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## Synthesis, crystal structure and properties of a 1D cadmium(II) coordination polymer with 2,6-dimethyl-3,5-bis(pyrazo-3-yl)pyridine

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A new coordination polymer $\{[Cd(H_2dmbpzp)I_2]\cdot CH_3CH_2OH\}_n$ ($H_2dmbpzp$ = 2,6-dimethyl-3,5-bis(pyrazo-3-yl)pyridine) has been prepared by the reaction of $H_2dmbpzp$ in aqueous ethanolic solution at room temperature with $CdI_2$. The compound has been characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis (TGA) and single crystal X-ray diffraction. Photoluminescence properties have also been examined. The complex exhibits a 1D chain structure.

**Keywords**: Syntheses, Crystal structures, Cadmium coordination polymers, 2,6-Dimethyl-3,5-bis(pyrazo-3-yl)pyridine

Coordination polymer (CP) research is a fast developing research area for its potential applications in separations[1-3], gas storage[4-6], and catalysis[7]. It has also been studied for chemical sensing[8], light-harvesting[9,10] and drug delivery[11]. However, in comparison to a typical organic reaction, it still remains a considerable challenge to control the structures of CPs[12-14] due to many external factors including coordination requirements of the central metal, features of organic ligand, solvent systems, pH values, reaction time and temperatures[15,16]. Nevertheless, the versatility of organic ligands is the basis of coordination polymers. Judicious selection/design of organic ligands is the key approach to obtain the desired structures and functions[17].

Similar to that of imidazolates, due to its strong coordination ability and neutral or deprotonated forms on binding with the metal center, monopyrazole is a widely used ligand in the synthesis of interesting polynuclear metal complexes[18]. However, owing to the simple coordination mode, small bridging angle, and short bridging distances of monopyrazolates, their coordination polymers still have quite limited structure types[19].

Due to the adjustable length and geometry of the donor groups, polypyrazolates are beneficial for the rational design of targeted coordination polymers and have received considerable attention[19-24]. Moreover, in the coordination polymers, inorganic anions such as $Cl^-$, $NO_3^-$, $I^-$ and $SO_4^{2-}$ also act as terminal ligands or bridging linkers to impart their influence on the structure of self-assemblies of CPs[25]. In the past few years, several coordination polymers consisting of bipyrazoles and transition metals[17,19-24] have been prepared, however, to the best of our knowledge, the coordination polymers containing the ligand 2,6-dimethyl-3,5-bis(pyrazo-3-yl)pyridine ($H_2dmbpzp$) has not been reported to date.

Herein, we report a new 1D Cd(II) coordination polymer with 2,6-dimethyl-3,5-bis(pyrazo-3-yl)pyridine prepared at room temperature. The complex was characterized by single crystal X-ray diffraction, elemental analysis, IR, and thermogravimetric analysis (TGA). The photoluminescence properties of the complex and ligand are also investigated.

### Experimental

The 2,6-dimethyl-3,5-bis(pyrazo-3-yl)pyridine ligand was synthesized by a modified reported procedure[26]. Other reagents and solvents were commercially available and were used without further purification. IR spectra were obtained from KBr pellets on a Bruker EQUINOX 55 FTIR spectrometer in the 400–4000 $cm^{-1}$ region. Elemental analysis (C, H, N) was performed on a PerkinElmer 240 elemental analyzer. Fluorescent spectra were obtained from an Edinburgh FLS920 spectrometer equipped with a continuous Xe900 Xenon lamp and a F900 microsecond flash lamp.

For the synthesis of $[CdI_2(H_2dmbpzp)C_2H_5OH]_n$(**1**), a solution of $CdI_2$ (36.6 mg, 0.1 mmol) in 4 mL of water was mixed with 4 mL of an absolute ethanol solution of 2,6-dimethyl-3,5-bis(pyrazo-3-yl)pyridine (23.9 mg, 0.1 mmol). The resulting mixture was allowed to evaporate for one month to yield colorless block-shaped crystals and then filtered, washed with water, and dried in air to afford 45.4 mg (Yield: 75% based on Cd) of the product. For $C_{15}H_{17}N_5OI_2Cd$ Calcd: (%) C 27.74; H 2.64; N 10.78. Found: C 27.71; H 2.61; N 10.85%. IR (KBr; *ν*, $cm^{-1}$): $\nu$ = 3446 w, 2967 w, 2359 w, 1733 w, 1607 m, 1558 s, 1423 s, 1340 w, 1297 w, 1177 w, 1123 s, 1063 w, 1064 w, 951 m, 765 s, 652 w, 563 w (supplementary data, Fig. S1).

