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Square planar Ni(II) complexes of pyridine-4-carbonyl-hydrazine carbodithioate, 1-phenyl-3-pyridin-2-yl-isothiourea and 4-(2-methoxyphenyl)piperazine-1-carbodithioate involving N–S bonding: An approach to DFT calculation and thermal studies

P. Bharati [a], A. Bharti [a], M.K. Bharty [a,*], B. Maiti [a], R.J. Butcher [b], N.K. Singh [a,*]

[a] *Department of Chemistry, Banaras Hindu University, Varanasi 221005, India*
[b] *Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA*

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ABSTRACT

Three new complexes $[H_2en][Ni(pchc)_2]$ (**1**) (pchc = pyridine-4-carbonyl-hydrazine carbodithioate), $[Ni(Hppith)_2]$ (**2**) (H_2ppith = 1-phenyl-3-pyridin-2-yl-isothiourea) and $[Ni(mppcdt)_2]$ (**3**) {mppcdt = 4-(2-methoxyphenyl)piperazine-1-carbodithioate} have been synthesized and characterized by elemental analyses, IR and single crystal X-ray diffraction data. The ligand H_2ppith and complexes $[H_2en][Ni(pchc)_2]$ (**1**) $[Ni(Hppith)_2]$ (**2**) and $[Ni(mppcdt)_2]$ (**3**) crystallize in monoclinic, orthorhombic, monoclinic and triclinic system with space group $P21/n$, $Icab$, $C2/c$ and $P\bar{1}$, respectively. The nitrogen and sulfur donor sites of the bidentate ligands chelate Ni(II) forming two five-membered CSN_2M chelate rings in the complex **1**, two six membered C_2SN_2M rings in complex **2** and the sulfur donor sites of the bidentate ligand chelate Ni(II) forming two four membered CS_2M rings in complex **3**. The Ni(II) complexes are diamagnetic and have distorted square planar geometry. The crystal structure of the complexes are stabilized by various types of inter and intramolecular extended hydrogen bonding providing supramolecular framework. Results obtained from quantum chemical calculations at the density functional theory level corroborate our experimental findings from IR and UV. The course of the thermal degradation of complexes **1**, **2** and **3** has been investigated by TG-DTA. Thermogravimetric analyses of the complexes indicate NIO/NIS as the end residue.

1. Introduction

Nickel(II) complexes of nitrogen sulfur containing chelating ligands have recently attracted much attention because of their use as a model for the nickel center of enzymes such as bifunctional carbon monoxide dehydrogenase/acetyl–CoA synthase and nickel-containing superoxide dismutase [1]. Nickel(II) complexes with nitrogen and sulfur donor ligands are also highly interesting because several hydrogenases and carbon monoxide dehydrogenases contain such nickel complexes as their active site [2,3]. Nickel is a nutritionally essential trace metal for at least several animal species, micro-organisms and plants, and therefore toxicity symptoms can occur under the conditions of either its deficiency or excess. Isonicotinic acid hydrazide being an antimicrobial agent has been used as anti-tubercular drug and its dithio derivatives may exhibit both N–S and S–S bonded chelating behavior forming interesting M(N,S) and M(S,S) bonded compounds with increased electron delocalization which may lead to improved biological activity [4–6]. The uninegative thio ligands exhibit different modes of bonding in mononuclear Ni(II) complexes [7]. The dithiocarbazates and their substituted derivatives containing nitrogen sulfur donor atoms have been of great interest to researchers because of their wide variation in structure and properties. Their complexes have tunable electronic behavior which may result in nonlinear optical (NLO) materials with unique magnetic and electrochemical properties [7,8] and show selective biological activity [9–11]. Substituted dithiocarbazates containing hetero atoms behave as bidentate [7,8], tridentate [9,10] or multidenate [11] chelating agents. In the literature, thiosemicarbazone ligands based on aldehydes have generally formed *trans* square planar complexes, while ketone based thiosemicarbazones have formed only *cis* square planar complexes [12–14]. Thiourea/isothiourea ligands may exhibit monodentate, bidentate or multidentate behavior in the resulting complexes [15–24], which opens a multiplicity of bonding schemes. Thus the presences of different donor atoms as well as the various structures of thiourea derivatives result in a variety of complexes. In view of

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* Corresponding authors. Tel.: +91 5422318529; fax: +91 5422368127 (N.K. Singh).

E-mail addresses: manoj_vns2005@yahoo.co.in (M.K. Bharty), singhnk_bhu@yahoo.com (N.K. Singh).

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this, we have prepared and characterized the Ni(II) complexes of pyridine-4-carbonyl-hydrazine carbodithioate, 1-phenyl-3-pyridin-2-yl-isothiourea and 4-(2-methoxyphenyl) piperazine-1-carbodithioate, all of which contain nitrogen–sulfur donor atoms.

