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Synthesis, crystal structure, spectral characterization and photoluminescence property of three Cd(II) complexes with a pyrazole based Schiff-base ligand

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ABSTRACT

Substituted pyrazole containing Schiff-base ligand, 5-methyl-3-formylpyrazole-N-(2′-methylphenoxy) methyleneimine, (MPzOA), afforded three new Cd(II) complexes, $[Cd(MP_zOA)Cl_2]_2.CH_3OH$ (**I**), $[Cd(MP_zOA)_2(H_2O)_2](ClO_4)_2$ (**II**) and $[Cd(MP_zOA)(H_2O)(NO_3)_2]$ (**III**). In the reported complex species the coordination number and geometry of Cd(II) vary. In complex **I** and **II,** Cd(II) adopts six and in (**III**) it adopts eight coordination modes, with prismatic, octahedral and distorted dodecahedral geometry, respectively. All the complexes are characterized by IR, ^{1}H NMR, UV–Vis spectral parameters and X-ray analyses. The complexes have 1D, 2D and 3D supramolecular frameworks formed by non-covalent interactions, like hydrogen bonding, π … π stacking, C–H … π interactions.

1. Introduction

Supramolecular architectures formed by metal-organic moieties have growing interest for structural diversity and potential application in the development of molecular sensors, catalysts, new pharmaceutical therapies, design of supramolecular electronics, molecular recognition and also in green chemistry [1]. 1D, 2D and 3D supramolecular frameworks formed by self-assembly of metal-organic moieties with association of various kinds of hydrogen bonds, metal coordination, hydrophobic forces, van der Walls forces, electrostatic forces and π–π stacking interactions are well known in this field. The structure of ligands, orientation and flexibility of binding sites and coordination geometry of metal centre play the key role in construction of these architectures. Nowadays asymmetrical N-heterocyclic Schiff-base ligands, have received much attention in the crystal engineering of coordination polymers, one of them are pyrazole based ligands [2–7]. Pyrazoles are π-excessive, better π-donors and weaker π-acceptors than the six membered heterocycles and can act as hard donor site [8]. Due to presence of basic and acidic NH group, it can form large number of hydrogen bonds leading to supramolecular architecture.

On the other hand Cd(II) has been shown to form various complexes with different donors having coordination numbers 4, 5, 6, 7 and 8 in different coordination geometries like tetrahedral, trigonal bipyramidal, octahedral and distorted dodecahedral along with 1D, 2D and 3D polymeric architectures [9–18]. This may be attributed to larger radius and d^{10} electronic configuration of Cd^{2+} cation. The d^{10} electronic configuration of Cd(II) reduces the ligand field effects so that it can be able to form bonds with different donors simultaneously with diverse geometries and the larger radius brings flexibility to adopt various coordination numbers. The wide variety of cadmium complexes and their supramolecular structures are well-studied in the literature [9–18].

Herein, we report the synthesis, characterization and crystal structures of three cadmium complexes of a pyrazole based Schiff-base ligand, 5-methyl-3-formylpyrazole-N-(2′-methylphenoxy)-methyleneimine (MPzOA) (Fig. 1). There occurs a structural diversification in the complexes, which might be entailed by the

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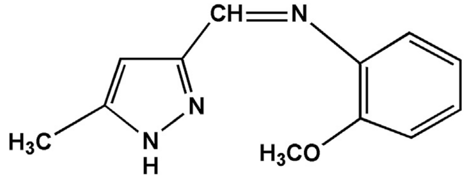

Fig. 1. Structural formulation of the ligand, MP_zOA.

presence of counter anions. The Cd(II) centres adopt different coordination numbers and geometry with Cl^- and NO_3^- as counter anions. Complex **I**, $[Cd(MP_zOA)Cl_2]_2$, is a chloro bridged binuclear complex; each Cd(II) ion in the complex species is six coordinate and resides in a distorted octahedral environment, whereas, in complex **III,** $[Cd(MPzOA)(H_2O)(NO_3)_2]$, the Cd(II) ion is eight coordinate having a distorted dodecahedron geometry around it. In complex **II**, $[Cd(MP_zOA)_2(H_2O)_2](ClO_4)_2$, the Cd(II) centre adopts six coordinate octahedral geometry. The primary ligand (MPzOA), acts as an NNO tridentate system in complexes **I** and **III**, but for **II**, it acts an NN bidentate one. All the complexes reported here are fluorescence active and exhibit 1D, 2D and 3D supramolecular frameworks via non-covalent interactions, like hydrogen bonding, π … π stacking and C–H … π interactions.

