure analysis were obtained after slow evaporation of solutions of the compounds in dichloromethane–methanol and few drops of water.



$$RSO_2N{=}CS_2K_2.2H_2O \xrightarrow[-8H_2O,\ -2KCl]{NiCl_2.6H_2O,\ 2PPh_3,\ EtOH/H_2O} [Ni(PPh_3)_2(RSO_2N{=}CS_2)]$$

**1, 2, 3**

**1** ($R = 2\text{-}CH_3C_6H_4$), **2** ($R = 4\text{-}CH_3C_6H_4$), **3** ($R = 4\text{-}BrC_6H_4$)

Scheme 1.

#### *2.2.1. Bis(triphenylphosphine)2-methylphenyldithiocarbimatenickel(II) (**1**)*

Elemental analysis: Found (Calc.): C, 63.39 (63.78); H, 4.37 (4.50); N, 1.70 (1.69); Ni, 7.01 (7.08)%. M.p. (°C): 165.5–166.0. UV–Vis (nm): 197; 236; 320; 426 and 557. IR (most intense bands) ($cm^{-1}$): 1440 $\nu$(C=N); 1300 $\nu_{ass}(SO_2)$; 1120 $\nu_{sym}(SO_2)$; 920 $\nu_{ass}(CS_2)$ and 345 $\nu$(NiS). $^1H$ NMR ($\delta$): 7.88–7.79 (m, 1H, H2′ (R group)); 7.42–7.05 (m, 33H, H3′, H4′, H5′, R group and triphenylphosphine signals) and 2.63 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR ($\delta$): 197.35 ($N{=}CS_2$); 140.77 (C1′); 137.98 (C2′); 131.49 (C3′); 129.02 (C5′); 127.94 (C6′); 125.09 (C4′) and 20.84 ($CH_3$). Triphenylphosphine signals: 134.39 (t, $J = 7$, C2″ and C6″); 130.89 (s, C4″); 129.35 (d, $J = 31$, C1″); 128.45 (t, $J = 7$, C3″ and C5″). $^{31}P$ NMR ($\delta$): 31.69 (s).

#### *2.2.2. Bis(triphenylphosphine)4-methylphenyldithiocarbimatenickel(II) (**2**)*

Elemental analysis: Found (Calc.): C, 63.91 (63.78); H, 4.39 (4.50) N, 1.72 (1.69); Ni, 7.11 (7.08)%. M.p. (°C): 166.5–167.0. UV–Vis (nm): 197; 234; 320; 429 and 557. IR (most intense bands) ($cm^{-1}$): 1445 $\nu$(C=N); 1300 $\nu_{ass}(SO_2)$; 1135 $\nu_{sym}(SO_2)$; 910 $\nu_{ass}(CS_2)$ and 344 $\nu$(NiS). $^1H$ NMR ($\delta$): 7.69–7.57 (m, 2H, H2′ and H6′ (R group)); 7.44–7.20 (m, 30H triphenylphosphine signals); 7.17–7.15 (m, 2H, H3′ and H5′ (R group)) and 2.39 (s, 3H, CH3). $^{13}C\{^1H\}$ NMR ($\delta$): 197.37 (N=CS2); 142.58 (C1′); 139.42 (C4′); 128.94 (C3′ and C5′); 127.49 (C2′ and C6′); 21.78 ($CH_3$). Triphenylphosphine signals: 134.29 (t, $J = 6$, C2″ and C6″); 130.64 (s, C4″); 129.25 (d, $J = 46$, C1″); 128.27 (t, $J = 5$, C3″ and C5″). $^{31}P$ NMR ($\delta$): 30.47 (s).

#### *2.2.3. Bis(triphenylphosphine)4-bromophenyldithiocarbimatenickel(II) (**3**)*

Found (Calc.): C, 57.29 (57.80); H, 3.79 (3.84); N, 1.60 (1.57); Ni, 6.61 (6.57)%. M.p. (°C): 169.0–170.5. UV–Vis (nm): 193; 247; 308; 426 and 557. IR (most intense bands) ($cm^{-1}$): 1435 $\nu$(C=N); 1310 $\nu_{ass}(SO_2)$; 1135 $\nu_{sym}(SO_2)$; 915 $\nu_{ass}(CS_2)$ and 335 $\nu$(NiS). $^1H$ NMR ($\delta$): 7.68–7.65 (m, 2H, H2′ and H6′ (R group)); 7.45–

