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Synthesis, spectroscopic, crystal structures and photoluminescence studies of cadmium(II) complexes derived from di-2-pyridyl ketone benzoylhydrazone: Crystal structure of a rare eight coordinate cadmium (II) complex

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ABSTRACT

Four cadmium(II) complexes, [CdL$_2$] (**1**), [Cd(HL)Cl$_2$] (**2**), [Cd(HL)Br$_2$] (**3**) and [Cd(HL)(NO$_3$)$_2$(H$_2$O)] (**4**) of di-2-pyridyl ketone benzoylhydrazone (HL) have been synthesized and characterized by different physico-chemical methods. The tetradentate aroylhydrazone acts as a tridentate ligand in all the complexes, bonding through iminol or amido oxygen, azomethine and pyridyl nitrogens. The molecular structures of all monomeric complexes were determined by single crystal X-ray diffraction studies. The complexes, [CdL$_2$] (**1**) and [Cd(HL)Cl$_2$] (**2**) got crystallized in a monoclinic space group whereas the other two complexes [Cd(HL)Br$_2$] (**3**) and [Cd(HL)(NO$_3$)$_2$(H$_2$O)] (**4**) in a triclinic crystal system. The complex [CdL$_2$] (**1**) has a distorted octahedral geometry with two deprotonated monoanionic hydrazone moieties satisfying the coordination whereas in [Cd(HL)Cl$_2$] (**2**) and [Cd(HL)Br$_2$] (**3**), the pentacoordination around Cd(II) is satisfied by neutral N, N, O – chelated hydrazone and two anions chloride and bromide respectively. In [Cd(HL)(NO$_3$)$_2$(H$_2$O)] (**4**), cadmium shows octacoordination and nitrate ion binds both in anisobidentate and bidentate fashion. The thermal stability and the nature of water molecule in complex [Cd(HL)(NO$_3$)$_2$(H$_2$O)] (**4**) was studied. The nature of emission was found to be quenched in all complexes.

1. Introduction

Hydrazones and their metal complexes have been widely investigated by researchers in the recent years due to their applications in diverse fields [1–6]. The interest remains unwavering and was further fueled by the inherent ability of hydrazones to exhibit tautomerism which in turn displays versatile coordination modes during complexation. The reaction parameters such as nature and denticity of the hydrazone, metal ion and its concentration and the pH of the medium [7,8] contributes to the coordinating ability of hydrazone and resulting in diverse geometries and nuclearities [9–11]. Among d^{10} metals, the heavy metal cadmium forms a plethora of complexes with wide variety of coordination numbers ranging from four to eight [12]. Recently cadmium(II) ion is also found to serve as the catalytic center in carbonic anhydrase [13]. Moreover the d^{10} metal ions also find potential applications as photoluminescence materials and the nature of fluorescence can be of Chelation Enhanced Fluorescence effect (CHEF) or Chelation Enhanced Quenching effect (CHEQ) or both effects coupled with red or blue shift in emission band.

Extensive studies have been done on the transition metal complexes of di-2-pyridyl ketone, a versatile polydentate ligand with three potential donor sites and the study began since 1967, when the first Cu(II) complex of di-2-pyridyl ketone was reported by Osborne and McWhinnie [14]. Transition metal complexes of di-2-pyridyl ketone derived ligand systems have also gained considerable interest [9,15]. In this paper, we report the syntheses as well as structural characterization of four cadmium(II) complexes of di-2-pyridyl ketone benzoylhydrazone. The quenching nature in the emission spectra of aroylhydrazone as well as complexes were also studied.

2. Experimental

2.1. Materials

All chemicals used were of analar quality and purchased from commercial source. Di-2-pyridyl ketone (Aldrich), benzhydrazide (Aldrich), cadmium(II) acetate dihydrate (E-Merck), cadmium(II)

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chloride (Aldrich), cadmium(II) bromide tetrahydrate (Aldrich) and cadmium(II) nitrate tetrahydrate (Qualigens) were used as supplied. Solvents, methanol and DMF were purchased from Spectrochem and used without further purification. The aroylhydrazone (HL), di-2-pyridyl ketone benzoylhydrazone was synthesized according to the reported procedure [16].

