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Syntheses, crystal structure and spectroscopic characterization of novel 1,2-bis(diphenylphosphine)ethane-(*N*-R-sulfonyldithiocarbimato)nickel(II) complexes

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Abstract

Three new complexes of the general formula: [Ni($RSO_2N{=}CS_2$)(dppe)], where R = CH_3 (**1**), CH_3CH_2 (**2**), 2-$CH_3C_6H_4$ (**3**) and dppe = 1,2-bis(diphenylphosphine)ethane, were obtained in crystalline form by the one-pot reaction of the appropriate potassium *N*-R-sulfonyldithiocarbimate: $RSO_2N{=}CS_2K_2 \cdot 2H_2O$ and 1,2-bis(diphenylphosphine)ethane with nickel(II) chloride hexahydrate in ethanol/water mixture. The complex **1** forms monoclinic crystals ($P2_1/c$) with two molecules in the asymmetric unit ($Z = 8$), while the crystals of the complexes **2** and **3** are orthorhombic, *Pbca* ($Z = 8$) and $P2_12_12_1$ ($Z = 4$) respectively, with one molecule in the asymmetric unit. All complexes present a distorted square-planar environment around the Ni atom. The elemental analyses and the IR, ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra are consistent with the formation of the nickel(II) complexes with mixed ligands.

Keywords: Dithiocarbimates; 1,2-bis(Diphenylphosphine)ethane; Nickel complexes; Crystal structure

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1. Introduction

Dithiocarbamate derivatives show a wide range of applications. For example, they are very active accelerators in vulcanization [1–3] and many dithiocarbamates, anions and complexes, show biological activity and are used as fungicides [1,4].

Many authors have investigated complexes of nickel(II) with diphosphines. These systems are quite attractive in view of their importance as precursors in catalytic reactions [5]. Complexes containing the $NiXS_2P$ chromophore (X = halide, S_2 = dithiocarbamate, P = phosphine) are usually obtained by reacting NiX_2 with dithiocarbamates and PR_3 (R = alkyl/aryl) [6]. Nickel(II) dithiocarbamates normally react with phosphines to form complexes with the NiS_2P_2 chromophore [7–12].

Some nickel complexes with dithiocarbimates and phosphines with general formulae [Ni($R'N{=}CS_2$)($(PR_3)_2$)] (R and R′ = alkyl/aryl) have been obtained [13]. However, only the nickel complexes with general formulae [Ni($RSO_2N{=}CS_2$)($(PPh_3)_2$)] with R = 2-$CH_3C_6H_4$, 4-$CH_3C_6H_4$ and 4-BrC_6H_4 [14] and with R = 2,5-$Cl_2C_6H_3$ [15] have had their structures determined by X-ray diffraction techniques.

We decided to study dithiocarbimato complexes due to their similarities with the dithiocarbamate compounds. As part of these studies three new nickel(II)-dithiocarbimato-diphosphine complexes of the general formula: [Ni($RSO_2N{=}CS_2$)(dppe)], where R = CH_3 (**1**), CH_3CH_2

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(**2**), 2-$CH_3C_6H_4$(**3**) and dppe = 1,2-bis(diphenylphosphine)-ethane, were obtained in crystalline form by the reaction of $NiCl_2 \cdot 6H_2O$ with the diphosphine and dithiocarbimate anions derived from sulfonamides. The complexes here studied are the first examples of nickel(II)–sulfonyldithiocarbimato–diphosphine complexes prepared and characterized by single crystal X-ray diffraction techniques. The compounds were also characterized by IR, ^{1}H, ^{13}C and ^{31}P NMR and elemental analyses for C, H, N and Ni.

2. Experimental

2.1. Methods and materials

The solvents were purchased from Merck and used without further purification. The sulfonamides, nickel(II) chloride hexahydrate and 1,2-bis(diphenylphosphine)ethane were purchased from Aldrich. Carbon disulfide and potassium hydroxide were purchased from Vetec. The *N*-R-sulfonyldithiocarbimate potassium salts dihydrate were prepared in dimethylformamide from sulfonamides analogously as described in the literature [16]. Melting points were determined with a Mettler FP5 equipment. Microanalyses for C, H and N were obtained from a Perkin–Elmer 2400 CHN. Nickel was analysed 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 KBr pellets and nujol mulls between CsI plates. The ^{1}H (400 MHz), ^{13}C (100 MHz) and ^{31}P (162 MHz) NMR spectra of the complexes were recorded at 300 K on a Bruker Advance RX-400 spectrophotometer in $CDCl_3$ with TMS (H_3PO_4 for ^{31}P NMR spectra) as internal standard. Additionally, the ^{31}P (162 MHz) NMR spectra were recorded at 240 K.