2. Experimental

2.1. Reagents and instrumentation

All reagents were of AR grade/molecular biology grade and were obtained from commercial sources and used without further purification. Spectrograde solvents were used for spectral and conductance measurements. Elemental analyses (C, H and N) were done with a Perkin–Elmer 2400 CHNS/O analyser. The molar conductance of the complexes in methanol solutions was measured with a Systronics 306 digital conductivity metre. ^1H NMR spectra were recorded with a Bruker AC 400 NMR spectrometer. The electronic spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. IR spectra (4000-450 cm^{-1}) were recorded on a Perkin Elmer L120-000A FT-IR spectrophotometer with KBr pellets. The fluorescence spectra of the complexes in methanol were recorded using a Perkin–Elmer LS 55 Fluorescence Spectrometer.

2.2. Syntheses

2.2.1. Preparation of 5-methyl-3-formylpyrazole-N-(2′-methylphenoxy)methyleneimine, (MPzOA)

The title ligand, 5-methyl-3-formylpyrazole-N-(2′-methylphenoxy)methyleneimine, (MPzOA) (Fig. 1), was synthesized by a similar but appropriately modified method [19a] involving conversion of 5-methyl pyrazole-3-carbohydrazide [19b] into its benzene sulphonyl derivative, followed by treatment with o-anisidine in alkaline ethylene glycol medium (160 °C) leading to the pale yellow coloured crystalline product with a yield of *ca.* 68–70%. (m.p. 190–191 °C). Anal. Calcd. (%) for $C_{12}H_{13}N_3O$: C, 66.9; H, 6.1; N, 19.5. Found (%): C, 66.7; H, 6.2; N, 18.9. *m*/*z*: 216.06 (M^+, 98%). IR (KBr): ν (cm^{-1}) = 3312 (ν_{NH}), 1602 ($\nu_{CH=N,}$ azomethine), 1520 ($\nu_{C=N,}$ pyrazole) and 1032 ($\nu_{N\text{-}NPZ}$). ^1H NMR ($CDCl_3$) δ(ppm): 12.94 (s, 1H, NH pyrazole); 8.44 (s, 1H, CH═N); 6.76–7.41 (m, 4H, Ar-ring); 6.67 (s, 1H, C_4–H); 3.89 (s, 3H, O–CH_3); 2.35 (s, 3H, C_5–CH_3).

2.2.2. Synthesis of the cadmium (II) complexes: $[Cd(MP_zOA)Cl_2]_2.CH_3OH$, $[Cd(MP_zOA)(H_2O)(O_2NO)_2]$ and $[Cd(MP_zOA)_2(H_2O)_2](ClO_4)_2$

The Cd(II) complexes were synthesized by refluxing the ethanol solution of the ligand (0.226 gm, 0.00105 mol) and the corresponding hydrated Cd(II) salt in 1:1/2:1 M ratio for ~1 h on water bath. On slow evaporation of pale yellow coloured solutions, the desired Cd(II) complex separated out in each case, was filtered off, washed with cold ethanol and dried over anhydrous $CaCl_2$. (Yield ~ 70–80%). X-ray quality single crystals of $[Cd(MP_zOA)Cl_2]_2.CH_3OH$ (**I**) were obtained from slow diffusion of benzene into methanol solution of the complex. Whereas, single crystals of $[Cd(MP_zOA)_2(H_2O)_2](ClO_4)_2$ (**II**) and $[Cd(MP_zOA)(H_2O)(O_2NO)_2]$ (**III**) were obtained from slow evaporation of ethanol solution of the respective complex. Anal. Calcd. (%) for $C_{26}H_{34}N_6O_4Cd_2Cl_4$ (**I**): C, 36.3; H, 3.9; N, 9.8; Cd, 26.1. Found (%): C, 36.1; H, 3.6; N, 9.5; Cd, 25.9. IR (KBr) ν (cm^{-1}): 1591 ($\nu_{CH=N,\ azomethine}$), 1563 ($\nu_{C=N,\ pyrazole}$), 1040 ($\nu_{N\text{–}N,\ pyrazole}$) and 483 ($\nu_{Cd\text{–}N,\ azomethine}$). UV–Vis. (MeOH, $\lambda_{max,}$ nm): 327, 244 ($n\rightarrow \pi^*$), 203 ($\pi\rightarrow \pi^*$). Emission (MeOH, λ_{em}^{max}, $\lambda_{ex,}$ nm): 425, 327. ^1H NMR ($CDCl_3$) δ(ppm): 13.48 (NH pyrazole); 9.81 (s, 1H, CH═N); 8.40 (s, 1H, C_4–H); 6.83–7.48 (m, 4H, Ar-ring); 3.95 (s, 3H, O–CH_3); 1.04 (s, 3H, C_5–CH_3).

