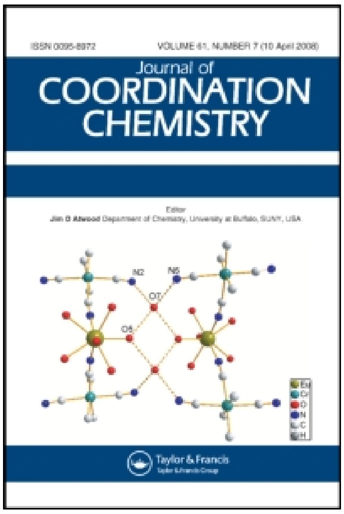

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Synthesis, crystal structure and fluorescent property of a novel one-dimensional chain coordination polymer generated from cadmium(II) and bridging ligand carbamyldicyanomethanide anion

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SYNTHESIS, CRYSTAL STRUCTURE AND FLUORESCENT PROPERTY OF A NOVEL ONE-DIMENSIONAL CHAIN COORDINATION POLYMER GENERATED FROM CADMIUM(II) AND BRIDGING LIGAND CARBAMYLDICYANOMETHANIDE ANION

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The novel one-dimensional chain coordination polymer $\{[\mathrm{Cd}(cda)_2\mathrm{H_2O}]\cdot\mathrm{H_2O}\}_n$ (cda = carbamyldicyanomethanide anion) has been synthesized and its crystal structure determined by X-ray crystallography. The complex crystallizes in a triclinic system with a space group $P\bar{1}$ and $a = 7.217(2)$, $b = 7.641(2)$, $c = 11.806(3)$ Å, $\alpha = 79.403(4)$, $\beta = 79.859(4)$, $\gamma = 72.028(4)^\circ$. The cadmium(II) ion is coordinated by four nitrogen atoms from four nitrile groups and two oxygen atoms, one from an amide group and one from a water molecule. The coordination environment of the cadmium(II) is a distorted octahedron. The bridging ligand *cda* displays two coordination modes, $\mu_{1,5}$-*cda* and μ_3-*cda*, and a one-dimensional chain is formed through these two kinds of coordination. A solution of the coordination polymer exhibits strong fluorescence.

Keywords: Synthesis; Crystal structure; Cadmium complex; Fluorescence; Polynitrile bridging ligand

INTRODUCTION

Polynitrile ligands, such as TCNE [1–5], TCNB [6,7], TCNQ [8–13], TCNP, tcm [14–16], dca [17–24] and so on [25–30], are ideal multi-functional ligands; many complexes with polynitriles as ligand and electron acceptors have displayed significant magnetic properties [1] and a few exhibit electrical conductivities [31–33] and microporous structure [6]. Complexes of Zn(II), Co(II), Ni(II) and Cu(II) with carbamyldicyanomethanide as a polynitrile ligand have been reported [34,35], but the crystal structures and physical properties of these complexes were not reported. Interest in the excellent physical properties of polynitrile compounds resulted in synthesis and characterization of a few complexes [36–41] with *cda* as a bridging and terminal ligand. Here we report a novel *cda*-bridged one-dimensional cadmium(II) chain with its crystal structure and fluorescent property.

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EXPERIMENTAL

Materials

Sodium carbamyldicyanomethanide [Na(*cda*)] was prepared according to the literature [42]. Other chemicals were analytical grade and used without further purification.

Synthesis of the Complex

The one-dimensional complex $\{[Cd(cda)_2H_2O]\cdot H_2O\}_n$ was prepared as follows. Hydrated cadmium perchlorate (0.5158 g, 1.23 mmol) and Na(*cda*) (0.3264 g, 2.49 mmol,) were separately dissolved in $20\,cm^3$ H_2O, and the two solutions were mixed and stirred for a few minutes. Colorless single crystals were obtained after the solution was kept at room temperature for about a week. (Yield: 0.3812 g, 85%). Anal. calcd. for $C_8H_8CdN_6O_4$(%): C, 26.35; H, 2.21; N, 23.06; Cd, 30.83. Found: C, 26.30; H, 2.12; N, 23.41; Cd, 30.54.