2.2. Syntheses

The compounds were prepared according to the methodology applied for the syntheses of similar compounds with triphenylphosphine [14] (Scheme 1).

A solution of potassium *N*-R-sulfonyldithiocarbimate dihydrate (1.0 mmol) in water (10 mL) was added to a solution of 1,2-bis(diphenylphosphine)ethane (1.0 mmol) in ethanol (40 mL). Nickel(II) chloride hexahydrate (1.0 mmol) was added to the suspension and the reaction mixture was stirred for 5 h at room temperature. The colour of the suspension changed from green to orange/red. The solid product of the reaction was filtered, washed with distilled water and ethanol, and dried under reduced pressure for one day yielding [Ni($RSO_2N{=}CS_2$)(dppe)] (ca. 70%). Suitable crystals for X-ray structure analysis were obtained after slow evaporation of solutions of the compounds in dichloromethane/ethanol and few drops of water.

2.2.1. [Ni($CH_3SO_2N{=}CS_2$) (dppe)] (**1**)

Elemental *Anal.* Calc. C, 53.69; H, 4.34; N, 2.24; Ni, 9.37. Found C, 53.41; H, 4.46; N, 2.26; Ni, 9.40%. M.p. with decomposition (°C): 227.3–229.5. IR (most important bands) (cm^{-1}): 1463 ν(C=N); 1283 ν_{ass} (SO_2); 1128 ν_{sym} (SO_2); 923 ν_{ass} (CS_2) and 374 ν(NiS). ^{1}H NMR (δ), J (Hz): 7.79–7.69 (m, 8H, H2 and H6 of the aromatic rings); 7.56–7.43 (m, 12H, H3, H4 and H5 of the aromatic rings); 3.03 (s, 3H, CH_3) and 2.36 (d, 4H, $J_{HP} = 17$, CH_2CH_2). ^{13}C{^{1}H} NMR (δ), J(Hz): 198.67 (N=CS_2); 42.05 (CH_3). dppe signals: 132.91 (t, $J_{CP} = 5.4$, C2 and C6); 131.88 (s, C4); 129.41 (t, $J_{CP} = 5.2$, C3 and C5); 128.23 (t, $J_{CP} = 23$, C1); 26.10 (t, $J_{CP} = 23$, CH_2CH_2). ^{31}P NMR (300 K) (δ): 57.31 (s). ^{31}P NMR (240 K) (δ), J (Hz): 58.62 (d, $J_{PP} = 40.5$, P1); 57.78 (d, $J_{PP} = 40.5$, P2).

2.2.2. [Ni($CH_3CH_2SO_2N{=}CS_2$)(dppe)] (**2**)

Elemental *Anal.* Calc. C, 54.39; H, 4.56 N, 2.19; Ni, 9.17. Found: C, 52.49; H, 4.36; N, 2.09; Ni, 9.00%. M.p. with decomposition (°C): 217.0–219.0. IR (most important bands) (cm^{-1}): 1463 ν(C=N); 1275 ν_{ass} (SO_2); 1121 ν_{sym} (SO_2); 920 ν_{ass} (CS_2) and 344 ν(NiS). ^{1}H NMR (δ), J (Hz): 7.78–7.72 (m, 8H, H2 and H6 of the aromatic rings); 7.59–7.44 (m, 12H, H3, H4 and H5 of the aromatic rings); 3.12 (q, 2H, $J = 7.5$ CH_2SO_2); 2.36 (d, 4H, $J_{HP} = 17$, CH_2CH_2); 1.38 (t, 3H, $J = 7.5$ CH_3). ^{13}C{^{1}H} NMR (δ), J (Hz): 198.32 (N=CS_2); 48.65 (CH_2SO_2); 8.20 (CH_3). dppe signals: 132.88 (t, $J_{CP} = 5.7$, C2 and C6); 131.81 (s, C4); 129.36 (t, $J_{CP} = 5.2$, C3 and C5); 128.21 (t, $J_{CP} = 21$, C1); 25.94 (t, $J_{CP} = 23$, CH_2CH_2). ^{31}P NMR (300 k) (δ): 57.18 (s). ^{31}P NMR (240 k) (δ),J (Hz): 58.64 (d, $J_{PP} = 40.5$, P1); 57.75 (d, $J_{PP} = 40.5$, P2).

