

Article

Synthesis, Crystal Structure, and Luminescent Property of a Cd(II) Coordination Polymer with a *N*-Nicotinoylglycine Ligand

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Academic Editor: Helmut Cölfen

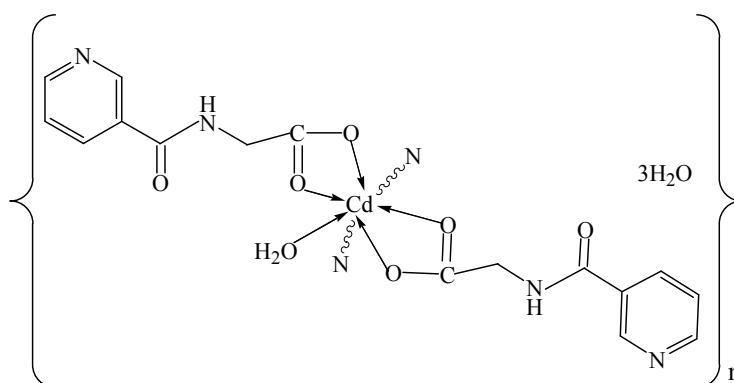
Received: 6 December 2016; Accepted: 23 January 2017; Published: 25 January 2017

Abstract: A new 1D Cd(II) coordination polymer, $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$ (HL = *N*-nicotinoylglycine), has been synthesized by the assembly of $Cd(NO_3)_2 \cdot 4H_2O$ with *N*-nicotinoylglycine, and its composition was determined by elemental analysis, infrared, and X-ray single-crystal diffraction analysis. In this complex, the Cd(II) is seven-coordinated by two N atoms of two *N*-nicotinoylglycine anions, four O atoms of two *N*-nicotinoylglycine anions, and one O atom of a coordinated water molecule. The complex forms a 1D looped coordination polymer by the bridging of the *N*-nicotinoylglycine anion. The luminescent property of the *N*-nicotinoylglycine ligand and the Cd(II) coordination polymer has also been studied.

Keywords: *N*-nicotinoylglycine; Cd(II) coordination polymer; synthesis; crystal structure; luminescence

1. Introduction

Metal-organic coordination polymers have received great attention as an important part of coordination chemistry. Many of them that are constructed by Cd(II) ions or bridging multipodal ligands show unique structures and excellent properties in gas storage, luminescence, catalysis, and magnetism [1–7]. In the past decades, many multipodal ligands containing two $-COO^-$ functional groups and neutral ligands, such as 4,4'-bipyridine and 1,10-phenanthroline, have been chosen to build coordination polymers [8–13]. Recently, our group has obtained some new Cd(II), Ca(II), Mg(II), and Zn(II) coordination polymer materials and have investigated their structures and properties [14–18]. In order to investigate the coordination behavior of ligands containing both $-COO^-$ and pyridine bifunctional groups and the property of their metal complexes, herein, a new 1D Cd(II) coordination polymer, $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$ (HL = *N*-nicotinoylglycine) has been synthesized and its luminescent property in the solid state has also been investigated. The chemical diagram of the Cd(II) complex is shown in Scheme 1.



Scheme 1. Chemical diagram of the Cd(II) complex.

2. Results and Discussion

2.1. Characterization of $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$

A comparison of the *N*-nicotinoylglycine ligand and Cd(II) complex was conducted with infrared data, and the ligand shows two characteristic absorption bands at 1725 cm^{-1} (ν (COO^-)) and 1634 cm^{-1} (ν (C(O)-NH)), and at 1675 cm^{-1} (ν (COO^-)) and 1636 cm^{-1} (ν (C(O)-NH)), respectively. The shift of COO^- is 50 cm^{-1} , indicating that the oxygen atom of the COO^- group coordinated to Cd(II). However, The shift of C(O)-NH is 2 cm^{-1} , indicating that the oxygen atom of the C(O)-NH group does not coordinate to Cd(II). The band at 3256 cm^{-1} proves that the Cd(II) complex contains water molecules [19].

