



Di-, tri-, tetranuclear clusters and polymeric cadmium compounds: Syntheses, structures and fluorescent properties with various linking fashions and high stability of orotates under the condition of strong bases

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ABSTRACT

Assembly reactions of orotic acid (H_3dtpc) and $CdCl_2 \cdot 2.5H_2O$ or $CdSO_4 \cdot 8H_2O$ yielded four new cadmium compounds $\{[Cd(H_2dtpc)(phen)(H_2O)_2] \cdot (H_2dtpc) \cdot 4H_2O\}_2$ (**1**: solution reaction, $pH=4-5$, in addition of phen), $[Cd_3(dtpc)_2(phen)_5] \cdot 13H_2O$ (**2**: hydrothermal reaction, initial $pH=14$, final $pH=7.5$), $[Cd(Hdtpc)(H_2O)_3]_4$ (**3**: solution reaction, initial $pH=6.5$, final $pH=6.0$), $\{[Cd(Hdtpc)(phen)(H_2O)] \cdot H_2O\}_n$ (**4**: hydrothermal reaction, initial $pH=8$; final $pH=6.5$), respectively. Compounds **1-4** have been characterized by IR, thermogravimetric analyses (TGA), photoluminescence analyses, single-crystal and powder X-ray diffraction (PXRD). Compound **1** is a binuclear, **2** is a trinuclear, **3** is a tetranuclear structure, and **4** possesses one-dimensional chain framework, respectively, in which the orotate ligands show seven different linking fashions in **1-4**. The orotate ligands as trivalence anions are observed in the formation of orotate-compounds, in which the orotates show high stability under the extreme condition of strong basic solution, high temperature and pressure.

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1. Introduction

Great interest has been focused on design and syntheses of novel metal-organic hybrid coordination compounds in recent decades, of which multinuclear clusters show unique catalysis and magnetism [1,2], and polymeric complexes can afford the intriguing topological network as well as many potential applications in many areas such as optical, separation and gas storage [3–5]. One of the key challenges in purposeful construction of the new hybrid frameworks depends particularly on appropriate organic ligands or building blocks, of which the cluster cores and multi-dentate bridging ligands are fine candidates in most cases [6].

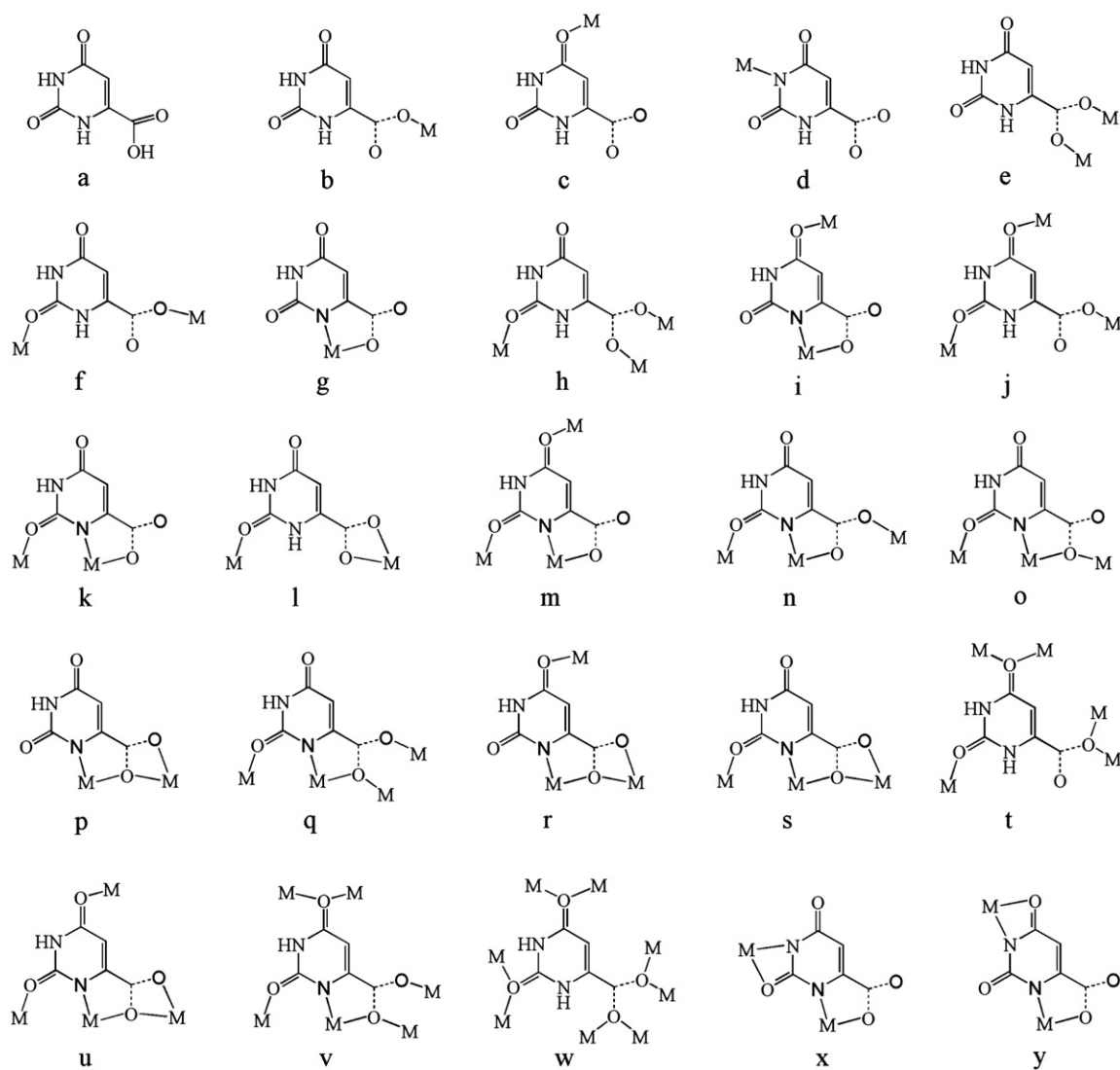
Orotic acid (2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid, H_3dtpc , Vitamin B_{13}), in addition to a unique role in bioinorganic and pharmaceutical chemistry [7], has been proven to be a good organic building block in coordination chemistry because of fascinating coordination behaviors, such as asymmetric geometry and multiple coordination sites. On the other hand, it contains a potential hydrogen-bond acceptor and hydrogen-bond donor, and can display different hydrogen-bonding interactions in supramolecular systems [8]. Various linking

