



## Syntheses, crystal structure and theoretical investigation of novel heteroleptic complexes of nickel(II) with *N*-*R*-sulfonyldithiocarbamate and phosphine ligands

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### ABSTRACT

Five new complexes of general formula:  $[\text{Ni}(\text{RSO}_2\text{N}=\text{CS}_2)(\text{dppe})]$ , where  $\text{R} = \text{C}_6\text{H}_5$  (**1**), 4- $\text{ClC}_6\text{H}_4$  (**2**), 4- $\text{BrC}_6\text{H}_4$  (**3**), 4- $\text{IC}_6\text{H}_4$  (**4**) and  $\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane and  $[\text{Ni}(4\text{-IC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)(\text{PPh}_3)_2]$  (**5**), where  $\text{PPh}_3 =$  triphenylphosphine, were obtained in crystalline form by the reaction of the appropriate potassium *N*-*R*-sulfonyldithiocarbamate  $\text{K}_2(\text{RSO}_2\text{N}=\text{CS}_2)$  and  $\text{dppe}$  or  $\text{PPh}_3$  with nickel(II) chloride in ethanol/water. The elemental analyses and the IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR spectra are consistent with the formation of the square planar nickel(II) complexes with mixed ligands. All complexes were also characterized by X-ray diffraction techniques and present a distorted *cis*- $\text{NiS}_2\text{P}_2$  square-planar configuration around the Ni atom. Quantum chemical calculations reproduced the crystallographic structures and are in accord with the spectroscopic data. Rare C–H...Ni intramolecular short contact interactions were observed in the complexes **1–5**.

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### 1. Introduction

The interest in the syntheses and characterization of dithiocarbamate metal complexes is related to their similarities with the dithiocarbamate compounds, which have a wide range of applications. For example, dithiocarbamates are used in the rubber vulcanization process [1,2] as well as several dithiocarbamate salts and complexes have been used as fungicides [2,3]. In fact, recently it was demonstrated that dithiocarbamates are also fungicides and vulcanization accelerators [4,5]. Additionally, heteroleptic group 10 metal complexes with sulfonyldithiocarbamate and phosphines have shown interesting molecular electrical conducting and photoluminescent properties. Besides, their structures present rare C–H...M intramolecular short contact interactions [6,7].

Less than ten nickel(II) complexes of this class are structurally characterized:  $[\text{Ni}(\text{RSO}_2\text{N}=\text{CS}_2)(\text{PPh}_3)_2]$  ( $\text{R} = 2\text{-CH}_3\text{C}_6\text{H}_4$ , 4- $\text{CH}_3\text{C}_6\text{H}_4$ , 4- $\text{BrC}_6\text{H}_4$ , and 2,5- $\text{Cl}_2\text{C}_6\text{H}_3$ ) [8,9],  $[\text{Ni}(\text{RSO}_2\text{N}=\text{CS}_2)\text{dppe}]$  ( $\text{R} = \text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ , 2- $\text{CH}_3\text{C}_6\text{H}_4$  and 4- $\text{CH}_3\text{C}_6\text{H}_4$ ) [6,10]. Considering the need to increase the knowledge on the physical and chemical properties of this group of complexes, we have prepared five new compounds:  $[\text{Ni}(\text{RSO}_2\text{N}=\text{CS}_2)(\text{dppe})]$   $\text{R} = \text{C}_6\text{H}_5$  (**1**), 4- $\text{ClC}_6\text{H}_4$  (**2**),

4- $\text{BrC}_6\text{H}_4$  (**3**), 4- $\text{IC}_6\text{H}_4$  (**4**), and  $[\text{Ni}(4\text{-IC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)(\text{PPh}_3)_2]$  (**5**). The complexes were obtained in the crystalline form by the reaction of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with  $\text{PPh}_3$  or  $\text{dppe}$  and the dithiocarbamate anions derived from sulfonamides. These complexes were characterized by IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR, elemental analyses, single crystal X-ray diffraction techniques, and semiempirical quantum chemical calculations.