2. Experimental

2.1. Chemicals and starting materials

Commercial reagents were used without further purification and all experiments were carried out in open atmosphere. Isonicotinic acid hydrazide, Pyridine-2-yl amine, Isothiocyanato benzene, 1-(2-methoxyphenyl) piperazine (Sigma Aldrich), CS_2 (SD Fine Chemicals) and KOH (Qualigens) were used as received. All the synthetic manipulations were carried out in open atmosphere and at room temperature. The solvents were dried and distilled before use following the standard procedure. The complexes were analyzed for their metal content, after decomposition with a mixture of conc. HNO_3 and HCl, followed by conc. H_2SO_4 [25].

2.2. Physical measurements

Carbon, hydrogen, nitrogen and sulfur contents were estimated on a CHN Model CE-440 Analyser and on an Elementar Vario EL III Carlo Erbo 1108. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant and electronic spectra were recorded on a SHIMADZU 1700 UV–Vis spectrophotometer. IR spectra were recorded in the 4000–400 cm^{-1} region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a JEOL AL300 FT-NMR spectrometer using TMS as an internal reference. Thermogravimetric analyses (TG-DTA) were completed on a Perkin Elmer-STA 6000 thermal analyzer at a heating rate of 5 °C/min in N_2 atmosphere.

2.3. Synthesis

2.3.1. Synthesis of ethylenediammonium-pyridine-4-carbonyl-hydrazine carbodithioate $[(H_2en)(pchc)_2]$

The potassium pyridine-4-carbonyl-hydrazine carbodithioate was prepared by adding CS_2 (1.8 mL, 20 mmol) dropwise to a suspension of isonicotinic acid hydrazide (2.74 g, 20 mmol) in methanol (20 mL) in the presence of potassium hydroxide (1.2 g, 20 mmol). The reaction mixture was stirred continuously for 30 min and the separated yellow solid potassium pyridine-4-carbonyl-hydrazine carbodithioate was filtered, washed with EtOH and dried. The above potassium salt was dissolved in water and treated with a solution of chloroacetic acid (1.8 g, 20 mmol) neutralized with sodium carbonate. The solution was left overnight after adjusting the pH at 7. The reaction mixture was cooled in ice and acidified with conc. HCl, white precipitate was obtained which was dissolved in the aqueous solution of sodium hydroxide (1.89 g, 20 mmol) and ethylenediamine (1.6 mL, 25 mmol) diluted two times with water was added and the reaction mixture was kept for 3 h and then acidified with dil. HCl (40% v/v) in ice cold condition which gave a white precipitate. The precipitate was filtered, washed with water, dried under reduced pressure and recrystallized from a MeOH–$CHCl_3$ mixture (50:50 v/v). Yield: 0.69 g, 58%; m.p. 557 K. *Anal.* Calc. for $C_{16}H_{22}N_8S_4O_2$ (486.67): C, 39.48; H, 4.55; N, 22.81; S, 26.35. Found: C, 39.53; H, 4.49; N, 22.63; S, 26.46%. IR (KBr, cm^{-1}): ν(N–H) 3250, 3120; ν(C=O) 1622; ν(N–N) 1003; ν(C=S) 904. ^1H NMR (DMSO-d_6; δ ppm): 10.8, 11.5 (s, 2H, NH), 8.00–9.06 (m, 4H, pyridine ring protons), 4.45 ($-NH_3^+$), 4.05 (d, 4H, $-CH_2$). ^{13}C NMR (DMSO-d_6; δ ppm): 170.51 (C=S), 163.94 (C=O), 151.03–120.05 (aromatic carbons), 34.58 (CH_2, en).

2.3.2. Synthesis of 1-phenyl-3-pyridin-2-yl-isothiourea (H_2ppith)

To a solution of pyridine-2-yl amine (1.88 g, 20 mmol) in benzene (20 mL) was added phenylisothiocyanate (2.4 mL, 20 mmol) and the reaction mixture was refluxed for 4 h. A white precipitate was obtained upon cooling the reaction mixture in ice, which was filtered off, washed with methanol and ether and recrystallised from MeOH:$CHCl_3$ mixture (50:50 v/v). Yield: 0.87 g, 38%; m.p. 455 K. *Anal.* Calc. for $C_{12}H_{11}N_3S_1$ (229.30): C, 62.85; H, 4.83; N, 18.32; S, 13.98. Found: C, 62.87; H, 4.80; N, 18.34; S, 13.97%. IR (KBr, cm^{-1}): ν(NH) 3219, ν(C=N) 1598; ν(C–S) 772. ^1H NMR ($CDCl_3$; δ ppm): 7.25 (s, 2H, NH), 7.32–7.82 (pyridine ring protons), 6.67–7.12 (phenyl ring protons). ^{13}C NMR ($CDCl_3$; δ ppm): 180.89 (C=S), 162.09 (C=N), 159.67–118.22 (aromatic carbons). UV–Vis [λ_{max}, MeOH, cm^{-1}]: 43100, 42200 and 33220.