2.2. Structural Description of $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$

The coordination environment of the Cd(II) ion in $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$ is shown in Figure 1. Selected bond distances and bond angles are given in Table 1. Its crystal structure shows that each Cd(II) ion is seven-coordinated by four O atoms from two carboxyl group of two different *N*-nicotinoylglycine anion ligands, two N atoms from two different *N*-nicotinoylglycine anion ligands, and one O atom from a coordinated water molecule. Each Cd(II) ion adopts a distorted pentagonal bipyramidal coordination environment. The carboxyl groups of *N*-nicotinoylglycine anion ligands adopt a didentate coordination mode in the complex molecule. The distances of $\text{Cd} \cdots \text{Cd}$ separated by *N*-nicotinoylglycine anion ligands are 10.064 \AA and 9.933 \AA , respectively.

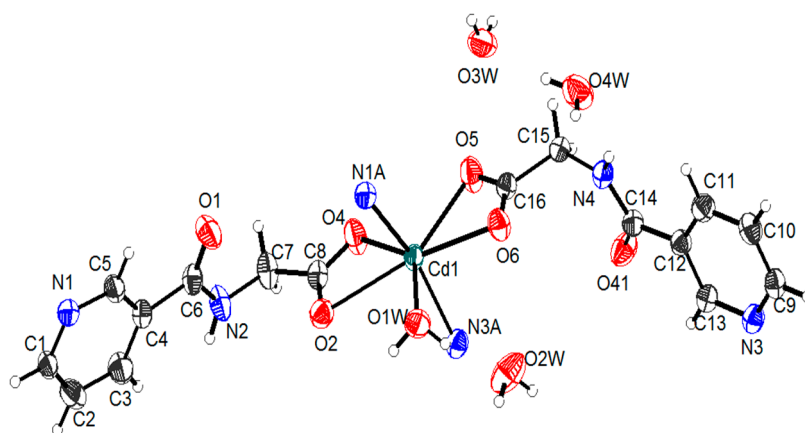


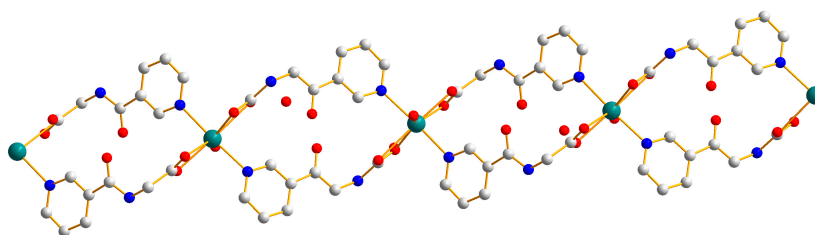
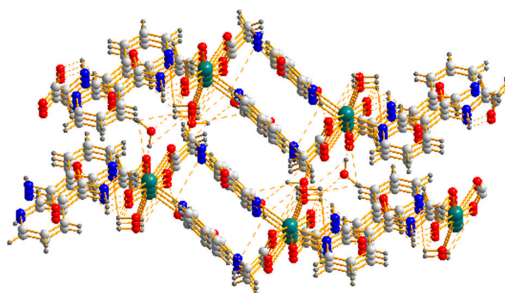
Figure 1. The coordination environment of the Cd(II) ion.

Table 1. Selected bond lengths d (Å) and bond angles ($^\circ$) for $[\text{CdL}_2(\text{H}_2\text{O})] \cdot (\text{H}_2\text{O})_3]_n$.

