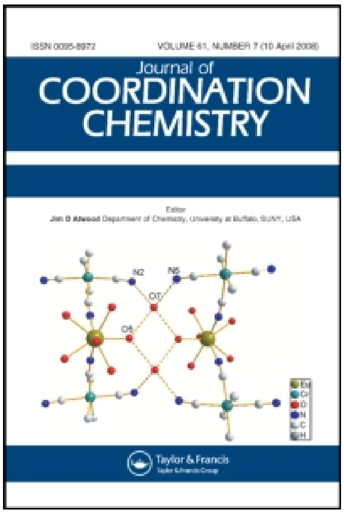

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Hydrothermal synthesis, crystal structure and characterization of a new 1-D supramolecular ladder based on a binuclear Cd^{II} complex [Cd_2L_4(3,5-DNBA)$_2$](H_2O) with L as a bridging ligand (L=3-(2-pyridyl)pyrazole; 3,5-DNBA=3,5-dinitrobenzoate)

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Hydrothermal synthesis, crystal structure and characterization of a new 1-D supramolecular ladder based on a binuclear Cd^{II} complex $[Cd_2L_4(3,5\text{-}DNBA)_2](H_2O)$ with L as a bridging ligand (L = 3-(2-pyridyl)pyrazole; 3,5-DNBA = 3,5-dinitrobenzoate)

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A new 1-D cadmium(II) mixed ligand dimer supramolecular ladder $[Cd_2\mathbf{L}_4(3,5\text{-}DNBA)_2]H_2O$ (**1**), (**L** = 3-(2-pyridyl)pyrazole and 3,5-DNBA = 3,5-dinitrobenzoate) was synthesized by hydrothermal methods. X-ray structural analysis of complex **1** revealed that two cadmium(II) cores are bridged by two deprotonated pyrazole groups of **L**, leading to dinuclear cadmium(II) $[Cd_2\mathbf{L}_4(3,5\text{-}DNBA)_2]$. The dimers are joined by hydrogen-bonding interactions between two different cadmium(II) dimers to form a one-dimensional ladder-like framework and stabilized by weak π–π interactions. Moreover, the fluorescence spectrum of compound **1** exhibits blue fluorescent emission in the solid state at room temperature.

Keywords: Hydrothermal synthesis; Cadmium(II) dimer; 3-(2-Pyridyl)pyrazole; Supramolecular framework

1. Introduction

Crystal engineering of supramolecular architectures based on metal and organic building blocks has been rapidly expanding in recent years owing to their novel and diverse topologies and potential applications in host-guest chemistry, catalysis, electrical conductivity, and magnetism [1–4]. Weaker intermolecular forces, such as hydrogen bonds, play an important role in fundamental biological processes and construction of complicated supramolecular arrays through self-assembly of molecules in the field of supramolecular chemistry [5–8]. 3,5-DNBA is an excellent ligand to construct supramolecular networks [9, 10] for the following reasons: (a) the carboxylate group can connect with metal ions with several coordination modes, (b) oxygen atoms from the nitro-group can form strong hydrogen bonds with other groups, acting not only as hydrogen-bond acceptors but also as hydrogen-bond donors. Furthermore, since the first comprehensive review by Trofimenko, the coordination chemistry

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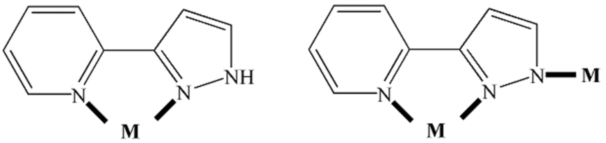


Scheme 1. The possible coordination modes of **L**.

of pyrazole-derived ligands has attracted much interest [11]. Among such ligands, 3-(2-pyridyl)pyrazole is used not only as a terminal building block but also as a bridging ligand in construction of a series of complexes, such as mononuclear Cu(II), Ni(II) and Zn(II) [12, 13], dinuclear Fe(II) [14], tetranuclear Fe(II) and Cu(II) [15, 16]. The possible coordination modes of the ligand **L** are shown in scheme 1. Reports on architectures based on mixed ligand complexes of Cd(II) have been rare [17].