fashions of the orotate ligands are displayed in Scheme 1: adopting monodentate modes (Scheme 1b–d) [8,9], bidentate modes (Scheme 1e–g) [10], tridentates (Scheme 1h–l) [11], tetradentates (Scheme 1m–p) [12], pentadentates (Scheme 1q–t) [13], hexadentate (Scheme 1u) [14], heptadentate (Scheme 1v) [15], and octadentate (Scheme 1w) [16], to yield mono- or multibinuclear clusters or one-, two-, three-dimensional frameworks.

In terms of coordination manners, orotic acid exhibits interesting behaviors, in which it employs its carbonyl oxygen or nitrogen atom to links metal ions and the carboxylate oxygen atoms remain free [8,9]. In terms of valences, orotic acid can act as mono or bi-valence anions to connect metal cations in general, as well as a neutral free ligand to locate in the lattices of the supramolecules sometimes [8]. However, trivalent anions of the orotates have not been observed in the past reports up to now as far as we know. In terms of redox activities, orotic acid could be oxidized to be oxalates to chelate metal ions under hydrothermal conditions [17]. Previous studies on the coordination chemistry of orotic acid mainly focused on lanthanides [8,17,18] and some other transition metals [9–16,19], and those on cadmium compounds were very limited [20]. We recently began to use orotic acid as organic ligands to synthesize cadmium compounds and study the coordination chemistry of cadmium–orotic acid for some novel structures. This paper will report systematical studies on the syntheses and characterizations of di-, tri-, tetranuclear

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Scheme 1. Coordination modes of the orotates.

clusters and one-dimensional cadmium-orotate compounds, in which trivalent anion modes of the orotates are observed in coordination compounds (Scheme 1x and y).

2. Experimental section

2.1. Materials and physical measurements

All chemicals used in the syntheses were of reagent grade and used without further purification. All aqueous solutions were prepared with doubly-distilled water. Other solvents were best available commercial quality and used as received. The FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. Elemental analyses of C, H and N were performed with an EA1110CHNS-0 CE analyzer. All photoluminescence measurements were carried out on a LS 50B Luminescence Spectrometer (Perkin-Elmer, Inc., USA). Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Focus X-ray diffractometer using Cu $K\alpha$ radiation. The calculated PXRD patterns were produced using the *SHELXTL-XPOW* program.

2.2. Preparation of complexes

2.2.1. Preparation of $[\{\text{Cd}(\text{H}_2\text{dtpc})(\text{phen})(\text{H}_2\text{O})_2\} \cdot (\text{H}_2\text{dtpc}) \cdot 4\text{H}_2\text{O}]_2$ (**1**)

A mixture of orotic acid (0.052 g, 0.3 mmol), $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (0.106 g, 0.3 mmol) and 1,10-Phenanthroline monohydrate (0.04 g, 0.2 mmol) in $\text{EtOH}/\text{H}_2\text{O}$ (1:2, 30 ml) was heated (80–90 $^{\circ}\text{C}$) and stirred for 20 min. A few drops of ammonia solution were added to adjust the pH value to 4.5 and the resulting mixture was filtered. Clear solution was allowed to stand at room temperature for three days; colorless columnar-like crystals suitable for single-crystal X-ray diffraction were collected and dried in air. Yield: 60% (based on Cd). Anal. Calcd. (%) for $\text{Cd}_2\text{C}_{44}\text{H}_{52}\text{N}_{12}\text{O}_{28}$: C, 37.17; H, 3.69; N, 11.82; Found (%): C, 37.38; H, 3.58; N, 11.73. IR (KBr, cm^{-1}): 3514(w), 3155(m), 3088(m), 3010(m), 2835(w), 1703(s), 1516(w), 1493(w), 1425(m), 1381(m), 1281(w), 1225(w), 1014(w), 924(w), 858(w), 773(w), 548(w), 444(w).

2.2.2. Preparation of $[\text{Cd}_3(\text{dtpc})(\text{dtpc})(\text{phen})_5] \cdot 13\text{H}_2\text{O}$ (**2**)

A mixture of orotic acid (0.11 g, 0.6 mmol), $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.142 g, 0.6 mmol), 1,10-Phenanthroline monohydrate (0.20 g, 1.0 mmol) and KOH (3.0 mmol) in H_2O (15 ml) (initial pH=14), was placed in a 25 ml stainless reactor fitted with a Teflon liner and heated to 160 $^{\circ}\text{C}$ for 2 days (resulting solution pH=7.5),

colorless block-like crystal of **2** were collected and dried in air. Yield: 40% (based on Cd). Anal. Calcd. (%) for $\text{Cd}_3\text{C}_{70}\text{H}_{68}\text{N}_{14}\text{O}_{21}$: C, 47.27; H, 3.85; N, 11.03; Found (%): C, 47.90; H, 3.78; N, 11.10. IR (KBr, cm^{-1}): 3406(s), 3061(m), 1589(vs), 1514(s), 1427(s), 1379(s), 1342(m), 1223(w), 1144(w), 1101(w), 1020(w), 850(m), 800(m), 729(s), 638(w), 420(w).

2.2.3. Preparation of $[\text{Cd}(\text{Hdtpc})(\text{H}_2\text{O})_3]_4$ (**3**)

A mixture of orotic acid (0.052 g, 0.3 mmol), $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (0.106 g, 0.3 mmol) in H_2O (20 ml) was heated (80–90 °C) and stirred for 20 min. A few drops of ammonia solution were added to adjust the pH value to 6.5 and the resulting mixture was filtered. Clear solution was allowed to stand at room temperature for two

Table 1
Structure determination summary for **1–4**.