Bond	d	Bond	d
Cd1-O4	2.283(3)	Cd1-O6	2.337(3)
Cd1-N1 ⁱ	2.357(3)	Cd1-O1W	2.361(3)
Cd1-N3 ⁱⁱ	2.370(3)	Cd1-O5	2.493(3)
Cd1-O2	2.609(3)	C6-O1	1.222(5)
C8-O2	1.229(5)	C8-O4	1.267(5)
C16-O5	1.251(5)	O6-C16	1.234(5)
C1-N1	1.337(5)	C5-N1	1.336(5)
C6-N2	1.330(5)	N2-C7	1.441(5)
N3-C13	1.331(5)	N3-C9	1.350(5)
N4-C14	1.327(5)	N4-C15	1.442(5)
C16-C15	1.517(5)	C2-C1	1.378(6)
C3-C2	1.383(6)	C4-C3	1.385(5)
C4-C5	1.380(5)	C4-C6	1.501(5)
C7-C8	1.528(5)	C9-C10	1.383(6)
C10-C11	1.379(6)	C11-C12	1.389(5)
Angle	ω	Angle	ω
O4-Cd1-O6	138.27(11)	O4-Cd1-N1 ⁱ	94.26(12)
O6-Cd1-N1 ⁱ	94.80(11)	O4-Cd1-O1W	138.23(11)
O6-Cd1-O1W	83.50(11)	O1W-Cd1-N1 ⁱ	79.14(12)
O4-Cd1-N3 ⁱⁱ	95.42(12)	O6-Cd1-N3 ⁱⁱ	87.58(11)
N1 ⁱ -Cd1-N3 ⁱⁱ	162.55(12)	O1W-Cd1-N3 ⁱⁱ	83.98(11)
O5-Cd1-O4	84.67(11)	O5-Cd1-O6	53.62(10)
N1 ⁱ -Cd1-O5	100.70(12)	O5-Cd1-O1W	137.09(10)
N3 ⁱⁱ -Cd1-O5	94.63(12)	O4-Cd1-O2	52.62(10)
O6-Cd1-O2	168.53(10)	O2-Cd1-N1 ⁱ	86.89(11)
O1W-Cd1-O2	85.69(10)	O2-Cd1-N3 ⁱⁱ	87.49(11)
O5-Cd1-O2	137.20(10)		

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

In the crystal, the looped structure is formed by the bridging of *N*-nicotinoylglycine anion ligands (Figure 2). The 3D network is generated by $\pi \cdots \pi$ stacking and hydrogen bond interactions (Figure 3).

**Figure 2.** One-dimensional chained structure by the bridging of ligands.**Figure 3.** 3D supramolecular network structure.

2.3. Luminescent Property

The luminescent behaviors of $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$ and the free ligand are investigated in the solid state on a multicrystalline bulk sample. The luminescent spectrum of the Cd(II) coordination polymer is shown in Figure 4. The Cd(II) coordination polymer shows a luminescent peak at 458 nm when excited at 358 nm, however, the *N*-nicotinoylglycine ligand does not have a luminescent peak. Thus, the luminescent emission of the Cd(II) coordination polymer may be due to the charge transfer of ligand-to-metal [20].

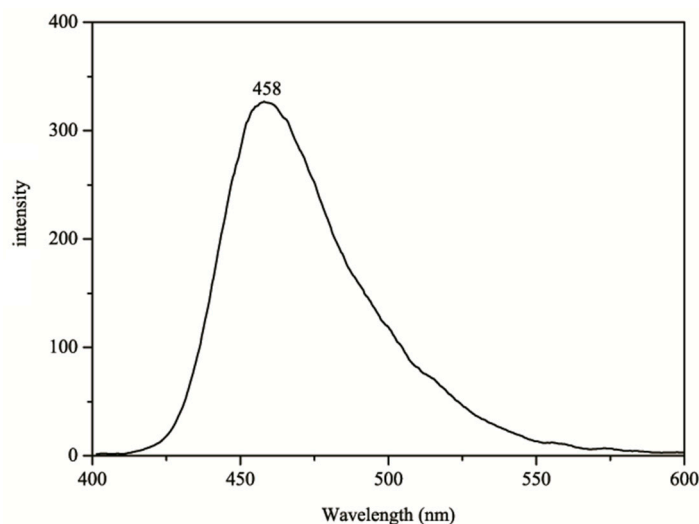


Figure 4. The luminescent spectrum of the Cd(II) coordination polymer.