2.2.3. [Ni(2-$CH_3C_6H_4SO_2N{=}CS_2$)(dppe)] (**3**)

Elemental *Anal.* Calc. C, 58.13; H, 4.45; N, 1.99; Ni, 8.36. Found: C, 57.40; H, 4.51; N, 1.89; Ni, 8.15%. M.p. with decomposition (°C): 230.0–232.0. IR (most important bands) (cm^{-1}): 1459 ν(C=N); 1304 ν_{ass} (SO_2); 1151 ν_{sym} (SO_2); 919 ν_{ass} (CS_2) and 357 ν(NiS). ^{1}H NMR (δ), J(Hz): 8.04 (d, $J = 7.6$, 1H, H6 of the aromatic ring of the dithiocarbimato) 7.76–7.67 (m, 8H, H2 and H6 of the aromatic rings of dppe); 7.51–7.41 (m, 12H, H3, H4 and

$$\mathrm{RSO_2N{=}CS_2K_2.2H_2O} \xrightarrow[\mathrm{H_2O/EtOH;\ -8H_2O,\ -2KCl}]{\mathrm{NiCl_2.6H_2O,\ dppe}} \underset{\mathbf{1,2,3}}{\mathrm{[Ni(RSO_2N{=}CS_2)dppe]}}$$

1 (R = CH_3), **2** (R = CH_3CH_2), **3** (R = 2-$CH_3C_6H_4$)

Scheme 1. Syntheses of **1**–**3**.

H5 of the aromatic rings of dppe); 7.36–7.28 (m, 1H, H5 of the aromatic ring of the dithiocarbimato); 7.20–7.13 (m, 2H, H3 and H4 of the aromatic ring of the dithiocarbimato); 2.68 (s, 3H, CH_3); 2.33 (d, 4H $J_{HP} = 17$, CH_2CH_2). $^{13}C\{^1H\}$ NMR (δ), J (Hz): 198.26 ($N{=}CS_2$); 140.80 (C1); 137.98 (C2); 131.69 (C4); 128.55 (C5); 125.19 (C6). dppe signals: 132.90 (t, $J_{CP} = 5.4$, C2 and C6); 131.78 (s, C4); 129.36 (t, $J_{CP} = 5.2$, C3 and C5); 128.35 (t, $J_{CP} = 23$, C1); 25.89 (t, $J_{CP} = 23$, CH_2CH_2). ^{31}P NMR (300 k) (δ): 56.80 (s). ^{31}P NMR (240 k) (δ), J (Hz): 58.10 (d, $J_{PP} = 40.5$, P1); 57.43 (d, $J_{PP} = 40.5$, P2).

2.3. X-ray crystallography

X-ray diffraction data collections for all crystals were performed on an Enraf-Nonius Kappa-CCD diffractometer (95 mm CCD camera on κ-goniostat) using graphite monochromated Mo Kα radiation (0.71073 Å), at room temperature for the complex **2** and at lower temperature for the complexes **1** and **3**. Data collections were carried out using the COLLECT software [17] up to 50° in 2θ with a redundancy of four. Final unit cell parameters were based on all reflections. Integration and scaling of the reflections, correction for Lorentz and polarization effects were performed with the *HKL* DENZO-SCALEPACK system of programs [18]. Numerical absorption correction (GAUSSIAN) were applied using the program SORTAV [19].

The structures were solved by direct methods with SHELXS-97 [20]. The models were refined by full-matrix least squares on F^2 using SHELXL-97 [21]. All the hydrogen atoms were stereochemically positioned and refined with the riding model [21]. Data collections and experimental details for the compounds are summarized in Table 1. The program ORTEP-3 [22] was used for graphic representation and the program WINGX [23] to prepare materials for publication. Selected bond and angles are presented in Table 2.

3. Results and discussion

The complexes are quite stable at ambient conditions. They are soluble in acetonitrile, dimethylformamide, dimethylsulfoxide, chloroform and dichloromethane, and insoluble in water, methanol and ethanol. 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**, their $\nu_{C=N}$ band being observed in the 1300–1260 cm^{-1} region [24,25]. These low values point to a great contribution of the canonical forms (a) and (b) for the resonance hybrid of the dithiocarbimate anions (Scheme 2). In the spectra of the bis(dithiocarbimato)