Physical Measurements

The IR spectra were recorded with a Shimadzu 408 IR spectrophotometer using KBr discs. Thermogravimetric analysis was carried out under flowing argon at a heating rate of 10°C/min on a Perkin-Elmer TGA-7 instrument. C, H and N elemental analyses were carried out on a Perkin-Elmer instrument, Model 240. The fluorescence spectra were obtained on a Perkin-Elmer LS-50 fluorescence spectrophotometer.

Crystal Structure Determination

A single crystal with dimensions $0.50 \times 0.40 \times 0.25$ mm was selected and its structure determined using graphite-monochromated Mo Kα radiation ($\lambda = 0.7103$ Å) on a Bruker Smart-1000 diffractometer using the ω scan mode. A total of 3165 reflections were collected in the range of $1.77 \leq \theta \leq 25.02°$ at 293(2) K, of which 2102 reflections were independent [R(int) = 0.0114] and 2025 reflections with $I > 2\sigma(I)$ were used in the succeeding refinement. Corrections for Lorentz and polarization factors were applied and all nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from a difference Fourier map and refined isotropically using the riding model with displacement parameters. The final refinement including hydrogen atoms converged to $R = 0.0215$ and $wR = 0.0571$, $w = 1/[\sigma^2(F_o)^2 + (0.0336P)^2 + 0.4408P]$ where $P = (F_o^2 + 2F_o^2)/3$, $S = 1.103$, $(\Delta\rho)_{\max} = 0.349\,e/Å^3$, $(\Delta\rho)_{\min} = -0.567\,e/Å^3$, $(\Delta/\sigma)_{\max} = 0.001$. The programs for structure solution and refinement are SHELXS97 and SHELXL97, respectively.

RESULTS AND DISCUSSION

Crystal Structure

$C_8H_8CdN_6O_4$, $M = 364.60$, triclinic, space group $P\bar{1}$, $a = 7.217(2)$. $b = 7.641(2)$, $c = 11.806(3)$ Å, $\alpha = 79.403(4)$, $\beta = 79.859(4)$, $\gamma = 72.028(4)°$, $V = 603.7(3)$ Å^3, $Z = 2$,

$D_c = 2.006\,\mathrm{g\,cm^{-3}}$, $F(000) = 356$, $\mu(\mathrm{MoK_\alpha}) = 1.830\,\mathrm{mm^{-1}}$. Selected bond distances and angles are listed in Table I.

Figure 1 shows the coordination diagram of the complex with the atom numbering scheme. The Cd(II) ion is coordinated by two oxygen atoms and four nitrogen atoms. One oxygen atom is from H_2O and the other from amide, and the four nitrogen atoms are from four nitrile-nitrogen groups. The bond lengths and the associated angles indicate that the Cd(II) ion lies in a distorted octahedral environment. Two kinds of coordination mode exist for *cda* anions. The first has the *cda* anion as a bidentate $\mu_{1,5}$-bridging ligand providing two nitrile-nitrogen atoms to coordinate two Cd(II) ions, identical with that of the one-dimensional zinc(II) complex [38] and the one-dimensional copper(II) complex [39]. This coordination mode is different from that in the europium(III) complex [37], in which *cda* acts as a bidentate $\mu_{1,5}$-bridging ligand and coordinates two europium(III) ions through one nitrile nitrogen atom and one amide oxygen atom. The second coordination mode has the *cda* anion as a tridentate μ_3-bridging ligand coordinating three Cd(II) ions through two nitrile-nitrogen

TABLE I Selected bond lengths (Å) and bond angles (°) for the complex

Cd(1)–N(5)	2.271(3)	Cd(1)–N(6A)	2.281(3)
Cd(1)–N(2)	2.287(3)	Cd(1)–N(3A)	2.321(3)
Cd(1)–O(3)	2.328(3)	Cd(1)–O(1B)	2.367(2)
N(5)–Cd(1)–N(6A)	94.86(10)	N(5)–Cd(1)–N(2)	179.26(11)
N(6A)–Cd(1)–N(2)	85.52(11)	N(5)–Cd(1)–N(3A)	86.69(10)
N(6A)–Cd(1)–N(3A)	178.44(9)	N(2)–Cd(1)–N(3A)	92.94(10)
N(5)–Cd(1)–O(3)	92.95(12)	N(6A)–Cd(1)–O(3)	93.73(13)
N(2)–Cd(1)–O(3)	86.40(13)	N(3A)–Cd(1)–O(3)	86.34(12)
N(5)–Cd(1)–O(1B)	89.75(9)	N(6A)–Cd(1)–O(1B)	89.32(10)
N(2)–Cd(1)–O(1B)	90.89(10)	N(3A)–Cd(1)–O(1B)	90.53(9)
O(3)–Cd(1)–O(1B)	175.74(11)		