7.19 (m, 32H, H3′, H5′ R group and triphenylphosphine signals). $^{13}C\{^1H\}$ NMR ($\delta$): 145.00 (C1′); 131.93 (C3′ and C5′); 128.88 (C2′ and C6′); 127.50 (C4′). Triphenylphosphine signals: 134.29 (t, $J = 6$, C2″ and C6″); 130.75 (s, C4″); 129.33 (d, $J = 54$, C1″); 128.33 (t, $J = 5$, C3″ and C5″). $^{31}P$ NMR ($\delta$): 31.75 (s).

### 2.3. *X-ray crystallography*

X-ray intensity data for all crystals were collected using graphite monochromatic Mo K$\alpha$ radiation on a four circle KUMA KM-4 diffractometer with a two-dimensional area CCD detector. The $\omega$-scan technique with $\Delta\omega = 0.75°$ for each image was used for data collection. The 960 images for six different runs covered over 90% of the Ewald sphere were performed. Initially the lattice parameters were refined on about 200 reflections obtained from 40 images for eight runs with different orientation in the reciprocal space. Finally the lattice parameters were refined by least-squares method based on the all reflection with $I > 4\sigma(F^2)$. One image was used as standard for monitoring the data collection after every 40 images, and no correction on the relative intensity variation was necessary. Integration of the intensities, correction for Lorenz and polarization effects were performed using a KUMA KM-4 CCD program system [16]. Total of 18 419 (9819 independent, $R_{int} = 0.0294$), 27 613 (10 354 independent, $R_{int} = 0.0750$) and 55 811 (9891 independent, $R_{int} = 0.0773$) reflections were collected for the complexes **1**–**3**, respectively. The face-indexed analytical absorption was calculated using the SHELXTL program [17].

The structures were solved by a Patterson heavy-atom method using the SHELXL-97 program [18]. The Patterson map revealed the positions of the nickel, sulfur, bromide (**3**) and some of the P and C atoms. The remaining non-hydrogen atoms were located from difference Fourier synthesis. The structures were refined with anisotropic thermal parameters. Difference Fourier maps gave electron density concentrations approximately located for all hydrogen atom positions; these positions were idealized (HFIX 43 for all hydrogen atoms of the phenyl rings with isotropic thermal parameters of 1.2 $U_{eq}$ of the carbon atoms joined directly to the hydrogen atoms, and HFIX 137 for the $CH_3$ group in the complexes **1** and **2** with isotropic thermal parameters of 1.5 $U_{eq}$ of the methyl carbon atom). Final differences Fourier maps showed no peaks of chemically significance. Details of data collection parameters and final agreement factors are collected in Table 1. Selected bond lengths and angles are listed in Table 2.

## 3. Results and discussion

The compounds are quite stables at the ambient conditions. In contrast to the dithiocarbamate Ni-complexes with the general formula of $[Ni(PR_3)_2(RN{=}CS_2)]$ which are soluble in THF, benzene and dichloromethane [12], these *N*-R-sulfonyldithiocarbimate Ni-complexes characterized in this paper are insoluble in most organic solvents and are slightly soluble in chloroform and dichloromethane. These complexes are stable up to the melting point without decomposition. Attempted to prepare the monotriphenylphosphine Ni-complexes like $K[NiCl(PPh_3)(N\text{-}RSO_2N{=}CS_2)]$ in the same conditions described above, with 1 equiv. of triphenylphosphine was unsuccessful.

The electronic spectra of the complexes show two shoulders (ca. 426 and 557) that are typical for square-planar nickel complexes and are assigned to d–d transitions [9]. The 190–300 nm region in the spectra of the complexes is dominated by three very intense bands of the triphenylphosphine and the dithiocarbimate ligands.