2.3.3. Synthesis of potassium 4-(2-methoxyphenyl)piperazine-1-carbodithioate $[K^+(mppcdt)^-]$

The potassium 4-(2-methoxyphenyl)piperazine-1-carbodithioate was prepared by adding CS_2 (1.8 mL, 20 mmol) dropwise to a suspension of 1-(2-methoxyphenyl) piperazine (3.51 mL, 20 mmol) in methanol (20 mL) in the presence of potassium hydroxide (1.2 g, 20 mmol). The reaction mixture was stirred continuously for 30 min in cold condition and the separated white solid potassium 4-(2-methoxyphenyl) piperazine-1-carbodithioate was filtered, washed with EtOH and dried under reduced pressure and recrystallized from a MeOH–$CHCl_3$ mixture (50:50 v/v). Yield: 0.211 g, 69%; m.p. 185 °C. *Anal.* Calc. for $C_{12}H_{15}N_2S_2OK$ (306.43): C, 47.05; H, 4.92; N, 9.13; S, 20.92. Found: C, 47.08; H, 4.91; N, 9.15; S, 20.90%. IR (KBr, cm^{-1}): ν(C–N) 1415; ν(C=S) 928; ^1H NMR (DMSO-d_6; δ ppm): 6.85–7.25 (m, 4H, aromatic protons), 3.08–3.27 (m, 8H, CH_2), 3.88 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6; δ ppm): 209.56 (C=S), 120.96–140.56 (aromatic carbons), 152.05 (C–N), 44.65–50.73 (CH_2), 55.39 (CH_3). UV–Vis [λ_{max}, DMSO, cm^{-1}]: 31250.

*2.3.4. Synthesis of $[H_2en][Ni(pchc)_2]$ (**1**)*

A methanol solution (25 mL) of $[(H_2en)(pchc)_2]$ (0.486 g, 1 mmol) was added slowly to the methanol solution of $NiCl_2\cdot 6H_2O$ (0.237 g, 1 mmol) and stirred for 2 h. A clear solution was obtained which was filtered and kept for crystallization. Blue crystals of **1** suitable for X-ray analyses were obtained by slow evaporation of the above solution over a period of 15 days. Yield: 0.43 g, 78%; m.p. (>633) K. *Anal.* Calc. for $C_{16}H_{20}Ni_1N_8S_4O_2$ (543.35): C, 35.33; H, 3.68; N, 20.61; S, 23.55. Found: C, 35.36; H, 3.66; N, 20.58; S, 23.57%. IR (KBr, cm^{-1}): ν(NH) 3116, ν(C=O) 1650, ν(N–N) 1032, ν(C=S) 850, (Ni–N) 503, (Ni–S) 407. ^1H NMR (DMSO-d_6; δ ppm): 10.08 (s, 1H, NH), 7.37–8.70 (m, 4H, pyridine ring protons), 4.59 ($-NH_3^+$), 3.03 (d, 4H, $-CH_2$). We have computed IR frequencies (using electronic structure method as described in Section 4) in the gas phase. These IR frequencies ν(cm^{-1}) are: (N–H) 3539, (C=O) 1642, (N–N) 1138, (C=S) 1019 and (Ni–S) 365. The significant deviations (in most cases higher in magnitude) in frequencies are probably due to usage of different phases (experiment in solid state; computation in gaseous state). Experimental UV–Vis [λ_{max}, DMSO, cm^{-1}]: 11450. The corresponding computed (using a TD-DFT: B3LYP/6-31G** method along with PCM model for solvation) absorption peak appears at 12276 cm^{-1}, which is close to the experimental value.

*2.3.5. Synthesis of $[Ni(Hppith)_2]$ (**2**)*

A methanol solution (25 mL) of H_2ppith (0.228 g, 2 mmol) was added slowly to the methanol solution of $Ni(OAc)_2\cdot 4H_2O$ (0.248 g, 1 mmol) and stirred for 2 h. The resulting clear solution was obtained which was filtered off and kept for crystallization. Reddish black crystals of **2** suitable for X-ray analyses were obtained by slow evaporation of the above solution over a period of 20 days. Yield: 0.58 g, 52%; m.p. 493 K. *Anal.* Calc. for $C_{15}H_{20}N_6S_2Ni$