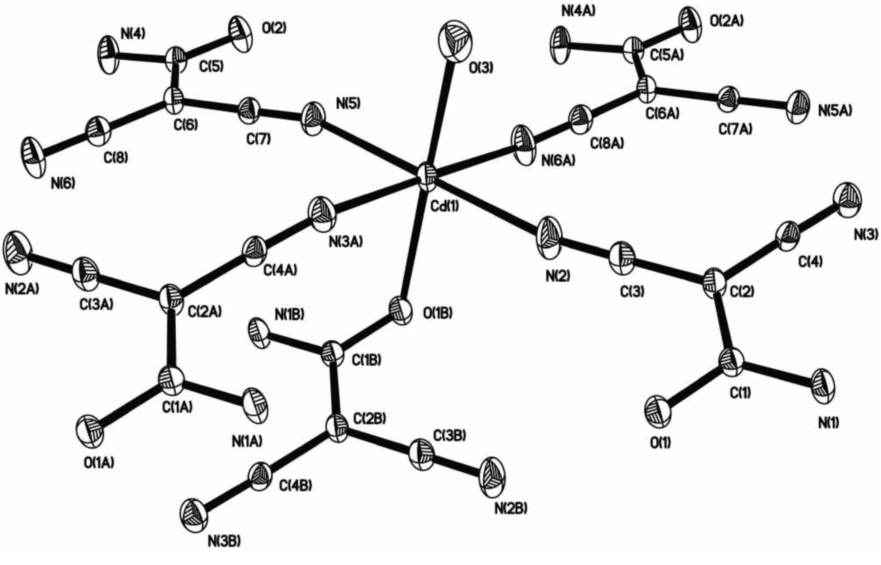

FIGURE 1 The coordination diagram of the complex with atom numbering scheme.

atoms and one amide-oxygen atom. In the three-dimensional manganese(III) complex [40] *cda* also shows this coordination mode. The cadmium complex is the first example in which *cda* exhibits two bridging coordination modes. Generally the coordination ability of amide-oxygen is very weak and it rarely takes part in coordination. The coordination of the amide-oxygen atom indicates that there exists strong conjugation in μ_3-*cda*. Figure 2 shows the one-dimensional chain structure consisting of two branched one-dimensional chains. The coordination bonding from the amide-oxygen atoms links the two branched one-dimensional chains into a single one-dimensional chain. Figure 3 shows the unit cell and crystal packing viewed from the *b* direction. In the crystal the one-dimensional chains lie parallel along the *b* axis, to form a sheet in the *bc* plane. The three-dimensional structure is constructed through sheets piling up along the *a* axis. The CCDC deposition number of this crystal is 161871.

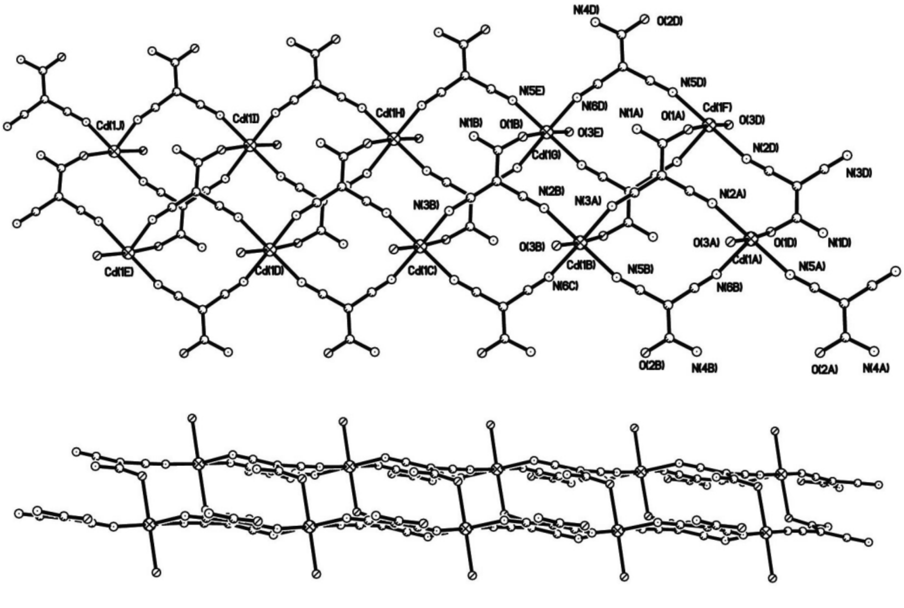

FIGURE 2 Diagrams of the one-dimensional chain viewed from a different direction.