Complex	1	2	3	4
Empirical formula	$\text{Cd}_2\text{C}_{44}\text{H}_{52}\text{N}_{12}\text{O}_{28}$	$\text{C}_{70}\text{H}_{68}\text{Cd}_3\text{N}_{14}\text{O}_{21}$	$\text{Cd}_4\text{C}_{20}\text{H}_{32}\text{N}_8\text{O}_{28}$	$\text{CdC}_{17}\text{H}_{14}\text{N}_4\text{O}_6$
Formula weight	1424.11	1782.18	1287.75	483.99
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Triclinic, $P-1$	Triclinic, $P-1$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
<i>a</i> (Å)	9.5220(3)	15.448(3)	7.0318(2)	10.6312(6)
<i>b</i> (Å)	11.8790(3)	15.639(3)	11.1243(2)	14.3635(7)
<i>c</i> (Å)	12.6141(3)	16.641(3)	22.1885(6)	11.5860(6)
α (deg.)	73.082(2)	64.025(2)	90	90
β (deg.)	81.100(2)	85.352(2)	94.215(3)	91.399(5)
γ (deg.)	78.073(2)	79.399(2)	90	90
<i>V</i> (Å ³)	1328.75(6)	3552.7(10)	1730.98(7)	1768.67(16)
<i>Z</i> , <i>D</i> _{calc} (Mg m ⁻³)	1, 1.777	2, 1.663	2, 2.460	4, 1.183
<i>F</i> (000)	720	1796	1248	960
Absorption coefficient (mm ⁻¹)	0.906	0.976	2.546	1.280
θ range for data collection (deg.)	3.85–25.00	1.34–27.53	3.68–25.00	2.84–27.48
Reflections collected	8191	31,400	10,399	13,339
Independent reflections	4563	16,028	3043	3871
Data [$I > 2\sigma(I)$]/parameters	4563/404	16,028/973	3043/299	3871/261
Goodness-of-fit on <i>F</i> ²	1.158	0.952	1.116	1.087
<i>R</i> ₁ indices ($I > 2\sigma(I)$)	0.0325	0.0549	0.0247	0.0260
w <i>R</i> ₂ indices (all data)	0.0902	0.1808	0.0609	0.0651
Largest diff. peak and hole (e Å ⁻³)	0.811 and -0.480	1.191 and -0.642	0.483 and -1.252	0.878 and -0.464

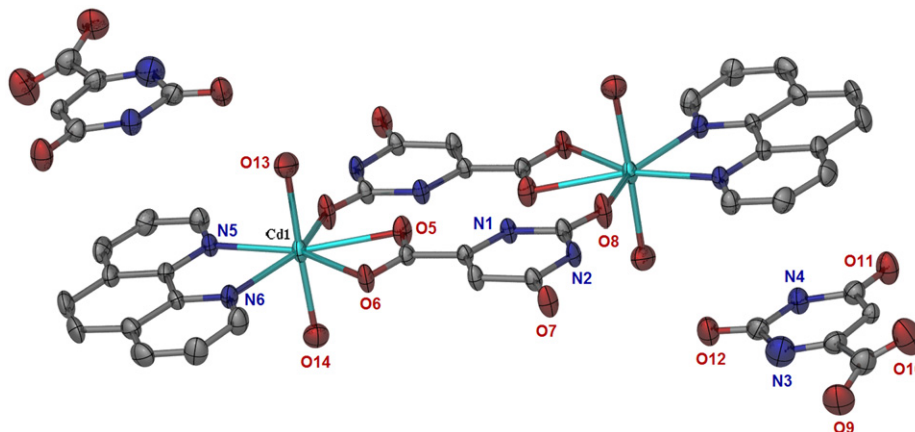
Table 2
Selected bond lengths (Å) and angles (deg.) for compounds **1** and **2**.

