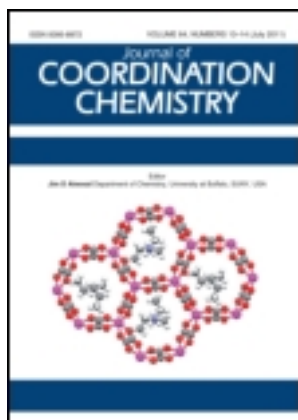


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Li-Ran Jia^a, Min Hu^a, Shao-Ming Fang^a & Chun-Sen Liu^a

^a Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Zhengzhou, Henan 450002, P.R. China

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Two Cd(II) complexes with xanthene-9-carboxylate ligand: syntheses, crystal structures, and emission properties

LI-RAN JIA, MIN HU, SHAO-MING FANG and CHUN-SEN LIU*

Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Zhengzhou, Henan 450002, P.R. China

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Two new Cd^{II} complexes, [Cd(L)₂(CH₃OH)₂]_∞ (**1**) and [Cd(L)₂(pyz)(H₂O)]_∞ (**2**), have been prepared by the reaction of xanthene-9-carboxylic acid (HL) and Cd(ClO₄)₂·6H₂O in the presence or absence of pyz co-ligand (L = xanthene-9-carboxylate and pyz = pyrazine). Their structures were determined by single-crystal X-ray diffraction. Complex **1** possesses a 1-D zigzag chain structure, whereas **2** has a 1-D linear chain that is further assembled into a 2-D network, and then an overall 3-D framework by inter-chain O–H···O hydrogen bonds and C–H···π supramolecular interactions. Both **1** and **2** are photoluminescent and their emission properties are closely related to their intrinsic structures.

Keywords: Cd^{II} complexes; Xanthene-9-carboxylate; Crystal structures; Luminescent properties

1. Introduction

Self-assembly of coordination polymers has attracted interest due to intriguing topological structures and potential applications as functional materials in catalysis, optics, magnetism, etc. [1]. The final structures of coordination polymers can be influenced by multiple factors, indicating geometrical and electronic properties of metal ions and ligands [2]. Cadmium(II) possesses variable coordination geometries and its complexes have fluorescent and second- or third-order nonlinear optical (NLO) properties [3]. Thus, much research interest has focused on cadmium inorganic–organic hybrid materials. Despite remarkable achievements [3–7], however, it remains a considerable challenge to predict and accurately control the framework structure. Among various ligands, organic ligands with carboxylic groups, especially benzene-, naphthalene-, and anthracene-based carboxylic acids, have been widely used to construct various Cd^{II} coordination complexes [4–7]. The introduction of 4,4'-bipyridyl-like linear bridging co-ligands into such reaction systems usually generate interesting coordination architectures [8]. In addition to coordination bonds, various weak interactions, such as intra- and/or inter-molecular hydrogen-bonding, π···π stacking, and C–H···π supramolecular interactions, also affect the final structures of

*Corresponding author. Email: chunsenliu@zzuli.edu.cn

coordination complexes, especially linking low-dimensional entities into higher dimensional supramolecular frameworks [9].

In comparison with the aromatic carboxylic acids mentioned above, the use of xanthene-based carboxylic acids [10], such as xanthene-9-carboxylic acid (**HL**) used here has been far less common. To explore the coordination architectures of **HL** with a bulky ring skeleton, we subsequently chose **HL** and reported the syntheses, structures, and thermal/luminescent properties of two Cd^{II} complexes, [Cd(**L**)₂(CH₃OH)₂]_∞ (**1**) and [Cd(**L**)₂(pyz)(H₂O)]_∞ (**2**) (**L** = xanthene-9-carboxylate and pyz = pyrazine).

2. Experimental

2.1. General methods

All the starting reagents and solvents were commercially available and used as received. IR spectra were measured on a TENSOR 27 (Bruker) FT-IR spectrometer with KBr pellets from 4000 to 400 cm⁻¹. Elemental analyses (C, H, and N) were performed on a Vario EL III elemental analyzer. The X-ray powder diffraction (XRPD) was recorded on a Bruker D8 Advance diffractometer (Cu-Kα, λ = 1.54056 Å) at 40 kV and 30 mA using a Cu-target tube and a graphite monochromator. The intensity data were recorded by continuous scan in a 2θ/θ mode from 3° to 80° with a step size of 0.02° and a scan speed of 2° min⁻¹. Simulation of the XRPD spectra was carried out from the single-crystal data and diffraction-crystal module of the commercially available Cerius2 program [11]. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Diamond SII thermal analyzer from room temperature to 900°C under nitrogen at a heating rate of 10°C min⁻¹. The emission/excitation spectra were recorded on an F-7000 (HITACHI) spectrophotometer at room temperature.