Crystallographic data of complex **1** was collected at room temperature with a Bruker Apex CCD diffractometer with graphite-monochromate Mo-Kα radiation ( λ = 0.71073 Å). Absorption correction was applied by using multi-scan program SADABS[27]. The structure was solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package[28]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The H atoms attached to C atoms were constrained, with C-H = 0.96 Å and $U_{iso}$ (H) = 1.5 $U_{eq}$ (C) of the attached C atoms for methyl H atoms, C-H = 0.97 Å and $U_{iso}$ (H) = 1.2 $U_{eq}$ (C) for methylene H atoms and C-H = 0.93 Å and $U_{iso}$ (H) =1.2 $U_{eq}$ (C) for methenyl H atoms. Due to the disorder of ethyl groups of ethanol molecules, two of them were split and SADI, EADP, ISOR, DELU and DFIX commands were used in the refinement. N-bond H atoms were constrained with N-H = 0.86 Å and $U_{iso}$ (H) = 1.2 $U_{eq}$ (N). Hydroxyl H atoms were located from a different Fourier map and restrained with O-H = 0.820(10) Å and $U_{iso}$ (H) = 1.5 $U_{eq}$ (O). Crystal data as well as details of data collection and refinement for complex 1 are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1 — Crystal data and structure refinement of complex **1**

| | |
|---|---|
| Formula | $C_{13}H_{11}CdI_2N_5\cdot CH_3CH_2OH$ |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Temperature, K | 293 |
| $a$ (Å) | 8.7373 (17) |
| $b$ (Å) | 16.078 (3) |
| $c$ (Å) | 15.719 (3) |
| $V$ (Å$^3$) | 2124.5 (8) |
| $Z$ | 4 |
| Radiation type | Mo-$K_\alpha$ |
| $\mu$ (mm$^{-1}$) | 3.95 |
| Crystal size (mm) | 0.30 × 0.27 × 0.25 |
| $T_{min}$, $T_{max}$ | 0.318, 0.373 |
| No. of measured | 15328 |
| No. of independent | 3707 |
| No. of obs. [$I > 2\sigma(I)$] reflections | 2201 |
| $R_{int}$ | 0.101 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.595 |
| $R[F^2 > 2\sigma(F^2)]$ | 0.066 |
| $wR(F^2)$ | 0.148 |
| $S$ | 1.03 |
| No. of Reflections | 3707 |
| No. of parameters | 226 |
| No. of restraints | 31 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.67, −0.71 |

## Results and discussion

Colorless block-shaped crystals of $[CdI_2(H_2dmbpzp)\cdot C_2H_5OH]_n$ **(1)** were obtained under ambient conditions of $H_2$dmbpzp and $CdI_2$ from the mixed solvent of $H_2O$ and ethanol after a period of one month. As shown in Fig. S2, the XRD pattern measured for the as-synthesized crystal sample is in good agreement with the XRD pattern simulated from the single-crystal X-ray data, indicating the phase purity of the synthesized sample. Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the monoclinic space group $P2_1/c$, and exhibits one-dimensional structure. In the asymmetric unit of complex **1,** there are one independent Cd(II) cation (lying on a twofold axis), one $H_2$dmbpzp ligand, two coordinated iodide anions and one crystalline ethanol molecule. As shown in Fig. 1, each Cd atom is bound to one pyrazolyl $N^1$ atom from one $H_2$dmbpzp ligand, one pyrazolyl $N^2$ atom belonging to another $H_2$dmbpzp ligand and two coordinated iodide anions forming irregular tetrahedral coordination geometry. The bond lengths of Cd-N2, Cd–N5A, Cd–I1 and Cd–I2 are 2.306(8), 2.265(8), 2.6898(15) and 2.7177(12) Å, respectively, which are in good agreement with the reported values[29]. The N-Cd-N angle is 101.1(3)°. The dihedral angles between the planes of the pyrazolyl rings and the 3,5-dimethylpyridyl ring are 27.038 and 55.54°, respectively. Due to the steric hindrance between the methyl groups, the dihedral angle between the two

