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## *КРАТКИЕ СООБЩЕНИЯ*

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# CRYSTAL STRUCTURES AND LUMINESCENCE PROPERTIES OF A ONE-DIMENSIONAL CADMIUM COORDINATION POLYMER DERIVED FROM A FLEXIBLE bis(IMIDAZOLE) LIGAND

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A new Cd(II) coordination polymer, namely $[Cd(pbmb)(mip)]_n$ (pbmb = 1,1′-(1,3-propane)bis-(2-methylbenzimidazole), $H_2$mip = 5-methylisophthalic acid), is hydrothermally synthesized and characterized by elemental analyses, infrared spectroscopy and single crystal X-ray diffraction analyses. It crystallizes in the triclinic space group $P\bar{1}$, $a = 0.2883(11)$, $b = 11.3409(12)$, $c = 13.2519(14)$ Å, $\alpha = 69.6950(10)°$, $\beta = 73.5850(10)°$, $\gamma = 63.8100(10)°$, $V = 1285.8(2)$ Å$^3$, $Z = 2$, $C_{28}H_{28}CdN_4O_5$, $M_r = 612.94$, $D_c = 1.583$ g/cm$^3$, $\mu = 0.896$ mm$^{-1}$. In the complex, adjacent dinuclear units $[Cd_2(pbmb)_2]$ are bridged by mip$^{2-}$ ligands in the $\mu_2$-$\eta^2$, $\eta^1$ coordination modes to construct 1D ladder-like chains which are additionally assembled into a 2D supramolecular network *via* C—H$\cdots\pi$ interactions. Moreover, the luminescence properties of the complex are described.

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**Keywords:** Cd(II) complex, crystal structure, luminescence property.

Over the past few years, the design and construction of metal-organic coordination polymers (MOCPs) have been rapidly developing because of their fascinating structural diversities and potential applications in gas storage and absorption, luminescence, magnetism, sensing and so on [ 1—4 ]. Generally, the construction of MOCPs can be controlled by the reasonable design and sensible choice of organic ligands, solvents, pH value, and metal atoms. Therefore, the selective design of organic ligands is usually crucial for the formation of novel metal-organic frameworks [ 5, 6 ]. Flexible bis(benzimidazole) ligands, such as 1,4-bis(5,6-dimethyl-benzimidazolyl)-2-butene, 1,3-bis(imidazol-1-ylmethyl)benzene and 1,4-bis(imidazol-1-ylmethyl)-benzene [ 7, 8 ], have been widely used and serve as N-containing ligands having rich structural information and free conformation. Due to the presence of a —$CH_2$— spacer this sort of bis(benzimidazole) ligands can act as bridges to construct high dimensional frameworks [ 9, 10 ]. Inside the series of bis(benzimidazole) derivatives, 1,1′-(1,3-propane)bis-(2-methylbenzimidazole)(pbmb) is especially outstanding for the 2-position methyl substituent of the benzimidazole ring can effectively enhance the electron donating ability of the ligand, which make pbmb exhibit a strong collaborative coordination ability with organic carboxyl ligands [ 11, 12 ]. When it comes to aromatic carboxylate ligands, which exhibit an abundant variety of coordination modes, isophthalic acid ($H_2$ip) has been extensively applied to prepare hybrid complexes [ 13—15 ]. In particular, $H_2$ip ramifications have a tender difference with $H_2$ip, and the variation may significantly influence the resulting MOCPs. Compared to $H_2$ip, one of the derivatives, $H_2$mip not only contains two potential bridging carboxylate sections but also possesses different assemblies in the aspect of their steric and electronic effects due to 5-position substituents which may display different physical and chemical properties [ 16, 17 ]. Hence, the synthesis and crystal structure of a novel coor-

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dination polymer [Cd(pbmb)(mip)]$_n$, based on 5-substituted isophthalate and flexible bis(benzimidazole) co-ligands (pbmb = 1,1′-(1,3-propane)bis-(2-methylbenzimidazole), $H_2$mip = 5-methylisophthalic acid) is reported. The luminescence properties of the complex are also investigated.