2.2. Syntheses of **1** and **2**

2.2.1. [Cd(L)₂(CH₃OH)₂]_∞ (1**).** Xanthene-9-carboxylic acid (0.05 mmol) and Cd(ClO₄)₂·6H₂O (0.05 mmol) were placed in methanol/H₂O media (10 mL, v/v = 1 : 1) in the presence of ammonia (pH = 12.0, 0.25 mL). The reaction mixture was stirred subsequently for *ca* 10 min at room temperature, the product was collected by filtration, and the resultant colorless filtrate was allowed to slowly evaporate under ambient conditions for 2 weeks to give colorless crystals of **1**. Yield: *ca* 40% based on **HL**. Anal. Calcd for C₃₀H₂₆CdO₈: C, 57.47; H, 4.18%. Found: C, 57.20; H, 4.39%. IR (KBr pellet, cm⁻¹): 3443m(br), 1604s, 1573s, 1482s, 1454s, 1381s, 1326w, 1304w, 1259vs, 1211w, 1183w, 1154w, 1120m, 1097m, 1036m, 941m, 871m, 801w, 746s, 692m, 664w, 570w, 490w.

2.2.2. [Cd(L)₂(pyz)(H₂O)]_∞ (2**).** The same procedure as that for **1** was used for this complex with exception of the introduction of auxiliary co-ligand pyz (0.05 mmol). Colorless crystals of **2** were obtained by slow evaporation of the solvents for 1 week. Yield: *ca* 50% based on **HL**. Anal. Calcd for C₃₂H₂₄CdN₂O₇: C, 58.15; H, 3.66; N, 4.24%. Found: C, 58.32; H, 4.37; N, 3.37%. IR (KBr pellet, cm⁻¹): 3366m(br), 1599m,

1563s, 1479s, 1455s, 1418m, 1376s, 1329m, 1299m, 1257s, 1236s, 1202m, 1175m, 1115m, 1047m, 954w, 909m, 869m, 847w, 803m, 765s, 747s, 717m, 694m, 619m, 547w, 446m.

2.3. Crystal structure determination

X-ray single-crystal diffraction data for **1** and **2** were collected on a Bruker Smart 1000 CCD area-detector diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) by ω scan mode. The program SAINT [12a] was used for the integration of the diffraction profiles. Semi-empirical absorption corrections were applied using SADABS [12b]. All the structures were solved by direct methods using SHELXS of the SHELXTL package and refined by full-matrix least-squares with SHELXL [12c]. Metals were located from the E -maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . The C-bound hydrogens were generated theoretically and refined with isotropic thermal parameters riding on the parent atoms. The hydrogens of CH₃OH or water in **1** and **2** were first located by difference Fourier E -maps and then treated isotropically as riding. Further details for structural analysis are summarized in table 1. Selected bond distances and angles as well as hydrogen-bonding geometries are listed in tables 2–4, respectively.

3. Results and discussion

3.1. IR characterization

IR spectra show features attributable to compositions of the complexes [13]. Strong broad bands centered at 3443 cm^{-1} for **1** and 3366 cm^{-1} for **2** indicate O–H stretch of

Table 1. Crystal data and structure refinement for **1** and **2**.

