

一种新型的 T 形一维镉配位聚合物



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$\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 和 4-(4-羧基吡啶)氨基苯甲醛通过温和条件下的水热反应制备了一种新型的中性 T 形一维链状配位聚合物, 聚合[(异烟酸根) (4-羧酸根基吡啶铵) 冰合硝酸镉]。该配合物显示了蓝色荧光性质。

关键词: 异烟酸根 一维镉配位聚合物 T 形 荧光

分类号: O614.24+2

A Novel T-shaped One-Dimensional Cadmium Coordination Polymer, [(Isonicotinato) (4-carboxylato-pyridinium) (nitrate) (aqua) cadmium]_n

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A meso-hydrothermal reaction between $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 4-(4'-pyridylcarbonyl) aminobenzaldehyde yields a novel neutral T-shaped one-dimensional chain coordination polymer [(isonicotinato) (4-carboxylatopyridinium) (nitrate) (aqua) · cadmium (II)]_n (I) which displays blue fluorescent emission in the solid state.

Keywords: isonicotinato cadmium one-dimension coordination polymer
T-shaped fluorescence

0 Introduction

Crystal engineering of new solid state coordination architectures with unsymmetric multidentate

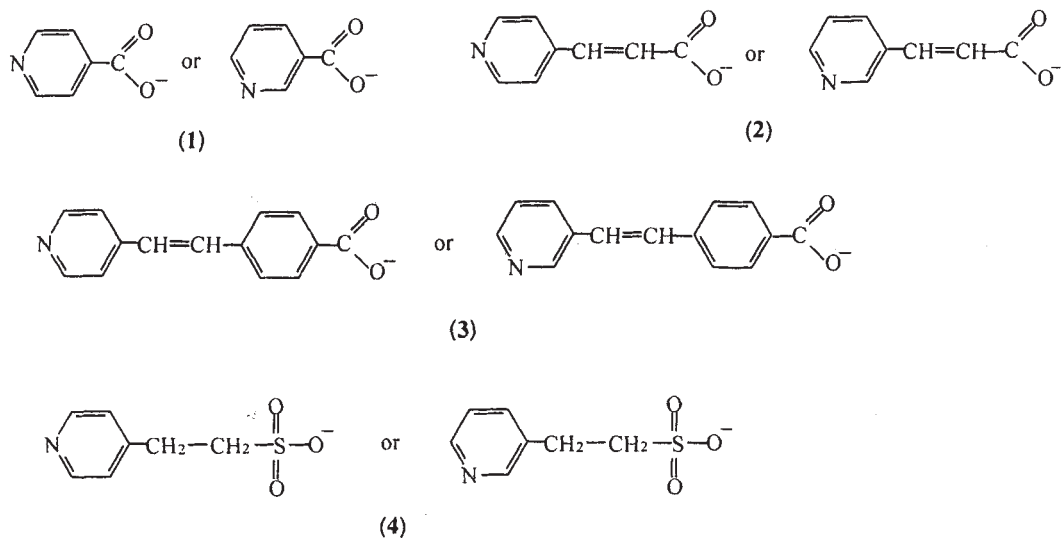
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ligands and a variety of transition metal ions offers an exciting approach to the exploration of novel multi-dimensional arrays which may possess fascinating physical properties. A variety of coordination polymers have been prepared from isonicotinic or nicotinic(**1**), 3- or 4-pyridylacrilate(**2**), 3- or 4-pyridylethenylbenzoate(**3**), and 4-pyridylethenylsulfonate(**4**). Structural motifs for coordination polymers include adamandoid^[1], square network^[2], inclined grid and double nets^[3] as well as octahedral networks features^[4]. Furthermore, it is very interesting to note that the use of precursors of these multidentate ligands, such as their cyano or estate derivatives is very crucial for the construction of the condensed materials. Also, these motifs are generally synthesized under hydrothermal conditions (beyond 110°C). Here, we report the synthesis, crystal structure and fluorescent properties of (I) which, to the best of our knowledge, represents the first example of the neutral T-shaped motif^[5].



1 Experimental

1.1 Synthesis

To our surprise, a novel T-shaped one-dimensional cadmium coordination polymer, (isonicotinato) (4-carboxylato-pyridinium) (nitrate) (aqua) cadmium (I), was obtained under 'meso' hydrothermal conditions using the precursor of isonicotinic acid, i. e. 4-(4'-pyridylcarbonyl) amino benzaldehyde. Once again, the starting material, 4-(4'-pyridylcarbonyl) aminobenzaldehyde was hydrolyzed to form isonicotinic acid. While Cd^{2+} ion reacts slowly with the fresh isonicotinic acid to give rise to (I). The temperature (70°C) is a key for the successful preparation of (I). The presence of carboxylate groups in (I) was clearly confirmed by the strong peak at 1600cm^{-1} and a weak peak at 1540cm^{-1} , respectively. The very strong peak at 1380cm^{-1} indicates the existence of NO_3^- anion. And a very broadly weak peak at 3400cm^{-1} also suggests that there is one coordinated water molecule.