**Materials and physical measurements.** All commercially available solvents and starting materials bought from Alfa Aesar Company were used as received without further purification. The pbmb ligand was prepared as previously reported [ 18 ]. Elemental analyses for C, H, and N were carried out with a Perkin-Elmer 240C automatic analyzer. IR spectra were recorded on a Nicolet FT-IR Avatar 360 spectrophotometer in the range 4000—400 cm$^{-1}$ using KBr pellets. The luminescence spectra for the powdered solid samples were performed on a Hitachi F-7000 spectrophotometer at room temperature.

**Synthesis of [Cd(pbmb)(mip)]$_n$.** A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (53 mg, 0.2 mmol), pbmb (61 mg, 0.2 mmol), $H_2$mip (36 mg, 0.2 mmol), NaOH (8 mg, 0.2 mmol), and $H_2O$ (10 ml) was sealed in a 25-ml Teflon-lined stainless vessel and heated to 140°C for 3 days under autogenous pressure, and then cooled down to room temperature at a rate of 10°/h. Colorless block crystals of the complex, suitable for X-ray diffraction, were obtained in a 56.8 % yield based on $Cd(OAc)_2 \cdot 2H_2O$. Anal. Calc. for $C_{28}H_{28}CdN_4O_5$ ($M_r$ = 612.94) (%): C 54.62, H 4.76, N 9.01. Found: C 54.87, H 4.60, N 9.14. IR (KBr, cm$^{-1}$): 1612 s, 1560 s, 1516 m, 1460 s, 1411 m, 1370 s, 1243 w, 758 s, 734 w.

**X-ray crystallography.** A single crystal with dimensions of 0.23×0.23×0.18 mm was selected for X-ray diffraction. The crystallographic data collections for the complex were carried out on a Bruker Smart 1000 CCD diffractometer with graphite monochromated Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) and the $\omega$-2$\theta$ scan mode at 296(2) K. A semi-empirical absorption correction was applied using the SADABS program [ 19 ]. The structure was solved by direct methods with the SHELXS-97 program [ 20 ] and refined with SHELXL-97 by the full-matrix least-squares fitting on $F^2$ [ 21 ]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. The summary of the crystallographic data and structure analysis are given in Table 1. The selected

Table 1

*Crystal data and structure refinements for the complex*

| | |
|---|---|
| Empirical formula | C28 H28 Cd N4 O5 |
| $M$, g/mol | 612.94 |
| $T$, K | 296(2) |
| Wavelength, Å | 0.71073 |
| Crystal system | Triclinic |
| $a$, $b$, $c$, Å | 10.2883(11), 11.3409(12), 13.2519(14) |
| Space group | $P\overline{1}$ |
| Volume, Å$^3$ | 1285.8(2) |
| $Z$ | 2 |
| Calculated density, g/cm$^3$ | 1.583 |
| Absorption coefficient, mm$^{-1}$ | 0.896 |
| $F$(000) | 624 |
| Crystal size, mm | 0.23×0.23×0.18 |
| $\theta_{min}$—$\theta_{max}$, deg. | 1.66—27.10 |
| Limiting indices | $-13 \le h \le 12$, $-14 \le k \le 4$, $-16 \le l \le 7$ |
| Reflections collected / unique ($R_{int}$) | 4217 / 3737 (0.0125) |
| Data / restraints / parameters | 3737 / 0 / 336 |
| Goodness-of-fit on $F^2$ | 1.096 |
| Final $R$ indices[$I > 2\sigma(I)$][a] | $R_1$ = 0.0302, $wR_2$ = 0.0874 |
| $R$ indices (all data) | $R_1$ = 0.0314, $wR_2$ = 0.0881 |

Table 2

*Selected bond lengths* (Å) *and angles* (deg.) *for the complex*

| Bond | | Angle | | | |
|---|---|---|---|---|---|
| Cd(1)—O(4)A | 2.208(2) | O(4)A—Cd(1)—O(2) | 90.12(9) | O(4)A—Cd(1)—N(1) | 104.94(10) |
| Cd(1)—N(1) | 2.248(2) | O(2)—Cd(1)—N(1) | 115.84(10) | O(4)A—Cd(1)—N(3)B | 115.06(10) |
| Cd(1)—O(1) | 2.530(3) | O(2)—Cd(1)—N(3)B | 110.01(11) | N(1)—Cd(1)—N(3)B | 117.63(9) |
| Cd(1)—O(2) | 2.224(3) | O(4)A—Cd(1)—O(1) | 144.08(9) | N(3)B—Cd(1)—O(1) | 85.27(10) |
| Cd(1)—N(3)B | 2.263(3) | N(1)—Cd(1)—O(1) | 89.01(9) | | |