3. Experimental Section

3.1. Materials and Instrumentation

N-nicotinoylglycine and $Cd(NO_3)_2 \cdot 4H_2O$ were purchased from Xi'ya Chemical Reagent Company and used as received. C, H, and N were determined on a Elementar Vario III EL elemental analyzer (Hanau, Germany). IR spectra were recorded on a Nicolet AVATAR 360 FTIR spectrophotometer (Nicolet Instrument Inc., Madison, WI, USA) (range 4000 cm^{-1} – 400 cm^{-1}) as KBr discs. Crystal structure of $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$ was determined on a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA). Luminescent spectra were recorded on a PE LS-55 spectrometer (PerkinElmer, Billerica, MA, USA).

3.2. Synthesis of $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$

A CH_3CH_2OH/H_2O ($v:v = 3:1$) solution of *N*-nicotinoylglycine (0.1802 g, 1.0 mmol) and NaOH (0.040 g, 1.0 mmol) was stirred to clarify, then a water solution (3 mL) of $Cd(NO_3)_2 \cdot 4H_2O$ (0.3085 g, 1.0 mmol) was added to the above mixture. The mixture was stirred for 5 h at 60°C and filtered. Colorless crystals suitable were obtained after 10 days by evaporation at room temperature. Yield 52%. Anal. Calcd. for $C_{16}H_{22}N_4O_{10}Cd$: C, 35.37; H, 4.05; N, 10.32. Found: C, 35.15; H, 4.47; N, 10.11. IR ν_{\max} (cm^{-1}): $\nu(H_2O)$: 3256 cm^{-1} , $\nu(COO^-)$: 1675 cm^{-1} , $\nu(C(O)-NH)$: 1636 cm^{-1} .

3.3. Crystal Structure Determination

Crystal data of $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$ were collected on a Bruker Smart APEX CCD diffractometer at 293(2) K using graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The structure was solved by direct method using the SHELX program [21], and refined by full-matrix

least squares on F^2 using the SHELXL program [22]. Technical details of the crystal structure solutions and refinements are listed in Table 2.

Table 2. Crystallographic data and structure refinement for $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$.

Empirical Formula	$C_{16}H_{22}N_4O_{10}Cd$
Formula weight	542.77
Temperature/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
$a/\text{\AA}$	8.3460(17)
$b/\text{\AA}$	8.5186(17)
$c/\text{\AA}$	16.727(3)
$\alpha/^\circ$	100.90(3)
$\beta/^\circ$	94.89(3)
$\gamma/^\circ$	116.16(3)
Volume/ \AA^3	1028.8(4)
Z	2
$\rho_{\text{calc}}/\text{mg}/\text{mm}^3$	1.752
μ/mm^{-1}	1.124
S	1.211
$F(000)$	548
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-21 \leq l \leq 18$
Reflections collected	9521
Independent reflections	4531 [$R(\text{int}) = 0.0293$]
Data/restraints/parameters	4531/14/304
Goodness-of-fit on F^2	1.212
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0381$, $wR_2 = 0.1024$
Final R indexes [all data]	$R_1 = 0.0442$, $wR_2 = 0.1055$
Largest diff. peak/hole/ $e \cdot \text{\AA}^{-3}$	1.460/−0.598

4. Conclusions

In summary, $[\{CdL_2(H_2O)\} \cdot (H_2O)_3]_n$ has been prepared and characterized by elemental analysis, infrared, and X-ray single-crystal diffraction analysis. The Cd(II) complex forms a 1D helix coordination polymer by the bridging of the *N*-nicotinoylglycine anion. The 3D network is generated by $\pi \cdots \pi$ stacking interactions. The luminescent property of the *N*-nicotinoylglycine ligand and the Cd(II) coordination polymer has also been studied.

Acknowledgments: This project was supported by the National Natural Science Foundation of China (No. 21171132), the National Natural Science Foundation of Shandong (ZR2014BL003), the Project of Shandong Province Higher Educational Science and Technology Program (J14LC01) and Science Foundation of Weifang.

Author Contributions: Tai Xi-Shi designed the method and wrote the manuscript. Wang Xin synthesized the Cd(II) coordination polymer. Li Peng-Fei analysed the crystal data of Cd(II) coordination polymer.

Conflicts of Interest: The authors confirm that this article content has no conflict of interest.

Appendix A

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1470820. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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