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研究简报

镉(Ⅱ)与对乙酰氨基苯甲酸、4,4′-联吡啶配位聚合物的合成、晶体结构及荧光性质

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关键词:镉(Ⅱ)配合物;对乙酰氨基苯甲酸;液层扩散法;晶体结构

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Synthesis, Crystal Structure and Fluorescence Characterization of Cadmium(Ⅱ) Coordination Polymer with 4-Acetamidobenzoic Acid and 4,4′-Bipyridine

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Abstract: The complex $\{[Cd_2(C_9H_8O_3N)_2(CH_3COO)_2(4,4'\text{-bipy})_2]\cdot(4,4'\text{-bipy})\cdot(H_2O)_4\}_n$ with 4-acetamidobenzoic acid and 4,4′-bipyridine has been synthesized with liquid diffusion method and characterized. It crystallizes in the monoclinic space group *C*2/*c*. The crystal structure shows that two neighboring cadmium(Ⅱ) ions are linked together by two bridging acetic acid radicals, forming a binuclear structure. Adjacent binnuclear structure is linked together by two bridging 4,4′-bipy molecules and the complex molecule forms an one-dimensional double-chain structure. The luminescent properties of the complex were studied. CCDC: 734878.

Key words: cadmium(Ⅱ) complex; 4-acetamidobenzoic acid; liquid diffusion method; crystal structure

In recent years, the design and assembly of coordination polymers with 1-, 2- or 3-dimensional ordered structure has been one of the briskest studies on supramolecular chemistry[1,2]. 4,4′-bipyridine, as a rigid linear bridging ligand, is often used in the design and construction of multi-dimensional coordination polymers. Many academic reports have referred to complexes with the ligands of 4,4′-bipyridine and carboxylic acid, but the carboxylic acids in these complexes are mostly rigid aromatic polycarboxylic acids[3~7]. Complexes with the ligands of 4,4′-bipyridine and rigid aromatic monocarboxylic acid are relatively few in chemical literature. 4-acetylaminobenzoic acid is a rigid aromatic monocarboxylic acid containing nitrogen atom. With its multiple coordination sites and potential hydrogen-bond identification points, it can be used as a ligand to construct new complexes[8]. With the aim of preparing stable functional coordination polymer, we have synthesized a compound $\{[Cd_2(C_9H_8O_3N)_2(CH_3COO)_2(4,4'\text{-bipy})_2]\cdot(4,4'\text{-bipy})\cdot(H_2O)_4\}_n$ in the way of liquid

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diffusion and determined structurally by means of X-ray diffraction crystal structure analysis. It is a new one-dimensional double-chain structure complex with 4,4′-bipyridine and 4-acetamidobenzoic acid as ligands.

1 Experimental

1.1 Reagents and instruments

4,4′-bipyridine and 4-acetamidobenzoic acid are analytically pure grade; acetic acid, triethylamine and $CdSO_4$ are chemically pure grade. IR spectra were recorded on Shimadzu FTIR-8700 spectrometer with KBr pellets in the 4 000~400 cm^{-1} regions. Crystal structure determination was carried out on a Bruker SMART 1000 CCD diffractometer. C, H, N analysis was performed on a PE-2400(Ⅱ) apparatus. Melting point measurement was executed on a XT4 binocular micromelting point apparatus (Beijing). Excitation and luminescence spectra were performed on a WGY-10 fluorescence spectrophotometetr (Tianjin).

1.2 Synthesis of the title complex

A mixture of $CdSO_4$ (2.0 mmol) and 4,4′-bipyridine (3.5 mmol) was dissolved in CH_3OH (12 mL) and placed in a 25 mL tube. 4-Acetamidobenzoic acid (2.0 mmol) was added to 6 mL mixed solvent of C_2H_5OH/H_2O (volume ratio: 2:1), then resultant mixture whose pH was adjusted to 5.5~6.5 with triethylamine and acetic acid was also transferred to the 25 mL tube along the wall of tube with care, which was sealed and undisturbed at room temperature. The yellow crystals suitable for X-ray diffraction were obtained after a month. Anal. Calcd. for $C_{52}H_{54}Cd_2N_8O_{14}$(%): C,50.39, H, 4.36, N, 9.04; found(%): C, 50.29, H, 4.34, N, 9.01. m.p.: 239.5~240.5 ℃. IR (ν/cm^{-1}): 3 406(s), 1 662(vs), 1 604(vs), 1 566(vs) 1 533(s), 1 412(s), 1 221(m), 1 007(m), 806(s), 630(s), 492(w), 413(w).