### 2. Experimental

#### 2.1. Material and reagents

The solvents, carbon disulfide and potassium hydroxide were purchased from Vetec and used without further purification. The benzenesulfonamide, 4-chlorobenzenesulfonamide, 4-bromophenylsulfonyl chloride, 4-iodophenylsulfonyl chloride, nickel(II) chloride hexahydrate, triphenylphosphine and 1,2-bis(diphenylphosphino)ethane were purchased from Aldrich. The 4-iodobenzenesulfonamide and the 4-bromobenzenesulfonamide were prepared from the appropriate sulfonyl chloride as described elsewhere [11]. The *N*-*R*-sulfonyldithiocarbamate potassium salts dihydrate were prepared in dimethylformamide from the sulfonamides analogously as described in the literature [12,13]. Melting points were determined with a Mettler FP5 equipment. Microanalyses for

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Structures were solved by direct methods (SHELXS-97) and refined (SHELXL-97) by full-matrix least-squares on all  $F^2$  data [17]. All the hydrogen atoms were placed in geometrically idealized positions [17]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. For **2**, the phenyl rings C14–C19 and C20–C25 of the dppe ligand were disordered over two different orientations with occupancy of 50%. In complex **3**, the phenyl ring C8–C13 of the dppe ligand was disordered over two sites with occupancy factors of 60% and 40%. In complex **5**, the phenyl ring C2–C7 and iodine atom of the dithiocarbamate ligand were disordered over two sites with occupancies 70% and 30%. For all disordered rings the bond lengths  $C_{ar}-C_{ar}$  and angles  $C_{ar}-C_{ar}-C_{ar}$  were fixed in 1.39 Å and 120.0°, respectively.

The absolute configuration of the compounds **1** and **4** were established by evaluation of the anomalous dispersion effects [18]. Structural diagrams were drawn using ORTEP3 [19] and the program WINGX 1.70.01 [20] was used to prepare materials for publication. Crystal data and details on data collection and refinement are summarized in Table 1. Selected bond and angles are given in Table 2.

#### 2.4. Theoretical calculations

The structures of the metal complexes **1–5** as determined by X-ray crystallography analysis were fully optimized with the PM6 semiempirical Hamiltonian [21] implemented in the MOPAC2009 software package [22]. The calculations were performed for the isolated complexes and their ligands using a SCF criterion of 0.0001 kcal/mol. For all complexes, the geometry and charge drifts were evaluated before and after the complex formation.

### 3. Results and discussion

The complexes **1–5** were prepared as shown in Scheme 1. They are quite stable at the ambient conditions. The dppe complexes

**Table 2**  
Selected geometrical parameters (°).

	1	2	3	4	5
<i>Bond length</i> (Å)					
Ni–S1	2.1870(6)	2.1884(5)	2.1889(8)	2.191(1)	2.184(1)
Ni–S2	2.2083(7)	2.2078(5)	2.2035(8)	2.1969(1)	2.2203(9)
Ni–P1	2.1659(7)	2.1754(4)	2.1681(7)	2.153(1)	2.2203(9)
Ni–P2	2.1650(7)	2.1728(4)	2.1703(8)	2.163(1)	2.2269(9)
C1–S1	1.744(2)	1.739(2)	1.7373(3)	1.724(4)	1.738(3)
C1–S2	1.746(3)	1.740(2)	1.735(3)	1.739(4)	1.735(3)
C1–N	1.290(3)	1.299(2)	1.303(3)	1.317(5)	1.295(4)
<i>Bond angle</i> (°)					
S1–Ni–S2	79.24(3)	79.02(2)	79.17(3)	79.79(4)	78.16(3)
P1–Ni–P2	86.57(3)	87.93(2)	88.00(3)	87.90(4)	98.87(3)
P1–Ni–S1	97.67(3)	94.693(7)	95.68(3)	94.64(4)	91.21(4)
P2–Ni–S2	96.53(3)	98.66(2)	97.52(3)	97.69(4)	92.53(4)
S1–C1–S2	106.7(1)	107.02(9)	107.5(1)	108.7(2)	106.2(2)
S1–C1–N	132.3(2)	131.1(1)	130.6(2)	131.6(3)	131.4(3)
S2–C1–N	120.8(2)	121.7(1)	121.9(2)	119.7(3)	122.4(3)
C1–N–S3	125.3(2)	120.6(1)	120.6(2)	122.4(3)	121.6(2)

**1–4** are soluble in acetonitrile, dimethylformamide, dimethylsulfoxide, chloroform and dichloromethane, and insoluble in water, methanol and ethanol. The complex **5** showed very little solubility in chloroform and dichloromethane and is insoluble in the other above mentioned solvents.

