

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE AND LUMINESCENT PROPERTIES OF
A ONE-DIMENSIONAL Cd(II) COORDINATION POLYMER CONSTRUCTED BY
4,4'-DI-*TERT*-BUTYL-2,2'-BIPYRIDINE AND 5-*TERT*-BUTYL ISOPHTHALIC ACID

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A one-dimensional Cd(II) complex $[\text{Cd}(\text{Bu}_2\text{bpy})(\text{tbip})\cdot\text{H}_2\text{O}]_n$ (**1**) (Bu_2bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine, H_2tbip = 5-*tert*-butyl isophthalic acid) is synthesized and characterized using single crystal X-ray diffraction, IR spectroscopy, and elemental analysis. The single crystal X-ray diffraction analysis reveals that complex **1** is a one-dimensional double chain polymer based on $\{\text{Cd}_2(\text{OCO})_2\}$ dimeric kernels with a Cd \cdots Cd separation of 4.3197(7) Å. The thermal stability and luminescent properties of the title complex are briefly investigated.

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Considerable efforts have been focused on the rational design and synthesis of coordination polymers not only because of their intriguing structural diversity and new topologies but also due to their potential applications in gas storage, chemical separations, microelectronics, nonlinear optics, heterogeneous catalysis, and so on [1—8]. It is well-known that the structure of the coordination polymer is usually influenced by several factors in the self-assembly process, such as organic ligands, solvents, metal atoms, temperature, and so on [9—14]. Among these factors, the choice of organic ligands plays a key role in directing the ultimate architectures of the complexes. In recent years, multi-carboxylate ligands have been widely used in the construction of coordination polymers because of their diversity in coordination modes and conformations [15—17].

5-*tert*-Butyl isophthalic acid (H_2tbip) as a substituted isophthalate ligands at *meta*-disposed position 5 is chosen to construct novel coordination polymers mainly because of the steric hindrance and electron-donating properties of the bulky *tert*-butyl group which can affect the coordination abilities and modes of the carboxylic groups [18—22]. However, to the best of our knowledge, coordination polymers constructed from 5-*tert*-butyl isophthalic acid (H_2tbip) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (Bu_2bpy) ligands have not been documented so far. In the present study, we have selected H_2tbip and Bu_2bpy as the organic ligands generating the title new Cd(II) coordination polymer $[\text{Cd}(\text{Bu}_2\text{bpy})(\text{tbip})\cdot\text{H}_2\text{O}]_n$ (**1**), the crystal structure of which we now report. In addition, the thermal and luminescent properties of complex **1** have been investigated.

Experimental. All reagents and solvents were commercially available and used without further purification. The infrared spectrum was obtained in the range 4000—400 cm^{-1} as KBr disks on a VECTOR 22 spectrometer. The elemental analysis was performed on a Perkin Elmer 240C elemental analyzer. The thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 TGA analyzer from room temperature to 950 °C with a heating rate of 20 °C·min⁻¹ under nitrogen. Solid-state fluorescence spectra were recorded on a Fluoro Max-P spectrophotometer at room temperature.

Table 1

Crystal data and structure refinement for complex 1

Parameter	
Empirical formula	C ₃₀ H ₃₈ CdN ₂ O ₅
Formula weight	619.03
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg.	14.125(3), 10.210(2), 20.477(4); 99.311(4)
<i>V</i> , Å ³	2914.2(10)
<i>Z</i>	4
ρ _{calcd} , g/cm ³	1.411
μ(MoK _α), mm ⁻¹	0.789
Crystal size, mm	0.21×0.19×0.17
θrange, deg.	2.02—26.75
<i>F</i> (000)	1280
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0414 / 0.0725
GOOF	0.912

Synthesis of [Cd(Bu₂bpy)(tbip)·H₂O]_{*n*}. A mixture of Cd(NO₃)₂·6H₂O (0.0346 g, 0.1 mmol), H₂tbip (0.0222 g, 0.1 mmol), Bu₂bpy (0.0268 g, 0.1 mmol), NaOH (0.008 g, 0.2 mmol) in H₂O (10 ml) was sealed in a 16 ml Teflon-lined stainless steel container and heated at 160 °C for 72 h. After cooling to room temperature, white block crystals were collected by filtration and washed with water and ethanol several times. (yield 31.8 %, based on H₂tbip). Elemental analysis for C₃₀H₃₈CdN₂O₅ (*M*_w = 619.03): C 58.21, H 6.19, N 4.53; found: C 58.39, H 6.21, N 4.54 %. Selected IR peaks (cm⁻¹): 3441 (m), 1633 (s), 1451 (s), 1215 (s), 838 (w), 756 (w), 719 (w).