Empirical formula	C ₃₀ H ₂₆ CdO ₈	C ₃₂ H ₂₄ CdN ₂ O ₇
Formula weight	626.91	660.94
Temperature (K)	294(2)	294(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Unit cell dimensions (Å, °)		
a	16.2261(19)	29.931(7)
b	18.8061(16)	6.2146(8)
c	9.0919(10)	15.078(3)
β	105.859(12)	103.55(2)
Volume (Å ³), Z	2668.8(5), 4	2726.6(9), 4
Calculated density (g cm ⁻³)	1.560	1.610
Absorption coefficient (mm ⁻¹)	0.869	0.855
$F(000)$	1272	1336
Crystal size (mm ³)	0.21 × 0.12 × 0.10	0.29 × 0.25 × 0.21
θ Range for data collection (°)	3.16 to 25.00	3.35 to 25.00
Reflections collected	19,056	4708
Independent reflection	4702 [$R(\text{int}) = 0.0375$]	2405 [$R(\text{int}) = 0.0273$]
Goodness-of-fit on F^2	1.003	0.967
Final R indices [$I > 2\sigma(I)$]	$R_1^a = 0.0263$, $wR_2^b = 0.0421$	$R_1^a = 0.0309$, $wR_2^b = 0.0408$
R indices (all data)	$R_1^a = 0.0477$, $wR_2^b = 0.0436$	$R_1^a = 0.0425$, $wR_2^b = 0.0417$

^a $R = \Sigma||F_o| - F_c|/|\Sigma|F_o|$; ^b $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

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

Cd1–O3	2.2239(16)	Cd1–O7	2.2880(17)
Cd1–O4 ^{#1}	2.2833(16)	Cd1–O2	2.3437(16)
Cd1–O8	2.2870(17)	Cd1–O1	2.4777(16)
Cd1 ^{#2} –O4	2.2833(16)		
O3–Cd1–O4 ^{#1}	98.81(6)	O8–Cd1–O2	91.29(7)
O3–Cd1–O8	102.54(6)	O7–Cd1–O2	145.85(7)
O4 ^{#1} –Cd1–O8	154.09(6)	O3–Cd1–O1	167.74(6)
O3–Cd1–O7	99.02(7)	O4 ^{#1} –Cd1–O1	78.09(6)
O4 ^{#1} –Cd1–O7	81.18(7)	O8–Cd1–O1	83.86(6)
O8–Cd1–O7	81.12(7)	O7–Cd1–O1	92.26(6)
O3–Cd1–O2	115.14(6)	O2–Cd1–O1	53.70(6)
O4 ^{#1} –Cd1–O2	92.81(6)		

Symmetry codes for **1**: #1 = $x, -y + 3/2, z - 1/2$; #2 = $x, -y + 3/2, z + 1/2$.Table 3. Selected bond distances (Å) and angles (°) for **2**.

Cd1–O4	2.270(3)	Cd1–N1 ^{#1}	2.3849(19)
Cd1–O1	2.379(2)	Cd1–O2 ^{#1}	2.3995(16)
Cd1–O1 ^{#1}	2.379(2)	Cd1–O2	2.3995(16)
Cd1–N1	2.3849(19)		
O4–Cd1–O1	138.66(5)	O4–Cd1–O1 ^{#1}	138.66(5)
O1–Cd1–O1 ^{#1}	82.69(9)	O4–Cd1–N1	87.39(7)
O1–Cd1–N1	89.35(8)	O1 ^{#1} –Cd1–N1	94.58(8)
O4–Cd1–N1 ^{#1}	87.39(7)	O1–Cd1–N1 ^{#1}	94.58(8)
O1 ^{#1} –Cd1–N1 ^{#1}	89.35(8)	N1–Cd1–N1 ^{#1}	174.77(14)
O4–Cd1–O2 ^{#1}	84.64(5)	O1–Cd1–O2 ^{#1}	136.69(7)
O1 ^{#1} –Cd1–O2 ^{#1}	54.03(7)	N1–Cd1–O2 ^{#1}	95.14(7)
N1 ^{#1} –Cd1–O2 ^{#1}	84.37(7)	O4–Cd1–O2	84.64(5)
O1–Cd1–O2	54.03(7)	O1 ^{#1} –Cd1–O2	136.69(7)
N1–Cd1–O2	84.37(6)	N1 ^{#1} –Cd1–O2	95.14(7)
O2 ^{#1} –Cd1–O2	169.28(11)		

Symmetry code for **2**: #1 = $-x, y, -z + 1/2$.Table 4. Hydrogen-bonding geometry (Å, °) for **2**.