Table 1
Crystal data and structure refinement for the complexes **1**–**3**

Complex	**1**	**2**	**3**
Empirical formula	$C_{28}H_{27}NNiO_2P_2S_3$	$C_{29}H_{29}NNiO_2P_2S_3$	$C_{34}H_{31}NNiO_2P_2S_3$
Formula weight (g mol^{-1})	623.34	640.36	702.43
Temperature (K)	210(2)	293(2)	210(2)
Crystal dimensions (mm)	0.310 × 0.270 × 0.140	0.388 × 0.177 × 0.014	0.407 × 0.149 × 0.117
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$	*Pbca*	$P2_12_12_1$
Unit cell dimensions			
a (Å)	19.3341(2)	16.1991(8)	12.4023(3)
b (Å)	19.1118(4)	15.1391(4)	12.8866(2)
c (Å)	15.9462(3)	23.5503(12)	20.1779(5)
β (°)	104.697(1)		
Volume (Å^3)	5699.48(17)	5775.5(4)	3224.9(1)
Z	8 ($Z' = 4$)	8	4
Calc. density (mg m^{-3})	1.46	1.473	1.447
μ (Mo Kα) (mm^{-1})	1.04	1.028	0.928
$F(000)$	2592	2656	1456
Transmission factors: minimum, maximum	0.739, 0.864	0.826, 0.986	0.803, 0.900
θ Range for data collection (°)	2.13–27.5	2.98–25.69	1.88–27.44
Index range	$-25 \leqslant h \leqslant 22$, $-22 \leqslant k \leqslant 24$, $-18 \leqslant l \leqslant 20$	$-19 \leqslant h \leqslant 16$, $-14 \leqslant k \leqslant 18$, $-28 \leqslant l \leqslant 28$	$-13 \leqslant h \leqslant 16$, $-15 \leqslant k \leqslant 16$, $-23 \leqslant l \leqslant 26$
Reflections collected	35271	36401	20282
Independent reflections [R_{int}]	13017 [0.0382]	5476 [0.1398]	7322 [0.0445]
Reflections $I > 2\sigma$(I)	9739	2901	6169
Number of parameters refined	667	345	388
Final R for $I > 2\sigma(I)$	$R_1 = 0.0388$ $wR_2 = 0.0779$	$R_1 = 0.0460$ $wR_2 = 0.0774$	$R_1 = 0.0361$ $wR_2 = 0.0793$
R indices [all data]	$R_1 = 0.0628$, $wR_2 = 0.0878$	$R_1 = 0.1285$ $wR_2 = 0.0961$	$R_1 = 0.0479$ $wR_2 = 0.0841$
Goodness-of-fit on F^2	1.011	0.924	1.033
Residual electron density (e Å^{-3})	0.395	0.481	0.332

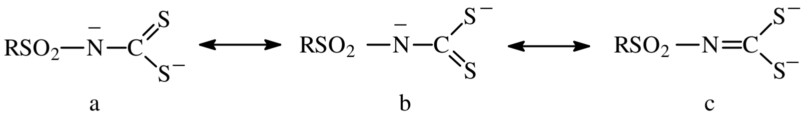
Table 2
Selected bond (Å) and angles (°) for the complexes **1**–**3**

	1		**2**	**3**
	Molecule 1	Molecule 2		
Bond length				
Ni–S1	2.1959(7)	2.1966(6)	2.201(1)	2.1822(7)
Ni–S2	2.1978(7)	2.1979(7)	2.203(1)	2.2065(8)
Ni–P1	2.1562(7)	2.1569(7)	2.171(1)	2.1718(7)
Ni–P2	2.1773(7)	2.1466(6)	2.166(1)	2.1672(7)
P1–C9	1.810(3)	1.821(2)	1.822(4)	1.812(3)
P1–C15	1.816(3)	1.814(2)	1.818(3)	1.818(3)
P1–C33	1.834(3)	1.840(2)	1.823(4)	1.834(3)
P2–C21	1.827(3)	1.813(2)	1.817(4)	1.821(3)
P2–C27	1.813(2)	1.823(2)	1.811(4)	1.819(3)
P2–C34	1.842(2)	1.841(2)	1.835(4)	1.844(3)
C1–S1	1.747(2)	1.744(2)	1.761(4)	1.749(3)
C1–S2	1.742(2)	1.738(2)	1.745(4)	1.745(3)
C1–N	1.286(3)	1.296(3)	1.287(4)	1.280(3)
N–S3	1.638(2)	1.635(2)	1.640(3)	1.641(2)
O1–S3	1.430(2)	1.418(2)	1.445(3)	1.426(2)
O2–S3	1.429(2)	1.433(2)	1.441(3)	1.444(2)
C2–S3	1.757(3)	1.740(3)	1.761(4)	1.776(3)
C2–C3			1.530(5)	1.386(4)
C33–C34	1.521(4)	1.530(3)	1.521(5)	1.526(4)
Bond angles				
S1–Ni–S2	79.14(2)	79.96(2)	79.33(4)	79.21(3)
P1–Ni–P2	86.52(3)	88.47(2)	86.40(4)	86.69(3)
S1–Ni–P1	96.44(3)	96.74(2)	99.31(4)	97.78(3)
S2–Ni–P2	98.89(3)	95.52(2)	95.27(4)	96.32(3)
Ni–P1–C33	109.19(9)	109.09(8)	107.8(1)	106.3(1)
Ni–P2–C34	109.14(9)	108.89(8)	109.7(1)	109.9(1)
S1–C1–S2	106.7(1)	108.4(1)	106.6(2)	106.4(1)
S1–C1–N	132.4(2)	130.6(2)	131.5(3)	132.2(2)
S2–C1–N	120.8(2)	121.0(2)	121.8(3)	121.4(2)
C1–N–S3	121.3(2)	120.2(2)	121.0(3)	124.0(2)
N–S3–O1	112.4(1)	113.7(1)	113.1(2)	105.8(1)
N–S3–O2	109.8(1)	108.7(1)	109.8(2)	107.9(1)
O1–S3–O2	117.5(2)	116.4(2)	116.2(2)	117.4(1)
N–S3–C2	99.3(1)	99.6(1)	99.8(2)	109.4(1)
O1–S3–C2	108.0(2)	108.8(2)	107.6(2)	109.0(1)
O2–S3–C2	108.6(2)	108.2(2)	108.9(2)	107.2(1)
S3–C2–C3			110.2(3)	117.3(2)
C9–P1–C15	107.6(1)	105.8(1)	106.4(2)	104.3(1)
C21–P2–C27	109.3(1)	105.6(1)	106.8(2)	106.7(1)

