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Crystal structures and luminescent properties of two cadmium complexes containing the *N,N′*-bis-(4-pyridylmethyl) piperazine ligand

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ABSTRACT

Two cadmium coordination polymers based on the flexible ligand *N,N′*-bis-(4-pyridyl-methyl) piperazine (bpmp), formulated as $\{[Cd(bpmp)(H_2O)(Cl)_2]\cdot C_2H_5OH\cdot 2H_2O\}_n$ (**1**) and $\{[Cd(bpmp)(H_2O)_4]\cdot 2NO_3\cdot 2H_2O\}_n$ (**2**), are reported. The crystal structures of the as-synthesized complexes were determined by single-crystal X-ray diffraction analyses. Complex **1** possesses a chloride-bridged two-dimensional (2-D) wave-like layer structure containing (6,3) networks, with the bpmp ligands displaying a *cis*-conformation. Complex **2** has a one-dimensional (1-D) chain structure built by octahedral Cd nodes and *trans*-bpmp bridges. Solid state emission spectra of both the two compounds have also been studied at room temperature.

1. Introduction

The rational design and synthesis of coordination polymers (CPs) remain an active and rapidly expanding research area, because of their potential applicability in diverse applications such as magnetism, luminescent materials, nonlinear optics, gas adsorption and catalysis [1–5]. A widely used strategy for the preparation of coordination polymers is based on the selection of metal center and ligand [6]. Construction of CPs based on transition- and lanthanide-metal ions and rigid organic ligands results in a great number of CPs with intriguing topological structures [7]. However, scientific research of the coordination chemistry focusing on flexible ligands has currently been undergoing an unparalleled development. This is mainly because of the much more difficulty in predicting and designing the assembly process, as well as understanding the versatile coordination modes of the functional groups. Inspired by our previous experience on the research of CPs with flexible carboxylate ligands [8], we now expand our research attention to a flexible ligand, *N,N′*-bis-(4-pyridyl-methyl) piperazine (bpmp). For this ligand, the methylene between the piperazine ring and the pyridyl group allows the bpmp ligand to adopt *cis*- or *trans*-conformation (Scheme 1). Some other coordination polymers incorporating this dipyridyl ligand have been reported [9]. In this paper, we report the syntheses and characterization of two cadmium coordination compounds based on the flexible bpmp ligand formulated as $\{[Cd(bpmp)(H_2O)(Cl)_2]\cdot C_2H_5OH\cdot 2H_2O\}_n$ (**1**) and $\{[Cd(bpmp)(H_2O)_4]\cdot 2NO_3\cdot 2H_2O\}_n$ (**2**).

2. Experimental

2.1. Material required and instrumentation

The piperazine-pyridine ligand, 1,4-bis-(pyridin-4-ylmethyl) piperazine (bpmp), was prepared according to a previously reported procedure [10]. All commercially available reagents and starting materials were of reagent-grade quality and used without further purification. Elemental analyses (C, H, N) were carried out on an Elementar Vario EL III analyzer. Infrared (IR) spectra were recorded on PerkinElmer Spectrum One as KBr pellets in the range 4000–400 cm^{-1}. Fluorescence spectroscopy of the compounds were performed on an Edinburgh Analytical instrument FLS920.

2.2. Syntheses

2.2.1. Synthesis of $\{[Cd(bpmp)(H_2O)(Cl)_2]\cdot C_2H_5OH\cdot 2H_2O\}_n$ (**1**)

A solution of $CdCl_2\cdot 2.5H_2O$ (22.8 mg, 0.1 mmol) in H_2O (5 ml) was poured into a test tube. Above it a mixture of water and ethanol (3 ml, 1:1 in volume proportion) was added slowly. Then the methanol solution (5 ml) of bpmp (26.8 mg, 0.1 mmol) was added above it. Colorless block crystals suitable for X-ray diffraction analysis were obtained after 3 days (30.6 mg, 55%, based on Cd). Elemental analysis (%): calcd. for $C_{18}H_{32}CdCl_2N_4O_4$ (551.79): C 39.18, H 5.85, N 10.15; found: C 39.29, H 5.76, N 10.37. IR (KBr, cm^{-1}): 3445 (s, br), 2946(w),

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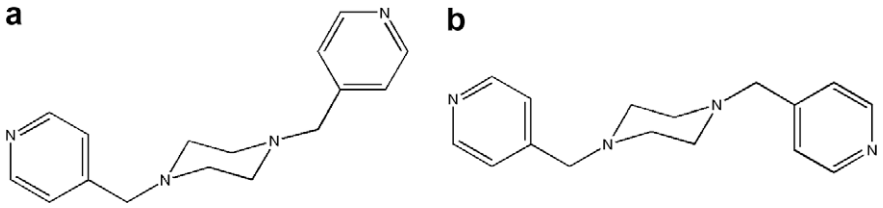

Scheme 1. Two conformations of bpmp ligands.