D–H...A	D–H	H...A	D...A	D–H...A
O4–H1W...O1 ^{#1}	0.85	1.84	2.670(4)	165
C10–H10...Cg1 ^{#2}	0.93	2.89	3.656(2)	140

Symmetry codes for **2**: #1 = $x, y - 1, z$; #2 = $-x + 1, -y + 2, -z - 1$. Cg1 is the centroid of the C9–C14 phenyl ring of **L** ligand in **2**.

the hydroxyl in methanol and water, respectively. IR absorptions of carboxylates are very complicated owing to its coordination diversity with metal ions. The characteristic bands of carboxylates in **1** and **2** appear at 1604–1563 cm^{-1} for the antisymmetric stretching vibrations and 1482–1454 cm^{-1} for the symmetric stretch. The $\Delta\nu$ values [$\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$] indicating the coordination modes of carboxylate in **1** are 122 and 109 cm^{-1} and 84 and 108 cm^{-1} for **2**, which are consistent with their solid structural features [14].

3.2. Description of crystal structures

3.2.1. $[\text{Cd}(\text{L})_2(\text{CH}_3\text{OH})_2]_\infty$ (1**).** Single-crystal X-ray diffraction reveals that **1** has a 1-D zigzag coordination array (figure 1a). Each asymmetric unit contains one crystallographically unique Cd^{II} , two **L**, and two coordinated methanols. The Cd^{II} is six-coordinate, surrounded by four carboxylate oxygens from three distinct **L** and two hydroxyl oxygens of methanol (figure 1a and table 2 for detailed bond parameters). The carboxylates in **1** adopt $\mu_1 - \eta^1 : \eta^1$ -chelating bidentate and $\mu_2 - \eta^1 : \eta^1$ -*syn*, *anti*-bridging coordination modes, respectively. Thus, two adjacent Cd^{II} ions are bridged by the carboxylate with $\mu_2 - \eta^1 : \eta^1$ -*syn*, *anti*-bridging mode in **L** to form a 1-D zigzag chain along the $[001]$ direction with the intrachain closest $\text{Cd} \cdots \text{Cd}$ separation of 4.680 Å (figure 1b). No effective interchain hydrogen-bonding or $\pi \cdots \pi$ stacking interactions were observed in **1**, as confirmed by PLATON procedure (the closest centroid-centroid separation between phenyl π planes of **L** ligands is 3.840 Å) (figure 1c).

3.2.2. $[\text{Cd}(\text{L})_2(\text{pyz})(\text{H}_2\text{O})]_\infty$ (2**).** When pyz, a rigid linear spacer, was introduced into the reaction system as a bridging co-ligand, a new 1-D coordination polymer was produced. The fundamental building unit contains one Cd^{II} , two **L**, one pyz, and one coordinated water molecule (figure 2a). The CdI adopts a distorted pentagonal-bipyramidal geometry by coordinating to five oxygens from two **L** and one water molecule in the equatorial plane and two nitrogens from two pyz at the axial sites with N–Cd–N angle of 174.77(14)°. As for **L**, only one $\mu_1 - \eta^1 : \eta^1$ -chelating coordination mode was observed, while pyz co-ligand serves as a bridging spacer (figure 2b), giving an infinite linear chain $[-\text{Cd}-\text{pyz}-\text{Cd}-\text{pyz}-]_n$.

Adjacent 1-D chains are arranged into a 2-D layer, parallel to the *bc*-plane, by inter-chain O–H \cdots O hydrogen-bonds between carboxylate of **L** and coordinated water (O4–H1W \cdots O1, table 4 and figure 2b). The structure of **2** also contains inter-chain C–H \cdots π interactions between the phenyl rings of adjacent **L** with an edge-to-face orientation [15] [$d = 2.890$ Å; $A = 140^\circ$; d and A stand for the H \cdots π separations and C–H \cdots π angles in the C–H \cdots π patterns, respectively], which further interlink the 2-D layer into an overall 3-D framework (figure 2c).

