Polyhedron 30 (2011) 990–996

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, spectral and X-ray structural studies of Ni(II) complexes of N′-acylhydrazine carbodithioic acid esters containing ethylenediamine or *o*-phenanthroline as coligands

M.K. Bharty [a], A.K. Srivastava [a], Ram Dulare [a], R.J. Butcher [b], N.K. Singh [a,*]

[a] Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India
[b] Department of Chemistry, Howard University, 525 College Street NW, Washington, DC 20059, USA

ARTICLE INFO

Article history:
Received 26 October 2010
Accepted 28 December 2010
Available online 9 January 2011

Keywords:
Carbodithioic acid ester
Ni(II) complexes
Mixed ligand complexes, Supramolecular architectures

ABSTRACT

The new complexes $[Ni(Hbstbh)_2(en)]$ (**1**) and $[Ni(Hpchce)(o\text{-phen})_2]Cl{\cdot}CH_3OH{\cdot}H_2O$ (**2**) with N′-benzoyl hydrazine carbodithioic acid benzyl ester (H_2bstbh) and [N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid ethyl ester (H_2pchce) have been synthesized, containing ethylenediamine (en) or *o*-phenanthroline (*o*-phen) as coligands. The ligands and their complexes have been characterized by elemental analyses, IR, magnetic susceptibility and single crystal X-ray data. $[Ni(Hbstbh)_2(en)]$ (**1**) and $[Ni(Hpchce)(o\text{-phen})_2]Cl{\cdot}CH_3OH{\cdot}H_2O$ (**2**) crystallized in the monoclinic and triclinic systems, space group *C*2/*c* and $P-1$, respectively. The (N, O) donor sites of the bidentate ligands chelate the Ni(II) center and form a five-membered CN_2ONi ring. The resulting complexes are paramagnetic and have a distorted octahedral geometry.

1. Introduction

S-Alkyldithiocarbazates behave as versatile ligands, either acting as monodentate (S or N2) donors or bidentate anionic (*via* N3-S or S, S) chelating ligands [1–3]. They have been widely studied for their biological activities and chemotherapeutic properties [4,5] which may be highly dependent on the nature of the metal ion and binding sites of the ligand. Some Schiff bases of S-alkyl esters of dithiocarbazic acid and their complexes were found to display antifungal and antibacterial properties [6–8]. Several papers are available on the syntheses and spectral characterization of metal complexes of dithiocarbazates [9–15]. Recently, bis chelated complexes of S-benzyl-β-N-(benzoyl) dithiocarbazate, a oxygen–sulfur donor ligand, have been reported [16], but there is no work on the mixed ligand complexes of the dithioester of N-acyl hydrazide, RC(O)NH–NH–C(S)SR which may coordinate *via* N, O/O, S/N, S. Following our interest in the coordination property of ligands containing the H–N–C=S moiety and with the aim of elucidating the coordination geometry of this class of biologically important ligands, N′-benzoyl hydrazine carbodithioic acid benzyl (H_2bstbh) and [N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid ethyl (H_2pchce) esters have been synthesized and the present paper reports the syntheses, spectral characterization and X-ray crystallography of $[Ni(Hbstbh)_2(en)]$ (**1**) and $[Ni(Hpchce)(o\text{-phen})_2]Cl{\cdot}CH_3OH$ (**2**) (*o*-phen = *o*-phenanthroline).

2. Experimental

2.1. Materials and methods

Commercial reagents were used without further purification and all experiments were carried out in the open atmosphere. Ethyl benzoate and isonicotinic acid hydrazide (Sigma–Aldrich), CS_2 (SD Fine Chemicals, India) and KOH (Qualigens) were used as received. All the solvents were purchased from Merck Chemicals, India and used after purification. Benzoic acid hydrazide and $[Ni(en)_2(NCS)_2]$ were prepared by reported methods [17,18].

