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Versatile binding properties of a di-2-pyridyl ketone nicotinoylhydrazone ligand: Crystal structure of a Cu(II) complex

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ABSTRACT

Six new copper complexes of di-2-pyridyl ketone nicotinoylhydrazone (HDKN) have been synthesized. The complexes have been characterized by a variety of spectroscopic techniques and the structure of $[Cu(DKN)_2]\cdot H_2O$ has been determined by single crystal X-ray diffraction. The compound $[Cu(DKN)_2]\cdot H_2O$ crystallized in the monoclinic space group $P2_1$ and has a distorted octahedral geometry. The IR spectra revealed the presence of variable modes of chelation for the investigated ligand. The EPR spectra of compounds $[Cu_2(DKN)_2(\mu\text{-}N_3)_2]$ and $[Cu_2(DKN)_2(\mu\text{-}NCS)_2]$ in polycrystalline state suggest a dimeric structure as they exhibited a half field signal, which indicate the presence of a weak interaction between two Cu(II) ions in these complexes.

1. Introduction

Acid hydrazides and their corresponding products, heteroaroylhydrazones, have attracted much attention in synthetic chemistry and inorganic chemistry due to their use in biological systems and analytical chemistry. Due to the chelating behavior, they are used in analytical chemistry as selective metal extracting agents as well as in spectroscopic determination of certain metals [1]. Mixed ligand metal complexes of hydrazones, have proved to be useful catalysts in reactions such as hydrogenation, oxidation, carbonylation and hydroformylation [2]. The applications of rhenium–carbonyl compounds as electrochemical sensors and the optosensing behavior of ruthenium(II), manganese(I) compounds of di-2-pyridyl ketone have been reported [3,4]. The use of these systems as molecular sensors is due to their high values of extinction coefficients and low values for their activation parameters. Interest in these ligands has been driven, in part, by potentially beneficial biological activity of the ligands and the metal complexes, including antimicrobial, antitumor, anti-convulsant, anti-inflammatory and antibacterial [5,6]. Some hydrazone analogues namely di-2-pyridyl ketone isonicotinoylhydrazone were found to effectively promote the efflux of intracellular Fe and inhibit the uptake of Fe from transferrin by tumor cells in culture [7]. Moreover they have been investigated as promising agents for the treatment of neoplasia and were suggested as potential oral chelating drugs for the treatment of genetic disorders such as thalassemia [8].

Recently we have reported the synthesis and characterization of some new hydrazones and their vanadium complexes [9]. We have been interested in the chemistry of polypyridyl containing ligands and as an extension of our previous work [9] we have used di-2-pyridyl ketone nicotinoylhydrazone as a precursor to synthesize and characterize a series of Cu(II) complexes. Di-2-pyridyl ketone nicotinoylhydrazone is an interesting synthon in the class of chelating agents. These ligands exhibit keto-enol tautomerism and can coordinate metal ions in neutral and monoanionic forms [10–12]. The choice of di-2-pyridyl ketone is mainly due to the fact that this heteroaromatic moiety can provide a further binding site for metal cations [13,14]. It is rigid, and provides two aromatic nitrogens whose unshared electron pairs are beautifully placed to act co-operatively in binding cations. Thus it seemed interesting to investigate the coordinating behavior of the ligand, and in this paper we report the spectral and structural aspects of some newly synthesized copper(II) complexes.

2. Experimental

2.1. Materials

Di-2-pyridyl ketone (Aldrich), nicotinic hydrazide (Aldrich), copper(II) chloride dihydrate (E-Merck), copper(II) acetate monohydrate (E-Merck), sodium azide (Reidel-De Haen), potassium thiocyanate (Merck), copper(II) bromide (Aldrich), copper(II) perchlorate hexahydrate (Aldrich) were used as supplied