As typical aromatic carboxylic acid ligands, benzene-based carboxylic acids have been widely used to construct metal–organic coordination architectures [16–20]. For instance, incorporating benzene-based carboxylates, parallelogram-like sheet $[\text{Cd}(\text{O}_2\text{CPh})_2(\text{bpa})_{1.5}]_n$ (1,2-bis(4-pyridyl) ethane, bpa) [16], T-shaped bilayer motif $\{[\text{Cd}_2(\text{bpt})(\text{ip})_2(\text{H}_2\text{O})_4]6\text{H}_2\text{O}\}_n$ (ip = isophthalate; bpt = 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole) [17], a 2-D coordination polymer $\{[\text{Cd}(\text{bpt})(\text{Hbtc})(\text{H}_2\text{O})](\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})_{1.5}\}_n$ (btc = 1,3,5-benzenetricarboxylate; bim = benzimidazole) [18], and a 3-D open framework $[\text{Cd}(\text{btcc})(\text{H}_2\text{mbix})]_n$ (btcc = 1,2,4,5-benzenetetracarboxylate; mbix = 1,3-bis(imidazol-1-ylmethyl)-benzene) [19] have been reported. In our previous work, a series of six Cd^{II} coordination complexes were prepared by using naphthalene-2,3-dicarboxylic acid (H_2ndc) and different *N*-donor auxiliary co-ligands (chelating or bridging), showing discrete tetranuclear motif as well as infinite 1-D, 2-D, and 3-D frameworks [8b]. When employing bulky anthracene-based carboxylates reacting with Cd^{II} sometimes incorporating different chelating/bridging co-ligands, one dinuclear, one 1-D, two 2-D, and two 3-D structures were obtained, which exhibited interesting