Table 2 — Selected bond lengths (Å) and angles (°) for **1**

| | | | |
|---|---|---|---|
| | Bond lengths (Å) | | |
| Cd1—N5A | 2.265(8) | Cd1—N2 | 2.306(8) |
| Cd1—I1 | 2.6898(15) | Cd1—I2 | 2.7177(12) |
| | Bond angles (°) | | |
| N5—Cd1—N2 | 101.1(3) | N5—Cd1—I1 | 106.2(2) |
| N2—Cd1—I1 | 110.4(2) | N5—Cd1—I2 | 106.2(2) |
| N2—Cd1—I2 | 102.96(19) | I1—Cd1—I2 | 127.05(4) |

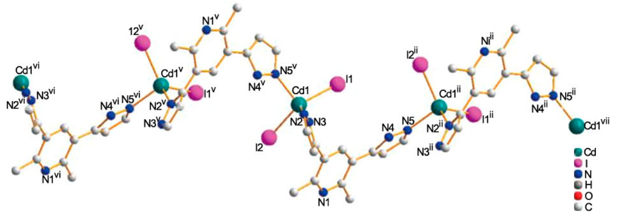

Fig. 1 — View of the coordination environment of the cadmium atoms and $H_2$dmbpzp. [Symmetric codes: ii: x, -y+1/2, z-1/2; v: x, -y+1/2, z+1/2; vi: x, y, z+1; vii: x, y, z-1. Hydrogen atoms are omitted for clarity].

pyrazolyl rings is 72.031° , which is similar to that of the complexes containing bispyrazole ligand 3,3',5,5'-tetramethyl-4,4'-bipyrazole($H_2$bpz)[30,31]. The ligand $H_2$dmbpzp serves as a bidentate ligand in a $\mu_2$-$N^1$, $N^2$ mode, which is different from that of the reported complexes[17,19-24]. Therefore, the $Cd^{2+}$ ions are bridged through the pyrazolyl $N^1$ and $N^2$ positions to form a one-dimensional chain composed of $M(pz)_2$ chains (pz = pyrazole) along the *a* axis (Fig. 2). Such $M(pz)_2$ chain is common in metal-pyrazolate complexes[19]. Moreover, there are weak hydrogen bonds involving the C or O atoms from the $H_2$dmbpzp ligand or ethanol molecules (as donors), the I atoms (as acceptors) ($O1{-}{-}{-}I2^{ii}$, $C7{-}{-}{-}I2^{iii}$, $C11{-}{-}{-}I2^{iv}$, C14---I1 and $C15B{-}{-}{-}I2^{i}$; see supplementary data, Table S1). There are also strong hydrogen bonds involving the N atoms from the $H_2$dmbpzp ligand (as donors) and the N from the $H_2$dmbpzp ligand or O atoms from ethanol molecules (as acceptors) ($N3{-}{-}{-}N1^{i}$ and N4---O1; Table S1). Together, these hydrogen bonds contribute to the formation of the three dimensional supramolecular structure (Fig. 3).

The thermal stability of complex **1** was investigated by thermogravimetric analysis (TGA) (Fig. S3). The TGA curve of complex **1** shows an initial mass loss of 6.62% from 24 to 303 °C, corresponding to the removal of one lattice ethanol molecule (calcd, 7.07%) and followed by continuous mass loss in the range of 303 to 442 °C (obsd, 38.70 %; calcd, 38.95%) which can be attributed to the loss of two coordinated iodide anions. On further increasing the temperature, the largest mass loss process was observed with the decomposition of the $H_2$dmbpzp ligand and the whole skeleton collapses rapidly.

