Synthesis, Crystal Structure and Theoretical Calculations of a Three-dimensional Supramolecular Cadmium(II) Coordination Polymer Postprint

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Date: 2017-11-05T00:00:00+00:00

Abstract

A new metal-organic cadmium coordination polymer [Cd(pzdc)0.5(L)]n · nH2O (1, H2pzdc = pyrazine-2,3-dicarboxylic acid, HL = 3-(2-pyridyl)pyrazole) has been successfully synthesized under hydrothermal conditions. The structure has been determined by single-crystal X-ray diffraction analysis, elemental analyses, IR and fluorescence spectrum. Brown crystals crystallize in the orthorhombic system, space group Fdd2 with a = 11.2636(9), b = 38.296(3), c = 10.5795(8) Å, V = 4563.5(6) Å3, C11H9CdN4O3, Mr = 357.62, Dc = 2.082 g/cm3, (MoK) = 1.924 mm-1, F(000) = 2800, Z = 16, the final R = 0.0169 and wR = 0.0443 for 2106 observed reflections (I > 2s(I)). It shows a two-dimensional network structure and extends into a three-dimensional supramolecular framework through - stacking interactions. Moreover, we analyzed Natural Bond Orbital (NBO) by using the PBE0/LANL2DZ method built in Gaussian 03 Program. The calculation results showed obvious covalent interaction between the coordinated atoms and Cd(II) ion.

Full Text

Preamble

Synthesis, Crystal Structure and Theoretical Calculations of a Three-dimensional Supramolecular Cadmium(II) Coordination Polymer

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ABSTRACT

A new metal-organic cadmium coordination polymer, [Cd(pzdc) . (L)] ·nH O (1, H pzdc = pyrazine-2,3-dicarboxylic acid, HL = 3-(2-pyridyl)pyrazole), has been successfully synthesized under hydrothermal conditions. Its structure was determined by single-crystal X-ray diffraction analysis, elemental analyses, IR spectroscopy, and fluorescence spectroscopy. The compound crystallizes as brown crystals in the orthorhombic system, space group Fdd2 with a = 11.2636(9), b = 38.296(3), c = 10.5795(8) Å, V = 4563.5(6) Å^3, C H CdN O , M = 357.62, Dc = 2.082 g/cm^3, (MoK) = 1.924 mm^{1}, F(000) = 2800, Z = 16, with final R = 0.0169 and wR = 0.0443 for 2106 observed reflections (I > 2 (I)). The complex exhibits a two-dimensional network structure that extends into a three-dimensional supramolecular framework through - stacking interactions. Moreover, Natural Bond Orbital (NBO) analysis was performed using the PBE0/LANL2DZ method implemented in the Gaussian 03 program. The calculation results revealed obvious covalent interactions between the coordinated atoms and the Cd(II) ion.

Keywords: hydrothermal synthesis; crystal structure; Cd(II) complex; natural bond orbital

DOI: 10.14102/j.cnki.0254-5861.2011-1735

1 INTRODUCTION

The designed synthesis and characterization of metal-organic coordination polymers have made significant progress in supramolecular chemistry and materials chemistry [1~8]. The growing interest in this field is justified not only by their aesthetic appeal and intriguing structural diversity but also by their potential applications as functional materials in catalysis, conductivity, luminescence, magnetism, spin-transition, non-linear optics, and porous materials [9-16]. The combination of metal ions with mixed neutral and anionic bridging ligands makes the assembly process more controllable than using a single ligand alone. The prospect of introducing second or additional organic ligands into a reaction system provides further impetus for research on metal-organic supramolecular frameworks. The construction of supramolecular architectures through selective and directional non-covalent forces such as hydrogen bonding, ··· , and C–H··· interactions in metal-organic frameworks has attracted considerable contemporary interest due to their potential applications as functional materials.

The hydrothermal technique is well-suited for the preparation of synthetic mineral crystals, new inorganic materials, and organometallic coordination polymers. Of particular interest is the construction of transition metal polymers with novel structural features using hydrothermal synthesis. We report herein the preparation and crystal structure of the title complex [Cd(pzdc) . (L)] · nH O (1), which exhibits a 3D supramolecular network formed through hydrogen bonds and - stacking interactions.