Polynuclear d^{10} metal (Cu(I), Ag(I), Au(I), Zn(II) or Cd(II)) complexes have attracted interest in recent years for appealing structures and photoluminescent properties [18].

We have synthesized a 1-D ladder-like supramolecular architecture $[Cd_2L_4(3,5\text{-DNBA})_2]H_2O$ with **L** and 3,5-dinitrobenzoic acid, in which **L** bridges and is also a terminal group. Complex **1** displays blue emission in the solid state.

2. Experimental

2.1. *General procedures*

All solvents and reagents for syntheses were commercially available and used as received. 3-(2-Pyridyl)pyrazole was synthesized by the literature method [19]. IR spectra were recorded in the range 400–4000 cm^{-1} on FTIR-8400 (SHIMADZU) spectrometer with pressed KBr pellets. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer. Excitation and emission spectra were obtained on a HITACHI F-4500 spectroflurometer equipped with a 150 W xenon lamp as the excitation source.

2.2. *Preparation of 1*

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.1 mmol), 3-(2-pyridyl)pyrazole (0.2 mmol), 3,5-DNBA (0.2 mmol), NaOH (0.35 mmol) and H_2O (15 mL), stirred for 20 min, was sealed in a Teflon-lined stainless steel autoclave (25 mL) and kept at 120°C for 12 h. After the mixture was slowly cooled to room temperature, yellow block crystals suitable for X-ray diffraction of **1** were obtained in 55% yield (based on Cd^{II} salt). Anal. Calcd for $Cd_2C_{46}H_{34}N_{16}O_{13}$(%): C, 44.44; H, 2.74; N, 18.04; Found: C, 44.30; H, 2.58; N, 18.12. IR (KBr, cm^{-1}): 1699 (m), 1624 (s), 1599 (s), 1570 (w), 1540 (s), 1520 (w), 1450 (m), 1431 (m), 1380 (m), 1365 (m), 1346 (s), 1215 (m), 1156 (m), 1126 (m), 1093 (m), 1068 (m), 1057 (m), 961 (s), 917 (m), 863 (w), 792 (m), 777 (s), 765 (s), 713 (s), 634 (w).

2.3. *X-ray crystallography*

The structure of **1** was determined by single crystal X-ray diffraction. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) at 293 K in the range of $3.00 < \theta < 27.48°$. A total of 12249 (5620 unique) reflections were measured ($-12 \le h \le 12$, $-14 \le k \le 14$, $-17 \le l \le 17$) for **1**. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXL-97 software [20, 21]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the Fourier difference maps. A summary of the crystallographic data and structural determination for the title compound are provided in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystal data and structure refinement summary for complex **1**.

Compound	**1**
Empirical formula	$Cd_2C_{46}H_{34}N_{16}O_{13}$
Formula weight	1241.70
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.4479(19)
b (Å)	11.240(2)
c (Å)	13.537(3)
α (°)	71.85(3)
β (°)	88.93(3)
γ (°)	67.79(3)
Volume (Å^3)	1256.6(4)
Z	1
D_{Calcd} (g cm^{-3})	1.643
$F(000)$	622
θ range (°)	3.00–27.48
Reflections collected/unique	12249/5620
Data/restraints/parameters	5620/0/352
Goodness-of-fit on F^2	1.015
Final R indices [$I > 2\sigma(I)$]	$R^a = 0.0351$, $wR^b = 0.0874$
R indices (all data)	$R^a = 0.0426$, $wR^b = 0.0899$
Largest diff. peak and hole (e Å^{-3})	0.557 and -0.492

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^bwR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

