

Square planar nickel(II) complexes derived from 5-bromo-2-hydroxybenzaldehyde *S*-ethylisothiosemicarbazone: Preparation, characterization and structural studies



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ARTICLE INFO

Article history:

Received 13 December 2013

Accepted 26 April 2014

Available online 9 May 2014

Keywords:

Isothiosemicarbazone

Nickel(II) complex

Spectroscopy

X-ray analysis

DFT

ABSTRACT

Three nickel(II) complexes, (5-bromo-2-hydroxybenzaldehyde *S*-ethylisothiosemicarbazono-*N,N'*,*O*)-(imidazole)-nickel(II) (**1**), (5-bromo-2-hydroxybenzaldehyde *S*-ethylisothiosemicarbazono-*N,N'*,*O*)-(4-dimethylaminopyridine)-nickel(II) (**2**) and (*S*-ethyl-1,4-bis(5-bromo-2-hydroxybenzaldehyde)-isothiosemicarbazido-*O,O'*,*N,N'*)-nickel(II) (**3**) have been synthesized and characterized by elemental analysis, molar conductivity, FT-IR, ¹H NMR and UV-Vis studies. For better definition of the molecular structures, the X-ray crystallographic analysis was carried out for the complexes. The complexes **1** and **2** show distorted square planar geometry around the central Ni(II) ion, with the ligand coordinated to the central metal as a tridentate chelate and the fourth coordination position occupied by imidazole and 4-dimethylaminopyridine in **1** and **2** respectively. Compound **3** also adopts a distorted square planar geometry with the tetradentate ligand occupying all coordination positions around the metal center. The deprotonated form of the N₂O₂ donor ligand is coordinated to nickel(II) via both deprotonated phenolic oxygen and azomethine nitrogen atoms. The complexes have been investigated by DFT calculation and the results were compared with the crystallographic data.

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1. Introduction

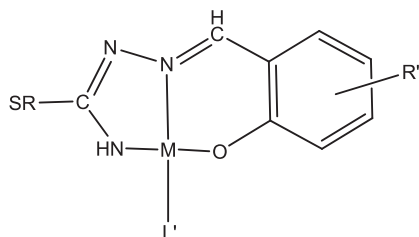
The condensation reaction between *S*-alkyl-isothiosemicarbazide and salicylaldehyde analogues affords Schiff bases that can act as tridentate NNO donor ligands, Scheme 1; they are called isothiosemicarbazones [1]. Isothiosemicarbazones are a potentially versatile class of ligands because by changing the nature of the substituents on sulfur and on salicylaldehyde, and by changing the metal ion and the additional ligand necessary for the completion of its coordination sphere, a fine tuning of the properties of the corresponding complexes can be achieved in principle.

Some articles have shown the biological activity of isothiosemicarbazone complexes that can actually display antimicrobial, antifungal and antibacterial properties [2–4]. *S*-alkylisothiosemicarbazones have an amino function that can further react with aldehydes. In particular, the template reaction of *S*-alkylisothiosemicarbazones with substituted salicylaldehydes, in the presence of metal ions prone to square planar coordination (e.g. V(IV), Cu(II), Ni(II)) can lead to tetradentate N₂O₂ ligands and complexes (Scheme 2). The structural features of this class of compounds are similar to the salen ligands. Although few structural studies of Ni(II) complexes with such tetradentate N₂O₂ ligands have been performed, their cytotoxic activity and electrochemical properties have been documented [2,5].