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Symmetry transformations used to generate equivalent atoms: A = $x+1, y, z$, B = $-x+1, -y, -z+1$.

bond lengths and bong angles are listed in Table 2. CCDC 1033548 contains the supplementary crystallographic data for the complex. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

**Crystal structure of [Cd(pbmb)(mip)]$_n$.** The single crystal X-ray diffraction analysis reveals that the complex crystallizes in the triclinic space group $P\overline{1}$. As depicted in Fig. 1, each Cd(II) atom is coordinated by three O(1), O(2), O(4)A oxygen atoms (symmetry code for A: $x+1, y, z$) from two distinct mip$^{2-}$ anions and two N(1), N(3)B nitrogen atoms (symmetry code for B: $-x+1, -y, -z+1$) of two different pbmb ligands. The bond angles around the Cd center range from 85.27(10)° to 144.08(9)°, leading to a certain extent of distortion towards a square pyramidal geometry, which is pointed out by a $\tau$ value of 0.59 [22]. The parameter is used to describe the degree of distortion of penta-coordinate complexes ($\tau = 1$ for an ideal trigonal bipyramid and $\tau = 0$ for an ideal square pyramid) [23]. Two pbmb ligands adopting the bis(monodentate) coordination mode bridge the adjacent cadmium atoms to form a dinuclear unit [Cd(pbmb)]$_2$ in which the dihedral angel between the mean planes of two benzimidazole rings is 59.97°. The mip$^{2-}$ carboxyl groups employ monodentate and chelate coordination fashions. The fully-deprotonated mip$^{2-}$ ligands connect the neighboring [Cd$_2$(pbmb)$_2$] dinuclear units to form a 1D ladder-like chain along the *a* axis where the [Cd$_2$(pbmb)$_2$] units lie on the crossbeams with a Cd···Cd distance being 8.1970(6) Å, and the [Cd$_2$(mip)$_2$] units locate in the columns with a Cd···Cd separation of 10.2883(11) Å (Fig. 2). In addition, two kinds of C—H···π interactions between pbmb and mip$^{2-}$ ligands lead the neighboring 1D ladder-like chains to generate a 2D supramolecular network, as shown in Fig. 3. The C—H···π bonding parameters (C—Cg distance and C—H···Cg angle) are 3.523(6) Å and 139° for C15—H15···Cg1C (Cg1: C2—C3—C4—C5—C6—C7, symmetry code for C: $x-1, y, z$) 3.681(6) Å and 143° for C46—H46A···Cg2D (Cg2: N1—C1—N2—C3—C2, symmetry code for D: $-x+1, -y, -z$).

**IR spectrum.** The features in the IR spectra of the complex are mainly attributed to the carboxyl group and pbmb ligands. The bands at about 1516 cm$^{-1}$ are assigned to $\nu_{C=N}$ of benzimidazole rings of the pbmb ligand [24]; the absorbance peaks at 1612 and 1370 ~ ~ 1460 cm$^{-1}$ are attributed to the asymmetric stretching

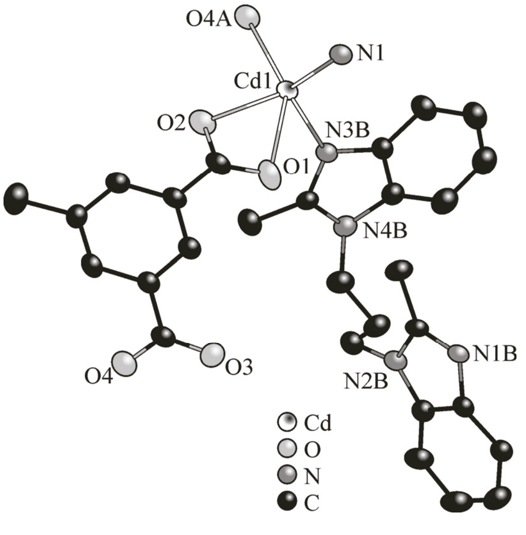


*Fig. 1.* Coordination environment of the Cd(II) ion in the complex. All the hydrogen atoms are omitted for clarity. (Symmetry codes: A = $x+1, y, z$; B = $-x+1, -y, -z+1$)