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

Compound **1**			
Cd(1)–N(6)	2.238(3)	Cd(1)–N(4)	2.331(2)
Cd(1)–N(7)#1	2.271(2)	Cd(1)–N(8)#1	2.393(3)
Cd(1)–O(2)	2.297(3)	Cd(1)–N(5)	2.498(3)
N(6)–Cd(1)–N(7)A	103.53(9)	N(6)–Cd(1)–O(2)	92.33(10)
N(7)#1–Cd(1)–O(2)	98.49(11)	N(6)–Cd(1)–N(4)	96.70(9)
N(7)#1–Cd(1)–N(4)	150.32(9)	O(2)–Cd(1)–N(4)	102.17(11)
N(6)–Cd(1)–N(8)#1	174.80(8)	N(7)#1–Cd(1)–N(8)#1	71.27(9)
O(2)–Cd(1)–N(8)#1	88.23(10)	N(4)–Cd(1)–N(8)#1	88.23(9)
N(6)–Cd(1)–N(5)	92.28(9)	N(7)#1–Cd(1)–N(5)	89.79(8)
O(2)–Cd(1)–N(5)	169.31(10)	N(4)–Cd(1)–N(5)	67.69(8)
N(8)#1–Cd(1)–N(5)	88.05(9)		

Symmetry code: #1 $-x$, $-y$, $-z+1$, #2: $-x$, $-y+1$, $-z$.

3. Results and discussion

3.1. *Structure description*

The structure of complex **1** consists of a [Cd_2L_4(3,5-DNBA)$_2$] dimer and lattice water. The dinuclear molecule consists of two asymmetric units, with Cd(1), N(6) and N(7) being the symmetry generated equivalents of Cd(1A), N(6A) and N(7A) with the complex located in an inversion centre. The coordination environment of cadmium(II) with atom labeling is shown in figure 1 (lattice water omitted for clarity). The coordination geometry around Cd^{II} could be described as a distorted octahedron generated by N(4)–N(6)–N(7A)–N(8A) occupying the equatorial plane, O(2) of 3,5-DNBA and N(5) in the axial positions.

In this complex, the four **L**s have two types of coordination mode. One occupies the axial position as a bidentate ligand chelated with the Cd^{II} center to result in a five-member ring, N(5)–C(11)–C(10)–N(4)–Cd^{II}(1); The other **L** occupies the equatorial plane as a tridentate ligand chelated with the Cd^{II} center to form a five-member chelated ring N(8)–C(19)–C(18)–N(7)–Cd^{II}(1A), while N(6A), N(6) and N(7A), N(7) of pyrazole groups connected Cd^{II}(1A) and Cd^{II}(1) to form a six-membered ring N(6)–N(7)–Cd^{II}(1A)–N(6A)–N(7A)–Cd^{II}(1). A schematic illustration of the coordination of the dimer core of **1** is shown in scheme 2. Two Cd^{II} centers are equivalently bridged by **L** with an intramolecular $Cd\cdots Cd$ separation of 4.139 Å. The Cd–N and Cd–O bond distances lie in the range of 2.239–2.497 Å and 2.302 Å, respectively, all being normal for such coordination bonds. Lattice water molecule is included in the dimer unit of the structure.

