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

Marcelo Ribeiro Leite Oliveira [a,*], Eduardo de Faria Franca [b], Celice Novais [b], Silvana Guilardi [b], Iterlandes Machado Jr. [a], Javier Ellena [c], Jorge Amim Jr. [a], Vito Modesto De Bellis [d], Mayura Marques Magalhães Rubinger [a]

[a] Departamento de Química, Universidade Federal de Viçosa, Viçosa MG, CEP 36571-000, Brazil
[b] Instituto de Química, Universidade Federal de Uberlândia, Uberlândia MG, CEP 38408-100, Brazil
[c] Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos SP, CEP 13500-970, Brazil
[d] Departamento de Química, Universidade Federal de Minas Gerais, Belo Horizonte MG, CEP 31270-901, Brazil

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ABSTRACT

Five new complexes of general formula: [Ni(RSO$_2$N=CS$_2$)(dppe)], where R = C_6H_5 (**1**), 4-ClC_6H_4 (**2**), 4-BrC_6H_4 (**3**), 4-IC_6H_4 (**4**) and dppe = 1,2-bis(diphenylphosphino)ethane and [Ni(4-IC_6H_4SO$_2$N=CS$_2$)(PPh$_3$)$_2$] (**5**), where PPh$_3$ = triphenylphosphine, were obtained in crystalline form by the reaction of the appropriate potassium *N*-R-sulfonyldithiocarbimate K$_2$(RSO$_2$N=CS$_2$) and dppe or PPh$_3$ with nickel(II) chloride in ethanol/water. The elemental analyses and the IR, ^{1}H NMR, ^{13}C NMR and ^{31}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*-NiS$_2$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**.

1. Introduction

The interest in the syntheses and characterization of dithiocarbimate 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 dithiocarbamates salts and complexes have been used as fungicides [2,3]. In fact, recently it was demonstrated that dithiocarbimates are also fungicides and vulcanization accelerators [4,5]. Additionally, heteroleptic group 10 metal complexes with sulfonyldithiocarbimate 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: [Ni(RSO$_2$N=CS$_2$)(PPh$_3$)$_2$] (R = 2-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 4-BrC_6H_4, and 2,5-$Cl_2C_6H_3$) [8,9], [Ni(RSO$_2$N=CS$_2$)dppe] (R = CH_3, CH_3CH_2, 2-$CH_3C_6H_4$ and 4-$CH_3C_6H_4$) [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: [Ni(RSO$_2$N=CS$_2$)(dppe)] R = C_6H_5 (**1**), 4-ClC_6H_4 (**2**), 4-BrC_6H_4 (**3**), 4-IC_6H_4 (**4**), and [Ni(4-IC_6H_4SO$_2$N=CS$_2$)(PPh$_3$)$_2$] (**5**). The complexes were obtained in the crystalline form by the reaction of NiCl$_2$·6H$_2$O with PPh$_3$ or dppe and the dithiocarbimate anions derived from sulfonamides. These complexes were characterized by IR, ^{1}H, ^{13}C and ^{31}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-iodobenzenesulphonamide and the 4-bromobenzenesulphonamide were prepared from the appropriate sulfonyl chloride as described elsewhere [11]. The *N*-R-sulfonyldithiocarbimate 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

* Corresponding author.
E-mail address: marcelor@ufv.br (M.R.L. Oliveira).

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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 ^{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.

2.2. Syntheses

The syntheses 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 suspension of the appropriate phosphine (2.0 mmol for PPh_3 and 1.0 mmol for dppe) in ethanol (40 mL). Nickel(II) chloride hexahydrate (1.0 mmol) was added to the suspension and the reaction mixture was stirred for six hours at room temperature. The color of the suspension changed from green to pink/red. The solid product was filtered, washed with distilled water and ethanol, and dried under reduced pressure for one day. The yield was *ca.* 80%. 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.

