



Supramolecular nickel complex based on thiosemicarbazone. Synthesis, transfer hydrogenation and unexpected thermal behavior



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ARTICLE INFO

Article history:

Received 30 September 2015

Accepted 3 February 2016

Available online 8 February 2016

Keywords:

Thiosemicarbazone

Transfer hydrogenation

Nickel

X-ray diffraction

Isopropyl alcohol

ABSTRACT

The cationic thiosemicarbazone complex of nickel containing triphenylphosphine as coligand was synthesized through the isopropanol-assisted hydrogen transfer reaction. The thiosemicarbazone ligand (LH₂) and its cationic nickel complex, [Ni(LH)(PPh₃)]⁺Cl⁻·(CH₃)₂CHOH, were characterized by elemental analysis, IR, ¹H NMR and UV–Vis spectroscopies. The molecular structure of the complex was also determined by single crystal X-ray diffraction technique. In addition computational studies at B3LYP/6-311G (d,p) (main group) and LANL2DZ (Ni) level were carried out for theoretical characterization of the ligand and complex. Structural analysis of the complex indicated the presence of square-planar coordination geometry (ONNP) about nickel in which the thiosemicarbazone ligand coordinated as mononegative tridentate. Isopropyl alcohol catalyzed efficiently the transfer hydrogenation and the cationic complex formed through inter conversion azinyl–azinylidene. All spectral data support the formation of the ligand and its nickel complex and the results calculated using theoretical methods coincide well with the experimental findings. The thermal degradation of the complex was investigated using thermogravimetric and differential thermal analyses techniques in nitrogen and oxygen atmosphere. The oxidative-thermal decomposition of the compound showed volatilization of nickel as unexpected behavior unlike nitrogen atmosphere.

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1. Introduction

Thiosemicarbazones are of great importance because of biological, medicinal, pharmacological and analytical properties [1–11]. They have more than one binding site for metal ions and their properties change depending on metal atom, coordination modes, connected aldehyde or ketone and substituents on aldehyde/ketone [12–16].

Thiosemicarbazones possess different coordination modes, can be in neutral or anionic form because of thione–thiol tautomerism and give generally neutral or rarely cationic metal complexes (Scheme 1) [17–25].

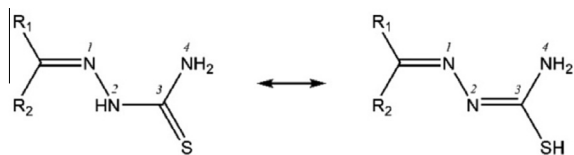
Supramolecular structures have attracted great attention in recent years and take place as a result of an intermolecular hydrogen bonding, pi–pi interactions, electrostatic effects, hydrophobic forces, metal coordination and van der Waals forces [26]. The non-covalent interactions are extremely significant in catalysis.

Although there are a great number of papers on thiosemicarbazones owning more than one donor atom, the papers are limited on supramolecular structures of metal complexes based on thiosemicarbazone [27–29].

As a continuation of our interest on thiosemicarbazone and its metal complexes, we present here the synthesis, structural, thermogravimetric and spectroscopic features of 5-bromo-2-hydroxybenzaldehyde-S-methyl-isothiosemicarbazido triphenylphosphine nickel chloride isopropyl alcohol. In this study, we isolated rarely occurring nickel complex salt form of S-methyl isothiosemicarbazone and triphenylphosphine, also containing one mole isopropyl alcohol as solvent in formula [Ni(LH)(PPh₃)]⁺Cl⁻·(CH₃)₂CHOH. Moreover, this solute–solvent complex has supramolecular structure (I). Despite many attempts in previous study, we were unable to put solvent molecule in the same crystal lattice as stable complex and the crystal did not contain chloride anion and the complex was in neutral form, [NiLPPH₃], (Scheme 2) [30]. By this study, we not only obtained rarely occurring cationic complex salt (I) by changing polarity of solvent, but we also saw that the isopropyl alcohol catalyzed efficiently the transfer hydrogenation and caused to supramolecular structure's formation.

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Scheme 1. Tautomerism of thiosemicarbazone.

Moreover, thermal decomposition of this crystal (**I**) showed an unexpected behavior in oxygen and nitrogen atmosphere. The oxidative decomposition of the complex unlike nitrogen atmosphere displayed volatilization of nickel. This property is preferable for volatile solid metallo-organic precursors for use in CVD applications for preparing thin films of metallic nickel [31,32].

2. Experimental

2.1. General remarks

All chemicals were of reagent grad and used as commercially purchased without further purification. The elemental analyses were determined on a Thermo Finnigan Flash EA 1112 Series Elemental Analyser and Varian Spectra-220/FS Atomic Absorption spectrometer. IR spectra of the compounds were recorded on KBr pellets with a Mattson 1000 FT-infrared spectrometer. The ^1H Nuclear Magnetic Resonance spectra were recorded in DMSO on Bruker AVANCE-500 model spectrometer. UV-Vis spectra were obtained with a Shimadzu 2600 UV-Visible Spectrometer as 5×10^{-5} M solutions in CHCl_3 . Magnetic measurements were carried out at room temperature by the Gouy technique with an MK I model device obtained from Sherwood Scientific. The molar