1.2 Crystallographic Data Collection and Structure Determination

A pale yellow crystal with slab shape of the title compound was selected and measured by an

X-ray single crystal diffraction study^[6]. Crystallographic data of complex (I) are shown in Table 1; The atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2, selected bond distances and angles in Table 3.

Table 1 Crystal Data and Structure Refinement for Cd(C₅H₄NCOO) · (C₅H₅NCOO) · (NO₃) · (H₂O)

identification code	Cd(C ₅ H ₄ NCOO) · (C ₅ H ₅ NCOO) · (NO ₃) · (H ₂ O)		
empirical formula	C ₁₂ H ₁₁ CdN ₃ O ₈		
formula weight	437. 64		
temperature	293(2)K		
wavelength	0. 71073Å		
crystal system	orthorhombic		
space group	Pbca		
unit cell dimensions	$a = 14. 411(1)\text{Å}$	$\alpha = 90^\circ$	
	$b = 13. 897(2)\text{Å}$	$\beta = 90^\circ$	
	$c = 14. 860(1)\text{Å}$	$\gamma = 90^\circ$	
volume	2976. 0(5)Å ³		
Z	8		
density (calculated)	1. 959Mg · m ⁻³		
absorption coefficient	1. 517mm ⁻¹		
$F(000)$	1728		
crystal size	0. 38 × 0. 18 × 0. 10mm3		
theta range for data collection	2. 45 ~ 27. 50°		
index ranges	$-1 \leq h \leq 18, -1 \leq k \leq 18, -19 \leq l \leq 1$		
reflections collected	4271		
independent reflections	3423[$R_{\text{int}} = 0. 0331$]		
completeness to theta = 27. 50°	100. 0%		
absorption correction	empirical		
max. and min. Transmission	0. 8631 and 0. 5964		
refinement method	full-matrix least-squares on F^2		
data/restraints/parameters	3423/2/225		
goodness-of-fit on F^2	0. 867		
final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0. 0338, wR2 = 0. 0695$		
R indices (all data)	$R1 = 0. 0705, wR2 = 0. 0777$		
largest diff. peak and hole	0. 429 and $-0. 614\text{e} \cdot \text{Å}^{-3}$		

Table 2 Atomic Coordinates (× 10⁴) and Equivalent Isotropic Displacement Parameters (Å⁻² × 10³) for Cd(C₅H₄NCOO) · (C₅H₅NCOO) · (NO₃) · (H₂O)

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)	atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Cd(1)	1964(1)	6456(1)	437(1)	27(1)	C(2)	- 654(2)	6359(3)	2004(3)	25(1)
O(1)	- 182(2)	6014(2)	509(2)	39(1)	C(3)	- 1593(3)	6383(4)	1832(3)	38(1)
O(2)	860(2)	6600(2)	1468(2)	35(1)	C(4)	- 2210(3)	6416(4)	2540(3)	40(1)
O(3)	2345(2)	6017(3)	- 1763(2)	50(1)	C(5)	- 1042(3)	6404(4)	3565(3)	45(1)
O(4)	3143(2)	6396(2)	- 531(2)	38(1)	C(6)	- 375(2)	6377(4)	2893(3)	37(1)
O(5)	1107(2)	7559(2)	- 544(2)	53(1)	C(7)	3067(3)	6186(3)	- 1338(3)	30(1)
O(6)	2109(2)	8230(2)	328(2)	43(1)	C(8)	3968(3)	6128(3)	- 1872(3)	28(1)
O(7)	1298(3)	9103(3)	- 582(3)	80(1)	C(9)	4814(3)	6155(3)	- 1429(3)	38(1)
N(1)	- 1955(2)	6412(3)	3400(2)	34(1)	C(10)	5620(3)	6156(4)	- 1923(3)	42(1)
N(2)	5590(2)	6144(3)	- 2821(2)	35(1)	C(11)	4795(3)	6118(3)	- 3265(3)	41(1)
N(3)	1497(2)	8303(3)	- 279(2)	38(1)	C(12)	3960(3)	6102(3)	- 2800(3)	34(1)
C(1)	49(2)	6319(3)	1255(3)	28(1)	O(1W)	1678(2)	4868(3)	246(2)	44(1)