There are no strong or medium bands in the 1400–1600 cm$^{-1}$ region in the IR spectra of the potassium dithiocarbimates related to the complexes **1**–**3**, the $\nu$(CN) band being observed around 1260 cm$^{-1}$ [14,19]. This low value indicates a great contribution of the canonical forms (a) and (b) for the resonance hybrid (Fig. 1). A strong band observed around 1455 cm$^{-1}$ in the spectra of the complexes was assigned to the $\nu$(CN). In the spectrum of the complex $[Ni(PPh_3)_2(4\text{-}CH_3C_6H_4N{=}CS_2)]$ that has no $SO_2$ group linked to the nitrogen atom, this band is located at 1500 cm$^{-1}$ [12]. In the case of the complex $[Ni(4\text{-}CH_3C_6H_4SO_2N{=}CS_2)_2]^{2-}$ this band is observed around 1345 cm$^{-1}$ [20]. This fact is probably due to a major negative charge on the Ni atom in this anionic complex in comparison to the complexes here synthesized. 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. This effect is also observed, for example when the spectrum of the complex $[Ni(dtc)_2]$ (dtc = *N*,*N*-diethyldithiocarbamate) ($\nu$(CN) band is observed in 1518 cm$^{-1}$) is compared with the spectrum of $[Ni(dtc)(PPh_3)_2]^+$ ($\nu$(CN) band is observed in 1530 cm$^{-1}$) [8]. The $\nu_{ass}(CS_2)$ were observed at higher frequency in the spectra of the potassium salts of dithiocarbimates (ca. 955 cm$^{-1}$) [19] than that in the spectra of the complexes here studied (ca. 915 cm$^{-1}$). The shifts observed in the $\nu_{ass}$(CS2) and $\nu$(CN) in the spectra of the complexes when compared with the spectra of the ligands, are consistent with the increased importance of the canonical form (c) after complexation (Fig. 1). The spectra of the complexes also show the expected medium band in the 300–400 cm$^{-1}$ range

Table 1
Crystallographic data

| Complex | **1** | **2** | **3** |
|---|---|---|---|
| Chemical formula | $C_{44}H_{37}NNiO_2P_2S_3$ | $C_{44}H_{37}NNiO_2P_2S_3$ | $C_{43}H_{34}BrNNiO_2P_2S_3$ |
| Formula weight | 828.61 | 828.61 | 893.48 |
| Crystal dimensions (mm) | 0.30 × 0.28 × 0.14 | 0.24 × 0.18 × 0.14 | 0.36 × 0.16 × 0.06 |
| Crystal system | triclinic | orthorhombic | orthorhombic |
| Space group | $P\bar{1}$ | *Pbcn* | *Pbcn* |
| $a$ (Å) | 10.000(2) | 16.556(3) | 16.497(3) |
| $b$ (Å) | 13.923(3) | 18.333(4) | 18.556(4) |
| $c$ (Å) | 14.953(3) | 25.412(5) | 25.364(5) |
| $\alpha$ (°) | 100.16(3) | | |
| $\beta$ (°) | 103.28(3) | | |
| $\gamma$ (°) | 95.20(3) | | |
| $V$ (Å$^3$) | 1975.7(7) | 7713(3) | 7764(3) |
| $Z$ | 2 | 8 | 8 |
| $D_{obsd}$ (g cm$^{-3}$) | 1.39 | 1.42 | 1.52 |
| $D_{calc}$ (g cm$^{-3}$) | 1.393 | 1.427 | 1.529 |
| $T$ (°C) | 295 | 295 | 295 |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 |
| $\mu$ (cm$^{-1}$) | 0.769 | 0.788 | 1.812 |
| Transmission factors: min, max | 0.8020, 0.8999 | 0.8334, 0.8977 | 0.5616, 0.8991 |
| $R(F^2)$ | 0.0433 | 0.0540 | 0.0449 |
| $R_w(F^2)$ | 0.1104 | 0.1385 | 0.0639 |
| $S$ | 1.015 | 1.140 | 1.004 |
| Residual electron density (e Å$^{-3}$) | +0.524 and −0.552 | +0.656 and −0.611 | +0.819 and −1.454 |

[a] Function minimized: $\Sigma\, w(|F_o|-|F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$; $[\Sigma\, w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$, where $N_o$, number of observations, $N_v$, number of variables. The final discrepancy factors: $R = \Sigma|F_o|-|F_c|/\Sigma|F_o|$ and $R_w = [\Sigma\, w(|F_o|-|F_c|)^2/\Sigma\, wF_o^2]^{1/2}$.

assigned to the NiS vibrations [21]. The $\nu$(NiP) band was not observed above 200 cm$^{-1}$.