complexes $[Ni(RSO_2N{=}CS_2)_2]^{2-}$ (R = CH_3, CH_3CH_2 and 2-$CH_3C_6H_4$) this band is observed in the 1400–1360 cm^{-1} region [25–27]. A strong band observed in the 1470–1450 cm^{-1} region in the spectra of the complexes **1**–**3** was assigned to the $\nu_{C=N}$. The mesomeric drift of electrons from the dithiocarbimate moiety towards the metal centre increases the contribution of the canonical form (c) (Scheme 2). This is reflected in the shift in $\nu_{C=N}$ values to higher wavenumbers when compared with those observed in the free ligands and in the analogous bis(dithiocarbimato) complexes spectra. This effect is also observed, for example, when the spectrum of the complex $[Ni(dpdtc)_2]$ (dpdtc = *N*,*N*-propyldithiocarbamato) ($\nu_{C=N}$ band is observed in 1508 cm^{-1}) is compared with the spectrum of $[Ni(dpdtc)(dppe)]^+$ ($\nu_{C=N}$ band is observed in 1526 cm^{-1}) [11]. The $\nu_{C–S}$ band were observed at higher frequency in the spectra of the potassium salts of dithiocarbimates (960–940 cm^{-1}) [24,25] than in the spectra of the complexes here studied (925–915 cm^{-1}), and in the spectra of analogous bis(dithiocarbimato) complexes (940–925 cm^{-1}) [25–27]. This band appears without any splitting, confirming the bidentate coordination of the dithiocarbimate moiety. The shifts observed in the $\nu_{C–S}$ in the spectra of the complexes are also consistent with the increased importance of the canonical form (c) after complexation (Scheme 2). The spectra of the complexes also show the expected medium band in the 300–400 cm^{-1} range assigned to the NiS vibrations [28]. The *v*NiP bands was not observed above 200 cm^{-1}.

The NMR spectra of **1**–**3** were typical for diamagnetic species supporting the assumption of a square planar geometry around the nickel atom. The ^1H NMR spectra of the complexes showed the signals for the hydrogen atoms of the dppe and the dithiocarbimate moiety. The integration curves on the ^1H NMR spectra were consistent with a 1:1 proportion between the dppe and the dithiocarbimate anion. The signals in the spectra of the free dithiocarbimates [24,25] and in the spectra of the complexes show approximately the same chemical shifts. Nevertheless, the $N{=}CS_2$ (C1) signal is shifted in the spectra of the complexes to higher field if compared to the spectra of the free ligands [24,25] and the correspondent bis(dithiocarbimato) complexes $[Ni(RSO_2N{=}CS_2)_2]^{2-}$ [25–27]. If the canonical form (c) (Scheme 2) is more important for the complexes than for the ligands, then the C1 carbon atom is expected to be more shielded in the complexes here studied.

Most of the diphosphine 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 [14,29]. The ^{31}P NMR spectra exhibited only one signal (*ca.* 58 *δ*) at 300 K, but the signal split into two doublets due P–P coupling at 240 K confirming that the phosphorus atoms in the molecules are not magnetically equivalent. Significant changes in the phosphorus chemical shifts in the spectra of the complexes when compared to



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

that of the free diphosphine (*ca.* −12 δ) [5] are caused by the nickel atom that deshields the phosphorus atoms considerably. Similar chemical shifts are also observed in the spectra of many complexes with NiX_2(P–P) chromophores (P–P = 1,2-bis(diphenylphosphine)ethane; X = Cl, Br, I, S) [5,8–12].