2 EXPERIMENTAL

2.1 Materials and Instruments

All chemicals were commercially purchased and used without further purification. Elemental analyses for C, H, and N were performed on an Elementar Vario III Elemental Analyzer. The IR spectrum was recorded in the range of 4000–400 cm ^{1} on a Nicolet 6700 spectrometer using KBr pellets. Powder X-ray diffraction (PXRD) patterns were collected in the 2 range of 5–50° with a scan speed of 0.1° • s ^{1} on a Bruker D8 Advance instrument using CuK radiation (= 1.54056 Å) at room temperature. Fluorescence studies were carried out on a computer-controlled JY FluoroMax-3 spectrometer at room temperature.

2.2 Synthesis

A mixture of H pzdc (0.067 g, 0.4 mmol), HL (0.030 g, 0.2 mmol), Cd(OAc) • 2H O (0.11 g, 0.4 mmol), and 18 mL H O was adjusted to pH 7 with 40% NaOH, sealed in a Teflon-lined stainless-steel vessel, and heated to 150 °C for 5 days, followed by slow cooling (a descent rate of 5 °C/h) to room temperature. Brown block crystals were obtained with a yield of 41%. Anal. Calcd. for C H CdN O : C, 36.94; H, 2.54; N, 15.67%. Found: C, 36.05; H, 2.01; N, 15.07%. IR (cm ^{1}): 3609(w), 3478(w), 2360(w), 1629(s), 1601(m), 1567(w), 1519(w), 1471(w), 1452(m), 1432(w), 1378(w), 1365(w), 1350(w), 1285(w), 1259(w), 1231(w), 1201(w), 1157(w), 1122(m), 1095(w), 1074(w), 1067(w), 1051(w), 1011(w), 978(w), 946(w), 880(w), 851(w), 822(w), 790(w), 752(m), 737(w), 709(w), 694(w), 670(w), 648(w), 638(w), 567(w), 509(w), 473(w), 444(w), 436(w).

2.3 X-ray Crystallography

All diffraction data for complex 1 were collected on a Bruker/Siemens Smart Apex II CCD diffractometer with graphite-monochromated MoK radiation (= 0.71073 Å) at 293(2) K. Data reductions and absorption corrections were performed using the SAINT and SADABS programs, respectively. The structure was solved by direct methods with the SHELXS-97 program [17(a)] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [17(b)]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of organic ligands were generated geometrically. For 1, a total of 6024 reflections were collected in the range of 2.13 26.13°, of which 2133 were independent (Rint = 0.0126). The final R = 0.0169 and wR = 0.0443 for observed reflections with I > 2 (I), and R = 0.0172 and wR = 0.0444 for all data, with (Δ)max = 0.796 and (Δ)min = -0.335 e • Å ^{3}. Selected bond lengths and bond angles of complex 1 are shown in Table 1 .

3 RESULTS AND DISCUSSION

3.1 Structural Description

Single-crystal X-ray diffraction analysis reveals that compound 1 crystallizes in the Fdd2 space group and consists of a two-dimensional network structure. The asymmetric unit contains one Cd(II) ion, one L ligand, half a H pzdc ligand, and one crystal water molecule (Fig. 1 [Figure 1: see original paper]). The Cd(1) ion is coordinated by three nitrogen atoms from two different L ligands and one nitrogen atom from a pzdc ligand in the equatorial plane (Cd(1)-N(1A) = 2.252(3), Cd(1)-N(2) = 2.268(3), Cd(1)-N(3) = 2.371(2), Cd(1)-N(4) = 2.416(3) Å) and by one oxygen atom from the pzdc ligand and one oxygen atom from another pzdc ligand at the axial sites (Cd(1)-O(1) = 2.514(2), Cd(1)-O(2B) = 2.273(2) Å). The coordination angles around the Cd(II) ion range from 67.59(9) to 167.33(9)°.