The NMR spectra of **1**–**3** were typical for diamagnetic species. The $^1$H NMR spectra of the complexes showed the signals for the hydrogen atoms of the triphenylphosphine. The remaining signals could be assigned to the $CH_3$ group of the aromatic moiety and the other aromatic hydrogen atoms. The integration curves on the $^1$H NMR spectra were consistent with a 2:1 proportion between the triphenylphosphine ligands and the dithiocarbimate anion. The signals in the spectra of the free dithiocarbimates [19] and in the complexes show approximate the same chemical shifts. The chemical shifts of the aromatic carbon atoms of the dithiocarbimate anions in the complexes are similar to those of the corresponding sulfonamides [22]. The $N=CS_2$ (C1) signal is shifted in the spectra of the complexes to higher field if compared with the spectra of the ligands (this signal is too weak and was not observed for **3**). Although the solvents are, necessarily different, this shift is expected. If the canonical form (c) (Fig. 1) is more important for the complexes than for the ligands, then the C1 carbon atom is expected to be more shielded in the complexes. The C1 signal for the complex **2** is also shifted to higher field when compared with the spectrum of the correspondent anionic complex $[Ni(4\text{-}CH_3C_6H_4SO_2N{=}CS_2)_2]^{2-}$ [20]. Most of the triphenylphosphine signals in the $^{13}$C NMR spectra appeared as pseudo triplets or doublets. This is consistent with square-planar geometry for the complexes. Doublets or pseudo triplets are commonly observed in the $^{13}$C NMR spectra of bis-phosphine transition metal *cis*-complexes [23]. As expected, the $^{31}$P NMR spectra exhibited only one signal (ca. 30 $\delta$) indicating that all phosphorus atoms in the molecules are magnetically equivalent.

The X-ray molecular structures of the **1**–**3** complexes are illustrated in Fig. 2(a–c), respectively. In all complexes, the nickel cation is coordinated by two triphenylphosphine ligands and chelated by two sulfur atoms of the *N*-R-sulfonyldithiocarbimate anion into a similarly distorted square-planar configuration. The P(1)–Ni(1)–S(1) and P(2)–Ni(1)–S(2) angles are less distorted from 90° than the P(1)–Ni(1)–P(2) and S(1)–Ni(1)–S(2) angles. The P(1)–Ni(1)–P(2) angle is significantly greater than 90° in all complexes due to the steric effect of the large triphenylphosphine ligands and the S(1)–Ni(1)–S(2) angle is smaller than 90° due to the chelation of the *N*-R-sulfonyldithiocarbimate ligand. The *N*-R-sulfonyldithiocarbimate anion $(RSO_2N{=}CS_2)^{2-}$ as an asymmetric didentate ligand forms a stable four membered ring by chelation through the two sulfur atoms ($NiS_2C$). The Ni(1)–S(1) bond lengths of 2.190(1) in **1**, 2.179(1) in **2** and 2.178(1) in **3** Å are shorter than the Ni(1)–S(2) [2.220(1), 2.219(1) and 2.224(1) Å in **1**, **2** and **3**, respectively]. These deviations are more obvious than those found in the $[Ni(CH_3SO_2N{=}CS_2)_2]^{2-}$ [24]. This fact may be ex-