2.2. Preparation of N′-benzoyl hydrazine carbodithioic acid benzyl ester (H_2bstbh)

H_2bstbh was prepared by the reaction of CS_2 (1.5 ml, 20 mmol) with a suspension of benzoic acid hydrazide (2.7 g, 20 mmol) in $CHCl_3$ (20 ml) in the presence of triethylamine (2.0 ml, 14 mmol). Benzyl chloride was added dropwise to the above clear solution and stirred continuously for 4 h at room temperature. The solvent was evaporated at room temperature and the residue was washed with water, which gave a colorless solid. Yield 66%; m.p. 426 K.

* Corresponding author. Tel.: +91 542 6702452.
E-mail addresses: mkbharty@bhu.ac.in (M.K. Bharty), singhnk_bhu@yahoo.com, nksingh@bhu.ac.in (N.K. Singh).

0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2010.12.043

Anal. Calc. for $C_{15}H_{14}N_2OS_2$ (302): C, 59.60; H, 4.63; N, 9.27; S, 21.19. Found: C, 59.45; H, 4.80; N, 9.36; S, 21.30%. IR (ν, cm^{-1}, KBr): ν(NH) 3205 and 3175, ν(C=O) 1685s; ν(N–N) 1060; ν(C=S) 966. ^1H NMR (DMSO-d_6; δ ppm): 11.80 and 11.60 (s, 2H, NH), 3.7 (s, 2H, CH_2) 7.0–7.8 (m, 10H aromatic protons). ^{13}C NMR (DMSO-d_6; δ ppm): 119.25 (C^1), 129.10 (C^2, C^6), 121.10 (C^3, C^5), 130.95 (C^4), 164.69 (C^7=O), 202.30 (C^8=S), 38.08 (C^9H_2), 134.05 (C^{10}), 128.52 (C^{11}, C^{15}), 130.65 (C^{12}, C^{14}), 127.30 (C^{13}) (Fig. 1).

2.3. Preparation of N′-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid ethyl ester

The ligand H_2pchce was prepared as described earlier [19].

2.4. Preparation of [Ni(Hbstbh)$_2$(en)]

[Ni(Hbstbh)$_2$(en)] was prepared by adding a MeOH–$CHCl_3$ solution of freshly prepared N′-benzoyl hydrazine carbodithioic acid benzyl ester (H_2bstbh) (0.604 g, 2 mmol) to a MeOH solution of [Ni(en)$_2$(NCS)$_2$] (0.230 g, 1 mmol). The resulting solution was filtered and kept for crystallization. Light pink single crystals of [Ni(Hbstbh)$_2$(en)] suitable for X-ray analyses were obtained by slow evaporation of its MeOH-$CHCl_3$ solution over a period of 15 days. Yield 60%; m.p. > 573 K. μ_{eff} = 3.0 BM. *Anal.* Calc. for $C_{32}H_{34}N_6NiO_2S_4$ (721.60): C, 53.21; H, 4.71; N, 11.64; S, 17.73. Found: C, 53.55; H, 4.90; N, 11.95; S, 17.85%; IR (ν, cm^{-1}, KBr): ν(NH) 3165; ν(C=O) 1640s; ν(N–N) 1096; ν(C=S) 956; ν(Ni–N) 450 and 475. The structure was further confirmed by XRD.

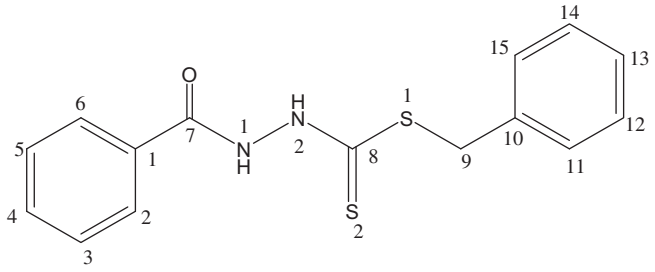


Fig. 1. N′-Benzoyl hydrazinecarbodithioic acid benzyl ester.