There are no strong or medium bands in the 1400–1600  $\text{cm}^{-1}$  region in the IR spectra of the potassium dithiocarbamates related to the complexes **1–5**, and their  $\nu_{\text{CN}}$  band was observed around 1260  $\text{cm}^{-1}$  [23,24]. This low value indicates a great contribution of the canonical forms (a) and (b) for the resonance hybrid (Scheme 2). A strong band observed around 1455  $\text{cm}^{-1}$  in the spectra of the complexes **1–5** was assigned to the  $\nu_{\text{CN}}$ . The  $\nu_{\text{asym}}\text{CS}_2$  was observed at higher frequency in the spectra of the potassium salts of dithiocarbamates (ca. 955  $\text{cm}^{-1}$ ) [23,24] than in the spectra of

**Table 1**  
Crystallographic data and structure refinement summary for complexes **1–5**.

Complex	1	2	3	4	5
Formula	$\text{C}_{33}\text{H}_{29}\text{NNiO}_2\text{P}_2\text{S}_3$	$\text{C}_{33}\text{H}_{28}\text{ClNNiO}_2\text{P}_2\text{S}_3$	$\text{C}_{33}\text{H}_{28}\text{BrNNiO}_2\text{P}_2\text{S}_3$	$\text{C}_{33}\text{H}_{28}\text{INNiO}_2\text{P}_2\text{S}_3$	$\text{C}_{43}\text{H}_{34}\text{INNiO}_2\text{P}_2\text{S}_3$
Formula weight	688.40	722.84	767.30	814.29	940.44
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$Pbca$
$T$ (K)	293(2)	210(2)	210(2)	293(2)	293(2)
Crystal size (mm)	$0.20 \times 0.20 \times 0.20$	$0.353 \times 0.328 \times 0.274$	$0.417 \times 0.132 \times 0.108$	$0.40 \times 0.40 \times 0.40$	$0.244 \times 0.128 \times 0.064$
Unit cell dimensions (Å)	$a = 12.3795(2)$ $b = 12.4137(2)$ $c = 19.7795(4)$	$a = 10.8105(2)$ $b = 27.6195(6)$ $c = 10.9922(2)$	$a = 10.7781(2)$ $b = 27.2057(6)$ $c = 11.4335(3)$	$a = 10.1544(2)$ $b = 15.1327(3)$ $c = 21.9260(5)$	$a = 16.5156(2)$ $b = 18.6092(3)$ $c = 25.5899(5)$
$\beta$ (°)		95.354(1)°	95.389(1)°		
$V$ (Å <sup>3</sup> )	3039.62(9)	3267.74(11)	3337.78(13)	3369.23(12)	7864.9(2)
$Z$	4	4	4	4	8
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.504	1.469	1.527	1.605	1.588
$\mu$ (Mo $K\alpha$ ) ( $\text{mm}^{-1}$ )	0.983	0.997	2.093	1.804	1.558
$F(000)$	1424	1488	1560	1632	3792
Transmission factors: minimum, maximum	0.8279, 0.9116	0.994, 1.008	0.59, 0.856	0.982, 1.021	0.752, 0.904
$\theta$ Range for data collection (°)	3.11–27.48	1.47–27.48	2.91–26.373	3.05–27.48	2.94–26.03
Index range	$-16 \leq h \leq 16$ $-16 \leq k \leq 11$ $-25 \leq l \leq 25$	$-13 \leq h \leq 14$ $-35 \leq k \leq 33$ $-14 \leq l \leq 14$	$-11 \leq h \leq 22$ $-32 \leq k \leq 34$ $-13 \leq l \leq 14$	$-12 \leq h \leq 13$ $-18 \leq k \leq 19$ $-28 \leq l \leq 28$	$-15 \leq h \leq 20$ $-22 \leq k \leq 14$ $-31 \leq l \leq 31$
Reflections collected	20659	26826	35481	21929	40896
Independent reflections ( $R_{\text{int}}$ )	6940 (0.0533)	7372 (0.0450)	6789 (0.0672)	7707 (0.0556)	7736 (0.0726)
Reflections $I > 2\sigma(I)$	5913	6731	4837	6201	5208
Number of parameters refined	379	376	382	388	481
Final $R$ for $I > 2\sigma(I)$ <sup>a</sup>	$R_1 = 0.0336$ $wR_2 = 0.0664$ $R_1 = 0.0477$ $wR_2 = 0.0705$	$R_1 = 0.0309$ $wR_2 = 0.0726$ $R_1 = 0.0351$ $wR_2 = 0.0750$	$R_1 = 0.0380$ $wR_2 = 0.0940$ $R_1 = 0.0662$ $wR_2 = 0.1080$	$R_1 = 0.0379$ $wR_2 = 0.0740$ $R_1 = 0.0596$ $wR_2 = 0.0824$	$R_1 = 0.0402$ $wR_2 = 0.1031$ $R_1 = 0.0757$ $wR_2 = 0.1233$
$R$ Indices (all data) <sup>a</sup>					
Absolute structure parameter	–0.001(9)	–	–	–0.012(13)	–
Goodness-of-fit (GOF) on $F^2$	1.030	1.070	1.049	1.031	1.068
Residual electron density ( $\text{e} \text{Å}^{-3}$ )	0.340 and –0.411	0.359 and –0.339	0.606 and –0.648	0.414 and –0.787	0.698 and –0.775