Anal. Calcd. (%) for $C_{24}H_{30}N_6O_{12}CdCl_2$ (**II**): C, 37.1; H, 3.9; N, 10.8; Cd, 14.5. Found (%): C, 36.9; H, 3.7; N, 10.7; Cd, 14.2. IR (KBr) ν (cm^{-1}): 1583 ($\nu_{CH=N,\ azomethine}$), 1573 ($\nu_{C=N,\ pyrazole}$), 1050 ($\nu_{N\text{–}N,\ pyrazole}$) and 481 ($\nu_{Cd\text{–}N,\ azomethine}$). UV–Vis. (MeOH, $\lambda_{max,}$ nm): 328, 245 ($n\rightarrow \pi^*$), 203 ($\pi\rightarrow \pi^*$). Emission (MeOH, λ_{em}^{max}, $\lambda_{ex,}$ nm): 443, 245. ^1H NMR ($CDCl_3$) δ(ppm): 13.46 (s, 1H, NH pyrazole); 9.81 (s, 1H, CH═N); 8.38 (s, 1H, C_4–H); 6.81–7.53 (m, 4H, Ar-ring); 3.93 (s, 3H, O–CH_3); 1.21 (s, 3H, C_5–CH_3).

Anal. Calcd. (%) for $C_{12}H_{15}N_5O_8Cd$ (**III**): C, 30.7; H, 3.2; N, 14.9; Cd, 23.9. Found (%): C, 30.6; H, 3.1; N, 15.0; Cd, 23.5. IR (KBr) ν (cm^{-1}): 1590 ($\nu_{CH=N,\ azomethine}$), 1570 ($\nu_{C=N,\ pyrazole}$), 1048 ($\nu_{N\text{–}N,\ pyrazole}$) and 479 ($\nu_{Cd\text{–}N,\ azomethine}$). UV–Vis. (MeOH, $\lambda_{max,}$ nm): 329, 243 ($n\rightarrow \pi^*$), 205 ($\pi\rightarrow \pi^*$). Emission (MeOH, λ_{em}^{max}, $\lambda_{ex,}$ nm): 436, 329. ^1H NMR ($CDCl_3$) δ(ppm): 13.47 (s, 1H, NH pyrazole); 9.80 (s, 1H, CH═N); 8.39 (s, 1H, C_4–H); 6.83–7.52 (m, 4H, Ar-ring); 3.94 (s, 3H, O–CH_3); 1.18 (s, 3H, C_5–CH_3);

2.3. X-ray crystallographic data collection and refinement

X-ray diffraction data of the suitable single crystals of $[Cd(MP_zOA)Cl_2]_2.CH_3OH$ (**I**), $[Cd(MP_zOA)_2(H_2O)_2](ClO_4)_2$ (**II**) and $[Cd(MP_zOA)(H_2O)(NO_3)_2]$ (**III**), were collected on Bruker Apex 2 and Agilent Xcalibur Ruby Gemini diffractometers, using Mo-K_α radiation and the data were corrected for absorption effects by using ω and ψ-scans. A multiscan and analytical absorption correction were applied using SADABAS software programme [20] and multifaceted crystal model [21]. The structures of complexes **I** and **II** were solved with Super flip [22] structure solution programme using Charge Flipping and refined with SHELXL-2013 [20] refinement package using Least Squares minimization. Whereas, the structure of complex **III** was solved by direct methods and refined by full matrix least squares based on $|Fobs|^2$ using SHELXL-97 programme [20]. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms, either located from difference electron density maps or generated using idealized geometry, were used in the structure factor calculations with isotropic thermal parameters using the "riding" model. Neutral atom scattering factors [23] were used and anomalous dispersion effects were included in F_{calc} [24].

3. Results and discussion

3.1. Structural description

3.1.1. Molecular and supramolecular structures of [Cd(MPzOA)Cl2] 2.CH3OH (I)

ORTEP diagram of complex **I** with atom numbering scheme is shown in Fig. 2. The crystallographic data and refinement