1					
Cd(1)–O(14)	2.260(3)	Cd(1)–N(6)	2.373(3)	Cd(1)–O(8)#1	2.401(2)
Cd(1)–O(13)	2.267(3)	Cd(1)–N(5)	2.377(3)	Cd(1)–O(5)	2.455(2)
Cd(1)–O(6)	2.575(2)				
O(14)–Cd(1)–O(13)	178.26(10)	O(13)–Cd(1)–N(6)	92.51(11)	O(13)–Cd(1)–N(5)	92.04(10)
O(14)–Cd(1)–N(6)	88.39(10)	O(14)–Cd(1)–N(5)	89.66(10)	N(6)–Cd(1)–N(5)	70.67(9)
O(14)–Cd(1)–O(8)#1	83.55(11)	N(6)–Cd(1)–O(8)#1	148.41(9)	O(14)–Cd(1)–O(5)	92.22(10)
O(13)–Cd(1)–O(8)#1	96.43(11)	N(5)–Cd(1)–O(8)#1	78.77(9)	O(13)–Cd(1)–O(5)	86.09(10)
N(6)–Cd(1)–O(5)	134.85(9)	O(8)#1–Cd(1)–O(5)	76.13(8)	O(13)–Cd(1)–O(6)	87.54(10)
N(5)–Cd(1)–O(5)	154.45(9)	O(14)–Cd(1)–O(6)	91.09(9)	N(6)–Cd(1)–O(6)	82.98(8)
N(5)–Cd(1)–O(6)	153.61(9)	O(8)#1–Cd(1)–O(6)	127.52(8)	O(5)–Cd(1)–O(6)	51.87(7)
2					
Cd(1)–N(5)		Cd(1)–N(1)	2.369(5)	O(8)–Cd(3)	2.360(4)
Cd(1)–N(4)	2.346(6)	Cd(1)–N(3)	2.423(5)	N(6)–Cd(2)	2.237(5)
Cd(1)–O(1)	2.353(5)	O(4)–Cd(2)	2.569(6)	N(7)–Cd(2)	2.388(6)
Cd(1)–N(2)	2.360(5)	O(6)–Cd(2)	2.617(5)	N(8)–Cd(2)	2.320(6)
N(9)–Cd(2)	2.244(5)	N(11)–Cd(3)	2.395(5)	N(13)–Cd(3)	2.362(5)
N(10)–Cd(3)	2.219(5)	N(12)–Cd(3)	2.402(5)	N(14)–Cd(3)	2.369(5)
N(5)–Cd(1)–N(4)	92.4(2)	N(4)–Cd(1)–N(2)	94.6(2)	O(1)–Cd(1)–N(1)	87.42(18)
N(5)–Cd(1)–O(1)	71.86(17)	O(1)–Cd(1)–N(2)	155.13(18)	N(2)–Cd(1)–N(1)	70.78(19)
N(4)–Cd(1)–O(1)	110.23(19)	N(5)–Cd(1)–N(1)	116.09(19)	N(5)–Cd(1)–N(3)	154.70(18)
N(5)–Cd(1)–N(2)	106.52(18)	N(4)–Cd(1)–N(1)	150.5(2)	N(4)–Cd(1)–N(3)	69.73(19)
O(1)–Cd(1)–N(3)	97.04(17)	N(6)–Cd(2)–N(8)	136.22(19)	N(8)–Cd(2)–N(7)	70.4(2)
N(2)–Cd(1)–N(3)	93.01(17)	N(9)–Cd(2)–N(8)	109.68(18)	N(6)–Cd(2)–O(4)	54.85(19)
N(1)–Cd(1)–N(3)	85.15(18)	N(6)–Cd(2)–N(7)	91.67(19)	N(9)–Cd(2)–O(4)	122.34(17)
N(6)–Cd(2)–N(9)	112.94(19)	N(9)–Cd(2)–N(7)	126.4(2)	N(8)–Cd(2)–O(4)	93.68(18)
N(7)–Cd(2)–O(4)	110.88(18)	N(7)–Cd(2)–O(6)	153.41(18)	O(8)–Cd(3)–N(13)	156.35(18)
N(6)–Cd(2)–O(6)	112.69(18)	O(4)–Cd(2)–O(6)	77.53(15)	N(10)–Cd(3)–N(14)	117.22(18)
N(9)–Cd(2)–O(6)	54.76(17)	N(10)–Cd(3)–O(8)	72.60(17)	O(8)–Cd(3)–N(14)	86.10(18)
N(8)–Cd(2)–O(6)	84.17(18)	N(10)–Cd(3)–N(13)	112.48(18)	N(13)–Cd(3)–N(14)	70.94(19)
N(10)–Cd(3)–N(11)	93.46(19)	N(14)–Cd(3)–N(11)	148.24(19)	N(13)–Cd(3)–N(12)	93.35(18)
O(8)–Cd(3)–N(11)	112.48(17)	N(10)–Cd(3)–N(12)	149.63(17)	N(14)–Cd(3)–N(12)	85.40(17)
N(13)–Cd(3)–N(11)	90.64(19)	O(8)–Cd(3)–N(12)	90.28(17)	N(11)–Cd(3)–N(12)	69.65(18)

Symmetry codes for **1**: #1 $-x+1, -y+1, -z$; **2**: x, y, z .

Table 3Selected bond lengths (Å) and angles (°) for compounds **3** and **4**.

3					
Cd(1)–N(1)	2.294(3)	Cd(1)–O(1)	2.386(3)	Cd(2)–N(3)	2.328(3)
Cd(1)–O(9)	2.307(3)	Cd(1)–O(10)	2.431(3)	Cd(2)–O(14)	2.332(3)
Cd(1)–O(11)	2.323(3)	Cd(1)–O(10)#1	2.463(3)	Cd(2)–O(5)	2.343(3)
Cd(1)–O(3)#1	2.331(3)	Cd(2)–O(12)	2.310(3)	Cd(2)–O(1)	2.371(3)
Cd(2)–O(13)	2.406(3)	Cd(2)–O(2)	2.539(3)		
N(1)–Cd(1)–O(9)	118.59(11)	O(11)–Cd(1)–O(3)#1	78.25(11)	N(1)–Cd(1)–O(10)	81.18(10)
N(1)–Cd(1)–O(11)	119.33(12)	N(1)–Cd(1)–O(1)	70.41(9)	O(9)–Cd(1)–O(10)	83.56(10)
O(9)–Cd(1)–O(11)	98.51(13)	O(9)–Cd(1)–O(1)	75.10(10)	O(11)–Cd(1)–O(10)	153.66(10)
N(1)–Cd(1)–O(3)#1	148.18(10)	O(11)–Cd(1)–O(1)	75.95(10)	O(3)#1–Cd(1)–O(10)	76.16(9)
O(9)–Cd(1)–O(3)#1	80.92(11)	O(3)#1–Cd(1)–O(1)	141.38(9)	O(1)–Cd(1)–O(10)	129.29(9)
N(1)–Cd(1)–O(10)#1	83.85(10)	O(10)–Cd(1)–O(10)#1	86.74(9)	N(3)–Cd(2)–O(5)	70.24(10)
O(9)–Cd(1)–O(10)#1	153.60(10)	O(12)–Cd(2)–N(3)	87.29(11)	O(14)–Cd(2)–O(5)	97.07(11)
O(11)–Cd(1)–O(10)#1	79.87(11)	O(12)–Cd(2)–O(14)	98.42(12)	O(12)–Cd(2)–O(1)	122.80(10)
O(3)#1–Cd(1)–O(10)#1	72.93(9)	N(3)–Cd(2)–O(14)	88.42(10)	N(3)–Cd(2)–O(1)	147.30(10)
O(1)–Cd(1)–O(10)#1	128.80(9)	O(12)–Cd(2)–O(5)	152.25(12)	O(14)–Cd(2)–O(1)	98.32(10)
O(5)–Cd(2)–O(1)	77.17(9)	O(5)–Cd(2)–O(13)	86.00(11)	O(14)–Cd(2)–O(2)	74.66(10)
O(12)–Cd(2)–O(13)	80.88(12)	O(1)–Cd(2)–O(13)	77.24(9)	O(5)–Cd(2)–O(2)	126.34(9)
N(3)–Cd(2)–O(13)	97.51(10)	O(12)–Cd(2)–O(2)	80.15(10)	O(1)–Cd(2)–O(2)	52.96(9)
O(14)–Cd(2)–O(13)	173.97(10)	N(3)–Cd(2)–O(2)	157.05(10)	O(13)–Cd(2)–O(2)	99.34(10)
4					
Cd(1)–N(1)	2.2403(17)	Cd(1)–N(4)	2.3153(19)	Cd(1)–N(3)	2.359(2)
Cd(1)–O(5)	2.291(2)	Cd(1)–O(2)	2.3482(16)	Cd(1)–O(4)#1	2.3595(16)
N(1)–Cd(1)–O(5)	85.85(7)	O(5)–Cd(1)–O(2)	94.51(7)	N(4)–Cd(1)–N(3)	71.87(7)
N(1)–Cd(1)–N(4)	119.01(7)	N(4)–Cd(1)–O(2)	160.73(7)	O(2)–Cd(1)–N(3)	90.36(7)
O(5)–Cd(1)–N(4)	102.58(8)	N(1)–Cd(1)–N(3)	100.64(7)	N(1)–Cd(1)–O(4)#1	153.95(6)
N(1)–Cd(1)–O(2)	70.61(6)	O(5)–Cd(1)–N(3)	172.92(7)	O(5)–Cd(1)–O(4)#1	82.53(7)
N(4)–Cd(1)–O(4)#1	86.35(7)	O(2)–Cd(1)–O(4)#1	87.12(6)	N(3)–Cd(1)–O(4)#1	92.60(7)