The ORTEP-3 view [22] of the solid-state molecular structures of the complexes **1**, **2** and **3** are illustrated in Figs. 1–3. Compound **1** crystallizes in the monoclinic system, space group $P2_1/c$, with two independent molecules in asymmetric unit ($Z = 8$), while the complexes **2** and **3** crystallize in the orthorhombic system, space groups *Pbca* ($Z = 8$) and $P2_12_12_1$ ($Z = 4$), respectively.

In all complexes, the nickel cation is coordinated by the two sulfur atoms of the dithiocarbimato ligand and by two phosphorus atoms of the 1,2-bis(diphenylphosphine)ethane into a distorted square-planar geometry. The P1–Ni–S1 and P2–Ni–S2 angles are more distorted from 90° than the P1–Ni–P2 angles. The S1–Ni–S2 angle is considerably smaller than 90° due to the chelation of the *N*-R-sulfonyldithiocarbimato ligand forming a four membered ring (NiS_2C). When the complex $[Ni(2\text{-}CH_3C_6H_4SO_2N{=}CS_2)(PPh_3)_2]$ [14] is compared with **3**, some interesting differences can be observed due to the chelation of dppe and its smaller steric effect. The P–Ni–P angle in **3** (86.69°) is smaller than in $[Ni(2\text{-}CH_3C_6H_4SO_2N{=}CS_2)(PPh_3)_2]$ (98.48°). The S–Ni–S angle in **3** (79.21°) is greater than in the bis(triphenylphosphine) complex (77.87°) and the Ni–P bond length in **3** (*ca.* 2.17 Å) is smaller than Ni–P bonding in the bis(triphenylphosphine) complex (*ca.* 2.21 Å).

The Ni–S bonds, in complexes **1** and **2** are symmetric. In **3**, this bond exhibits a small asymmetry, probably due to the repulsive interaction between the S1 atom and the large RSO_2 group. This group, in all complexes, is in *cis* position in relation to the S1 atom. The orientation of the RSO_2 group is also responsible for the difference between the angles S1–C1–N and S2–C1–N.

The C–S bond lengths in complexes **1**–**3** (*ca.* 1.74) are characteristic of partial double bonds (typical bond lengths: 1.81 Å for C–S and 1.69 Å for C=S). The C–N bond distances (*ca.* 1.285) are similar to that of the double bond C=N (1.275–1.300 Å) [30,31]. This behavior indicates that the π electron density is delocalized over S_2CN moiety. The CN bonds in these neutral complexes are shorter than in the bis(dithiocarbimato) complexes (Table 3) [25–27].

The crystallographic data are in accord with the spectroscopic data (Table 3). Both point to an increase on the contribution of the canonical form (c) (Scheme 2) in this sequence: free ligands < bis(dithiocarbimato) complexes < complexes **1**–**3** complexes.

The R-group in complex **3** lies in a significantly different conformation from that observed for the other complexes. The C1–N–S3–C2 torsion angle is 41.8(3)° for the complex **3**, 164.2(2)° for the molecule 1 and −172.0(2)° for the molecule 2 of the complex **1** and 157.0(3)° for the complex **2.**

The P–C_{sp3} and C_{sp3}–C_{sp3} distances in the dppe ligand, in all complexes, are similar to Ni(II) complexes with Ni(S–S)(P–P) chromophores [9,32–34]. The bond lengths and angles in the phenyl rings are in good agreement,