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

| | **1** | **2** | **3** |
|---|---|---|---|
| *Bond lengths* | | | |
| Ni(1)–S(1) | 2.190(1) | 2.179(1) | 2.178(1) |
| Ni(1)–S(2) | 2.220(1) | 2.219(1) | 2.224(1) |
| Ni(1)–P(1) | 2.206(1) | 2.134(1) | 2.227(1) |
| Ni(1)–P(2) | 2.224(1) | 2.230(1) | 2.184(1) |
| P(1)–C(11) | 1.833(3) | 1.846(4) | 1.840(4) |
| P(1)–C(21) | 1.837(3) | 1.805(3) | 1.808(3) |
| P(1)–C(31) | 1.825(3) | 1.829(4) | 1.823(4) |
| P(2)–C(41) | 1.838(3) | 1.821(4) | 1.820(3) |
| P(2)–C(51) | 1.852(3) | 1.812(4) | 1.837(3) |
| P(2)–C(61) | 1.834(3) | 1.830(4) | 1.834(4) |
| C(1)–S(1) | 1.751(3) | 1.739(4) | 1.764(3) |
| C(1)–S(2) | 1.740(3) | 1.743(4) | 1.725(3) |
| C(1)–N(1) | 1.279(3) | 1.288(5) | 1.296(4) |
| N(1)–S(3) | 1.631(2) | 1.655(3) | 1.626(3) |
| O(1)–S(3) | 1.441(2) | 1.435(3) | 1.430(2) |
| O(2)–S(3) | 1.431(2) | 1.441(3) | 1.422(2) |
| C(2)–S(3) | 1.783(3) | 1.767(4) | 1.776(4) |
| C(3)–C(8) | 1.497(4) | | |
| C(5)–C(8) | | 1.505(7) | |
| C(5)–Br(1) | | | 1.890(5) |
| *Bond angles* | | | |
| P(1)–Ni(1)–P(2) | 98.48(4) | 98.84(4) | 98.92(4) |
| S(1)–Ni(1)–S(2) | 77.87(4) | 78.18(4) | 78.14(3) |
| S(1)–Ni(1)–P(1) | 92.31(4) | 90.76(4) | 91.16(4) |
| S(1)–Ni(1)–P(2) | 168.21(3) | 168.58(4) | 167.95(4) |
| S(2)–Ni(1)–P(1) | 167.92(3) | 167.01(4) | 167.42(4) |
| S(2)–Ni(1)–P(2) | 91.96(4) | 92.94(4) | 92.53(4) |
| S(1)–C(1)–S(2) | 105.1(2) | 105.6(2) | 105.3(2) |
| S(1)–C(1)–N(1) | 132.0(2) | 132.2(3) | 131.0(3) |
| S(2)–C(1)–N(1) | 122.9(2) | 122.1(3) | 123.6(3) |
| C(1)–N(1)–S(3) | 120.7(2) | 120.6(3) | 121.5(2) |
| N(1)–S(3)–O(1) | 111.9(1) | 111.6(2) | 111.5(2) |
| N(1)–S(3)–O(2) | 106.0(1) | 104.2(2) | 105.8(2) |
| O(1)–S(3)–O(2) | 116.9(1) | 118.7(2) | 117.7(2) |
| N(1)–S(3)–C(2) | 105.7(1) | 107.3(2) | 107.7(2) |
| O(1)–S(3)–C(2) | 108.2(1) | 108.0(2) | 106.9(2) |
| O(2)–S(3)–C(2) | 107.5(1) | 106.5(2) | 106.8(2) |

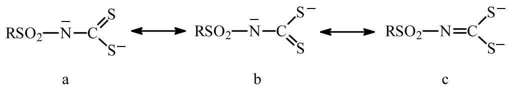


Fig. 1. Some possible canonical forms for the *N*-R-sulfonildithiocarbimate anion.

plained by the stereochemistry affecting the phenyl ring of the *N*-R-sulfonyldithiocarbimate ligand, which is located in *cis* position to the S1 atom. The C1–N1 bond lengths of 1.279(3), 1.288(3) and 1.296(4) in **1**–**3**, respectively, are shorter than the normal single C($sp^2$)–N($sp^2$) bond length (ca. 1.35 Å), and similar to that of the double bond C=N (1.275–1.295 Å) [25,26]. The C(1)–S(1) and C(1)–S(2) averaged bond lengths (1.745 Å) are slightly shorter than the typical C–S single bond length (ca. 1.81 Å) due to partial π-delocalization in the S–C–S group. The S(1)–C(1)–N(1) angles of 132.0(2)°,