Symmetry codes for **3**: #1 –x+1, –y+2, –z; **4**: #1 –x+1, y–1/2, –z+1/2.**Fig. 1.** Local coordination environment around the metal atom with 50% displacement ellipsoids for **1**, guest water molecules are omitted for clarity.

days; colorless block-like crystals were collected (resulting solution pH=6.0) and dried in air. Yield: 65% (based on Cd). Anal. Calcd. (%) for Cd₄C₂₀H₃₂N₈O₂₈: C, 18.74; H, 2.52; N, 8.74; Found (%): C, 18.96; H, 2.47; N, 8.66. IR (KBr, cm⁻¹): 3566(m), 3323(m), 3080(m), 1655(vs), 1473(m), 1419(m), 1381(s), 1356(m), 1335(m), 1317(m), 1155(w), 1020(w), 964(w), 816(w), 777(w), 654(w), 577(w), 438(w).

2.2.4. Preparation of {[Cd(Hdtpc)(phen)(H₂O)]·H₂O}_n (**4**)

A mixture solution of orotic acid (0.38 g, 0.2 mmol), CdCl₂·2.5H₂O (0.53 g, 0.2 mmol), 1,10-Phenanthroline monohydrate (0.029 g, 0.15 mmol) and H₂O (15 ml) was adjusted to the pH value to 8.0 using dilute solution of KOH, and then placed in a 25 ml stainless reactor fitted with a Teflon liner and heated to 140 °C for 3 days. After cooling to room temperature, the resulting solution was obtained (pH=6.5) and allowed to stand at room temperature for two days; pale yellow block-like crystal of **4** suitable for single-crystal X-ray diffraction were collected and

dried in air. Yield: 55% (based on Cd). Anal. Calcd. (%) for Cd₁₇H₁₄N₄O₆: C, 42.30; H, 2.92; N, 11.61; Found (%): C, 42.21; H, 3.01; N, 11.57. IR (KBr, cm⁻¹): 3400(m), 3236(m), 2971(m), 1696(s), 1624(vs), 1555(w), 1514(m), 1486(s), 1425(w), 1388(vs), 1342(m), 1229(w), 1204(w), 1144(w), 1100(w), 1020(s), 947(m), 851(vs), 782(vs), 726(vs), 686(w), 637(w).

2.3. X-ray crystallography

Data collection for **1–4** were performed on a Bruker-AXS diffractometer equipped with a graphite monochromated Mo-K α radiation ($\lambda=0.71073$ Å) at 293 K. All absorption corrections were applied using the SADABS program [21]. The structures were solved by direct methods, the metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from the successive difference Fourier Syntheses and refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically. The structures were refined on F^2 by full-matrix least-squares using

the SHELXTL-97 program package [22]. The crystallographic data of complex **1–4** are listed in Table 1 and the selected bond lengths and angles in Tables 2 and 3. Crystallographic data (excluding structure factors) for complex **1–4** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications.

3. Results and discussion

3.1. Syntheses of compounds

The coordination chemistry of H_3dtpc with transition metals has been studied in detail in recent years [9–16]. Studies on the lanthanide systems have received great attention in our lab [8,17,18]. By employing different synthetic techniques, ten Ln-complexes with four kinds of structures were successfully isolated by adjusting pH values of reaction systems. The radiuses of cadmium ions are close to ones of lanthanide ions, which trigger off our interesting on cadmium series. Our aim is to investigate the coordination chemistry of Cd-orotate for obtaining novel structures with special properties as well as to study the effects of pH values on the crystal structure formation. By employing different preparation techniques, four cadmium–orotate compounds were successfully isolated. The solution reactions of $CdSO_4 \cdot 8H_2O$ and orotic acid gave birth to a binuclear Cd-complex $\{[Cd(H_2dtpc)(phen)(H_2O)_2] \cdot (H_2dtpc) \cdot 4H_2O\}_2$ (**1**) (pH=4–5, in addition of phen), and a tetranuclear complex $[Cd(Hdtpc)(H_2O)_3]_4$ (**3**) (pH=6.0–6.5), respectively.