2.5. Preparation of [Ni(Hpchce)(o-phen)$_2$]Cl·CH_3OH·H_2O (**2**)

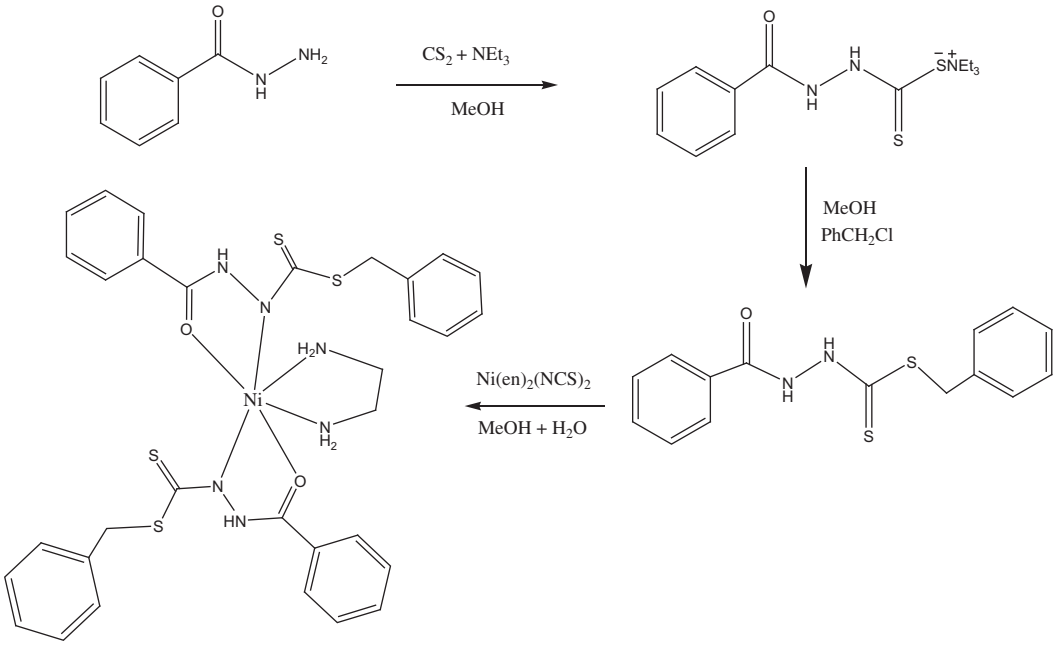
$NiCl_2·6H_2O$ (0.237 g, 1 mmol) and H_2pchce (0.482 g, 2 mmol) were dissolved separately in 20 ml MeOH, mixed together and stirred for 1 h. The brown solid which separated was filtered, washed successively with ethanol and air dried. A methanol solution of *o*-phen (0.400 g, 2 mmol) was added to the methanol suspension of the above compound and stirred for 2 h. The resulting clear brown solution was filtered and kept for crystallization. Brown single crystals of **2** suitable for X-ray analyses were obtained by slow evaporation of its methanol solution over a period of 10 days. Yield 55%; m.p. 483 K. μ_{eff} = 2.9 BM. *Anal.* Calc. for $C_{34}H_{29}ClN_7NiO_3S_2$ (741.92): C, 54.99; H, 3.90; N, 13.20; S, 8.62. Found: C, 55.00; H, 3.95; N, 13.30; S, 8.82%. IR (ν, cm^{-1}, KBr): ν(OH) 3457 and 3426; ν(NH) 3179; ν(C=O) 1630s; ν(N–N) 1097; ν(C=S) 985; ν(Ni–N) 455 and 478.

2.6. Physical measurements

Carbon, hydrogen and nitrogen contents were estimated on a Carlo Erba 1108 model microanalyser. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using Hg[Co(NCS)$_4$] as the calibrant. Electronic spectra were recorded on a Shimadzu 1700 UV–Vis spectrophotometer as Nujol mulls [20]. IR spectra were recorded in the 4000–400 cm^{-1} region as KBr pellets on a Varian 3100-FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a JEOL AL 300 FT NMR spectrometer using TMS as an internal reference.

3. Crystal structure determination

Data for the structure of **1** were obtained at 173(2) K on a Bruker three-circle diffractometer equipped with SMART 6000 CCD software, whereas the data for the structure of **2** were obtained



Scheme 1. Preparation of complex **1**.