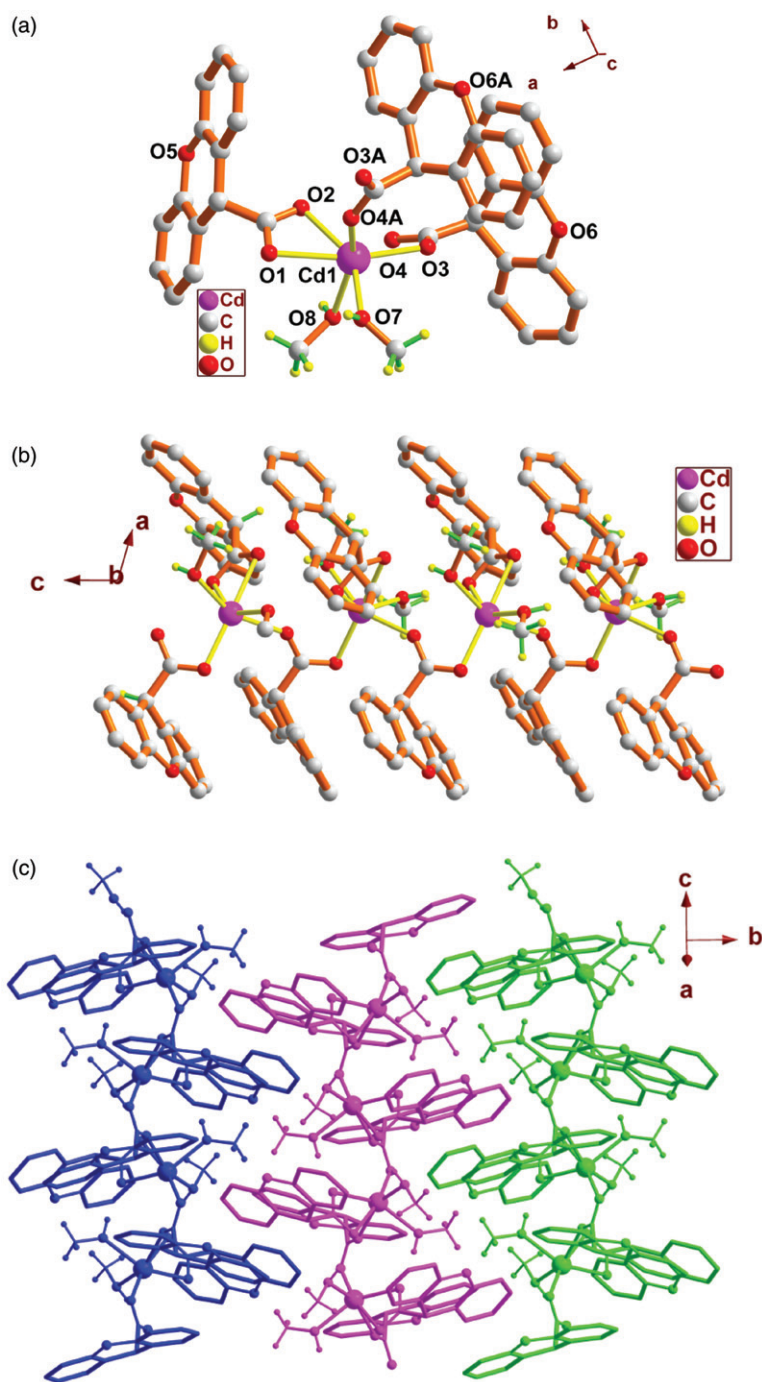


Figure 1. View of (a) the local coordination environment of Cd^{II} in 1, (b) the 1-D chain along the [001] direction, and (c) part of crystal packing. The symmetry-related atoms labeled with the suffix A are generated by the symmetry operation $(x, -y + 1.5, z - 0.5)$.