<sup>a</sup>  $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$ .



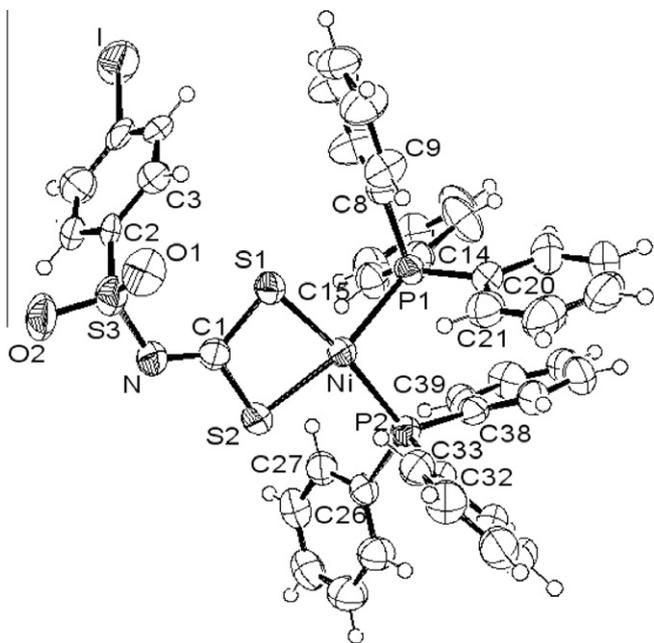


Fig. 5. X-ray molecular structure of **5**. Displacement ellipsoids are shown at the 50% probability level.

The  $^{31}\text{P}$  NMR spectra obtained at 300 K exhibited only one signal at *ca.* 56  $\delta$  for the complexes **1–4** and at *ca.* 33  $\delta$  for the triphenylphosphine complex **5**. These chemical shifts are in accordance to those observed for analogous complexes:  $[\text{Ni}(\text{RSO}_2\text{N}=\text{CS}_2)(\text{dppe})]$  ( $\text{R} = \text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$  and  $2\text{-CH}_3\text{C}_6\text{H}_4$ ) [10] and  $[\text{Ni}(\text{PPh}_3)_2(\text{RSO}_2\text{N}=\text{CS}_2)]$  ( $\text{R} = 2\text{-CH}_3\text{C}_6\text{H}_4$ ,  $4\text{-CH}_3\text{C}_6\text{H}_4$  and  $4\text{-BrC}_6\text{H}_4$ ) [8]. Although the phosphorus atoms are not equivalent, no split was observed at 300 K as observed for analogous complexes at 240 K [10].

The X-ray molecular structures of the complexes here studied are illustrated in Figs. 1–5. The complexes crystallize in monoclinic or orthorhombic system in  $P2_1/c$  (complexes **2** and **3**),  $P2_12_12_1$  (complexes **1** and **4**) or  $Pbca$  (complex **5**) space groups. In all complexes, the nickel atom is coordinated by two sulfur atoms of the dithiocarbamate ligand and by two phosphorus atoms of the phosphines. The *cis*- $\text{NiS}_2\text{P}_2$  fragment have a distorted square planar geometry due to the small angle  $\text{S1-Ni-S2}$  (*ca.* 79°) associated with the bidentate chelation of the dithiocarbamate moiety.

The Ni–P distances (Table 2) are symmetric in the complexes **1–5** (the difference between Ni–P1 and Ni–P2 is less than 0.01 Å), as reported for similar compounds [10]. The P–Ni–P angles in **1–4** (*ca.* 87.5°) are shorter than in **5** (98.87°) due to the steric repulsion

Table 4

Intra and intermolecular interactions parameters<sup>a</sup> (Å, °) for **1–5**.