2.2.1. [Ni($C_6H_5SO_2N$=CS_2)dppe] (**1**)

Anal. Calc. C, 57.57; H, 4.25; N, 2.05; Ni, 8.53. Found: C, 57.19; H, 4.38; N, 2.04; Ni, 8.16%. Mp with decomposition (°C): 201.5–202.5. IR (most important bands) (cm^{-1}): 1436 ν(C=N); 1310 $\nu_{ass}(SO_2)$; 1151 $\nu_{sym}(SO_2)$; 917 $\nu_{ass}(CS_2)$ and 360 ν(NiS). ^{1}H NMR (δ), *J*(Hz): 7.98–7.95 (m, 2H, H2 and H6 of the aromatic ring of the dithiocarbimato); 7.76–7.65 (m, 8H, H2 and H6 of the aromatic rings of dppe); 7.66–7.33 (m, 15H, H3, H4 and H5 of the aromatic rings of the dithiocarbimato and dppe); 2.34 (d, 4H J_{HP} = 17, CH_2CH_2). $^{13}C\{^{1}H\}$ NMR (δ): 199.32 (N=CS_2); 142.46 (C1); 131.62 (C4); 128.16 (C3 and C5); 127.44 (C2 and C6). dppe signals: 132.88 (t, J_{CP} = 5.3, C2 and C6); 131.79 (s, C4); 129.35 (t, J_{CP} = 5.2, C3 and C5); 128.23 (t, J_{CP} = 22, C1); 26.01 (t, J_{CP} = 23, CH_2CH_2). *^{31}P NMR (δ)*: 56.92 (s).

2.2.2. [Ni(4-$ClC_6H_4SO_2N$=CS_2)dppe] (**2**)

Anal. Calc. C, 54.83; H, 3.90; N, 1.94; Ni, 8.12. Found: C, 54.69; H, 3.74; N, 1.83; Ni, 8.00%. Mp with decomposition (°C): 220.0–221.1. *IR* (most important bands) (cm^{-1}): 1443 ν(C=N); 1308 $\nu_{ass}(SO_2)$; 1147 $\nu_{sym}(SO_2)$; 922 $\nu_{ass}(CS_2)$ and 355 ν(NiS). ^{1}H NMR (δ), *J*(Hz): 7,92–7,88 (m, 2H, H2 and H6 of the aromatic ring of the dithiocarbimato); 7.75–7.67 (m, 8H, H2 and H6 of the aromatic rings of dppe); 7.53–7.30 (m, 14H, H3, H4 and H5 of the aromatic rings of the dppe and H3 and H5 of the aromatic ring of the dithiocarbimato); 2.35 (d, 4H J_{HP} = 17, CH_2CH_2). $^{13}C\{^{1}H\}$ NMR (δ): 200.25 (N=CS_2); 141.04 (C1); 137.84 (C4); 128.36 (C3 and C5); 129.08 (C2 and C6). dppe signals: 132.88 (t, J_{CP} = 5.3, C2 and C6); 131.88 (s, C4); 129.39 (t, J_{CP} = 5.2, C3 and C5); 128.20 (t, J_{CP} = 22, C1); 26.06 (t, J_{CP} = 23, CH_2CH_2). ^{31}P NMR (δ): 57.23 (s).

2.2.3. [Ni(4-$BrC_6H_4SO_2N$=CS_2)dppe] (**3**)

Anal. Calc. C, 51.65; H, 3.68; N, 1.83; Ni, 7.65. Found: C, 51.40; H, 3.55; N, 1.80; Ni, 7.90%. Mp with decomposition (°C): 206.5–208.5. IR (most important bands) (cm^{-1}): 1443 ν(C=N); 1308 $\nu_{ass}(SO_2)$; 1150 $\nu_{sym}(SO_2)$; 922 $\nu_{ass}(CS_2)$ and 358 ν(NiS). ^{1}H NMR (δ), *J*(Hz): 7.85–7.81 (m, 2H, H2 and H6 of the aromatic ring of the dithiocarbimato); 7.71–7.67 (m, 8H, H2 and H6 of the aromatic rings of dppe); 7.51–7.45 (m, 14H, H3, H4 and H5 of the aromatic rings of the dppe and H3 and H5 of the aromatic ring of the dithiocarbimato); 2.35 (d, 4H J_{HP} = 17, CH_2CH_2). $^{13}C\{^{1}H\}$ NMR (δ): 200.92 (N=CS_2); 141.58 (C1); 133.04 (C4); 131.45 (C3 and C5); 126.51 (C2 and C6). dppe signals: 132.88 (t, J_{CP} = 5.3, C2 and C6); 132.00 (s, C4); 128.52 (t, J_{CP} = 5.2, C3 and C5); 128.30 (t, J_{CP} = 22, C1); 26.57 (t, J_{CP} = 23, CH_2CH_2). ^{31}P NMR (δ): 57.19 (s).