In the crystal structure of complex 1, each L ligand binds two cadmium(II) ions through a bidentate-monodentate mode, utilizing two nitrogen atoms to connect one cadmium(II) ion and one nitrogen atom to connect another cadmium(II) ion, whereas the H pzdc ligands adopt a coordination mode, with two carboxylate groups using four oxygen atoms to connect four different cadmium(II) ions and two nitrogen atoms bridging two different cadmium(II) ions. The coordination mode of the H pzdc molecule in 1 differs from that in our previously reported compound [Zn(pzdc)(mbix)] · nH O [18]. Consequently, four Cd(II) ions are linked by two pzdc and two L ligands, and each pair of tetranuclear subunits is bridged by pzdc ligands to yield a two-dimensional network structure, as depicted in Fig. 2 [Figure 2: see original paper]. The Cd(1) ion exhibits a distorted octahedral coordination geometry.

Further analysis of the crystal packing revealed - interactions in complex 1 between the N(3)C(4)C(5)C(6)C(7)C(8) pyridine ring of the L ligand. The centroid-to-centroid distances are 3.931(3) and 3.929(3) Å, with perpendicular distances of 3.411(2) and 3.484(2) Å, and the dihedral angle is 6°. Therefore, through - interactions, the two-dimensional networks are further extended into a three-dimensional supramolecular framework (Fig. 3 [Figure 3: see original paper]).

3.2 IR Analysis of Complex 1

The IR spectrum of 1 shows a broad absorption band at 3478 cm ^{1}, corresponding to the O-H stretching of the crystal water molecule in the complex. The C-N absorption peaks of pyridine can be observed at 1350 cm ^{1}. Asymmetric and symmetric COO stretching modes of the lattice pzdc^{2} anion were evidenced by very strong, slightly broadened bands at 1601 and 1452 cm ^{1} [19], which is consistent with the X-ray analysis results.

3.3 Powder X-ray Diffraction (PXRD)

To confirm the phase purity of complex 1, powder X-ray diffraction (PXRD) patterns were recorded and compared with the corresponding simulated patterns calculated from the single-crystal diffraction data (Fig. 4 [Figure 4: see original paper]), indicating a pure phase of the bulk sample.

3.4 Photoluminescent Properties

Luminescence properties are highly significant in photochemistry and photophysics [20, 21]. Therefore, in this study, we measured the solid-state photoluminescence spectra of 1 (Fig. 5 [Figure 5: see original paper]) at room temperature. Upon excitation at 440 nm, complex 1 exhibits blue emission with a maximum peak at 495 nm. To investigate the nature of these emission bands, we first analyzed the photoluminescence properties of the free L and H pzdc ligands and confirmed that they do not emit any luminescence in the range of 400–800 nm. Therefore, based on previous literature [22], the emission band can be attributed to ligand-to-metal charge transfer (LMCT). Owing to its strong fluorescent intensity, 1 appears to be a promising candidate for novel hybrid inorganic-organic photoactive materials.

4 THEORETICAL CALCULATIONS

All calculations in this manuscript were conducted with the Gaussian 03 program [23]. The molecular structure parameters for calculation were all derived from the experimental data of complex 1. Natural bond orbital (NBO) analysis was carried out using density functional theory (DFT) [24] with the PBE0 [25-28] hybrid functional and the LANL2DZ basis set [29].

The major natural atomic charges, natural electron configurations, Wiberg bond indices, and NBO bond orders (a.u.) for complex 1 are shown in Table 2 . The results indicate that the electronic configurations of the Cd(1) ion, N atoms, and O atoms are 5s $.^{2}$ 4d . 5p $.^{3}$, 2s^{1}.^{3} –1.412p^{3}. –4.16, and 2s^{1}. –1.692p . ^{1}–5.09, respectively. Based on these results, one can infer that the coordination of the Cd(1) ion with nitrogen and oxygen atoms primarily involves the 4d, 5s, and 5p orbitals. Nitrogen atoms form coordination bonds with the Cd(1) ion utilizing 2s and 2p orbitals, while oxygen atoms donate electrons from 2s and 2p orbitals to the Cd(1) ion to form coordination bonds. Thus, the Cd(1) ion gains some electrons from four nitrogen atoms of the L ligand and two oxygen atoms of the pzdc ligands [30, 31, 32].