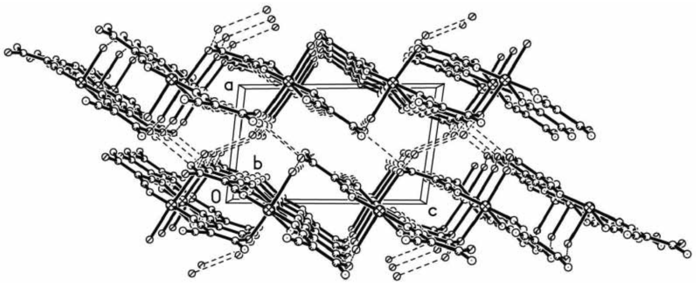

FIGURE 3 The unit cell and the arrangement of one-dimensional chains in the crystal viewed from the *b* direction.

Infrared Spectrum

Compared with the band of Na(*cda*), the characteristic bands of –C≡N have shifted from 2160 and 2200 cm^{-1} to 2152 and 2190 cm^{-1}. The sharp peaks at 3220, 3320 and 3455 cm^{-1} for $\nu(NH_2)$ were replaced by a strong and broad band at 3400 cm^{-1}. This band arises from vibration of H_2O and masks the peaks of $\nu(NH_2)$. The intense bands at 1440, 1560 and 1660 cm^{-1} for $-CONH_2$ have shifted to 1415, 1575 and 1650 cm^{-1}. The peak shapes of –CN and $-CO(NH_2)$ groups of the present complex are similar to those of other *cda*-bridging complexes [37–40], but the peak positions exhibit small shifts.

Thermogravimetric Analysis

Thermogravimetric analysis of the complex was carried out under flowing argon at a heating rate of 10°C/min. The amount of sample used was 3.705 mg and the temperature ranged from 50 to 419°C. From 50.00 to 226.78°C the weight loss is 10.57% indicating that both uncoordinated and coordinated H_2O were lost; intense loss of the H_2O began at about 140°C and ended at approximately 190°C. The ligand decomposed at about 260°C.

Fluorescence

The fluorescence spectra for Na(*cda*) and the complex were measured in aqueous solution at room temperature. The excited wavelength is 360 nm both for Na(*cda*) (1.5×10^{-3} M) and the complex (9.6×10^{-4} M).

The fluorescent experiment indicates that the maximum emission wavelengths are 409 nm for Na(*cda*) and 407 nm for the complex. Figure 4 shows the fluorescence spectra. Both fluorescence peak shapes are similar and the peak positions are very close, implying that the fluorescence emission of the complex comes from *cda*. The

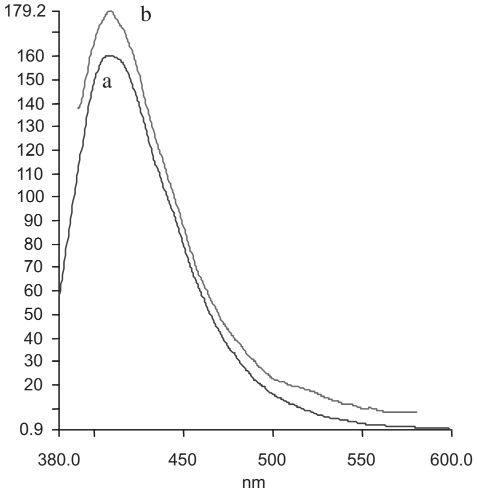

FIGURE 4 Fluorescence spectra of a, Na(*cda*); b, the complex.

fluorescence spectrum of the present complex is very similar to that of a zinc(II) complex, indicating that the fluorescence emission mechanism is also identical with that of zinc(II) complex [38].

Acknowledgment

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