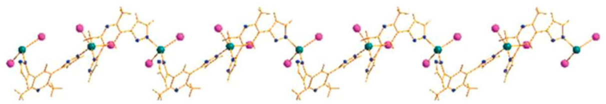

Fig. 2 — View of the one-dimensional ribbon of complex **1** along *a* axis.

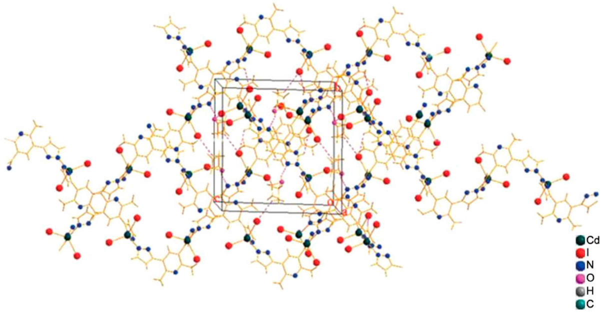

Fig. 3 — View of the crystal packing of complex **1** (hydrogen bonds are shown as red dashed lines).

The solid-state luminescence of free ligand $H_2$dmbpzp and complex **1** are investigated at room temperature. As depicted in Fig. 4, the main emission peak of the free $H_2$dmbpzp ligand is at 403 nm ($\lambda_{ex}$ = 281 nm). The emission band may be attributed to ligand-centered $\pi \rightarrow \pi^*$ electronic transitions[17]. The emission peak is observed at 379 nm (λex = 290 nm) for complex **1**. Compared with the free $H_2$dmbpzp ligand, the emission band of the complex **1** is blue shifted (by 24 nm). Due to the electrochemical inertness of $d^{10}$ configured Cd(II) ion, the emission band of complex **1** may be tentatively attributed to intraligand charge transfer transitions rather than LMCT or MLCT[32]. Compared to the free $H_2$dmbpzp ligand, complex **1** exhibits a relatively weak emission peak which may be attributed to the classic photoinduced electron transfer (PET) mechanism[33].

In summary, we have successfully prepared the 1D Cd(II) complex with the 2,6-dimethyl-3,5-bis(pyrazo-3-yl) pyridine ligand. In the crystal structure, the ligand $H_2$dmbpzp adopts a $\mu_2$-$N^1$, $N^2$ bridging mode, which is different from that of the reported complexes. It seems that the coordination modes of the ligand might play an important role in determining the structures. Although the ligand has many coordinate sites, we found that the pyridyl N atoms are not coordinated in this crystal structure, which may be due to the steric hindrance between the methyl groups. Further work is under progress in our laboratory, aimed at the discovery of new types of coordination polymers with the ligand.

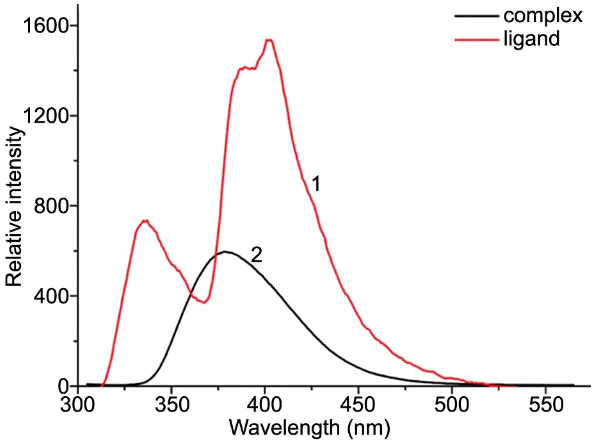

Fig. 4 — Solid-state photoluminescence spectra of free $H_2$dmbpzp (1) and complex **1**(2).

## Supplementary data

Crystallographic data for the structural analysis of complex **1** have been deposited with Cambridge Crystallographic Data Centre, under CCDC No. 1859167. Copy of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44-1223-336-033: Email: deposit@ccdc.cam.ac.uk). Other supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_58A(03)326-329_SupplData.pdf.

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