Donor–W...Acceptor	D–W	W...A	D...A	DWA
<b>1</b>				
C7–H7...O1	0.93	2.48	2.874(4)	106
C9–H9...S1	0.93	2.77	3.301(3)	117
C28–H28...O1 <sup>i</sup>	0.93	2.59	3.401(4)	147
C15–H15...Ni	0.93	2.83	3.396(3)	120
<b>2</b>				
C9–H9...S1	0.93	2.73	3.296(2)	120
C32–H32b...O2 <sup>i</sup>	0.97	2.40	3.350(2)	168
C18'...C1 <sup>ii</sup>	–	–	3.244(1)	–
*C15–H15...Ni	0.93	2.71	3.28(1)	120
*C15'–H15'...Ni	0.93	2.83	3.36(1)	118
<b>3</b>				
C3–H3...O1	0.93	2.57	2.937(4)	104
C9–H9...S1	0.93	2.65	3.29(2)	126
C12–H12...O2 <sup>i</sup>	0.93	2.57	3.39(1)	147
C32–H32b...O2 <sup>ii</sup>	0.97	2.44	3.397(4)	168
C5–Br...Cg <sup>iii</sup>	1.895(3)	3.4895(17)	5.019(4)	135.4(1)
C15–H15...Ni	0.93	2.68	3.259(4)	121
<b>4</b>				
C3–H3...O1	0.93	2.56	2.914(5)	103
C4–H4 O1 <sup>i</sup>	0.93	2.59	3.475(5)	159
C17–H17...O2 <sup>ii</sup>	0.93	2.53	3.279(6)	138
C31–H31...O2 <sup>iii</sup>	0.93	2.55	3.432(5)	159
C33–H33a...N <sup>iiii</sup>	0.97	2.55	3.269(5)	131
C33–H33b...S2 <sup>iii</sup>	0.97	2.85	3.394(5)	116
C5–I...O1 <sup>iv</sup>	2.103(4)	3.070(4)	5.164(4)	173.0(2)
C15–H15...Ni	0.93	2.85	3.405(5)	120
<b>5</b>				
C3–H3...O1	0.93	2.51	2.90(1)	105
C29–H29...O1 <sup>i</sup>	0.93	2.46	3.320(4)	154
C5–I...Cg <sup>ii</sup>	2.05(1)	3.720(3)	5.58(1)	148.7(3)
C5'–I'...Cg <sup>ii</sup>	2.15(3)	3.682(6)	5.47(3)	137.4(7)
C15–H15...Ni	0.93	2.73	3.339(4)	124
C33–H33...Ni	0.93	2.81	3.384(3)	121

Cg: centroid generated by the aromatic ring C26–C31; \*disordered atom.

<sup>a</sup> Symmetry codes for **1**: (i)  $x - 1/2$ ,  $5/2 - y$ ,  $2 - z$ ; for **2**: (i)  $1 + x$ ,  $y$ ,  $z$ ; (ii)  $x$ ,  $1/2 - y$ ,  $z - 1/2$ ; for **3**: (i)  $1 + x$ ,  $3/2 - y$ ,  $z - 1/2$ ; (ii)  $1 + x$ ,  $y$ ,  $z$ ; (iii)  $x$ ,  $1/2 - y$ ,  $-1/2 + z$ ; for **4**: (i)  $1/2 + x$ ,  $1/2 - y$ ,  $1 - z$ ; (ii)  $-1/2 + x$ ,  $1/2 - y$ ,  $1 - z$ ; (iii)  $1 - x$ ,  $1/2 + y$ ,  $1/2 - z$ ; (iv)  $-1 + x$ ,  $y$ ,  $z$ ; for **5**: (i)  $-1/2 + x$ ,  $y$ ,  $1/2 - z$ ; (ii)  $1/2 - x$ ,  $-y$ ,  $1/2 + z$ .

Table 5

Root mean square deviation (Å) of crystallographic and theoretical structures after fitting the second structure on the first one.

Complex	All structure fitting	Fitting between planar fragment $\text{NCS}_2\text{NiP}_2$
<b>1</b>	0.359	0.053
<b>2</b>	0.480	0.083
<b>3</b>	0.770	0.088
<b>4</b>	0.457	0.068
<b>5</b>	0.384	0.078

Table 3

Comparison between selected crystallographic and spectroscopic data for the CN bond in the complexes **1–5** and related compounds.