X-ray crystallography. The crystal structure of complex 1 was determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated MoK_α radiation (λ = 0.71073 Å) at 296 K. Absorption correction was performed using the SADABS program [23]. The structure was solved by a direct method using the SHELXL-97 program and refined by the full-matrix least-squares technique on *F*² using SHELXL-97 [24]. The disordered atoms (C12, C12B, C13, C13B, C14, C14B, C16, C16B, C17, C17B, C18, and C18B) were refined using C atoms split over two equally occupied sites with a total occupancy of 1. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. All H atoms were refined isotropically, with the isotropic vibrational parameters related to the non-H atom to which they are bonded. The crystallographic data are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

Table 2

Selected bond distances (Å) and angles (deg.) for complex 1

Cd(1)—N(1)	2.343(3)	N(1)—Cd(1)—N(2)	68.59(9)	N(1)—Cd(1)—O(1)	149.42(9)
Cd(1)—O(1)	2.387(2)	N(1)—Cd(1)—O(2)	100.83(9)	N(2)—Cd(1)—O(1)	88.07(9)
Cd(1)—O(3)#2	2.277(2)	N(2)—Cd(1)—O(2)	82.54(9)	O(2)—Cd(1)—O(1)	55.08(8)
Cd(1)—N(2)	2.361(3)	O(3)#2—Cd(1)—N(1)	102.81(9)	O(3)#2—Cd(1)—N(2)	169.54(9)
Cd(1)—O(2)	2.358(2)	O(3)#2—Cd(1)—O(1)	97.74(8)	O(3)#2—Cd(1)—O(2)	93.63(8)
Cd(1)—O(4)#1	2.222(2)	O(4)#1—Cd(1)—N(1)	110.72(9)	O(4)#1—Cd(1)—N(2)	91.62(9)
		O(4)#1—Cd(1)—O(1)	88.60(9)	O(4)#1—Cd(1)—O(2)	143.24(9)
		O(4)#1—Cd(1)—O(3)#2	97.19(8)		

#1 *x*, *y*-1, *z*; #2 -*x*+1, -*y*+1, -*z*+1.

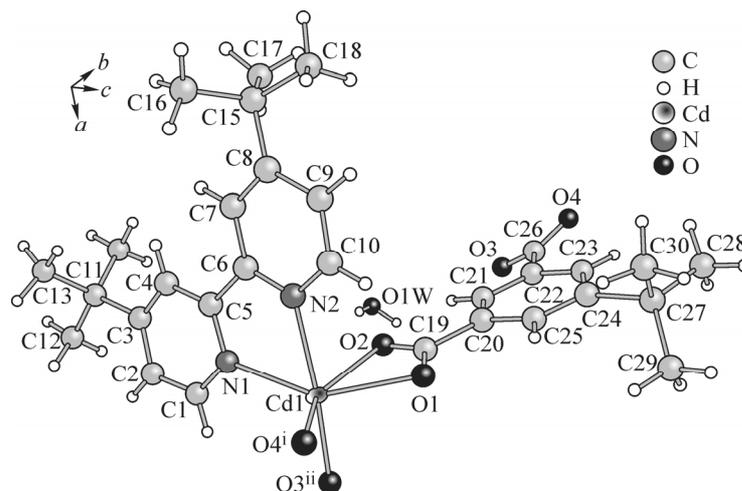


Fig. 1. Coordination environment of the Cd(II) ion in complex **1** showing 30 % ellipsoid probability.

Symmetry codes: ⁱ $x, y-1, z$; ⁱⁱ $-x+1, -y+1, -z+1$

Results and discussion. Single crystal X-ray diffraction revealed that complex **1** crystallized in the monoclinic space group $P2_1/n$ with an asymmetric unit consisting of a cadmium atom, one bridging tbip^{2-} dianion, one Bu_2bpy chelating ligand, and one water molecule of crystallization. As shown in Fig. 1, the Cd1 cadmium atom possesses a distorted $\{\text{CdN}_2\text{O}_4\}$ octahedron bound by a chelating carboxylate group from a tbip^{2-} ligand, single oxygen atom donors from two other different tbip^{2-} ligands, and two nitrogen atoms from one chelating Bu_2bpy ligand. The Cd—N bond lengths (2.343(3)—2.361(3) Å) and Cd—O bond lengths (2.222(2)—2.387(2) Å) are comparable with the corresponding values found in other Cd(II) complexes [25, 26]. The key bond lengths and bond angles are listed in Table 2.