2.2.4. [Ni(4-$IC_6H_4SO_2N$=CS_2)dppe] (**4**)

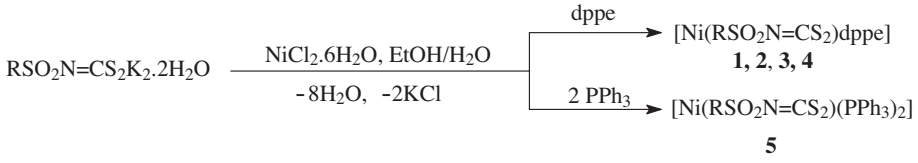
Anal. Calc. C, 48.67; H, 3.47; N, 1.72; Ni, 7.21. Found: C, 48.40; H, 3.32; N, 1.92; Ni, 6.89%. Mp with decomposition (°C): 203.5–207.3. IR (most important bands) (cm^{-1}): 1463 ν(C=N); 1301 $\nu_{ass}(SO_2)$; 1120 $\nu_{sym}(SO_2)$; 920 $\nu_{ass}(CS_2)$ and 335 ν(NiS). ^{1}H NMR (δ), *J*(Hz): 7,72–7,65 (m, 10H, H2 and H6 of the aromatic ring of the dithiocarbimato and dppe); 7.52–7.41 (m, 14H, H3, H4 and H5 of the aromatic rings of the dppe and H3 and H5 of the aromatic ring of the dithiocarbimato); 2.35 (d, 4H J_{HP} = 17, CH_2CH_2). $^{13}C\{^{1}H\}$ NMR (δ): 200.58 (N=CS_2); 142.30 (C1); 137.31 (C3 and C5); 129.18 (C2 and C6); 98.79 (C4). dppe signals: 132.87 (t, J_{CP} = 5.3, C2 and C6); 131.87 (s, C4); 129.40 (t, J_{CP} = 5.2, C3 and C5); 128.25 (t, J_{CP} = 22 C1); 26.13 (t, J_{CP} = 23, CH_2CH_2). ^{31}P NMR (δ): 58.46 (s).

2.2.5. [Ni(4-$IC_6H_4SO_2N$=CS_2)(PPh_3)$_2$] (**5**)

Anal. Calc. C, 54.91; H, 3.64; N, 1.49; Ni, 6.24. Found: C, 54.85; H, 3.58; N, 1.43; Ni, 6.10%. Mp with decomposition (°C): 192.9–194.3. IR (most important bands) (cm^{-1}): 1451 ν(C=N); 1315 $\nu_{ass}(SO_2)$; 1151 $\nu_{sym}(SO_2)$; 933 $\nu_{ass}(CS_2)$ and 341 *ν(NiS)*. ^{1}H NMR (δ): 7,75–7,26 (m, 34H, aromatic rings). $^{13}C\{^{1}H\}$ NMR (δ): 141.99 (C1); 137.16 (C3 and C5); 128.57 (C2 and C6); 98.75 (C4) triphenylphosphine signals: 134.30 (C2 and C6); 130.75 (C4); 129.57 (C1); 128.37 (C3 and C5). ^{31}P NMR (δ): 33.68 (s).

2.3. X-ray diffraction studies

Diffraction data for all crystals were collected on an Enraf–Nonius Kappa-CCD diffractometer using a graphite monochromator with Mo Kα radiation (0.71073 Å), at room temperature for the complexes **1**, **4** and **5** and at lower temperature for the complexes **2** and **3**. Data collections were made using the COLLECT program [14] up to 50° in 2θ with 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 [15]. Multi-scan absorption corrections were applied for the complexes **1**, **2** and **4** and numerical absorption corrections (GAUSSIAN) were applied for the complexes **3** and **2** using the program SORTAV [16].



1 (R = C_6H_5), **2** (R = 4-ClC_6H_4), **3** (R = 4-BrC_6H_4), **4** and **5** (R = 4-IC_6H_4)

Scheme 1. Syntheses of **1**–**5**.