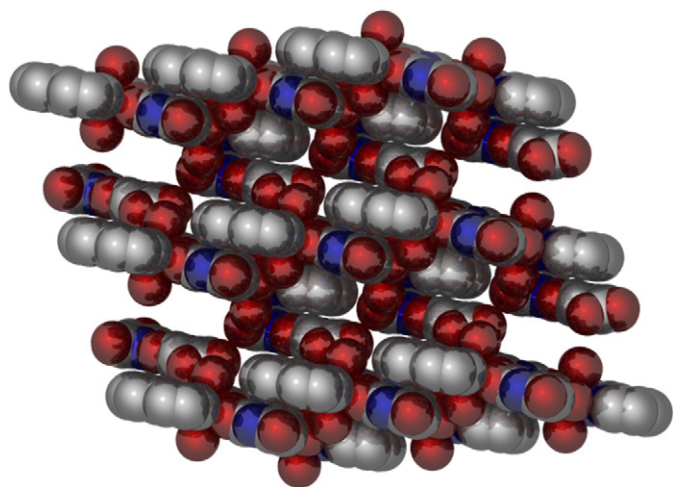


Fig. 2. Three dimensional supramolecular framework for **1**.

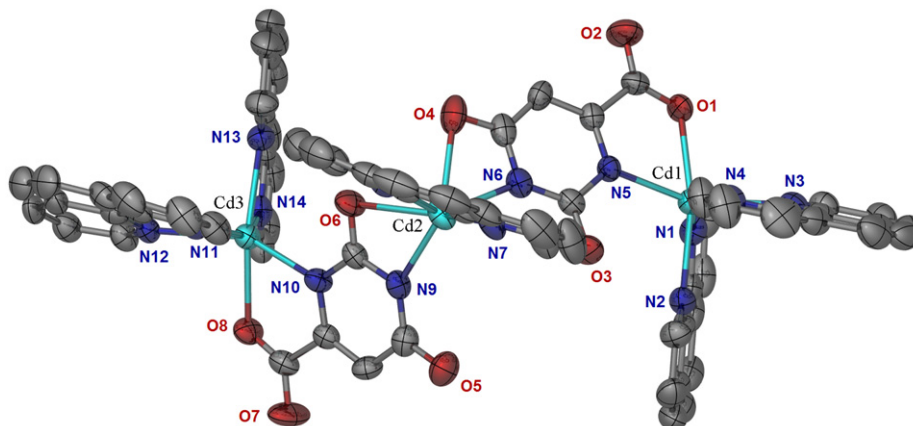


Fig. 3. Local coordination environment around metal atom with 50% displacement ellipsoids for **2**, guest water molecules and hydrogen bond linking are omitted for clarity.

Hydrothermal reactions of $CdSO_4 \cdot 8H_2O$ or $CdCl_2 \cdot 2.5H_2O$, phen and orotic acids yielded a trinuclear complex $[Cd_3(dtpc)_2(phen)_5] \cdot 13H_2O$ (**2**) (initial pH=14; final pH=7.5), and one -dimensional complex $\{[Cd(Hdtpc)(phen)(H_2O)] \cdot H_2O\}_n$ (**4**) (initial pH=8; final pH=6.5), respectively. Different crystal structures above indicate that pH values of reaction mixture and reaction atmospheric pressures play an important role in the formation of crystal structures in these reaction systems.

It's intriguing that the orotate ligands as trivalence anions connect metal ions but not hydrolyzing into oxalate under extremely strong basic solution, very high temperature and pressure in the formation of compound **2**, in which coordinating modes of the orotates are shown in Scheme 1(x and y). In our previous contribution, parts of the orotate ligands hydrolyzed into oxalate under hydrothermal condition (pH=6–7) [17], which could result from the Ln(II) or Co(II) metal-mediated catalysis oxidation to the orotates in hydrothermal reactions. The Cd(II) ions being the valence electronic structures of the $4d^{10}$, may have not catalysis oxidation to the orotates even in extreme condition of the strong basic solution, high temperature and pressure. So the orotates have to throw away its all active hydrogen atoms in strong basic reaction system for coordination to Cd(II) ions as the trivalence anions, which are first observed in the coordination chemistry of the orotates.

3.2. Description of crystal structures

3.2.1. Description of $\{[Cd(H_2dtpc)(phen)(H_2O)_2] \cdot (H_2dtpc) \cdot 4H_2O\}_2$ (**1**)

Single crystal X-ray analysis reveals that complex **1** belong to triclinic system, space group $P-1$, a binuclear structure. The local coordination environment around Cd^{2+} ion (Fig. 1) shows that the cadmium center is coordinated by two nitrogen atoms from the phen ligand, three oxygen from different orotates, and two oxygen from the coordinated water molecules (in the axial positions), forming a slightly distorted pentagonal bipyramid with Cd–O distances ranging from 2.260 to 2.575 Å and Cd–N distance ranging from 2.373 to 2.377 Å. In **1**, the orotate ligands acts as a μ_2 -bridge to link two Cd^{2+} atoms, in which the deprotonated carboxylate group chelates one Cd^{2+} ion and the carbonyl oxygen atom connects to another Cd^{2+} ion (${}^1H_2dtpc^-$, Scheme 11). The binuclear unit contains two phen, two Cd^{2+} ions, two coordinated orotates, two uncoordinated orotates, four coordinated water and eight guest water molecules. The π - π stacking interactions among the phen ligands, coordinated orotates and uncoordinated orotates heterocyclic rings (distances from 3.6 to 3.8 Å) along with the various hydrogen bonding interactions result in final three dimensional supramolecular framework (Fig. 2).

3.2.2. Description of $[Cd_3(dtpc)_2(phen)_5] \cdot 13H_2O$ (**2**)

Complex **2** belonging to triclinic system, space group $P\bar{1}$, has a trinuclear structure. In the asymmetry unit, Cd^{2+} ion has two different coordination environments (Fig. 3): (a) Cd1 and Cd3 have the same coordination mode, which are connected by four nitrogen atoms from two phen ligands, one nitrogen atom from the orotate and one oxygen from the carboxylate group; (b) Cd2 is coordinated by two oxygen atoms from the carbonyl oxygens, two nitrogen atoms from two orotates and two nitrogen atoms from the phen ligand with Cd–O distances ranging from 2.353 to 2.617 Å and Cd–N distances ranging from 2.219 to 2.423 Å. The orotate as a trivalent anion affords the *trans*- and *cis*-fashions to link cadmium ions in **2** (Scheme 1x and y), which is observed for the first time in Cd–orotate coordination compounds. The various hydrogen bonding interactions and the π – π stacking interactions

between neighboring phen rings give birth to final supramolecular framework (Fig. 4).