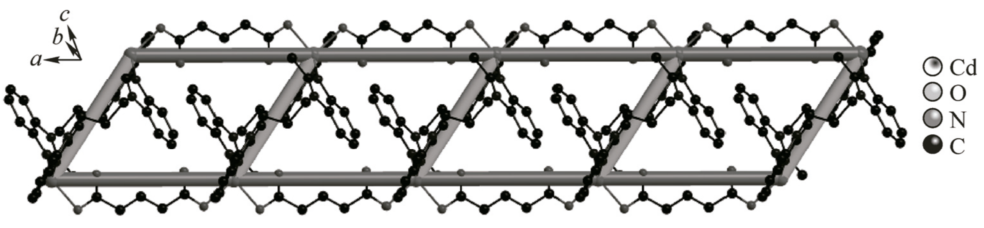


*Fig. 2.* 1D infinite ladder-like chain structure

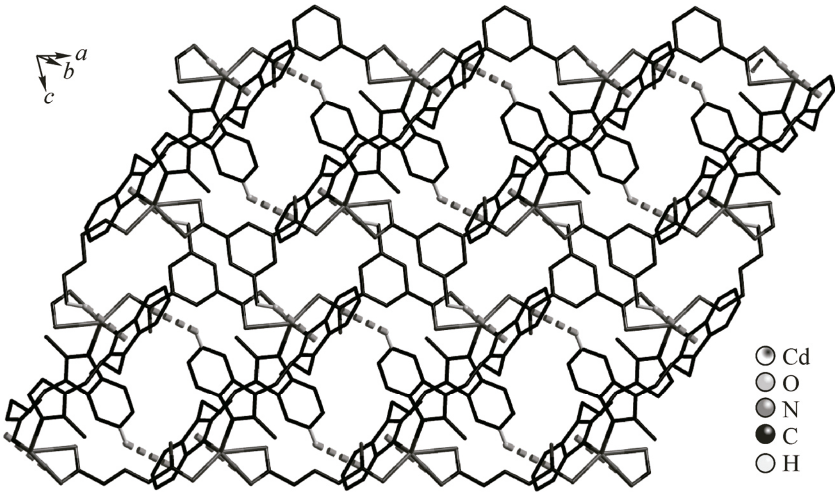
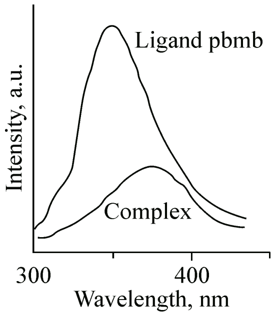


*Fig. 3.* 2D supramolecular network constructed by C—H···π hydrogen bonds. The dashed lines indicate C—H···π bonds

*Fig. 4.* Solid-state luminescence spectra of the free pbmb ligand and the complex



and symmetric stretching vibrations of the carboxylate groups, respectively. In the IR spectra of the complex, the absence of bands in the 1690 ~ 1730 $cm^{-1}$ region suggests the complete deprotonation of carboxylate groups in $mip^{2-}$, which is in agreement with the crystallographic structural analysis [ 25 ].

**Luminescence properties.** The solid state luminescence properties of the free pbmb ligand and the complex were investigated at room temperature. As depicted in Fig. 3, the complex exhibits a band emission at $\lambda_{em} = 375$ nm ($\lambda_{ex} = 210$ nm). The free pbmb ligand displays an intense emission band at 349 nm upon excitation at 310 nm, which may be attributed to π—π* transitions [ 26 ]. Compared to the free pbmb and $H_2$mip ($\lambda_{em} = 357$ nm and $\lambda_{ex} = 315$ nm) ligands, a small red shift of cal. 26 nm between the complex and the pbmb ligand can be tentatively attributed to the π—π* transition of the coordinated ligands since the Cd(II) ion is difficult to oxidize or to reduce due to its $d^{10}$ configuration [ 27 ].

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