Polyhedron 29 (2010) 1902–1909

Contents lists available at ScienceDirect

Polyhedron

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

Synthesis, spectral and structural studies of a Mn(II) complex of [N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid ethyl ester and Mn(II) and Ni(II) complexes of [N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl ester

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ARTICLE INFO

Article history:
Received 25 July 2009
Accepted 26 February 2010
Available online 15 March 2010

Keywords:
Carbodithioic acid ester
Mn(II) complexes
Ni(II) complexes
o-Phenanthroline
Metalloaromaticity

ABSTRACT

The new complexes [Mn(Hpchce)$_2$(*o*-phen)], {2[Mn(pchcm)(*o*-phen)$_2$]}·7H$_2$O and [Ni(Hpchcm)(*o*-phen)$_2$]Cl·CH$_3$OH with [N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid ethyl ester (H$_2$pchce) and [N′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl ester (H$_2$pchcm) have been synthesized, containing *o*-phenanthroline (*o*-phen) as a coligand. These ligands and their complexes have been characterized by elemental analyses, IR, magnetic susceptibility and single crystal X-ray data. H$_2$pchce (**2**), [Mn(Hpchce)$_2$(*o*-phen)] (**3**) {2[Mn(pchcm)(*o*-phen)$_2$]}·7H$_2$O (**4**) and [Ni(Hpchcm)(*o*-phen)$_2$]Cl·CH$_3$OH (**5**) crystallized in the monoclinic system, space group *Pc*, *C*2/*c*, *P*21/*n* and *P*21/*n*, respectively. The (N, O) donor sites of the bidentate ligands chelate the Mn(II) and Ni(II) centers forming a five-membered CN$_2$OM ring. The resulting complexes are paramagnetic and have a distorted octahedral geometry.

1. Introduction

Metal complexes of sulfur–nitrogen chelating ligands derived from S-alkyl esters of dithiocarbazic acid have been studied over the past two decades [1–10], not only because of their intriguing coordination chemistry, but also because of their pronounced biological activities against microbes, viruses and cancer cells [2–4]. Some Schiff bases of S-alkyl esters of dithiocarbazic acid and their complexes were found to display antifungal and antibacterial properties [5–7]. Although several papers on the syntheses and spectral characterization of metal complexes of dithiocarbazates have been reported [1–10], there is no work on the dithioester of N-acyl hydrazide, RC(O)NH–NH–C(S)SR, which also contains an NH–C=S moiety as the S-alkyl ester of dithiocarbazic acid. Following our interest in the coordination properties 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′-(pyridine-4-carbonyl)-hydrazine]-carbodithioic acid methyl (H$_2$pchcm) and ethyl (H$_2$pchce) esters have been synthesized, and the present paper reports the syntheses, spectral characterization and X-ray crystallography of H$_2$pchce, [Mn(Hpchce)$_2$(o-phen)], {2[Mn(pchcm)(*o*-phen)$_2$]}·7H$_2$O and [Ni(Hpchcm)(*o*-phen)$_2$]Cl·CH$_3$OH (*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. Isonicotinic acid hydrazide (Sigma Aldrich), CS$_2$ (S D Fine Chemicals, India) and KOH (Qualigens) were used as received. All the solvents were purchased from Merk Chemicals, India and used after purification.

2.2. Preparations of [K$^+$(H$_2$L)$^-$]

The potassium N-(pyridine-4-carbonyl)-hydrazine carbodithioate [K$^+$(H$_2$L)$^-$] was prepared by adding CS$_2$ (1.5 ml, 20 mmol) dropwise to a suspension of isonicotinic acid hydrazide (2.7 g, 20 mmol) in methanol (30 ml) in the presence of potassium hydroxide (1.2 g, 20 mmol). The reaction mixture was stirred continuously for 30 min and the yellow solid [K$^+$(H$_2$L)$^-$] which separated was filtered, washed with EtOH and dried. Yield: 77%. M.p. 578 K. ^{1}H NMR (DMSO-d$_6$; δ ppm): 10.60 (s, 2H, NH), 8.65, 7.85 (m, 4H, pyridine ring). ^{13}C NMR (DMSO-d$_6$; δ ppm): 203.03 (>C=S), 163.88 (>C=O), 131.77 (C3), 150.56 (C6), 140.27 (C5), 121.01 (C4), 118.63 (C7). IR (ν cm^{-1}, KBr): ν(NH) 3289m, 3182m; ν(C=O) 1676s; ν(N–N) 1062s; ν(C=S) 993s; pyridine ring 667. *Anal.*

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doi:10.1016/j.poly.2010.02.038

Calc. for $C_7H_6N_3OS_2K$ (251.36): C, 33.45; H, 2.41; N, 16.72; S, 25.51. Found: C, 33.40; H, 2.35; N, 16.76; S, 25.45%.