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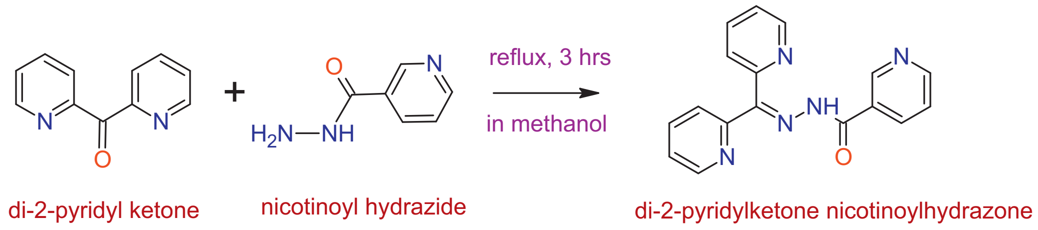

Scheme 1. Synthesis of di-2-pyridyl ketone nicotinoyl hydrazone.

and solvents were purified by standard procedures before use.

2.2. Synthesis of di-2-pyridyl ketone nicotinoylhydrazone hemihydrate (HDKN·0.5H_2O)

The ligand di-2-pyridyl ketone nicotinoylhydrazone hemihydrate (HDKN·0.5H_2O) was prepared as reported by us earlier [9]. To a methanolic solution of nicotinoyl hydrazide (0.137 g, 1 mmol), di-2-pyridyl ketone (0.184 g, 1 mmol) in methanol was added. The reaction mixture was refluxed for 5 h and was kept at room temperature for slow evaporation. After a week, a white compound was separated, filtered and washed with ether and dried over P_4O_{10} *in vacuo*. Yield: 84%, Color: colorless, M.P.: 159 °C, Elemental *Anal.* Found (Calcd.) (%): C: 65.94 (65.37), H: 4.26 (4.52), N: 22.47 (22.42) for HDKN·0.5H_2O. Selected IR (cm^{-1}) bands: ν(N–H) 2928 w; ν(C=O) 1689 vs; ν(C=N) 1579 s.

Electronic absorption bands (MeCN) λ_{max} (nm): 223, 269, 318 (Scheme 1).

2.3. Syntheses of complexes

2.3.1. Synthesis of [Cu(DKN)$_2$] (**1**)

Complex **1** was prepared by refluxing a methanolic solution of HDKN·0.5H_2O (1 mmol, 0.312 g) and $Cu(CH_3COO)_2·H_2O$ (1 mmol, 0.199 g) for 5 h. The resulting solution was allowed to stand at room temperature and after slow evaporation, dark green crystalline compound was separated, filtered and washed with ether and dried over P_4O_{10} *in vacuo*.

[Cu(DKN)$_2$] (**1**): Yield: 81%, λ_m (DMF): 5 Ω^{-1} cm^2 mol^{-1}, μ_{eff} (B.M.): 1.72, Elemental *Anal.* Found (Calcd.) (%): C: 60.86 (61.12), H: 3.58 (3.62), N: 20.36 (20.96).

2.3.2. Syntheses of [Cu(HDKN)Cl$_2$] (**2**), [Cu(DKN)Br] (**3**) and [Cu$_2$(DKN)$_2$](ClO$_4$)$_2$·2H$_2$O (**4**)

Complexes **2**, **3** and **4** were prepared by refluxing equimolar methanolic solutions of HDKN with corresponding copper salt solutions. The resulting solution was allowed to stand at room temperature and after slow evaporation, the green products were separated, filtered and washed with ether and dried over P_4O_{10} *in vacuo*.

[Cu(HDKN)Cl$_2$] (**2**): Yield: 75%, λ_m (DMF): 9 Ω^{-1} cm^2 mol^{-1}, μ_{eff} (B.M.): 1.89, Elemental *Anal.* Found (Calcd.) (%): C: 46.56 (46.64), H: 2.67 (2.99), N: 15.56 (16.00).

[Cu(DKN)Br] (**3**): Yield: 78%, λ_m (DMF): 12 Ω^{-1} cm^2 mol^{-1}, μ_{eff} (B.M.): 1.86, Elemental *Anal.* Found (Calcd.) (%): C: 45.26 (45.81), H: 2.96 (2.71), N: 15.20 (15.71).