2.2. Synthesis of aroylhydrazone (HL) and its cadmium(II) complexes

2.2.1. Synthesis of di-2-pyridyl ketone benzoylhydrazone (HL)

The aroylhydrazone, HL was prepared by refluxing equimolar methanolic solutions of benzhydrazide (0.136 g, 1 mmol) and di-2-pyridyl ketone (0.184 g, 1 mmol) for 4 h along with two drops of conc. HCl. The resulting solution was kept aside for slow evaporation at room temperature. Colorless crystals were obtained within a period of 2–3 days. The product obtained was filtered and dried. Yield: 0.222 g (55%).

2.2.2. Syntheses of cadmium(II) complexes

*2.2.2.1. Synthesis of [CdL_2] (**1**).* Methanolic solutions of aroylhydrazone, HL (0.302 g, 1 mmol) and cadmium(II) acetate dihydrate (0.267 g, 1 mmol) were mixed and refluxed for three hours. The resulting yellow colored solution is allowed to stand for slow evaporation under room temperature. Yellow crystals are obtained within a period of a week. The crystals were then filtered off, washed with methanol and dried over P_4O_{10} *in vacuo* (Scheme 1).

For [CdL_2] (**1**): Yield: 57% (0.407 g). Color: Yellow. *Anal*. Calc. for $C_{36}H_{26}CdN_8O_2$ (M.W.: 715.05 g mol^{-1}) C, 60.47; H, 3.66; N, 15.67. Found: C, 60.63; H, 3.6; N, 15.49%. λ_M (DMF): 3.5 mho cm^2 mol^{-1}.

*2.2.2.2. Syntheses of [$Cd(HL)Cl_2$] (**2**) and [$Cd(HL)Br_2$] (**3**).* To the methanolic solution of aroylhydrazone, HL (0.302 g, 1 mmol), methanolic solution of appropriate cadmium(II) salt (1 mmol) was mixed and the resulting yellow colored solutions were refluxed for three hours. On cooling, yellow microcrystalline product of the respective compounds formed were filtered off and washed with methanol and dried. Single crystals suitable for X-ray analysis were obtained on recrystallization from DMF solution of the crude yellow microcrystals of **2** and **3**. The crystals were filtered off, washed with methanol dried *in vacuo* over P_4O_{10} (Scheme 1).

For [$Cd(HL)Cl_2$] (**2**): Yield: 71% (0.344 g). Color: Yellow. *Anal*. Calc. for $C_{18}H_{14}N_4OCdCl_2$ (M.W.: 485.64 g mol^{-1}) C, 44.52; H, 2.91; N, 11.54. Found: C, 44.58; H, 2.83; N, 11.31%. λ_M (DMF): 22 mho cm^2 mol^{-1}.

For [$Cd(HL)Br_2$] (**3**): Yield: 77% (0.442 g). Color: Yellow. *Anal*. Calc. for $C_{18}H_{14}N_4OCdBr_2$ (M.W.: 574.54 g mol^{-1}) C, 37.63; H, 2.46; N, 9.75. Found: C, 38.03; H, 2.73; N, 10.09%. λ_M (DMF): 26 mho cm^2 mol^{-1}.

*2.2.2.3. Synthesis of [$Cd(HL)(NO_3)_2(H_2O)$] (**4**).* To the ethanolic solution of aroylhydrazone, HL (0.302 g, 1 mmol), ethanolic solution of cadmium(II) nitrate tetrahydrate (1 mmol, 0.308 g) was added, mixed and refluxed for three hours. On cooling, yellow block shaped single crystals suitable for X-ray analysis were formed within a period of five days. The crystals were separated and dried *in vacuo* over P_4O_{10} (Scheme 1).

For [$Cd(HL)(NO_3)_2(H_2O)$] (**4**): Yield: 63% (0.351 g). Color: Yellow. *Anal*. Calc. for $C_{18}H_{16}CdN_6O_8$ (M.W.: 556.78 g mol^{-1}) C, 38.83; H, 2.90; N, 15.09. Found: C, 38.92; H, 2.93; N, 14.01%. λ_M (DMF): 136 mho cm^2 mol^{-1}.