U(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3 Bond Lengths (Å) and Angles (°) for $\text{Cd}(\text{C}_5\text{H}_4\text{NCOO}) \cdot (\text{C}_5\text{H}_5\text{NCOO}) \cdot (\text{NO}_3) \cdot (\text{H}_2\text{O})$

bond distances					
Cd(1)-O(2)	2.218(3)	Cd(1)-O(6)	2.480(3)	O(5)-N(3)	1.241(5)
Cd(1)-O(4)	2.227(3)	O(1)-C(1)	1.234(5)	O(6)-N(3)	1.265(4)
Cd(1)-O(1W)	2.263(3)	O(2)-C(1)	1.273(4)	O(7)-N(3)	1.233(5)
Cd(1)-N(1)#1	2.328(3)	O(3)-C(7)	1.239(5)	N(1)-C(4)	1.330(5)
Cd(1)-O(5)	2.449(3)	O(4)-C(7)	1.240(5)	N(1)-C(5)	1.339(5)
Angle					
O(2)-Cd(1)-O(4)	175.23(10)	O(1W)-Cd(1)-N(1)#1	100.94(13)	O(4)-Cd(1)-O(6)	86.02(11)
O(2)-Cd(1)-O(1W)	92.50(11)	O(2)-Cd(1)-O(5)	89.63(11)	O(1W)-Cd(1)-O(6)	167.62(12)
O(4)-Cd(1)-O(1W)	91.24(11)	O(4)-Cd(1)-O(5)	91.36(11)	N(1)#1-Cd(1)-O(6)	91.05(12)
O(2)-Cd(1)-N(1)#1	88.21(10)	O(1W)-Cd(1)-O(5)	116.35(12)	O(5)-Cd(1)-O(6)	51.76(10)
O(4)-Cd(1)-N(1)#1	88.18(10)	O(2)-Cd(1)-O(6)	90.93(11)	N(1)#1-Cd(1)-O(5)	142.71(12)

Symmetry transformations used to generate equivalent atoms: #1 $x+1/2, y, -z+1/2$; #2 $x-1/2, y, -z+1/2$

2 Results and discussion

The one-dimensional polymeric structure of (I) was revealed by an X-ray single crystal diffraction study in which the coordination environment around the Cd^{2+} center in (I) is a slightly distorted octahedron (Fig. 1). To balance the Cd^{2+} charge, one of two N atoms in isonicotinato pyridine ring was protonated. So, the N atom remains uncoordinated. As a result, the extended framework looks like T-shaped one-dimensional chain structure type, as shown in Fig. 2. Moreover, the approximate plane composed of O(4), O(5), O(2) and N(1A) deviates from the idea plane about 0.341 Å while water O(1w) and O(6) occupy the apical positions. It is noteworthy that the plane composed of three isonicotinato ligands deviates from the idea plane about 0.0555 Å (calculated from C(1), O(1), O(2), Cd(1), O(3), O(4), C(7), and N(1A)). As a result,

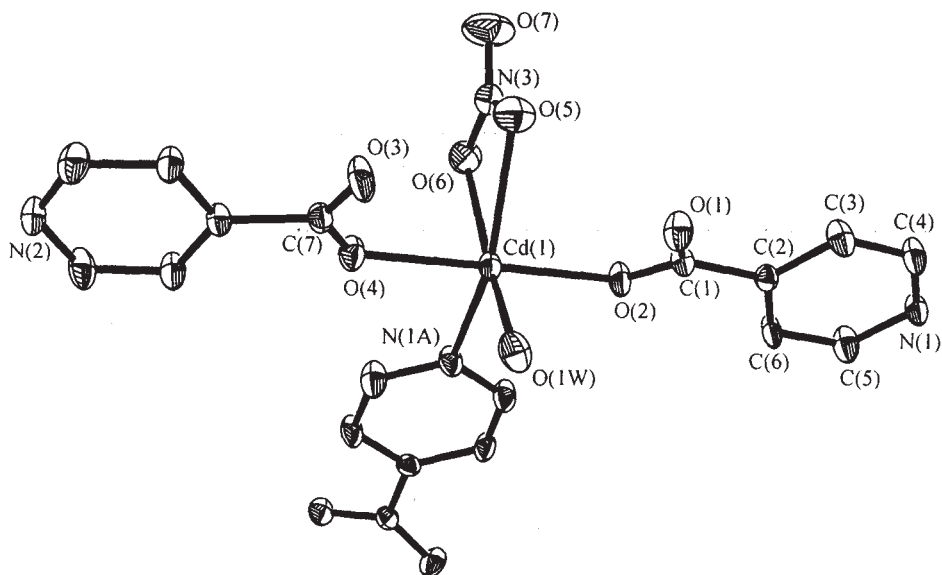


Fig. 1 Structure of complex (I) $[\text{Cd}(\text{C}_5\text{H}_4\text{NCOO}) \cdot (\text{C}_5\text{H}_5\text{NCOO}) \cdot (\text{NO}_3)(\text{H}_2\text{O})]$ with atomic labelling scheme at 35% probability level

