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Research paper

Cd(II) and Ni(II) complexes from aroyl hydrazones: Unravelling the intermolecular interactions and electronic, crystal structures through experimental and theoretical studies

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ABSTRACT

Three complexes of Cd(II) **1**, **2** and Ni(II), **3** were prepared from two different aroyl hydrozone ligands (HL^1 ($C_{15}H_{13}N_3O_4$) & HL^2 ($C_{20}H_{17}N_3O_2$)) using their respective metal bromides. Crystal structures of all the three complexes have been established and the anionic/neutral nature of the coordinating ligand is mainly dictated by the nature of the metal center used. Quantification of intermolecular interactions is done using Hirshfeld surface and 2D finger print analysis. The Electrostatic Potential (ESP) analysis reveals that **2** has a collective concentration of negative electrostatic potentials to one side of the molecule giving a perfect separation of charges. DFT/semiempirical calculations revealed the same, giving a very high dipole moment for the optimized geometry of **2**. Analysis of frontier orbitals is done through DFT calculations at the B3LYP/def2-TZVP level of theory and atomic charge distributions are predicted using AIM method.

1. Introduction

Schiff bases, particularly hydrazones have been active in the synthetic scenario for a long time thanks to the versatility and tunability of coordination modes that they own [1–3]. The degree of metamorphism achieved by these class of ligands and their chelating capability is unmatched by any other. This qualifies them as privileged ligands and aroyl hydrazones are no exception. These ligands and their metal complexes exhibit gripping magnetic [4,5], optical [6,7], catalytic [8,9] and pharmacological applications [10,11]. Out of these myriad of applications, the one that stands out the most is the antibacterial activity [12–14] that they exhibit.

Quantification of intermolecular interactions present in a crystal system has further opened the realm of understanding these interactions. One important tool in this regard is the calculation of a molecular Hirshfeld surface. It is no wonder that the number of publications incorporating this relatively young aspect is increasing daily [15]. A Hirshfeld surface is a single 3D surface that sums up the crystal packing and this 3D surface can further be reduced to a 2D finger plot which is unique for a molecule, thus deciphering the interactions present in the system [16]. The basic ideas of a Hirshfeld surface and its fingerprint plots are well defined by Spackman et al. [17].

On the other hand, visualization of electrostatic potential surfaces [18–20] can rationalize the intermolecular interactions in the system and the degree of reactivity of the molecules [21]. Apart from the easy visualization of the electrophilic and nucleophilic regions within a chemical species, this mapping will assist in the prediction of reactivity and noncovalent interaction which helps in great detail in dissecting the intermolecular interactions [22,23].

In continuation of our work on aroyl hydrazones and their complexes [24], herein, we report synthesis, characterization and structural study of three new Cd(II) and Ni(II) complexes from two different aroyl hydrazone ligands, HL^1 ($C_{15}H_{13}N_3O_4$) and HL^2 ($C_{20}H_{17}N_3O_2$). A Ni(II) metal center,{$[Ni(L^2)_2]\cdot H_2O$, **3**; $L = C_{20}H_{16}N_3O_2$},was used in this study since Ni(II) complexes can show interesting biological and electrochemical properties [25]. On the other hand, a Cd(II) metal center, {$[Cd(HL^1)_2Br_2]$, **1** and $[Cd(HL^2)_2Br_2]$, **2**}, is reported to enhance luminescence intensity of the ligand system which can be used for optoelectronic applications [26]. The work described here indicates the versatility in the behavior of the aforementioned ligand systems as in the three complexes synthesized; the ligands exhibit all the possible permutation and combinations of coordination/electronic properties that are

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possible. For instance, in the first two cases (**1** and **2**), the ligand coordinates in the neutral form and among these two, the two ligand units coordinate to a single metal ion only in the first case. The story is entirely different in the third case where the ligand is coordinated in the monoanionic form. The relatively high conductivity value of **2** prompted us to calculate the theoretical dipole moment which gave high value which is supported using molecular electrostatic potential maps mapped on electron density isosurfaces. The electronic features and frontier orbitals of these complexes are also viewed from a theoretical point of view using DFT studies.