Compounds	CN length (Å)	$\nu\text{CN}$ ( $\text{cm}^{-1}$ )	$^{13}\text{C}$ NMR ( $\text{NCS}_2$ ) (ppm)	Charge on C(1)
$\text{K}_2(\text{C}_6\text{H}_5\text{SO}_2\text{N}=\text{CS}_2) \cdot 2\text{H}_2\text{O}^{\text{a,b}}$	1.342(9)	1267	223.19	0.639
$[\text{Ni}(\text{C}_6\text{H}_5\text{SO}_2\text{N}=\text{CS}_2)(\text{dppe})]$ ( <b>1</b> )	1.290(3)	1452	199.32	0.397
$\text{K}_2(4\text{-ClC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2) \cdot 2\text{H}_2\text{O}^{\text{a,b}}$	1.354(5)	1261 <sup>*</sup>	225.72	0.654
$[\text{Ni}(4\text{-ClC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)(\text{dppe})]$ ( <b>2</b> )	1.299(2)	1430	200.25	0.395
$\text{K}_2(4\text{-BrC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2) \cdot 2\text{H}_2\text{O}^{\text{a}}$	–	1261 <sup>*</sup>	225.74	0.651
$[\text{Ni}(4\text{-BrC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)(\text{dppe})]$ ( <b>3</b> )	1.303(3)	1443	200.92	0.394
$\text{K}_2[4\text{-IC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2] \cdot 2\text{H}_2\text{O}^{\text{c}}$	–	1280	225.62	0.648
$[\text{Ni}(4\text{-IC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)(\text{dppe})]$ ( <b>4</b> )	1.317(5)	1463	200.58	0.396
$[\text{Ni}(4\text{-IC}_6\text{H}_4\text{SO}_2\text{N}=\text{CS}_2)(\text{PPh}_3)_2]$ ( <b>5</b> )	1.295(4)	1451	not observed	0.392

<sup>\*</sup> This work.

<sup>a</sup> Ref. [24].

<sup>b</sup> Ref. [13].

<sup>c</sup> Ref. [23].

**Table 6**  
Atomic charges on the atoms of the fragment N=CS<sub>2</sub> of the dithiocarbamate moiety.

Complex	Before complexation				After complexation			
	S1	S2	C1	N	S1	S2	C1	N
<b>1</b>	−0.988	−0.848	0.639	−0.926	−0.560	−0.429	0.397	−0.819
<b>2</b>	−0.975	−0.841	0.654	−0.945	−0.540	−0.442	0.395	−0.825
<b>3</b>	−0.974	−0.838	0.651	−0.942	−0.543	−0.442	0.394	−0.824
<b>4</b>	−0.960	−0.841	0.648	−0.944	−0.552	−0.442	0.396	−0.824
<b>5</b>	−0.960	−0.841	0.648	−0.944	−0.547	−0.432	0.392	−0.818

between the phenyl rings of the PPh<sub>3</sub>. This effect is also responsible for the greater Ni–P distances in bis(triphenylphosphine) complex **5** (*ca.* 2.22 Å) than in the diphosphine complexes **1–4** (*ca.* 2.17 Å). The Ni–S bonds in complexes **1–5** are in the same range of analogous compounds [10].

In all complexes the C–S bond lengths, of the NCS<sub>2</sub> fragment, are nearly equal and are slightly shorter than typical C–S single bonds (*ca.* 1.81 Å) due to partial  $\pi$ -delocalization in the S–C–S group. The spectroscopic data and X-ray experiments showed that the C–N bond have a greater double bond character and are shorter than in the free ligands for **1** and **2** [13] (Table 3). Similar behavior is observed for others nickel complexes with dithiocarbamate ligands [10].

The S1–C1–N angles are significantly greater than S2–C1–N due to the repulsive interaction between the RSO<sub>2</sub> group and S1 atom, which are in *cis* position in relation to the C1–N bond. The torsion angles of C1–N–S3–C2 describing the conformation of the dithiocarbamate ligand are almost equal in the compounds **2**, **3** and **4** bearing halogen atoms in the RSO<sub>2</sub> group [−70.0(2)°, −68.4(3)° and −70.5(4)°, respectively]. The complex **1** (with no substituent in the phenyl ring) has similar conformation with a dihedral angle of −38.3(3)°. This angle in the complex **5** [64.2(5)° for the most occupied position] agrees, in modulus, with observed values in other analogous complexes [8].