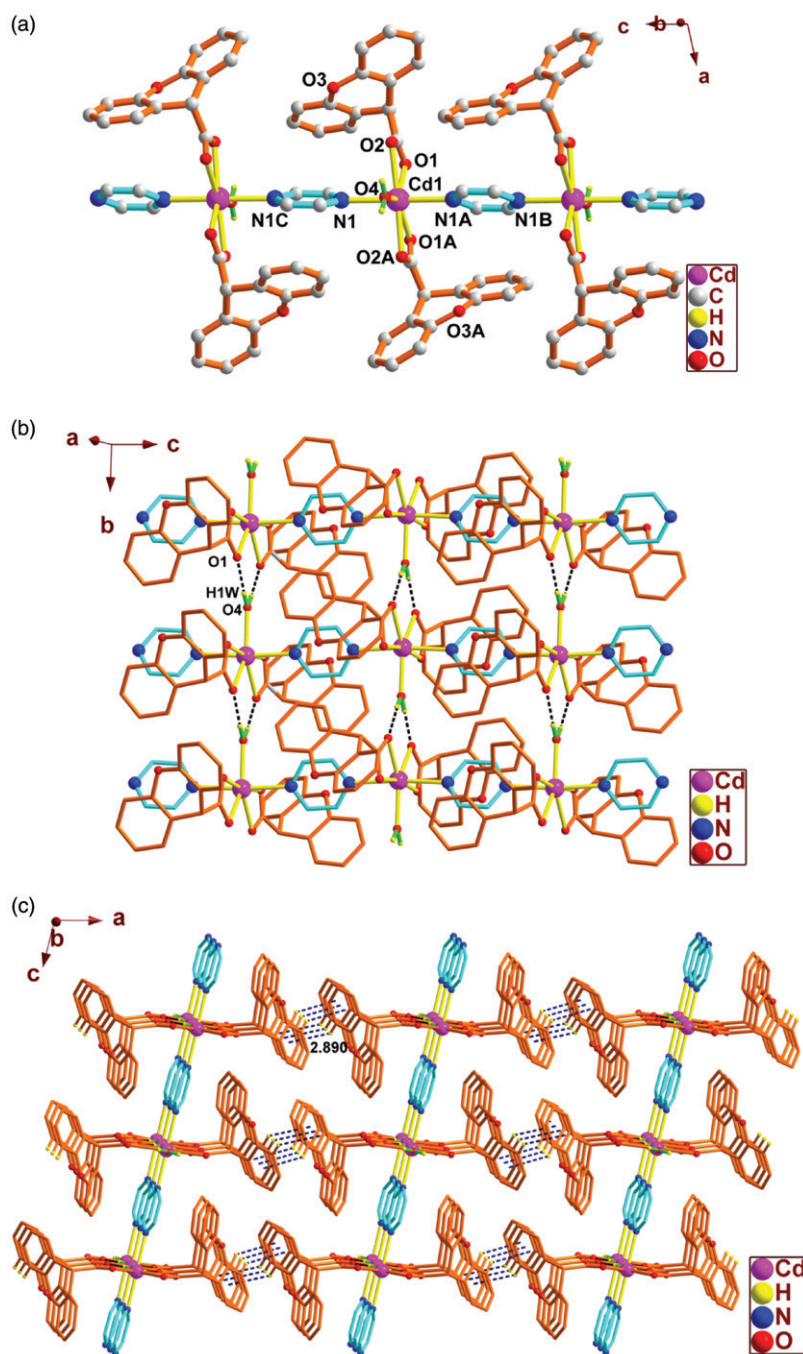


Figure 2. View of (a) the 1-D chain along the [001] direction in **1**, showing the local coordination environment of Cd^{II}, (b) the 2-D network, running parallel to the *bc*-plane, formed by the inter-chain O-H...O hydrogen-bonding interactions (black dashed lines), and (c) the 3-D framework, viewed along the [010] direction, formed by the inter-chain C-H... π interactions (blue dashed lines). The symmetry-related atoms labeled with the suffixes A, B, and C are generated by the symmetry operations $(-x, y, -z + 0.5)$, $(x, -y + 1, z + 0.5)$, and $(-x, -y - 1, -z)$. Only hydrogens involved in the interactions were shown for clarity.

luminescent properties [7, 21]. In this study, two 1-D Cd^{II} coordination polymers with xanthene-9-carboxylate ligand were obtained in the presence or absence of bridging pyz. The present finding exhibits a new example of the coordination versatility of simple monocarboxylic acid with a bulky xanthene ring skeleton.

3.3. XRPD result

To confirm whether the crystal structure is truly representative of the bulk material, XRPD experiments have been carried out for **1** and **2**. The XRPD experimental and computer-simulated patterns of the corresponding complexes are shown in Supplementary material. Although the experimental patterns have a few unindexed diffraction lines and some are slightly broadened in comparison with those simulated from the single-crystal modes, it can still be considered that the bulk synthesized materials and the as-grown crystals are homogeneous for **1** and **2**, respectively.

3.4. Luminescent property

The luminescent properties of **1** and **2** were investigated in the solid state at room temperature (Supplementary material). Complex **1** exhibits intense fluorescence with the emission maximum at 485 nm upon excitation at 418 nm. Excited at 412 nm, **2** displays a fluorescence emission at 468 nm. Both **1** and **2** have 1-D chain structure, and their emission properties are closely associated with their intrinsic structure arrangements. To further analyze the nature of these emission bands, the photoluminescent properties of HL have also been investigated under the same experimental conditions. By comparing the locations and profiles of its excitation/emission peaks with those of **1** and **2**, we can presume that the emissions should be assigned to neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) in nature [8b, 22], and can be probably ascribed to the intraligand charge transfer of L, since free HL exhibits a similar fluorescent emission peak at 474 nm while excited at 426 nm.

3.5. Thermogravimetric analysis

TGA experiments were performed from room temperature to 900°C with a heating rate of 10°C min⁻¹ under nitrogen (Supplementary material). The weight loss curve of **1** indicates that the first weight loss of 10.15% occurred between 80°C and 140°C (obsd: peaking at 126°C), which indicates loss of the coordinated methanol (Calcd: 10.22%). The remaining substance is stable to 300°C. With that, the decomposition of the residual occurs with two consecutive steps of weight loss (peaking at 337°C and 618°C). The weight loss of 70.83% observed from 300°C to 610°C is very close to the calculated value of 71.85%, which corresponds to L. With regard to **2**, the first weight loss of 2.81% from 130°C to 160°C corresponds to coordination water (Calcd: 2.73%). Decomposition of the remaining components occurs with many consecutive steps of weight loss. The endothermic peaks (164°C, 205°C, 339°C, and 617°C) in the DTA curve also recorded the weight loss processes of the various groups.

4. Conclusions

We obtained two 1-D Cd^{II} coordination polymers with xanthene-9-carboxylate (**L**), [Cd(**L**)₂(CH₃OH)₂]_∞ (**1**) and [Cd(**L**)₂(pyz)(H₂O)]_∞ (**2**). Complexes **1** and **2** can be excited directly and emit intense luminescence at room temperature, which suggest that they can be utilized as potential fluorescent materials. Also, isolation of **1** and **2** shows coordination versatility of monocarboxylic acid ligand bearing a bulky ring skeleton, which might be generally used to react with different transition metal ions for constructing other coordination complexes with fascinating structures and properties.

Supplementary material

Crystallographic data (excluding structure factors) for the crystal structures reported in this article have been deposited with the Cambridge Crystallographic Data Center and allocated the deposition numbers CCDC 805681 and 805682. The materials can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk.

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