1.3 Crystal structure determination

A crystal with dimensions of 0.41 mm×0.23 mm×0.22 mm was put on Bruker SMART CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) by using φ-ω scan mode at 291(2) K. Total of 20 173 reflections were collected in the range of $2.32° \leqslant \theta \leqslant 25.50°$, of which 5 124 were independent with R_{int}=0.028 2, and 4 249 with $I>2\sigma(I)$ were considered as observed. Corrections for Lp factors and empirical adsorption adjustment were applied. The crystal structure was solved with direct method using SHELXS-97 program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinement including hydrogen atoms converged to R_1=0.028 6, wR_2=0.073 9, $w=1/[s^2(F_o^2)+(0.045\,0P)^2+1.910\,0P]$, where $P=(F_o^2+2F_c^2)/3$, and $(\Delta/\sigma)_{max}$=0.000, S=1.054, $(\Delta\rho)_{max}$=396 e·nm^{-3} and $(\Delta\rho)_{min}$=−294 e·nm^{-3}. Crystallographic data of the complex are shown in Table 1.

CCDC: 734878.

Table 1　Crystallographic data for the complex

Empirical formula	$C_{52}H_{54}Cd_2N_8O_{14}$	D / (g·cm^{-3})	1.493
Formula weight	1 239.83	Z	4
Size / mm	0.41×0.23×0.22	F(000)	2520
θ range for data collection / (°)	2.32~25.50	μ (Mo $K\alpha$) / mm^{-1}	0.841
Crystal system	Monoclinic	Reflections collected	20173
Space group	$C2/c$	Independent reflections	5 124 (R_{int}=0.028 2)
a / nm	2.738 9(3)	Final GooF	1.054
b / nm	1.172 52(14)	R_1, wR_2 [$I>2\sigma(I)$]	0.028 6, 0.073 9
c / nm	1.760 6(2)	R_1, wR_2 (all data)	0.038 0, 0.080 6
β / (°)	102.642(2)	Largest difference peak and hole / (e·nm^{-3})	396, −294
V / nm^3	5.516 9(11)		

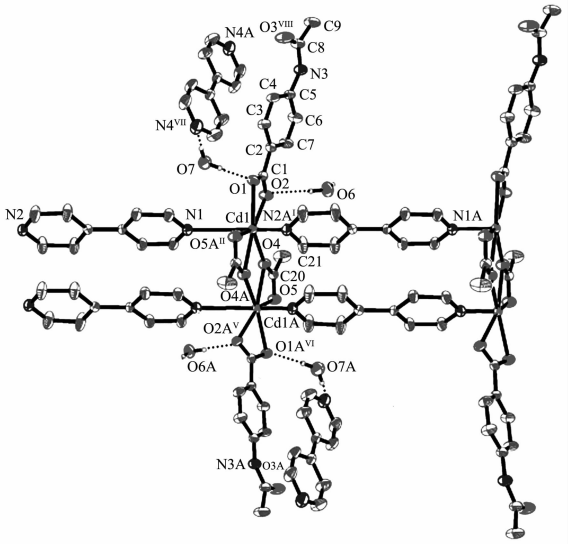
2 Results and discussion

2.1 Crystal structure of the complex

The crystal structure of the complex is revealed in Fig.1, and the main bond lengths and bond angles of the complex are shown in Table 2, Hydrogen bond lengths and bond angles are shown in Table 3.

As shown in Fig.1, in the complex, two acetic acid

radicals coordinate with two Cd(Ⅱ) ions by chelating-bridging tridentate way, respectively, and they surround two Cd(Ⅱ) to form a binuclear structure. Adjacent binuclear structure is linked together by two bridging 4,4′-bipy molecules to form an one-dimensional double-chain structure.



I x, y+1, z; II $-x$+2, y, $-z$+1/2; V $-x$+1, y, $-z$+3/2; VI $-x$+1, $-y$+2, $-z$+1; VII x, $-y$+1, z+1/2; VIII x−1/2, $-y$+3/2, z+1/2

Fig.1 Crystal structure of the complex

Each Cd(Ⅱ) ion is coordinated with two oxygen atoms from one 4-acetamidobenzoic acid radical, three oxygen atoms from two acetic acid radicals and two nitrogen atoms from two 4,4′-bipy molecules to give a seven-coordinated distorted pentagonal bipyramid coordination geometry, where O(1), O(2), O(4), O(4A) and O (5A) locate at equator position and N (1) and N (2A) locate at axial position. Here, the sum of the angles O(1)-Cd(1)-O(2), O(2)-Cd(1)-O(4), O(4)-Cd(1)-O(4A), O(4A)-Cd(1)-O(5A) and O(5A)-Cd(1)-O(1) is 359.96°. Strong hydrogen bonds can be observed in the title complex. Hydrogen bonds are shaped by oxygen atom and nitrogen atom of 4-acetamidobenzoic acid radical and neighboring H proton of uncoordinated H_2O. In addition, Uncoordinated 4,4′-bipy molecules exist in the complex via hydrogen bonds.