2829 (w), 1611(s), 1504(w), 1428(m), 1366(w), 1324(w), 1226(w), 1132(w), 1068(w), 1011(m), 837(m), 806(w), 724(w), 612(w).

*2.2.2. Synthesis of {[Cd(bpmp)(H_2O)$_4$]·2NO_3·2H_2O}$_n$ (**2**)*

A solution of $Cd(NO_3)_2{\cdot}4H_2O$ (30.8 mg, 0.1 mmol) in H_2O (5 ml) was added dropwise to a stirred solution of bpmp (26.8 mg, 0.1 mmol) in CH_3OH (10 ml). The reaction mixture was then stirred for 1 h. Slow evaporation of the solvent at room temperature for almost 1 month gave colorless rod crystals suitable for X-ray diffraction analysis(46.4 mg, 48%, based on Cd). Elemental analysis (%): calcd. for $C_{16}H_{20}CdN_6O_{12}$ (600.78): C 31.99, H 3.36, N 13.99; found: C 31.82, H 3.51, N 13.87. IR (KBr, cm^{-1}): 3465 (s, br), 2932(w), 2811(w), 2776(w), 1618(m), 1385(s), 1228(w), 1152(w), 1134(w), 1066(w), 1009(m), 838(m), 802(w), 604(w).

2.3. Crystal structure determination

Suitable single crystals of compounds **1** and **2** with approximate dimensions ($0.28 \times 0.20 \times 0.15 mm^3$ for **1** and $0.20 \times 0.13 \times 0.10 mm^3$ for **2**) were put on glass fiber and used for data collection respectively [11]. The intensity data were collected on a SCXmini CCD (for both complexes **1** and **2**) performed at ambient temperature. The absorption corrections were performed with the procedure contained within the CrystalClear software package [12]. The structure was solved by direct methods with the SHELXL-97 program package [11]. All data were refined by full-matrix least-squares minimizations of $\sum(F_o - F_c)^2$ with anisotropic thermal parameters for all nonhydrogen atoms. The organic hydrogen atoms were generated geometrically, and the hydrogen atoms bonded to water oxygen atoms were not located. The crystallographic data for **1** and **2** are listed in Table 1, and the selected bond lengths and angles are given in Table 2.

3. Results and discussion

3.1. Crystal structures

*3.1.1. {[Cd(bpmp)(H_2O)(Cl)$_2$]·C_2H_5OH·2H_2O}$_n$ (**1**)*

Single-crystal X-ray diffraction analysis reveals compound **1** crystallizes in the monoclinic space group *C2/c*. The local coordination environment around Cd(II) is shown in Fig. 1. The cadmium atom is coordinated by two nitrogen atoms (N1, N4B) from two pyridine ring of two different bpmp ligands, one coordinated water molecule (O1) and two bridged chlorine atom (Cl1, Cl1A) and a terminal chlorine atom (Cl2) in a slightly distorted octahedral geometry. The average Cd–N and Cd–Cl bond distance is 2.380(3) Å and 2.6428(8) Å respectively, while the Cd–O bond distance is 2.366(3) Å. As expected, the central piperazine ring of the bpmp ligand adopts a standard "chair" conformation. This preferred structure character gives the ligand some rigidity. The bpmp ligands displays a *cis*-conformation (Fig. 1), and all the ligands act as bis(monodentate) bridging ligand linking the Cd(II) ions to form a one-dimensional chain structure. Then the chlorine atoms act as μ_2-bridges linking the [Cd(bpmp)] chains to form a

Table 1
Crystallographic data for two compounds.

	1	**2**
Empirical formula	$C_{18}H_{32}CdCl_2N_4O_4$	$C_{16}H_{20}N_6O_{12}Cd$
Formula weight	551.79	600.78
T (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*P2$_1$/c*
a (Å)	18.343(5)	11.513(6)
b (Å)	10.345(2)	7.453(4)
c (Å)	23.242(6)	15.136(8)
β (°)	94.373(3)	101.486(9)
V (Å^{-3})	4397.5(19)	1272.8(11)
Z	8	2
D_{calc} (mg m^{-3})	1.649	1.568
μ (mm^{-1})	1.268	0.925
F(0 0 0)	2208	604
Transmission range	2.23–27.48	2.75–27.52
Reflections collected total, independent	16554/5044	9558/2919
Parameters	252	155
Goodness-of-fit on F^2	1.074	1.109
R_1 ($I > 2\sigma(I)$)[a]	0.0496	0.0406
wR_2 (all data)[b]	0.1492	0.1309
Residual electron density (eÅ^{-3})	1.280 and −0.828	0.704 and −0.619

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.