The intra and intermolecular contacts are shown in Table 4. All complexes exhibit intramolecular interactions and C–H...O intermolecular contacts. The complexes which have 4-XC<sub>6</sub>H<sub>4</sub> fragments show intermolecular interactions involving the halogen atoms in [0 0 1] (compounds **2**, **3** and **5**) or [1 0 0] (compound **4**) directions. The monoclinic compounds (**2** and **3**) present a weak C<sub>sp3</sub>–H...O intermolecular interaction involving the same atoms (C32–H32...O2). Only compound **4** have intermolecular interactions C–H...N and C–H...S.

C15–H...Ni intramolecular interactions with distances between 2.68 and 2.85 Å (angles 117.9–123.8°) were observed in compounds **1–5**. These are rare cases of short contact interactions in planar d<sup>8</sup> systems [6,7,26]. Interactions characterized by M...H distances between 2.3 and 2.9 Å might be important for catalytic applications [26]. Compound **3** presented the shorter CH...Ni distance (2.68 Å) as shown in Table 4.

The semiempirical quantum chemical calculations reproduced correctly the crystallographic structure, showing a small root mean square deviation (RMSD) as displayed in Table 5. Dihedral angles analysis showed that complexes conformations are affected by the presence of the halogen, independently of the physical state of these compounds. The complexes **2** and **3** (crystallized in the monoclinic system) presented greater RMSD. These high correlations between theoretical and experimental results suggest that the quantum chemical calculations can be used to describe the electronic structure of the studied complexes.

We have related the decrease of the distance of the C=N bond of dithiocarbamate metal complexes when compared to free ligands to the raise in the importance of the canonical form (c) upon complexation (Scheme 2) [8–10]. The shift of the signal of C1 to higher fields in the <sup>13</sup>C NMR, and the increase of the wavenumber of the

$\nu$ C=N band in the IR spectra of the complexes have been explained in the same terms. The quantum chemical calculations for compounds **1–5** are in accord with these assumptions. Before the complexation there was a negative charge density concentrated around N, S1 and S2 atoms of the *N*-R-sulfonyldithiocarbamate ligands, correlated to the canonical forms (a) and (b) (Scheme 2). After the complexation, a large drift of electrons from the SO<sub>2</sub>NCS<sub>2</sub> fragment to the Ni atom was observed. The major charge variation occurs on the sulfur atoms bonded to the Ni atom, as shown on Table 6. It is interesting to note that the charge in the carbon atom of the N=CS<sub>2</sub> group change from *ca.* 0.65–0.39. This fact is in accord with the <sup>13</sup>C NMR data (Table 3) for an increase of the shielding in this atom leads to a shift in the signal of the dithiocarbamate carbon from *ca.*  $\delta$  225 in the spectra of the ligands to *ca.*  $\delta$  200 in the spectra of the complexes.

An electron drift from the halogen atoms is also observed, but there are no significant charge transfer involving the phenyl rings. The only significant electron drift on the dppe and PPh<sub>3</sub> ligands occurs from the phosphorus atoms to the metal. The calculated charges on the phosphorus atoms of the dppe and PPh<sub>3</sub> are *ca.* 0.39 and 0.38, respectively. These values raise to *ca.* 0.84 for dppe and 0.83 for PPh<sub>3</sub> after the complexation.

#### 4. Conclusion

The five new complexes obtained in this work showed interesting relation between spectroscopic and crystallographic data. For all of the complexes it was observed an increase in the shielding of the carbon of the dithiocarbamate group (S<sub>2</sub>C=N) in the <sup>13</sup>C NMR spectra, the increase of the wavenumber of the  $\nu$ C=N in the IR spectra and the shortening of the N=C bond with respect to the corresponding data for the free ligands. Semiempirical quantum chemical calculation confirmed the charge distribution and the bond characteristics initially suggested by the spectroscopic experiments. The charge distribution in S<sub>2</sub>C=N group before and after the complexation are in accord with the spectroscopic and crystallographic data and confirm the increase of the importance of the canonical structure (c) in complexes **1–5** when compared to the parent potassium dithiocarbamates. The complexes showed interesting inter and intramolecular interactions. Especially rare cases of C–H...Ni short contact interactions were observed in **1–5** complexes involving one of the *ortho*-hydrogen atoms of the aromatic rings of the phosphines **1–4** and two *ortho*-hydrogens in the compound **5**. Compound **3** presented the shorter CH...Ni distance (2.68 Å).