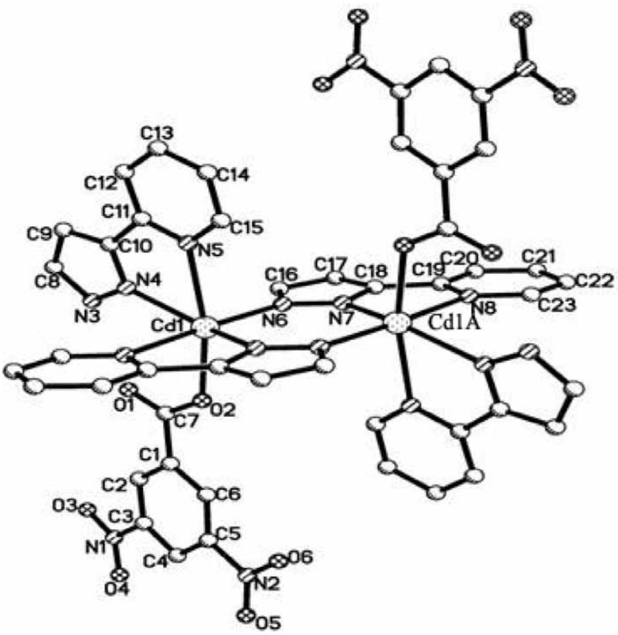
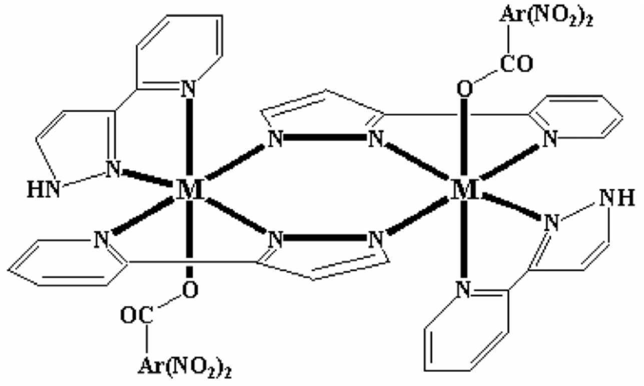


Figure 1. The binuclear complex of **1** (lattice water molecule and H atoms were omitted for clarity).



Scheme 2. Schematic illustration of the coordination of the dimer core of **1**.

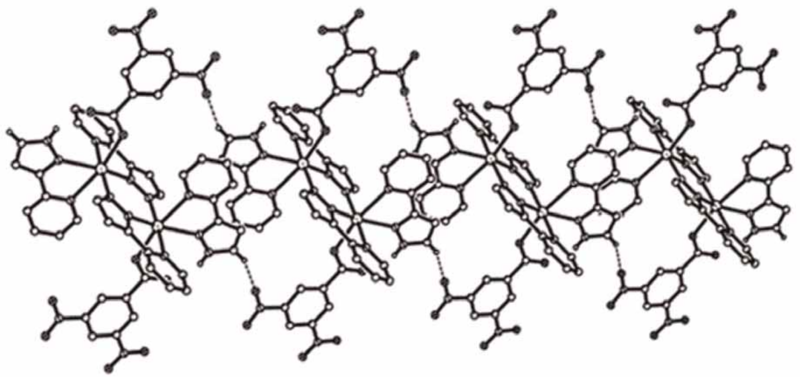


Figure 2. The view of the 1-D ladder-like chain formed through H-bonding of **1** along the *a* axis.

Analysis of the crystal packing of complex **1** reveals a 1-D ladder-type motif. The four nitrogen donors from two deprotonated tridentate bridging ligands **L** connect two Cd^{II} cores to form a dimer, and the dimers are further linked to result in a ladder type 1-D supramolecular network through intermolecular C–H ⋯ O hydrogen-bonding interactions (C(8)–H(8) ⋯ O(6))(x, $1+y$, z) between the chelating **L** and $–NO_2$ group of the other adjacent 3,5-DNBA as illustrated in figure 2. For the hydrogen bonds, the H ⋯ O distances are 2.46 Å; the C ⋯ O separations are 3.33 Å. All the relevant hydrogen-bonding geometries are in the normal range for such weak interactions [22]. In addition, between two adjacent chelating **L** molecules from two different dimers, the shortest aryl–aryl separation of 3.89 Å indicates that weak π–π stacking interactions further stabilize this 1-D ladder hydrogen-bonding structure, as depicted in figure 3.