2.3. Physical measurements

The elemental analyses of the aroylhydrazone and its cadmium (II) complexes were carried out using a Vario EL III CHNS analyzer. FT-IR spectra of the compounds were recorded on a JASCO – 4100 FT-IR Spectrophotometer in the range 4000–400 cm^{-1} using KBr pellets. Electronic spectra in DMF solutions were recorded on a Thermo scientific evolution 201 UV–Vis double beam spectrometer in the 200–800 nm range. The emission properties were studied using Shimadzu RF-5301PC spectrometer (solution). The TG-DTG analysis of the complex **4** was carried out in a Perkin Elmer Pyris Diamond TG/DTA analyzer under nitrogen at a heating rate of 10 °C min^{-1} in the 50–700 °C range. The molar conductivities of the complexes in DMF (10^{-3} M) solutions at room temperature were measured using a Systronic model 303 direct reading conductivity bridge.

2.4. Crystallographic data collection and refinement

Single crystals of the compounds [CdL_2] (**1**), [$Cd(HL^1)Cl_2$] (**2**), [$Cd(HL^1)Br_2$] (**3**) and [$Cd(HL)(NO_3)_2(H_2O)$] (**4**) with suitable dimensions were selected for X-ray diffraction measurements and mounted on a Bruker SMART APEXII CCD diffractometer, equipped with a graphite crystal, incident-beam monochromator and a fine focus sealed tube with Mo Kα (λ = 0.71073 Å) radiation as the X-ray source. The unit cell dimensions were measured and the data collection was performed. The programs SAINT and XPREP were used for data reduction and APEX2 and SAINT were used for cell refinement [17]. Absorption corrections were carried out using SADABS based on Laue symmetry using equivalent reflections [18]. The structure was solved by using SHELXS-97 direct methods and refined by full-matrix least-squares refinement on F^2 using SHELXL-2014/7 [19] as well as WinGX software package [20]. The molecular and crystal structures were plotted using ORTEP-3 [20] and DIAMOND version 3.2 g [21].

In complex **1**, one of the four pyridyl rings was disordered over five closely positioned sets of sites (N2/C8/C9/C10/C11) with a site-occupation factor of 0.684(19) for the major-occupied and 0.316 (19) for the minor-occupied sites. The hydrogens in pyridine ring and its disordered counterpart were fixed using HFIX instruction. The distances were restrained to be equal using SADI instruction. The connectivity array and planarity were restrained using DELU and FLAT instructions. In all cadmium(II) complexes, anisotropic refinement were performed for all non-hydrogen atoms and all H atoms on C were placed in calculated positions, guided by difference maps, with C–H bond distances 0.93–0.96 Å. H atoms were assigned as U_{iso} = 1.2 Ueq (1.5 for Me). In [$Cd(HL^1)Cl_2$] (**2**), [$Cd(HL^1)Br_2$] (**3**) and [$Cd(HL)(NO_3)_2(H_2O)$] (**4**) the hydrogen atom H4′ attached to N4 was located from Fourier map and restrained to a distance of 0.88 ± 0.01. The hydrogen atoms, H8A and H8B attached to the oxygen atom O8 of the coordinated water molecule in **4** were located from difference map and their distances and angles were restrained using DFIX and DANG instructions with distance restraint of O–H = 0.86 ± 0.01 Å and H· · ·H = 1.36 ± 0.02 Å followed by refinement of their displacement parameters. Some reflections were omitted for all complexes owing to bad disagreement. The extinction coefficient have value of 0.02389 in complexes **2**. The crystallographic data and structure refinement parameters for compounds **1**–**4** are given in Table 1.

3. Results and discussion

Four cadmium(II) complexes of tetradentate di-2-pyridyl ketone benzoylhydrazone (HL) were synthesized and characterized by elemental analysis and molar conductivity measurements, IR, electronic and ^1H NMR spectral studies. The reaction of cadmium (II) salts with aroylhydrazone in appropriate solvent yielded monomeric complexes **1**–**4**. In all the complexes, the HL acts as a tridentate NNO donor ligand bonding through iminol and amido oxygen, azomethine nitrogen and one of the pyridyl nitrogen