3.2.3. Description of $[Cd(Hdtpc)(H_2O)_3]_4$ (**3**)

Complex **3** is a tetranuclear structure with monoclinic system, space group $P2(1)/n$. Two types of coordination modes of orotate ligands are presented in the structures: (a) a bidentate chelate fashion to coordinate one Cd^{2+} ion through its carboxylate oxygen and nitrogen atom (Scheme 1g); (b) a bis-bidentate chelate and bridging fashion to link three Cd^{2+} ions, in which two carboxylate oxygen atoms chelating one Cd^{2+} ion, one carboxylate oxygen and one nitrogen atom chelating one Cd^{2+} ion, and the carbonyl oxygen atom connecting another Cd^{2+} ion (Scheme 1s). In the asymmetry unit, Cd^{2+} ions hold two different

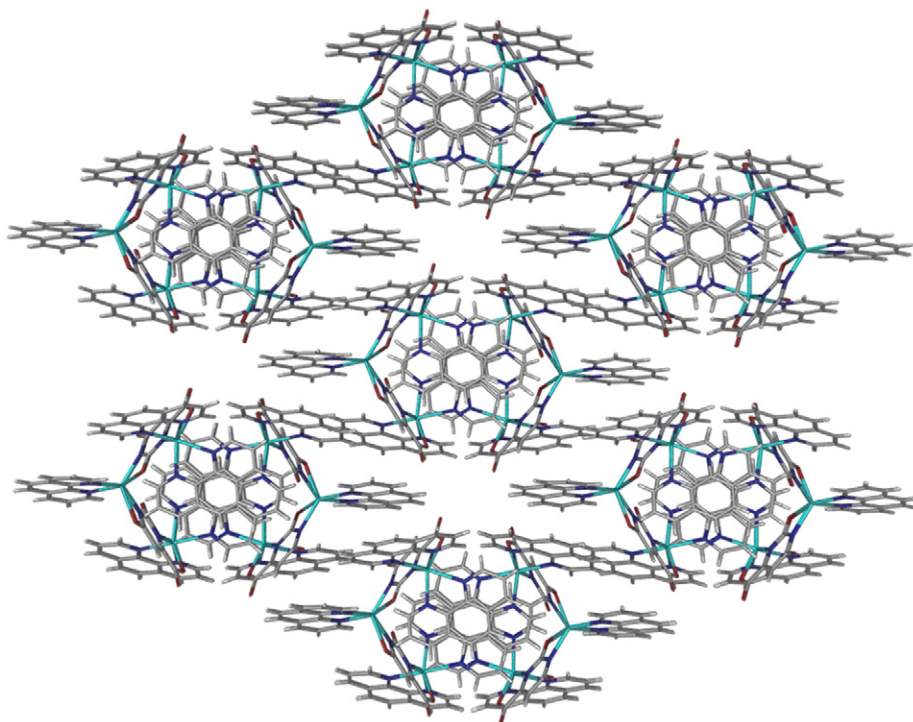


Fig. 4. View of supramolecular framework along the *a* axis for **2**, guest water molecules and hydrogen bond linking are omitted for clarity.

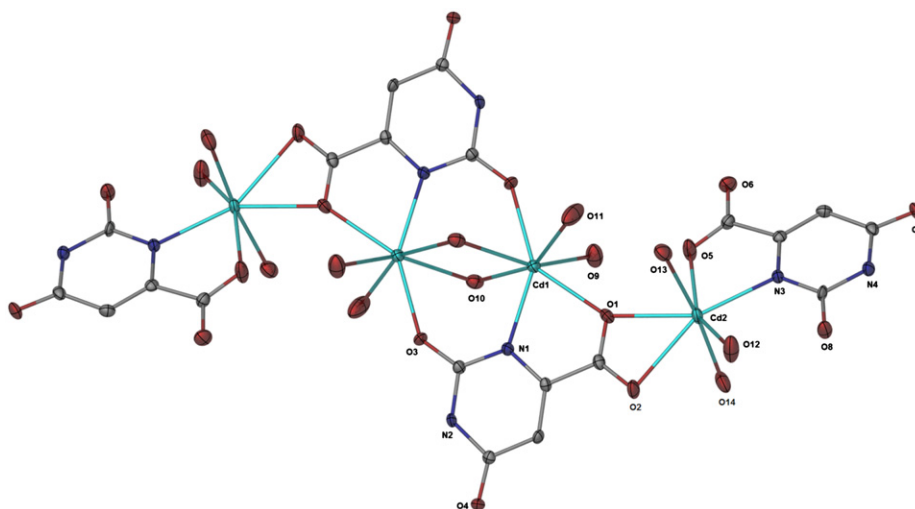


Fig. 5. Local coordination environment around metal atom with 50% displacement ellipsoids for **3**.

coordination environments (Fig. 5): (a) Cd1 is coordinated by one nitrogen atom and six oxygen atoms, of which one from carbonyl oxygen, one from carboxylate group, and four from water molecules; (b) Cd2 is linked by one nitrogen atom and six oxygen, of which three from carboxylates, three from water molecules with Cd–O distances ranging from 2.307 to 2.539 Å. The tetranuclear units are further linked by intermolecular hydrogen bonding and π – π interaction to be a final supramolecular structure (Fig. 6).