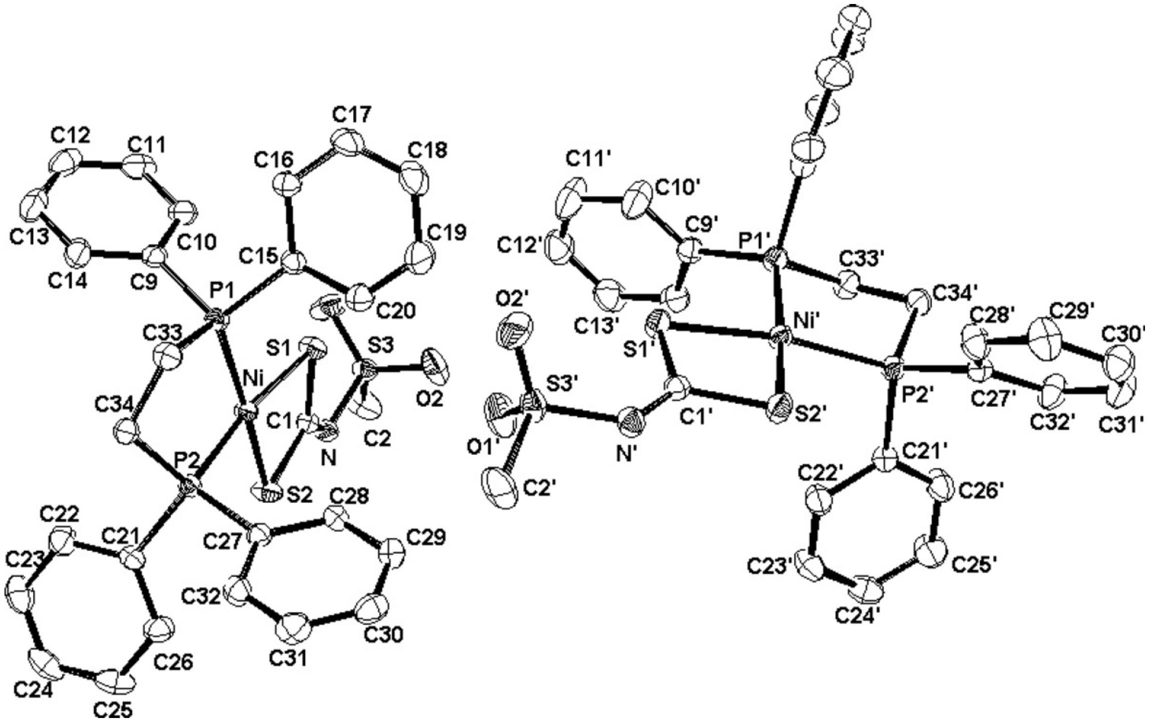


Fig. 1. The molecular structure of **1**. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

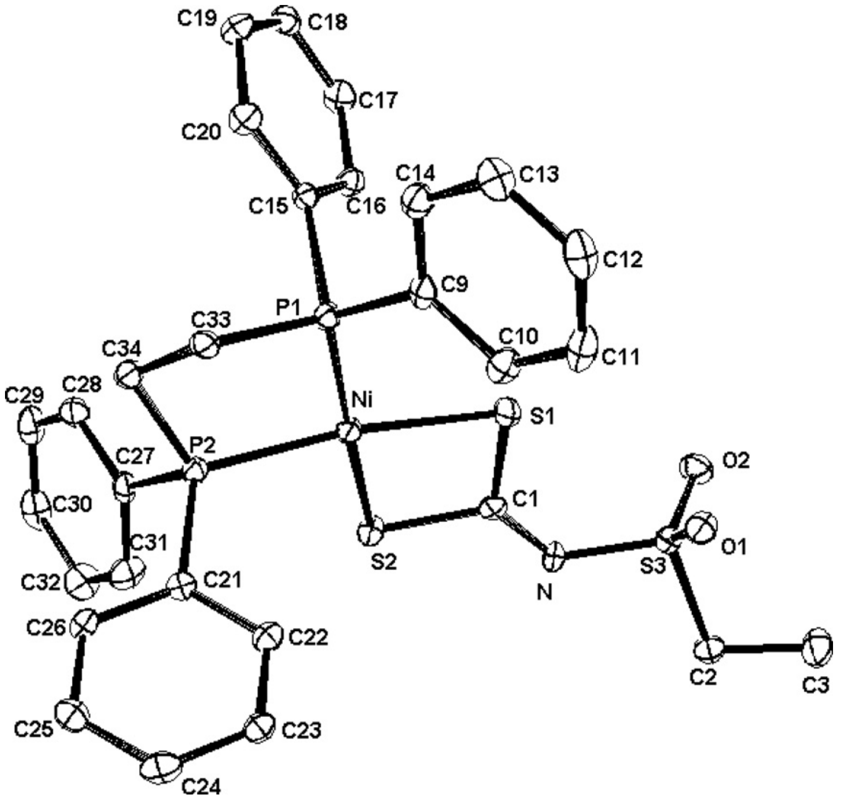


Fig. 2. The molecular structure of **2**. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

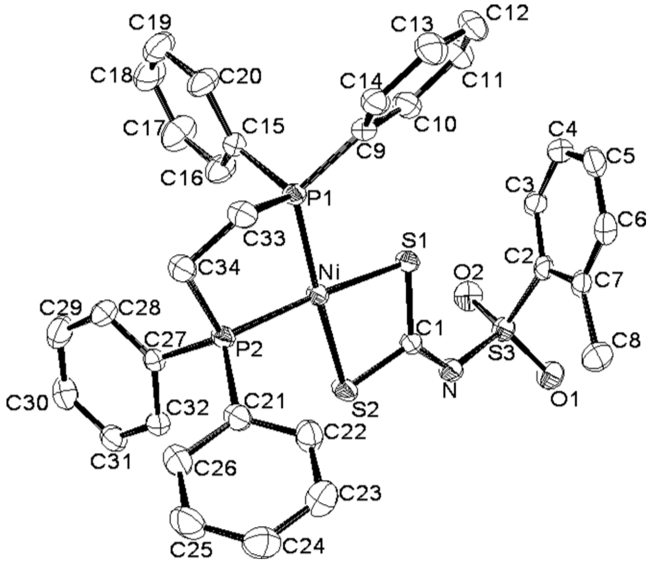


Fig. 3. The molecular structure of **3**. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