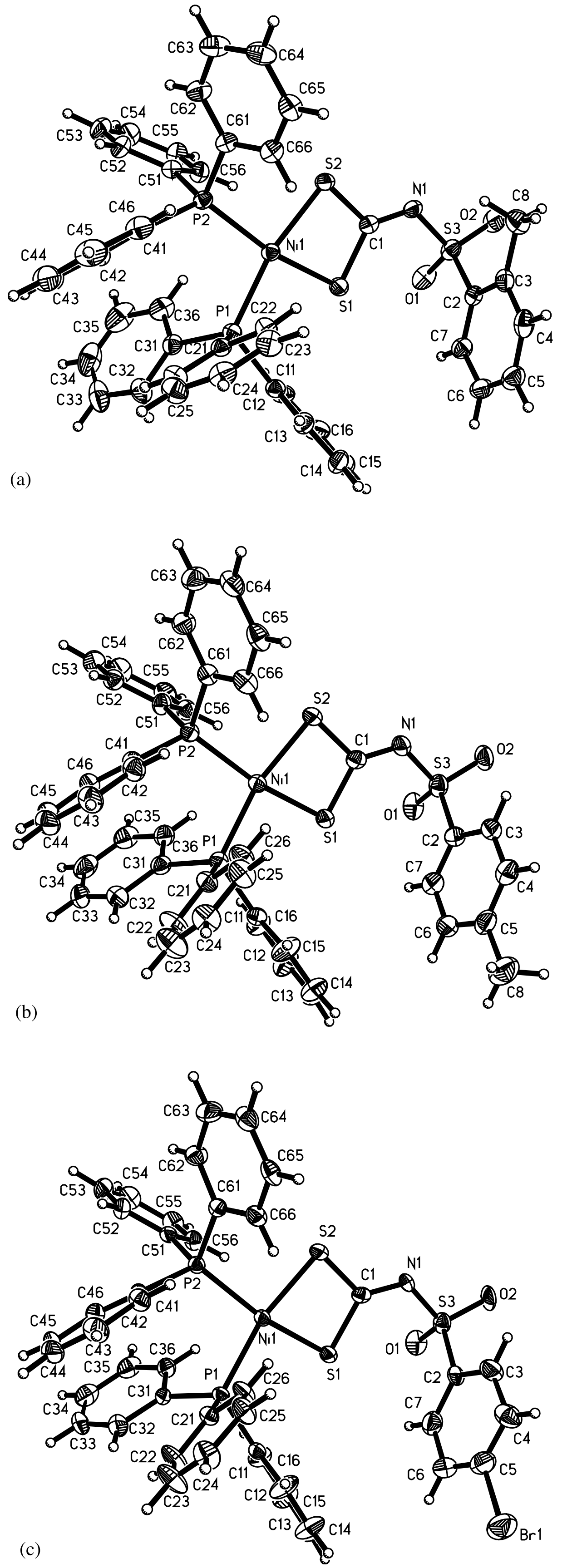
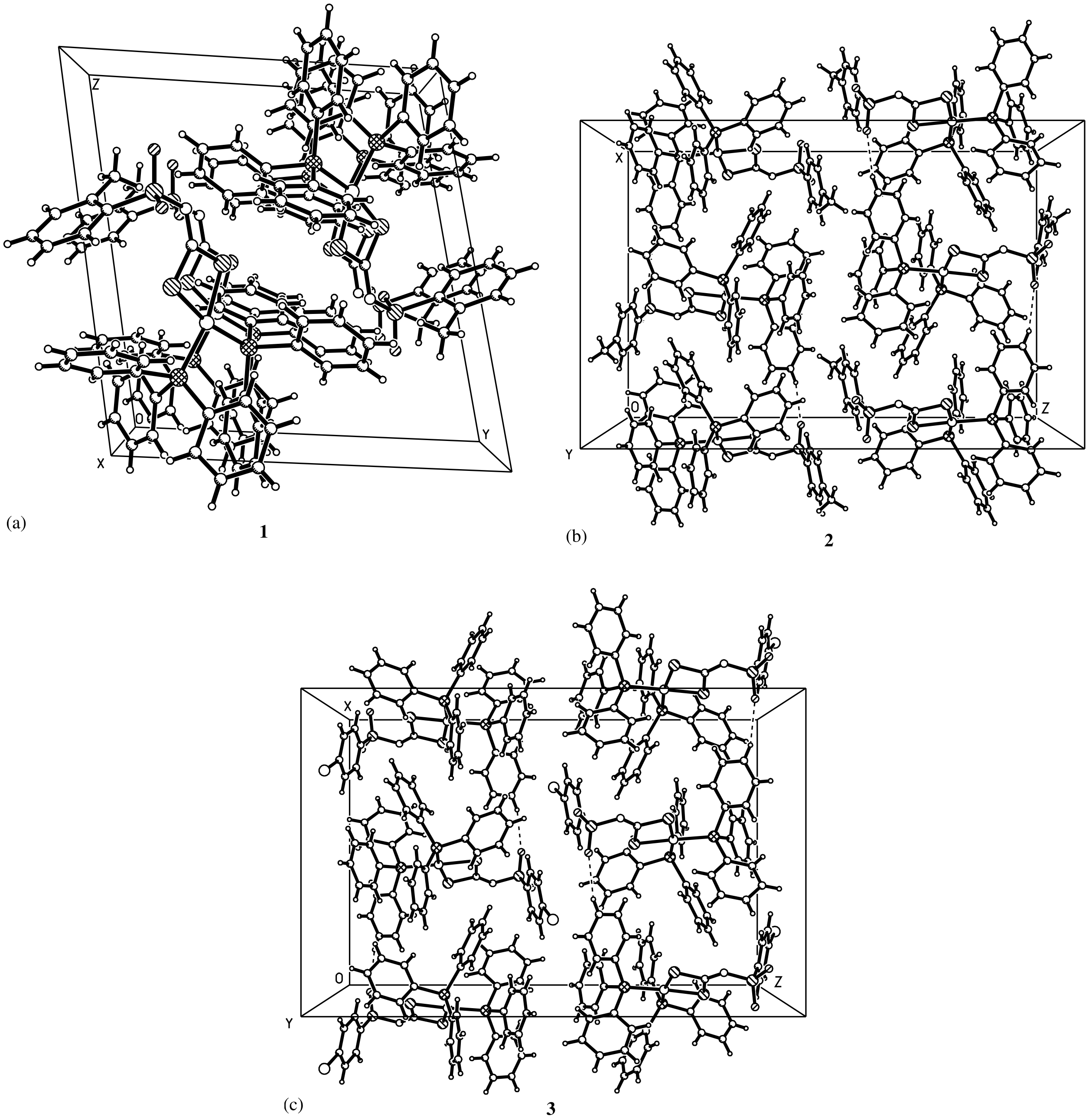