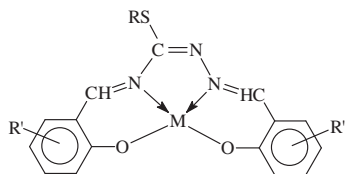
In the present paper we have explored both coordination abilities of *S*-alkylisothiosemicarbazones shown in Schemes 1 and 2, and we report on the synthesis and full characterization including spectroscopic methods, single crystal X-ray analysis and DFT theoretical calculations of three nickel(II) complexes: **1** (R = Et, R' = 5-Br, L' = imidazole in Scheme 1), **2** (R = Et, R' = 5-Br, L' = 4-dimethylaminopyridine in Scheme 1) and **3** (R = Et, R' = 5-Br in Scheme 2). Ni(II) was chosen as the metal, because of its ability to form square planar complexes and of our interest in advanced functional materials containing Ni(II) [6–8]. Bromine was chosen as the substituent on the salicylaldehyde moiety because of possible use of the complexes in cross-coupling reactions aimed at the synthesis of metal containing conjugated molecules for advanced applications.

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Scheme 1. Chemical diagram of complexes with tridentate isothiosemicarbazone ligand (R = Me, Et, allyl and ... , R' = H, OMe, Br and ... , L' = pyridine, imidazole and ...).



Scheme 2. Chemical diagram of a complex with a tetradentate isothiosemicarbazone ligand (R = Me, Et, allyl and ... , R' = H, OMe, Br and ...).

2. Experimental

2.1. Experimental and instrumentation

The H_2L ligand (R = Et, R' = 5-Br in **Scheme 1**) was prepared according to our previous article [9]. Other chemicals were of analytical grade and used without any further purification. FT-IR spectra (400–4000 cm^{-1}) were recorded on a FT-IR 8400-SHIMADZU spectrophotometer with samples prepared as KBr pellets. UV-Vis spectra were carried out on a SHIMADZU model 2550 UV-Vis spectrophotometer at 2×10^{-5} and 1×10^{-3} mol L^{-1} concentration in DMF. C, H, N elemental analyses were performed on a Thermo Finnigan Flash Elemental Analyzer 1112EA instrument. Electric conductance measurements were measured with a Metrohm 712 Conductometer. 1H NMR spectra were measured Bruker BRX 250 AVANCE spectrometers.

2.2. X-ray crystallography

Single crystals of **1**, **2** and **3** suitable for X-ray analysis were grown from ethanol. Data were collected on a Bruker-Nonius Kappa-CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 173 K. Absorption correction was performed using the multi-scan method [10]. Structures were solved by direct methods [11] and refined by the full matrix least squares method [12] on F^2 against all reflections, using anisotropic displacement parameters for non-H atoms, with the aid of the program WinGX [13]. H atoms were determined stereochemically and refined by the riding model, with exception for H atoms bonded to N atoms in **1** and **2**, whose positions were determined in difference Fourier maps and whose coordinates were refined. For all H atoms, U_{iso} was not refined and was fixed at $U_{iso} = 1.2U_{eq}$ of the carrier atom. In the case of **3** molecules enter the crystal in two orientations with complete superposition of all atoms but those of the ethylthio tail which, as a matter of fact, is disordered over two sites; moreover, the methylene group of the tail is coincident in the two positions. The two split positions were refined with some restraints on bond lengths. A summary of crystal, collection and refinement data is shown in **Table 1**. The analysis of the crystal packing was performed using the program Mercury [14].

Table 1

Crystal, collection and refinement data for **1**, **2** and **3**.

Compound	1	2	3
Chemical formula	$C_{13}H_{14}BrN_5NiOS$	$C_{17}H_{20}BrN_5NiOS$	$C_{17}H_{13}Br_2N_3NiO_2S$
Formula weight	426.97	481.06	541.89
T (K)	173(2)	173(2)	173(2)
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (\AA)	7.517(6)	8.5030(10)	9.3727(8)
b (\AA)	8.955(8)	10.5170(8)	9.7280(7)
c (\AA)	12.925(9)	10.7640(10)	11.0290(12)
α ($^\circ$)	73.98(5)	94.588(7)	111.034(7)
β ($^\circ$)	85.27(3)	103.499(6)	102.914(7)
γ ($^\circ$)	68.75(5)	94.605(10)	97.457(6)
V (\AA^3)	779.3(11)	928.11(16)	890.15(14)
Z	2	2	2
Density (g/cm^3), μ (mm^{-1})	1.820, 3.950	1.721, 3.327	2.022, 5.714
Reflection collected, max. θ	5196, 25.0 $^\circ$	11706, 27.5 $^\circ$	12053, 27.49 $^\circ$
Independent reflection (R_{int})	2689 (0.0625)	4232 (0.0288)	4082 (0.0902)
Data/restraints/parameter	2689/0/209	4232/0/244	4082/3/254
R, wR ($I > 2(I)$)	0.0535, 0.1258	0.0251, 0.0493	0.0537, 0.0767
R, wR (all data)	0.0877, 0.1431	0.0399, 0.0536	0.1159, 0.0918
Max. peak and hole ($e/\text{\AA}^3$)	0.681, -0.674	0.376, -0.306	0.706, -0.586