2.2.1. Synthesis of N′-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid methyl ester (*1*)

The N′-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid methyl ester (H_2pchcm) was synthesized by the dropwise addition of methyl iodide (1 ml, 8 mmol) to a suspension of freshly prepared potassium [N′-(pyridine-4-carbonyl) hydrazine] carbodithioate $[K^+(H_2L)^-]$ (2 g, 8 mmol) in methanol (15 ml), and the reaction mixture was stirred continuously for 2 h at room temperature and filtered to remove the residue. On evaporation of the solvent and acidification of the product with dilute CH_3COOH (20% v/v), a yellow precipitate was obtained. This was suction filtered, washed with water and dried in *vacuo*. The yellow solid was crystallized from MeOH. Yield (70%). M.p. 443 K. *Anal.* Calc. for $C_8H_9N_3OS_2$ (227.30): C, 42.27; H, 3.99; N, 18.48; S, 28. 21. Found: C, 42.20; H, 4.05; N, 18.36; S, 28.30%. IR (ν cm^{-1}, KBr): ν(NH) 3241m, 3199m; ν(C=O) 1691s; ν(N–N) 1062s; ν(C=S) 908m; pyridine ring 681; (CH_3) 2926. ^{1}H NMR (DMSO-d_6; δ ppm): 11.55, 11.75 (m, 2H, –NH), 7.8, 8.9 (4H, pyridine ring), 1.5 (s, 3H, –CH_3). ^{13}C NMR (DMSO-d_6; δ ppm): 138.82 (C3), 121.36 (C4), 150.62 (C5), 150.49 (C6), 121.28 (C7), 164.04 (>C2=O), 204.11 (>C1=S), 16.92 (C8).

2.2.2. Synthesis of N′-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid ethyl ester (*2*)

The N′-(pyridine-4-carbonyl)-hydrazinecarbodithioic acid ethyl ester (H_2pchce) was synthesized by the dropwise addition of ethyl iodide (1 ml, 8 mmol) to a suspension of freshly prepared potassium [N′-(pyridine-4-carbonyl) hydrazine] carbodithioate $[K^+(H_2L)^-]$ (2 g, 8 mmol) in methanol (15 ml), and the reaction mixture was stirred continuously for 2 h at room temperature. The resulting yellow solution was filtered off. On evaporation of the solvent and acidification of the residue with acetic acid (20% v/v), the solid obtained was washed twice with portions of an ethanol–water mixture (50:50) and finally dried in *vacuo*. Colorless needle shaped crystals of the compound suitable for X-ray analyses were obtained by slow evaporation of its methanol solution over a period of 12 days. Yield 62%. M.p. 438 K; *Anal.* Calc. for $C_9H_{11}N_3S_2O$ (241.33): C, 44.75; H, 4.55; N, 17.40; S 26.51. Found: C, 44.30; H, 4.62; N, 17.65; S, 26.36%. IR (cm^{-1}, KBr): ν(NH) 3281m, 3169m; ν(C=O) 1688s; ν(N–N) 1061; ν(C=S) 909; pyridine ring 692. ^{1}H NMR (DMSO-d_6; δ ppm): 7.8, 8.8 (m, 4H pyridine ring), 11.60 (s, 2H, NH), 1.2 (t, 3H, J = 5.4 Hz), 3.25 (q, 2H, J = 6.3 Hz). ^{13}C NMR (DMSO-d_6; δ ppm): 203.12 (>C=S), 163.90 (>C=O), 150.88 (C1), 121.41 (C2), 150.47 (C3), 139.36 (C4), 119.65 (C5), 28.55 (C8), 14.33 (C9). MS (FAB) m/z = 242 $[M]^{+\cdot}$. The structure was further confirmed by XRD.