Fig. 2. View of the molecular structure of the complexes **1** (a), **2** (b) and **3** (c).

132.2(3)° and 131.0(3)° in the complexes **1**–**3**, respectively, are significantly greater than S(2)–C(1)–N(1) [122.9(2) in **1**, 122.1(3)° in **2** and 123.6(3)° in **3**] due to the interaction between the $SO_2R$ group and the S(1) atom, which are joined in *cis* position in relation to the C(1)–N(1) bond. The steric effect of the R-sulfonyl group is greater than the effect of the lone-pair of electron at the N(1) atom, since the C(1)–N(1)–S(3) angle is greater than 120° in all complexes. If R is a small group such as $-SO_2CH_3$ [24] or $-C{\equiv}N$ [27] the repulsive interaction predicted by the valence-shell electron pair repulsion theory (VSEPR) [28] between the lone-pair of electron at the N(1) atom and the S(2) atom is greater than the steric effect and the angle S(2)–C(1)–N(1) is greater than the angle S(1)–C(1)–N(1). In other dithiocarbimate complexes with larger R groups, the steric effect between S(1) and R group is more important and similarly as in the **1**–**3** complexes the angle S(1)–C(1)–N(1) is greater than S(2)–C(1)–N(1) [29].

The C(1)–N(1)–S(3) fragment of the *N*-R-sulfonyldithiocarbimate ligand (Fig. 2(a–c)) is coplanar with the $NiS_2P_2$ fragment, thus the P(1)P(2)Ni(1)S(1)S(2)C(1)-N(1)S(3) atoms lie in plane. The phenyl ring of the *N*-R-sulfonyldithiocarbimate ligand is inclined by about



(a) **1**

(b) **2**

(c) **3**

Fig. 3. Molecular arrangements of the complexes **1** (a), **2** (b) and **3** (c) in the unit cells.

Table 3
Comparison between selected crystallographic and spectroscopic data for the CN bond in compound **2** and related compounds

| Parameters | **2** | $[Ni(4\text{-}CH_3C_6H_4SO_2N{=}CS_2)]^{2-}$ [b] | $(4\text{-}CH_3C_6H_4SO_2N{=}CS_2)^{2-}$ [a] |
|---|---|---|---|
| CN length (Å) | 1.288(5) | 1.35(2) | |
| $\nu$(CN) (cm$^{-1}$) | 1445 | 1390 | 1260 |
| $^{13}$C chemical shift (NCS$_2$) (ppm) | 197.37 | 210.07 | 225.19 |

[a] Ref. [19].
[b] Ref. [20].