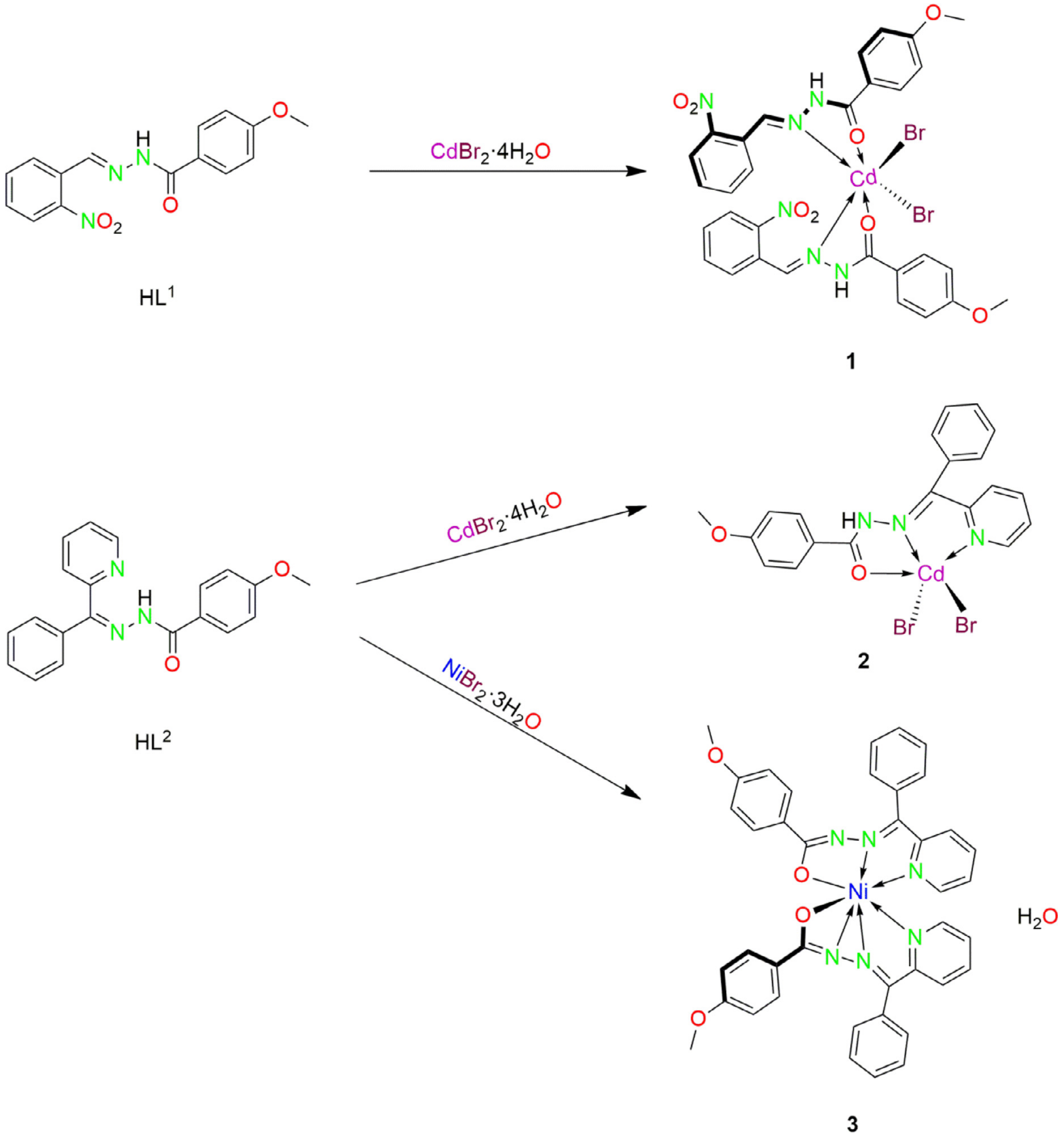
2. Experimental

2.1. General remarks

Commercially available AR grade reagents and chemicals were used as received without further purification. Both ligands were formed *in situ* through an equimolar (1:1) condensation reaction of 4-methoxybenzhydrazide with 2-nitrobenzaldehyde [2-nitrobenzaldehyde-4-methoxybenzhydrazone (HL^1)] and with 2-benzoylpyridine [2-benzoylpyridine-4-methoxybenzhydrazone (HL^2)] (Scheme S1) and one pot method was adopted for the syntheses of the complexes.

2.2. Methods and instrumentation

Elemental analyses of the compounds were done on a Vario EL III CHNS elemental analyzer at the SAIF, STIC, CUSAT, Kochi, India. IR spectra of the complexes were recorded on a JASCO FT-IR-5300 Spectrometer in the range 4000–400 cm^{-1} using KBr pellets and the electronic spectra of the compounds were taken on a Thermo scientific Evolution 220 spectrophotometer in the 200–900 nm range. Molar conductivities of the prepared complexes were



Scheme 1. Synthetic pathway to complexes **1, 2** and **3**.