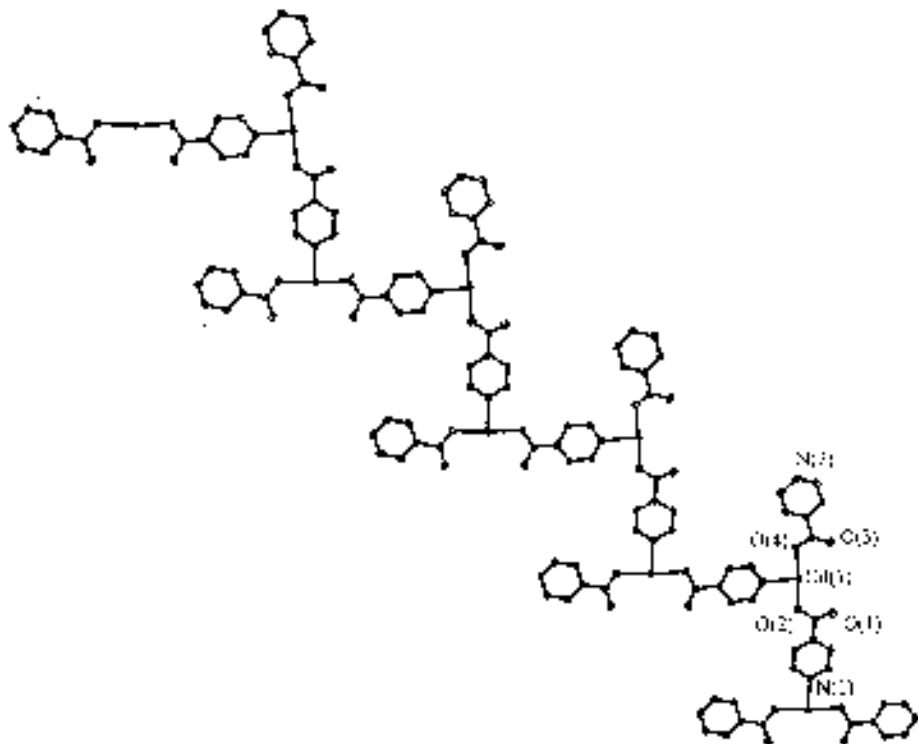


Fig. 2 A infinite T-shaped chain diagram running along the *b*-axis, omitting the nitrate and water for clarity

three isonicotinato groups almost are co-planar so that it makes (I) a perfect T-shaped one-dimensional chain polymer. The bond lengths of Cd-N and Cd-O are in good agreement with those found in $\text{Cd}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{EtOH})_2$ with the bond distances of Cd-N (2.343(5) ~ 2.366(5) Å) and Cd-O (2.279(5) ~ 2.664(4) Å), the bond distances of C-C, C-O, C-N and N-O are unexceptional.

It is noteworthy that the coordination polymer (I), exhibits medium fluorescent emission.

Clearly the fluorescence comes from that of ligand because the similar fluorescent properties was observed for the isonicotinato (Fig. 3). To evaluate the thermal stability of (I), thermogravimetric analysis (TGA) was performed on the polycrystalline sample, indicating that one weak weight loss step occurred at 160°C (3.4%), probably corresponding to the removal of the one coordinated water (4.39% calculated). Furthermore, one striking weight loss step occurred at 300°C, relative to the loss of one isonicotinic acid. It was found that (I) almost was insoluble in common solvents such water, ethanol, acetonitrile and benzene. Thus, it makes (I) good candidate for blue fluorescent emission (ca. 410nm) materials^[7].

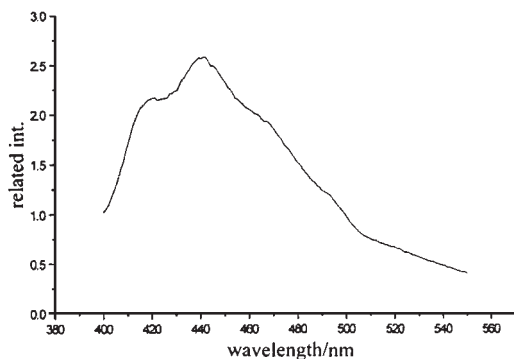


Fig. 3 A solid state fluorescent spectrum of (I)

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