88.6(2)° in the complex **1**, and 78.1(2)° and 79.1(2)° in the isostructural crystals of the **2** and **3** complexes, respectively. The torsion angle of C(1)–N(1)–S(3)–C(2) describing the conformation of the ligand along the N(1)–S(3) bond is more similar in the complexes **1** and **2** [−65.2(2)° and −65.0(1)°], since both have a methyl group in the phenyl ring, than in **3** [−61.4(2)°], containing a Br-substituted aromatic ring. The S(3) atom has an expected slightly distorted tetrahedral geometry. The S(3)–O(1) and S(3)–O(2) bond lengths indicate their double bond character (S=O); a typical distance of the double S=O bond ranging from 1.431 to 1.442 Å [27]. The S(3)–C(2) bond with a distance ranging from 1.767(4) to 1.783(3) Å is well correlated with the $C_{Ar}$–S bond length in the related complexes which comprise the $C_{Ar}$–$SO_2$–N fragment [26]. The S(3)–N(1) bond length with a value ranging from 1.626(3) to 1.655(3) Å indicates a single bond nature; the typical value of the N(sp$^2$)–S bond distance is 1.623–1.659 Å [26]. Both P atoms of the triphenylphosphine ligands have similar tetragonal geometry. The phenyl ring C(21)–C(26) of the P(1) triphenylphosphine is almost parallel to the phenyl ring C(41)–C(46) of the P(2) triphenylphosphine, the dihedral angle being equal to 9.3(2)° in the complex **1**, and 15.2(2)° and 15.8(2)° in isostructural **2** and **3** complexes. Although the crystal of the complex **1**, is not isostructural with the crystals of **2** and **3** the structure analysis clearly shows that the geometry of the molecules of the compound **1** is quite similar to that of **2** and **3**. The differences between the **1** and **2** and/or **3** may be found in the molecular arrangement and the crystal packing. The complexes **1** and **2** differ only in the position of the methyl group substituted in the aromatic ring of the *N*-R-sulfonyldithiocarbimate ligands (**1** in *ortho* and **2** in *para* position). The crystal of the isomer **2** is more compacted since the molecules interact more effectively than in compound **1**. The arrangement of molecules in both **2** and **3** crystals is quite similar since both have *para*-substituents. These structures are slightly stabilized by weak C–H···O intermolecular hydrogen interactions of neighbouring molecules to form a polymeric structure. The C–H···O interactions with C···O of approximately 3.37 and 3.36 Å distances in **2** and **3** compounds, respectively, lead to the formation of the pseudo mono-dimensional columns aligned along the *a*-axis in the crystal (Fig. 3(b–c)). Although the intermolecular C–H···O are weak, we suppose that they are important for the crystal packing, since this can be the reason for the more compacted arrangement of the molecules in **2** and in **3** in relation to the crystal of **1**, in which the C–H···O interactions were not observed.

## 4. Conclusion

Three novel bis(triphenylphosphine)*N*-R-sulfonyldithiocarbimatenickel(II) complexes were prepared and characterized by UV–Vis, IR, $^1$H, $^{13}$C and $^{31}$P NMR, elemental analyses for C, H, N, Ni and by single crystal X-ray diffraction techniques.

The spectroscopic and X-ray data for the complex $[Ni(4\text{-}CH_3C_6H_4SO_2]^{2-}$ [20] show an interesting relation with the data obtained for compound **2** (Table 3). The C(1)–N(1) bond length in **2** is shorter than in $[Ni(4\text{-}CH_3C_6H_4SO_2N{=}CS_2)_2]^{2-}$ [20]. The wavenumber for the $\nu$(CN) in the IR spectrum of **2** is greater than that in the spectrum of the related anionic complex and this band is observed in smaller wavenumber in the spectrum of the parent dithiocarbimate ligand [19]. The NMR spectra show that the carbon atom of the dithiocarbimate group of **2** is more shielded than that of the anionic complex and in the parent ligand. These facts are in accord with an increase of the contribution of the (c) canonical form (Fig. 1) to the resonance hybrid from the ligands to the complexes, with a consequent increase of the CN double bond character.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 181695, 181696 and 181697 for the compounds **1**–**3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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