3.2. *IR spectrum of complex 1*

The IR spectrum of **1** exhibits characteristic bands due to the ligand vibrations, including ν_{PR} at 1624 and 1599 cm^{-1} (PR = pyridine ring) of **L**, the absorption bands at

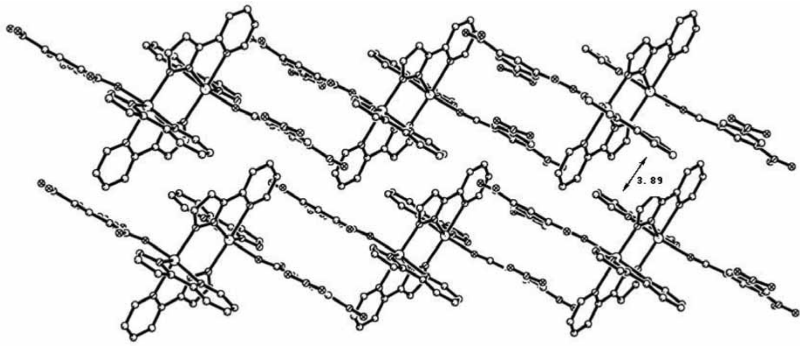


Figure 3. Stacking diagram along *b* axis showing the π–π interactions (lattice water molecule and H atoms were omitted for clarity).

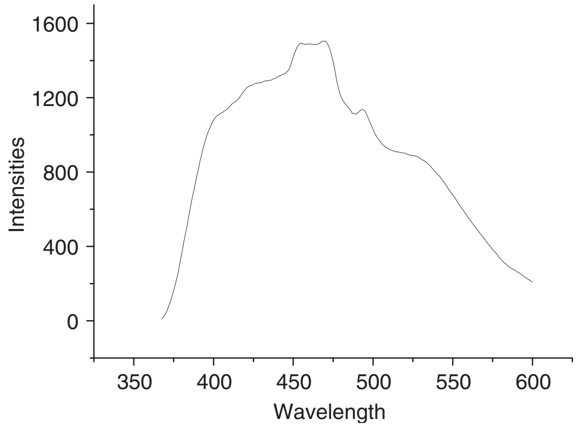


Figure 4. Solid state fluorescence spectrum of compound **1** ($\lambda_{ex} = 354$ nm) at room temperature.

1540 and 1346 cm^{-1} arise from the nitro-group of 3,5-DNBA. The absence of strong peaks around 1470 and 1440 cm^{-1} indicates that all carboxylic groups are deprotonated in compound **1**. The absorption bands in the 1400–1600 cm^{-1} region arise from the skeletal vibrations of the aromatic rings of the ligands.

3.3. *The fluorescence of complex 1*

The fluorescence spectrum shows that the solid-state emission occurred at 455, 470 and 493 nm ($\lambda_{ex} = 354$ nm), as shown in figure 4 with fluorescence intensity ($\lambda_{em} = 493$ nm) of compound **1** relatively slight. The emission of compound **1** is neither ligand-to-metal charge transfer (LMCT) nor metal-to-ligand charge transfer (MLCT) in nature, and probably can be assigned to intraligand fluorescent emission since a very similar emission is also observed for free **L** ligand ($\lambda_{em} = 452$ and $\lambda_{em} = 493$, $\lambda_{ex} = 354$ nm). Owing to the blue emission of **1**, it may be a potential material for blue-light-emitting diode devices. These condensed supramolecular framework materials may be good candidates for solvent-resistant blue fluorescent material because **1** is insoluble in common polar and non-polar solvents.

In summary, a new 1-D cadmium(II) mixed ligand dimer supramolecular ladder constructed through H-bonding and stabilized by weak π–π interactions has been prepared under hydrothermal conditions. Compound **1** exhibits good blue fluorescent emission that can be used as a candidate for potential photoactive materials.

Supplementary data

Full lists of atomic positional parameters and isotropic temperature factors are available from the authors. Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 279676 for **1**. Copies of the data can be obtained free of charge on application to CCDC (Fax: +44-1223336-033; Email: deposit@ccdc.ac.uk).

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