2.3. Computational details

The geometries of the complexes were fully optimized with the density functional theory (DFT) by the Gaussian98 program package [15]. In the calculations, the B3LYP method using the 6-31G* (d,p) basis set was applied for the H, C, N, O, S and Br atoms and Lan12dz [16,17] basis set for the metal centers in the gas phase. The frequency calculations were done to provide evidence of full optimizations. The Natural Bond Orbital (NBO) analyses have been performed using the NBO-code, included in GAUSSIAN98 [18].

2.4. Preparation of **1**

The complex **1** was synthesized by reaction of H_2L , imidazole and $NiCl_2 \cdot 6H_2O$ in molar ratio 1:2:1 in ethanol. Suitable crystals of complex **1** for crystallographic analysis were grown by slow evaporation of the reaction solution after one week.

Yield 0.31 g (73%). m.p. 163 $^\circ C$. *Anal.* Calc. for $C_{13}H_{14}BrN_5NiOS$ (426.95 $g\ mol^{-1}$): C, 36.57; H, 3.31; N, 16.40. Found: C, 35.37; H, 3.12; N, 16.87%. FT-IR (KBr, cm^{-1}): $\nu(NH)_{imidazole}$ 3452 m; $\nu(NH)$ 3448 m; $\nu(CH)$ 2896–2962w; $\nu(C=N) + \nu(C=C)$ 1604vs, 1512s; $\nu(C=C)$ 1450 m; $\delta(NH)_{opb}$ 1312; $\nu(C-O)$ 1141 m; $\nu(N-N)$ 1049w; $\delta(C-H)_{opb}$ 702w. UV-Vis (λ (nm), $\log \epsilon$ ($L\ mol^{-1}\ cm^{-1}$)): 268(4.23), 306(3.75), 390(4.22), 506(2.53), 568(1.85). Molar Conductivity (1×10^{-3} mol L^{-1} ; DMF): 12 $\Omega^{-1}\ cm^2\ mol^{-1}$. 1H NMR (250 MHz, DMSO- d_6 , ppm): 9.33 (brs, 1H, N3-H), 6.69–8.52 (m, 6H, CH of aromatic ring, imidazole ring and azomethinic), 4.3 (brs, 1H, N5-H), 3.05 (q, 2H, C9H₂), 1.40 (t, 3H, C10H₃).

2.5. Preparation of **2**

The complex **2** was synthesized by reaction of H_2L , 4-dimethylaminopyridine and $NiCl_2 \cdot 6H_2O$ in molar ratio 1:2:1 in ethanol. The resulted solid was recrystallised in DMF to obtain dark-red single crystal of complex **2** suitable for X-ray diffraction.

Yield 0.34 g (71%). m.p. 234 $^\circ C$. *Anal.* Calc. for $C_{17}H_{20}BrN_5NiOS$ (481.04 $g\ mol^{-1}$): C, 42.45; H, 4.19; N, 14.56. Found: C, 41.87; H, 4.32; N, 14.67%. IR (KBr, cm^{-1}): $\nu(NH)$ 3425 m; $\nu(CH)$ 2843–3003w; $\nu(C=N) + \nu(C=C)$ 1620vs, 1603m; $\nu(C=N)_{py} + \nu(C=C)_{py}$

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