As for the tbip^{2-} anion, the carboxylate groups are all bonded to Cd, with a bridging pair of Cd atoms at one terminus and acting as monodentate donors at another one. Thus, the tbip^{2-} anion serves as an exotridentate ligand with a $\mu_3\text{-}\kappa^3\text{O}_3\text{O}'\text{:O}''\text{:O}'''$ binding mode, connecting three Cd1 atoms. Pairs of Cd1 atoms are linked by two *anti-syn* carboxylate bridges to construct $\{\text{Cd}_2(\text{OCO})_2\}$ dimeric kernels which have a Cd \cdots Cd contact separation of 4.3197(7) Å. The latter are connected into 1D $[\text{Cd}(\text{tbip})]_n$ ribbons oriented parallel to the crystallographic b axis. The chelating Bu_2bpy ligands are extended on both sides of the chain (Fig. 2). Approximately 4.0 % of the crystal volume is occupied

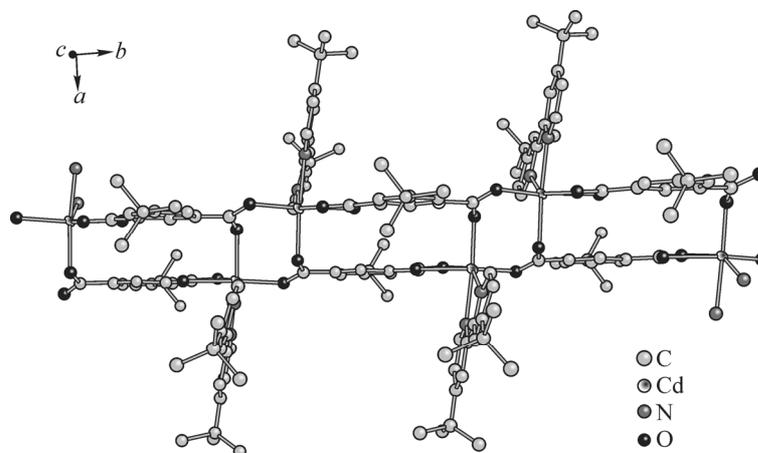


Fig. 2. The one-dimensional chain structure of complex **1** along the crystallographic b axis, all hydrogen atoms are omitted for clarity

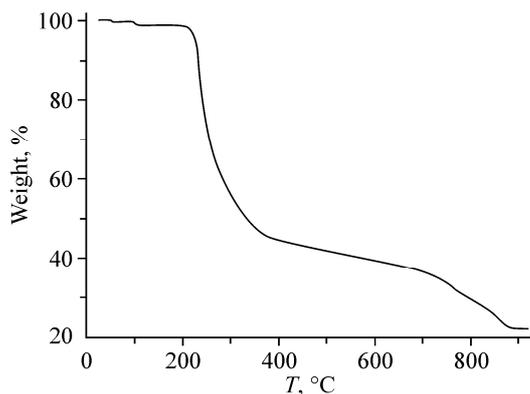


Fig. 3. The TG curve of complex **1**

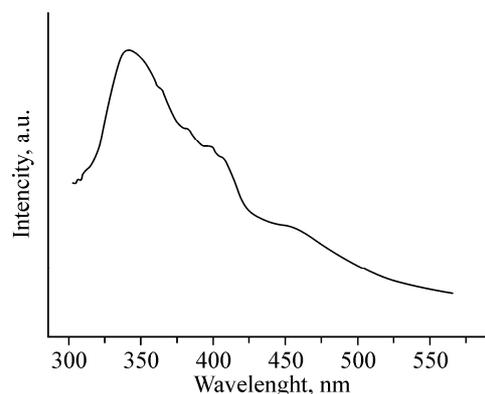


Fig. 4. Solid-state emission spectrum of complex **1** at room temperature

by solvent molecules with a volume of $\sim 115.1 \text{ \AA}^3$ in each cell unit (2914.3 \AA^3), according to the PLATON calculation [27].

The thermal stability of complex **1** was investigated. As shown in Fig. 3, the water molecules of crystallization were ejected from 100 °C to 108 °C (3.2 % weight loss observed, 2.9 % calcd). The removal of the organic ligands occurs in the temperature range of 210 °C to 900 °C. The final residue was proved to be CdO. The calculated result (20.9 %) is basically comparable with the observed one (20.7 %).

The fluorescent property of complex **1** was studied in the solid state at room temperature. The free H_2tbp ligand shows emission peaks at 320 nm [18]. Irradiation of crystalline samples of complex **1** with ultraviolet light ($\lambda_{\text{ex}} = 295 \text{ nm}$) in the solid state resulted in intense emission with a λ_{max} of 343 nm (Fig. 4). According to a recent review of the d^{10} metal coordination polymer luminescence, the emissive behavior of **1** can be ascribed to ligand-centered electronic transitions [28–31].

In summary, we have presented the synthesis and crystal structure of a new 1D Cd(II) complex $[\text{Cd}(\text{Bu}_2\text{bpy})(\text{tbp}) \cdot \text{H}_2\text{O}]_n$ (**1**). The single crystal X-ray diffraction analysis reveals that complex **1** is a one-dimensional double chain polymer based on $\{\text{Cd}_2(\text{OCO})_2\}$ dimeric kernels with a Cd...Cd separation of $4.3197(7) \text{ \AA}$. Moreover, the thermal stability and luminescent properties of the title complex have been briefly investigated.

Crystallographic data for the structural analysis of complex **1** has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 912615. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EQ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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