[Cu$_2$(DKN)$_2$](ClO$_4$)$_2$·2H$_2$O (**4**): Yield: 90%, λ_m (DMF): 165 Ω^{-1} cm^2 mol^{-1}, μ_{eff} (B.M.): 1.26, Elemental *Anal.* Found (Calcd.) (%): C: 42.38 (42.25), H: 2.99 (2.92), N: 14.61 (14.49).

2.3.3. Synthesis of [Cu$_2$(DKN)$_2$(μ-N$_3$)$_2$] (**5**)

Complex **5** was prepared by stirring methanolic solution of HDKN (1 mmol, 0.312 g) and aqueous solution of NaN_3 (1 mmol, 0.065 g) for half an hour and then $Cu(CH_3COO)_2·H_2O$ (1 mmol, 0.199 g) in distilled water was added to the mixture and again stirred for 2 h. Green precipitate obtained was filtered, washed with methanol and dried over P_4O_{10} *in vacuo*.

[Cu$_2$(DKN)$_2$(μ-N$_3$)$_2$] (**5**): Yield: 85%, λ_m (DMF): 8 Ω^{-1} cm^2 mol^{-1}, μ_{eff} (B.M.): 1.24, Elemental *Anal.* Found (Calcd.) (%): C: 49.73 (50.06), H: 2.40 (2.97), N: 27.68 (27.47).

2.3.4. Synthesis of [Cu$_2$(DKN)$_2$(μ-NCS)$_2$] (**6**)

Complex **6** was prepared in a similar manner as complex **5** by using KSCN instead of NaN_3. Green crystalline complex obtained was filtered, washed with methanol and dried over P_4O_{10} *in vacuo*.

[Cu$_2$(DKN)$_2$(μ-NCS)$_2$] (**6**): Yield: 70%, λ_m (DMF): 3 Ω^{-1} cm^2 mol^{-1}, μ_{eff} (B.M.): 1.42, Elemental *Anal.* Found (Calcd.) (%): C: 50.55 (51.00), H: 2.31 (2.85), N: 19.82 (19.82).

Caution! Although no problems were encountered during this research, azide and perchlorate salts of metal complexes with organic ligands are potentially explosive. So they should be prepared in small quantities and handled with care.

2.4. Physical measurements

C, H and N analyses of the ligand and the complexes were performed on a Vario EL III CHNS analyzer at SAIF, Kochi, India. The IR spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared spectrometer using KBr pellets in the range 400–4000 cm^{-1}. Electronic spectra in acetonitrile solutions were recorded on a Spectro UV–vis Double Beam UVD-3500 spectrometer in the 200–900 nm range. The molar conductances of the complexes in DMF (10^{-3} M) solutions were measured at 298 K with a Systronic model 303 direct-reading conductivity bridge. Magnetic susceptibility measurements at 298 K were made using a MSB mk1 magnetic susceptibility balance from Sherwood Scientific Limited. EPR spectra of complexes in solid state at 298 K and in frozen DMF at 77 K were recorded on a Varian E-112 spectrometer at X-band, using TCNE as standard with 100 kHz modulation frequency and 9.1 GHz microwave frequency at SAIF, IIT Bombay, India.

2.5. X-ray crystallography

X-ray quality crystals of [Cu(DKN)$_2$]·H$_2$O (**1a**) were grown from a solution of **1** in methanol-acetonitrile mixture. Hydrogen atoms of water could not be located and were not included in the model. The determination of the crystal structure was carried out on a Bruker P4 X-ray diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 153 K. The data were solved using Bruker SHELXTL by direct method and refined by the full matrix least squares method on F^2 using Bruker SHELXTL [15]. The Bruker SAINT software was used for data reduction and Bruker SMART for cell refinement. The atoms C(32) and C(33) of a pyridine ring are disordered over two sites with relative occupancies of 58 and 42% for A and B components respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms attached to carbons were placed in calculated positions with