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#### Appendix A. Supplementary material

CCDC 812069, 812070, 812071, 812072 and 812073 contain the supplementary crystallographic data for complexes **1**, **2**, **3**, **4** and **5**,

respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2011.06.025](https://doi.org/10.1016/j.ica.2011.06.025).

## References

- [1] P.J. Nieuwenhuizen, A.W. Ehlers, J.G. Haasnoot, S.R. Janse, J. Reedijk, E.J. Baerends, *J. Am. Chem. Soc.* 121 (1999) 163.
- [2] D. Hogarth, *Prog. Inorg. Chem.* 53 (2005) 71.
- [3] A.K. Malik, W. Faubel, *Pestic. Sci.* 55 (1999) 965.
- [4] L.C. Alves, M.M.M. Rubinger, R.H. Lindemann, G.J. Perpétuo, J. Janczak, L.D.L. Miranda, L. Zambolim, M.R.L. Oliveira, *J. Inorg. Biochem.* 103 (2009) 1045.
- [5] L.M.G. Cunha, M.M.M. Rubinger, J.R. Sabino, L.L.Y. Visconte, M.R.L. Oliveira, *Polyhedron* 29 (2010) 2278.
- [6] N. Singh, B. Singh, K. Thapliyal, M.G.B. Drew, *Inorg. Chim. Acta* 363 (2010) 3589.
- [7] N. Singh, B. Singh, S.K. Singh, M.G.B. Drew, *Inorg. Chem. Commun.* 13 (2010) 1451.
- [8] M.R.L. Oliveira, H.P. Vieira, G.J. Perpétuo, J. Janczak, V.M. De Bellis, *Polyhedron* 21 (2002) 2243.
- [9] C. Novais, S. Guilardi, I. Machado Jr., M.R.L. Oliveira, *Acta Crystallogr., Sect. E* 63 (2007) m1981.
- [10] M.R.L. Oliveira, J. Amim Jr., I.A. Soares, V.M. De Bellis, C.A. Simone, C. Novais, S. Guilardi, *Polyhedron* 27 (2008) 253.
- [11] A.I. Vogel, *A Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis*, third ed., Longmans, London, 1956, p. 543.
- [12] K. Hartke, *Archiv der Pharmazie* 299 (1966) 164.
- [13] H.U. Hummel, U.Z. Korn, *Naturforsch B* 44 (1989) 24.
- [14] Enraf-Nonius COLLECT, Nonius BV, Delft, The Netherlands, 1997–2000.
- [15] Z. Otwinowski, W. Minor, in: C.W. Carter Jr., R.M. Sweet (Eds.), *Methods in Enzymology*, vol. 276, Academic Press, New York, 1997, p. 307.
- [16] R.H. Blessing, *Acta Crystallogr., Sect. A* 51 (1995) 33.
- [17] G.M. Sheldrick, SHELXS-97, SHELXL-97, Programs for Crystal Structure Solution and Refinement, Göttingen University, Göttingen, Germany, 1997.
- [18] H.D. Flack, *Acta Crystallogr., Sect. A* 39 (1983) 876.
- [19] L.J. Farrugia, ORTEP-3 for Windows, *J. Appl. Crystallogr.* 30 (1997) 565.
- [20] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [21] J.J.P. Stewart, *J. Mol. Model.* 13 (2007) 1173.
- [22] J.J.P. Stewart, MOPAC2009, Stewart Computational Chemistry, Colorado Springs, CO, USA, 2008.
- [23] E.F. Franca, M.R.L. Oliveira, S. Guilardi, R.P. Andrade, R.H. Lindemann, J. Amim Jr., J. Ellena, V.M. De Bellis, M.M.M. Rubinger, *Polyhedron* 25 (2006) 2119.
- [24] M.R.L. Oliveira, V.M. De Bellis, *Trans. Met. Chem.* 24 (1999) 127.
- [25] K. Nakamoto, *Infrared and Raman of Inorganic and Coordination Compounds*, third ed., John Wiley and Sons, Inc., New York, 1978, p. 339.
- [26] H.V. Huynh, L.R. Wong, P.S. Ng, *Organometallics* 27 (2008) 2231.