Therefore, based on valence-bond theory, the atomic net charge distribution and NBO bond orders of complex 1 (Table 4) exhibit obvious covalent interaction between the coordinated atoms and the Cd(1) ion. The differences in NBO bond orders for Cd–O and Cd–N bonds result in different bond lengths [31], which is in good agreement with the X-ray crystal structural data of compound 1.

As can be seen from Fig. 6 [Figure 6: see original paper], the lowest unoccupied molecular orbital (LUMO) mainly consists of the L ligand, whereas the highest occupied molecular orbital (HOMO) is primarily composed of the pzdc ligand. Thus, charge transfer from ligand to ligand may be deduced from some contours of the molecular orbitals of complex 1.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1

Distance	Value	Distance	Value
Cd(1)-O(1)	2.514(2)	Cd(1)-O(2B)	2.273(2)
Cd(1)-N(2)	2.268(3)	Cd(1)-N(3)	2.371(2)
Cd(1)-N(1A)	2.252(3)	Cd(1)-N(4)	2.416(3)

Angle	Value	Angle	Value
N(1A)-Cd(1)-N(2)	97.41(10)	N(1A)-Cd(1)-O(2B)	103.34(10)
N(2)-Cd(1)-O(2B)	71.65(11)	N(1A)-Cd(1)-N(3)	160.98(12)
N(2)-Cd(1)-N(3)	71.57(9)	O(2B)-Cd(1)-N(3)	91.81(11)
N(1A)-Cd(1)-N(4)	95.61(10)	N(2)-Cd(1)-N(4)	161.95(10)
O(2B)-Cd(1)-N(4)	101.84(10)	N(3)-Cd(1)-N(4)	92.39(10)
N(1A)-Cd(1)-O(1)	85.15(9)	N(2)-Cd(1)-O(1)	101.10(8)
O(2B)-Cd(1)-O(1)	167.33(9)	N(3)-Cd(1)-O(1)	81.99(11)
N(4)-Cd(1)-O(1)	67.59(9)		

Symmetry codes: A: -x+5/2, -y+5/2, z; B: 2-x, -y+5/2, z+1/2

Table 2. Natural Atomic Charges, Natural Valence Electron Configurations, Wiberg Bond Indices and NBO Bond Orders (a.u.) for 1

Atom/Interaction	Charge	Electron Configuration	Wiberg Index	NBO Bond Order
Cd(1)		[core]5s(0.29)4d(9.98)5p(0.30)		
O(1)		[core]2s(1.69)2p(5.01)		
O(2)		[core]2s(1.68)2p(5.09)		
N(1)		[core]2s(1.41)2p(3.95)		
N(2)		[core]2s(1.39)2p(4.04)		
N(3)		[core]2s(1.34)2p(4.16)		
N(4)		[core]2s(1.35)2p(4.14)		
Cd(1)-O(1)				
Cd(1)-O(2)				
Cd(1)-N(1)				
Cd(1)-N(2)				
Cd(1)-N(3)				
Cd(1)-N(4)				

Symmetry codes: (A) -x, -y, z; (B) -x+1/2, -y, z-1/2

Fig. 1. Coordination environment of the Cd(II) center in 1. Symmetry codes: (A) -x+5/2, -y+5/2, z; (B) 2-x, -y+5/2, z+1/2

Fig. 2. View of the two-dimensional network structure along the b axis (carbon atoms of HL ligand were omitted for clarity)

Fig. 3. View of the 3D supramolecular architecture of 1 formed by - interactions along the a axis (carbon atoms of HL ligand were omitted for clarity)

Fig. 4. PXRD analysis of the title complex 1: bottom—simulated, top—experimental

Fig. 5. Solid-state emission spectrum of 1 at room temperature

Fig. 6. Frontier molecular orbitals of complex 1

Note: Figure translations are in progress. See original paper for figures.

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