Table 3
Comparison between selected crystallographic and spectroscopic data for the CN moiety in the complexes **1**–**3** and related compounds

Compounds	CN length (Å)	νCN (cm^{-1})	^{13}C NMR (δ)
$CH_3SO_2N{=}CS_2K_2$[a]		1260	223
$(Bu_4N)_2[Ni(CH_3SO_2N{=}CS_2)_2]$[b]	1.31(2)	1390	210
$[Ni(CH_3SO_2N{=}CS_2)dppe]$ (**1**)	1.296(3); 1.286(3)	1463	199
$CH_3CH_2SO_2N{=}CS_2K_2$[c]		1300	224
$(Bu_4N)_2[Ni(CH_3CH_2SO_2N{=}CS_2)_2]$[c]	1.309(2)	1399	209
$[Ni(CH_3CH_2SO_2N{=}CS_2)dppe]$ (**2**)	1.287(5)	1463	198
$2\text{-}CH_3C_6H_4SO_2N{=}CS_2K_2$[a]		1280	223
$(Bu_4N)_2[Ni(2\text{-}CH_3C_6H_4SO_2N{=}CS_2)_2]$[d]	1.311(3)	1365	209
$[Ni(2\text{-}CH_3C_6H_4SO_2N{=}CS_2)dppe]$ (**3**)	1.280(3)	1459	198

[a] Ref. [24].
[b] Ref. [27].
[c] Ref. [25].
[d] Ref. [26].

within experimental accuracy, with the values found in the literature [30].

The angles between the planes of the phenyl rings on each phosphorus, P1 and P2 are, respectively: 82.9(1)° and 52.19(8)° (molecule 1) and 63.4(1)° and 61.50(9)° (molecule 2) in complex **1**, 69.7(1)° and 76.4(1) in complex **2** and 87.3(1)° and 68.5(1)° in complex **3**. In all complexes there are weak intermolecular interactions among C33 atom of the ethane group and oxygen, with donor-acceptor distances ranged from 3.209 to 3.405 Å. The complex **2** have another weak interaction [C18–H18…O2 ($-x$, $-y+1$, $-z$)] with C…O of 3.409 Å and the complex **1** have two more intermolecular interactions C–H…O involving the carbon atom of the CH_3SO_2 group.

4. Conclusion

Three novel 1,2-bis(diphenylphosphino)ethane(*N*-R-sulfonyldithiocarbimato)nickel(II) complexes were prepared and characterized by IR, ^1H, ^{13}C and ^{31}P NMR, elemental analyses for C, H, N, Ni and by single crystal X-ray diffraction techniques. They are the first examples of nickel(II) complexes with the mixed ligands *N*-R-sulfonyldithiocarbimate and diphosphine.

When the analogous bis(dithiocarbimato) complexes [25–27] are compared with the compounds here studied, the spectroscopic and X-ray data show that the substitution of a dithiocarbimate group by a diphosphine ligand causes a drift of electrons from the dithiocarbimate to the metallic center, increasing the contribution of the canonical form (c) (Scheme 2) to the resonance hybrid, with a consequent increase of the CN double bond character. Therefore, the wavenumbers for the $\nu_{C=N}$ in the IR spectra of **1**–**3** are greater than those in the spectra of the related bis(dithiocarbimato) complexes and this band is observed in smaller wavenumbers in the spectra of the free ligands. Accordingly, the NMR spectra show that the carbon atom of the dithiocarbimate group of **1**–**3** is more shielded than that of the bis(dithiocarbimato) complex and in the parent ligand (see Table 3). Similar behavior is observed for complexes with general formulae $[Ni(RSO_2N{=}CS_2)(PPh_3)_2]$ with $R = 2\text{-}CH_3C_6H_4$, $4\text{-}CH_3C_6H_4$ and $4\text{-}BrC_6H_4$ [14] and with $R = 2,5\text{-}Cl_2C_6H_3$ [15].

The comparison between bis(triphenylphosphine)-*N*-R-sulfonyldithiocarbimato-nickel(II) complexes [14,15] and **1**–**3** show that the substitution of two bulky triphenylphosphine ligands by a diphosphine chelating ligand leads to an increase on the S1–C1–S2 angle, and a decrease on the P–Ni–P angle and on the P–Ni bond length.

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Appendix A. Supplementary material

CCDC 653767, 653768 and 653766 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.11.001.

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