2.2.3. Preparation of [Mn(Hpchce)$_2$(o-phen)] (*3*)

$Mn(OAc)_2 \cdot 4H_2O$ (0.244 g, 1 mmol) and H_2pchce (**2**) (0.482 g, 2 mmol) were dissolved separately in 20 ml methanol, mixed together and stirred for 1 h. The yellow solid which separated was filtered, washed successively with an ethanol–water mixture (50:50) and air dried. A methanol solution of *o*-phen (0.20 g, 1 mmol) was added to the methanol suspension of the above compound and stirred for 3 h. The resulting clear yellow solution was filtered and kept for crystallization. Pale yellow single crystals of **3** suitable for X-ray analyses were obtained by slow evaporation of its methanol solution over a period of 14 days. Yield 58%. M.p. 489 K. μ_{eff} = 5.9 BM. *Anal.* Calc. for $C_{30}H_{28}MnN_8O_2S_4$ (715.78): C, 50.29; H, 3.91; N, 15.64; S 17.88. Found: C, 50.10; H, 3.98; N, 15.81; S, 17.62%. IR (cm^{-1}, KBr): ν(NH) 3132m; ν(C=O) 1614s; ν(N–N) 1097; ν(C=S) 905; pyridine ring 969, 662.

2.2.4. Preparation of {2[Mn(pchcm)(o-phen)$_2$]}·7H$_2$O (*4*)

A solution of H_2pchcm (**1**) (0.454 g, 2 mmol) in MeOH (10 ml) was added to a MeOH solution (10 ml) of $Mn(OAc)_2 \cdot 4H_2O$ (0.244 g, 1 mmol). This mixture was magnetically stirred for 3 h at room temperature. The resulting precipitate was filtered off, washed thoroughly with EtOH and air dried. This was suspended in MeOH to which *o*-phen (0.400 g, 2 mmol) was added and magnetically stirred for 2 h at room temperature. The resulting clear red solution was filtered off and kept for crystallization. Light red single crystals of **4** suitable for X-ray analysis were obtained by slow evaporation of the above methanolic solution over a period of 12 days. Yield 58%. M.p. 493 K. μ_{eff} = 6.00 BM. *Anal.* Calc. for $C_{64}H_{60}Mn_2N_{14}O_9S_4$ (1407.38): C, 54.62; H, 4.29; N, 13.97; S, 9.11. Found: C, 54.79; H, 4.30; N, 13.58; S, 9.10%. IR (ν cm^{-1}, KBr): ν(>C=N) 1591s; ν(N–N) 1096; ν(>C=S) 908; pyridine ring 636; CH_3 2962. The structure was further confirmed by XRD.

2.2.5. [Ni(Hpchcm)(o-phen)$_2$]Cl·CH$_3$OH (*5*)

$NiCl_2 \cdot 6H_2O$ (0.237 g, 1 mmol) and H_2pchcm (**1**) (0.454 g, 2 mmol) were dissolved separately in 20 ml methanol, mixed together and stirred for 1 h. The brown solid which separated was filtered, washed successively with an ethanol–water mixture (50:50) 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 **5** suitable for X-ray analyses were obtained by slow evaporation of its methanol solution over a period of 10 days. Yield 60%. M.p. 503 K. μ_{eff} = 2.87 BM. *Anal.* Calc. for $C_{33}H_{28}ClN_7NiO_2S_2$ (712.90): C, 55.54; H, 3.92; N, 13.74; S, 8.97. Found: C, 55.55; H, 3.90; N, 13.75; S, 8.96%. IR (ν cm^{-1}, KBr): ν(OH) 3427; ν(NH) 3169; ν(>C=O) 1676s; ν(N–N) 1062; ν(>C=S) 993. The structure was further confirmed by XRD.

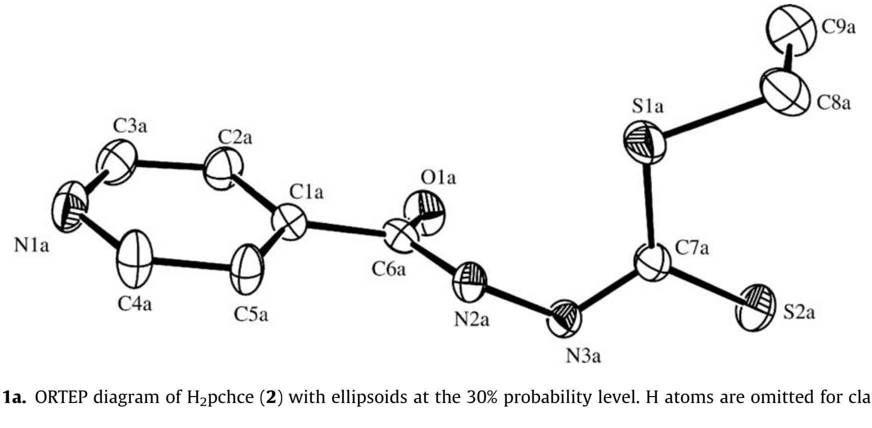

Fig. 1a. ORTEP diagram of H_2pchce (**2**) with ellipsoids at the 30% probability level. H atoms are omitted for clarity.