Table 2 Selected bond lengths (nm) and bond angles (°) of the complex

Cd(1)-N(1)	0.231 3(2)	Cd(1)-O(1)	0.235 96(19)	Cd(1)-O(5A)II	0.245 9(2)
Cd(1)-N(2A)I	0.233 0(2)	Cd(1)-O(2)	0.240 9(2)	O(4)-Cd(1A)II	0.242 1(2)
Cd(1)-O(4)	0.234 0(2)	Cd(1)-O(4A)II	0.242 1(2)	O(5)-Cd(1A)II	0.245 9(2)
N(1)-Cd(1)-N(2A)I	177.19(8)	O(4)-Cd(1)-O(2)	89.69(7)	O(2)-Cd(1)-O(4A)II	163.22(7)
N(1)-Cd(1)-O(4)	89.29(7)	O(1)-Cd(1)-O(2)	54.95(7)	N(1)-Cd(1)-O(5A)II	91.44(7)
N(1)-Cd(1)-O(1)	94.53(7)	N(1)-Cd(1)-O(4A)II	89.78(7)	O(4A)II-Cd(1)-O(5A)II	52.87(7)
O(4)-Cd(1)-O(1)	144.42(7)	O(4)-Cd(1)-O(4A)II	73.54(8)	O(4)-Cd(1)-O(5)II	126.40(7)
N(1)-Cd(1)-O(2)	90.82(7)	O(1)-Cd(1)-O(4A)II	141.68(7)	O(1)-Cd(1)-O(5A)II	88.91(7)

Symmetry transformation used to generate equivalent atoms: I x, y+1, z; II $-x$+2, y, $-z$+1/2.

Table 3 Hydrogen bond lengths and bond angles

D–H…A	D-H / nm	H–A / nm	D…A / nm	∠DHA / (°)
N(3)–H(3D)…O(7)V	0.086	0.200	0.286 0(3)	173.4
O(7)–H(4W)…O(1)VI	0.083	0.208	0.289 8(3)	170.7
O(7)–H(3W)…N(4)VII	0.083	0.200	0.282 2(4)	168.6
O(6)–H(2W)…O(3)VIII	0.083	0.210	0.290 2(3)	162.6
O(6)–H(1W)…O(2)V	0.083	0.204	0.286 9(3)	176.8

Symmetry transformations used to generate equivalent atoms: V $-x$+1, y, $-z$+3/2; VI $-x$+1, $-y$+2, $-z$+1; VII x, $-y$+1, z+1/2; VIII x−1/2, $-y$+3/2, z+1/2.

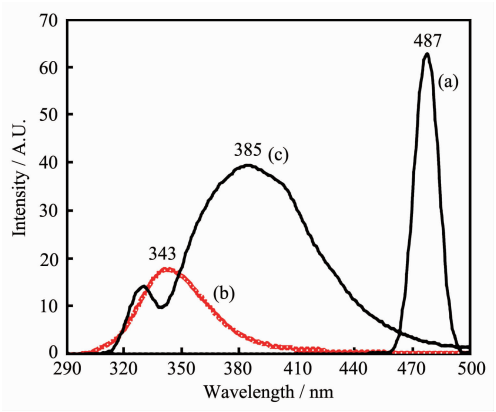
2.2 IR spectrum of the title complex

The wide adsorption peak at about 3 406 cm^{-1} is characteristic peak of OH group of H_2O. Two strong peaks at 1 604 and 1 533 cm^{-1} could be assigned to the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ stretching vibration of carboxyl in 4-acetamidobenzoic acid ligand. The $\Delta\nu[\nu_{as}(COO^-)-\nu_s(COO^-)]$ is 71.4 cm^{-1}, indicating that carboxyl of 4-acetamidobenzoic acid adopts a bi-dentate chelating coordination mode with Cd(Ⅱ)[9,10]. Besides, ν_{as} and ν_s stretching vibration peaks of carboxyl in acetic acid

shift from 1 714, 1 414 cm^{-1} to 1 662, 1 566, and 1 412 cm^{-1} respectively, suggesting an obvious shift. As far as 4,4′-bipy, its adsorption peaks are 806 and 630 cm^{-1} respectively. The above analysis is consistent with crystal structure.

2.3 Luminescence properties

The emission spectra of 4-acetamidobenzoic acid, 4,4′-bipy and the title complex in CH_3CH_2OH at the room temperature are shown in Fig.2. The complex displays a blue fluorescence emission maximum at 478 nm (λ_{ex}=473 nm), however, the maximum emission wavelength of 4-acetamidobenzoic acid and 4,4′-bipy are 343 nm (λ_{ex}=308 nm) and 385 (λ_{ex}=238 nm), respectively. The luminescence emission of the complex can probably be assigned to the intraligand (π-π^*) fluorescent emission of ligands since the cadmium (Ⅱ) ion is difficult to oxidize or to reduce due to its d^{10} configuration. Compared with the free ligands, the enhancement and significant red-shift of the emission occurs in the title complex, which is probably due to the chelating of the ligands to the metal ion which effectively increase the rigidity of the ligands.



a: Title complex; b: 4-acetamidobenzoic acid; c: 4,4′-bipy

Fig.2　Emission spectra of the title complex and ligands

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