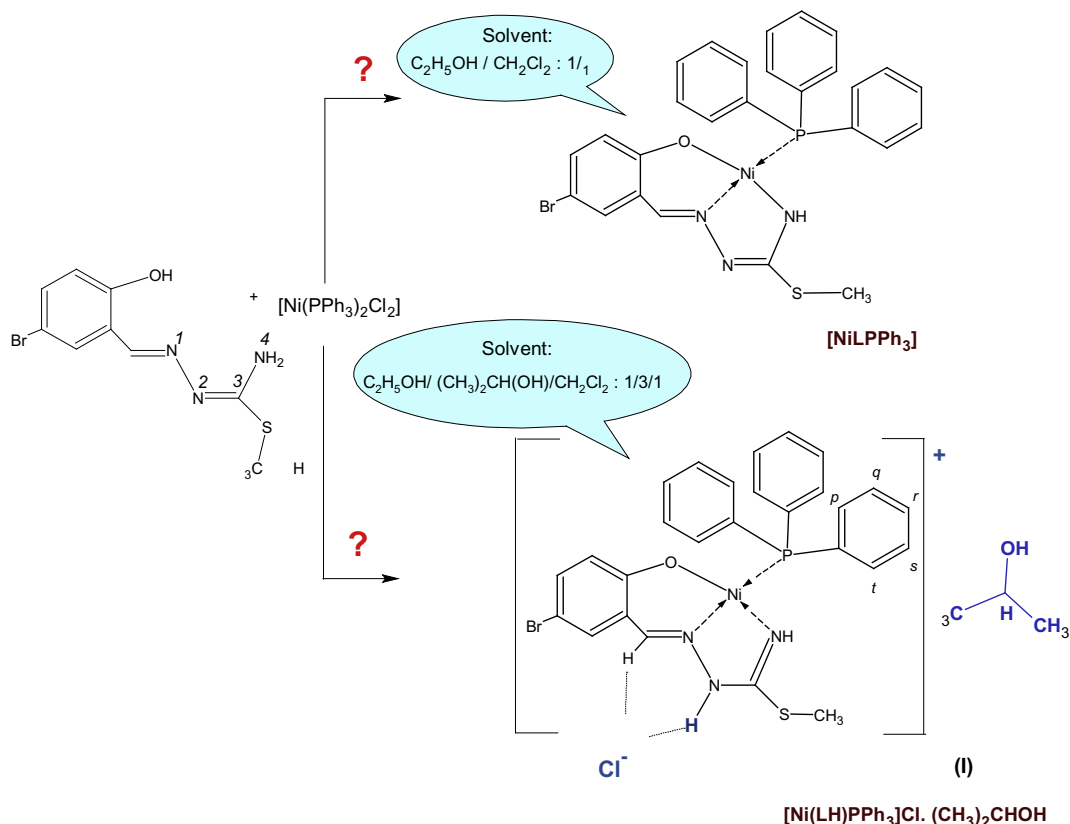
conductivities of the compounds were measured in 10^{-3} M DMSO solution at 25 ± 1 °C using a digital WPA CMD 750 conductivity meter. Thermal study of complex was carried out on a Seiko Exstar 6000 TG/DTA 6300 instrument between the 0 and 1000 °C at a heating rate of 5 °C/min. under air and nitrogen atmosphere using platinum crucibles.

2.1.1. Synthesis of 5-bromo-2-hydroxy-benzaldehyde-*S*-methyl-isothiosemicarbazone (LH_2)

The ligand was prepared according to common procedures [30]. The color; m.p. (°C); yield (%); elemental analysis; UV-Vis [$\lambda_{\text{max}}(\epsilon)$: nm ($\text{mM}^{-1} \text{cm}^{-1}$); IR (cm^{-1}) and ^1H NMR (ppm, J in Hz) data of the ligand were given as follows: Yellow; 199; 91; *Anal. Calc.* for $\text{C}_9\text{H}_{10}\text{BrN}_3\text{OS}$ (288.16 g/mol): C, 37.51; H, 3.50; N, 14.58; S, 11.13. Found: C, 37.53; H, 3.49; N, 14.57; S, 11.11%; UV-Vis: 241 (4.05), 298 (5.12), 309 (4.06), 342 (4.06), 356 (4.01); IR: $\nu_{\text{d}}(\text{NH}_2)$ 3476; $\nu_{\text{s}}(\text{NH}_2)$ 3276; $\nu(\text{OH})$ 3084; $\delta(\text{NH}_2)$ 1632; $\nu(\text{C}=\text{N}^1)$ 1620; $\nu(\text{C}=\text{N}^2)$ 1607; $\nu(\text{C}-\text{O})$ 1153; ^1H NMR: 11.65, 10.79 (*cis/trans* ratio: 3/2, s, 1H, OH), 8.43, 8.33 (*syn/anti* ratio: 2/3, s, 1H, $\text{CH}=\text{N}^1$), 7.01 (s, 2H, N^4H_2), 7.76 (d-d, $J = 2.52$, 1H, c), 7.35 (m, 1H, b), 6.86 (d-d, $J = 1.52$, $J = 8.7$, 1H, a), 2.45, 2.39 (*cis/trans* ratio: 3/2, s, 3H, S- CH_3).

2.1.2. Synthesis of $[\text{Ni}(\text{LH})(\text{PPh}_3)]^+\text{Cl}^-(\text{CH}_3)_2\text{CHOH}$

The compound (**I**) was prepared with small modifications of literature method (Scheme 2) [33]. $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ (0.65 g, 1 mmol) in 25 mL absolute alcohol was added to the solution of LH_2 (0.29 g, 1 mmol) in mixture of ethanol, isopropyl alcohol and dichloromethane (20 ml:60 mL:20 mL). The reaction mixture was refluxed for 48 h. After standing for six days, the precipitated dark red crystals were filtered off and washed with *n*-hexane (10 ml). The color; m.p. (°C); yield (%); μ_{eff} . value (BM); molar conductivity ($\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$); elemental analysis; UV-Vis [$\lambda_{\text{max}}(\epsilon)$: nm



Scheme 2. Formation of $[\text{NiLPP}_3]$ and $[\text{Ni}(\text{LH})(\text{PPh}_3)]^+\text{Cl}^-(\text{CH}_3)_2\text{CHOH}$ (**I**).

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