3.2.4. Description of $\{[Cd(Hdtpc)(phen)(H_2O)] \cdot H_2O\}_n$ (**4**)

Compound **4** consists of Cd^{2+} ions together with phen and H_3dtpc ligands belonging to monoclinic system, space group $P2(1)/c$. Single X-ray diffraction analysis reveals that the asymmetric unit of **4** contains one Cd(II) ion, one orotate, one phen, one coordination water, and one guest water molecule. The coordination geometry of Cd^{2+} ion is a distorted octahedral, O5 and N3 occupy the axial positions, one carboxyl oxygen atom and one

carbonyl oxygen from two different orotate ligands (O2, O4), two nitrogen atoms from phen and orotate ligand (N1, N4) stand in the equatorial plane with Cd–O distances ranging from 2.291 to 2.360 Å and Cd–N distances ranging from 2.240 to 2.359 Å. The structure units are further joined by orotate ligands (Scheme 1i) in different direction to complete a zig-zag chain with Cd–Cd distance being 8.001 Å (Fig. 7). The chains are assembled by the intermolecular hydrogen bonding to form a two-dimensional structure (Fig. 8), which is further extended into a final three-dimensional framework by the π – π stacking interaction with the separation of 3.79 Å from the nearest two benzene rings.

3.3. Powder X-ray diffraction (PXRD)

In an attempt to confirm the homogeneity of the material synthesized under the hydrothermal or solution conditions, we have analyzed the PXRD patterns of **1–4** and correlated the results

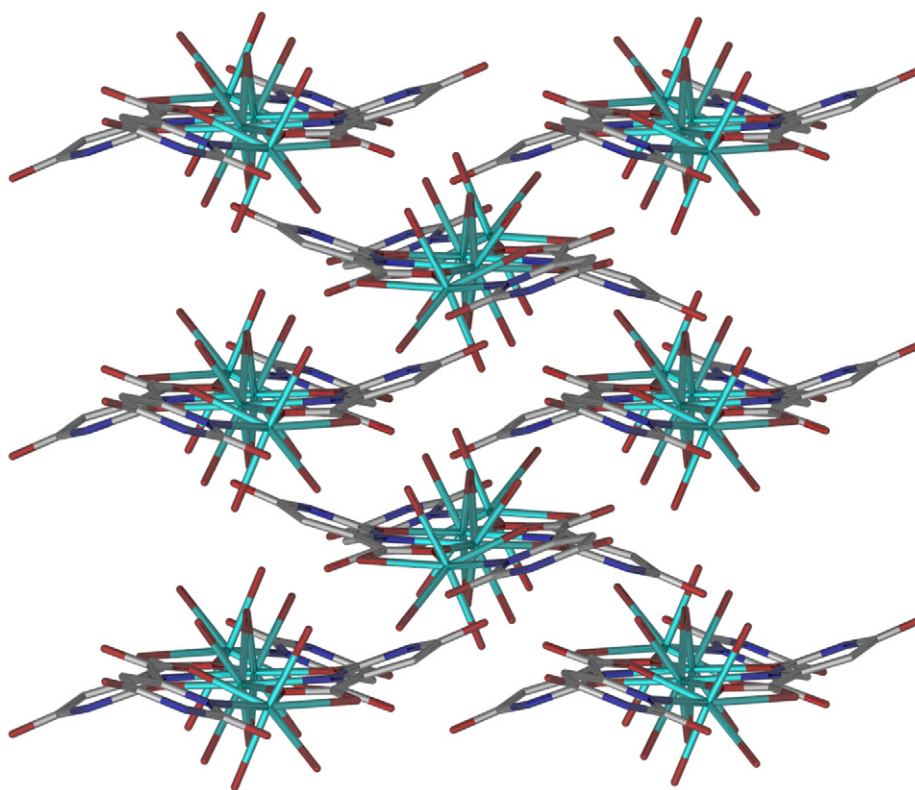


Fig. 6. View of supramolecular framework along the *c* axis for **3**.

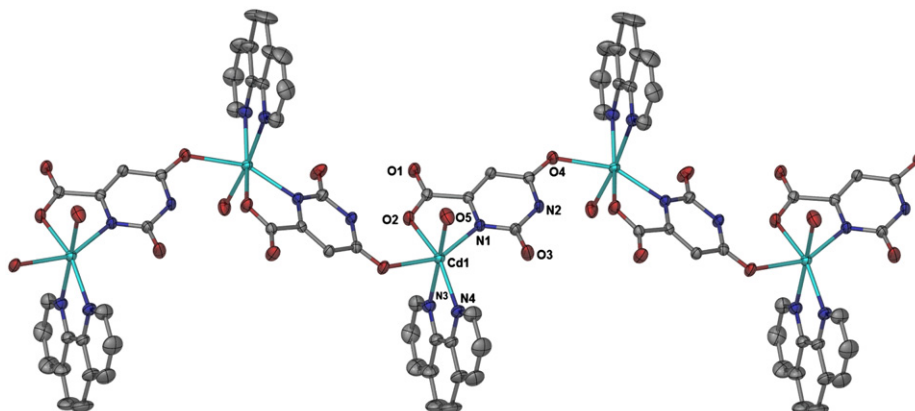


Fig. 7. One dimensional chain structure for **4**, guest waters are omitted for clarity.

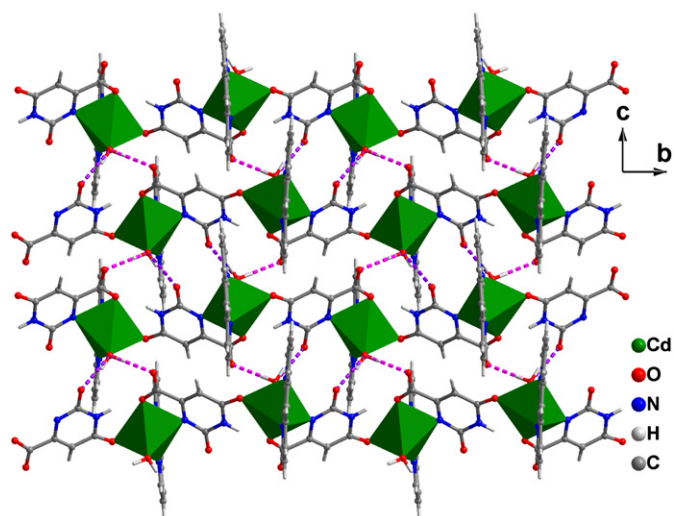


Fig. 8. Two-dimensional structure formed by the intermolecular hydrogen bonding for **4**.

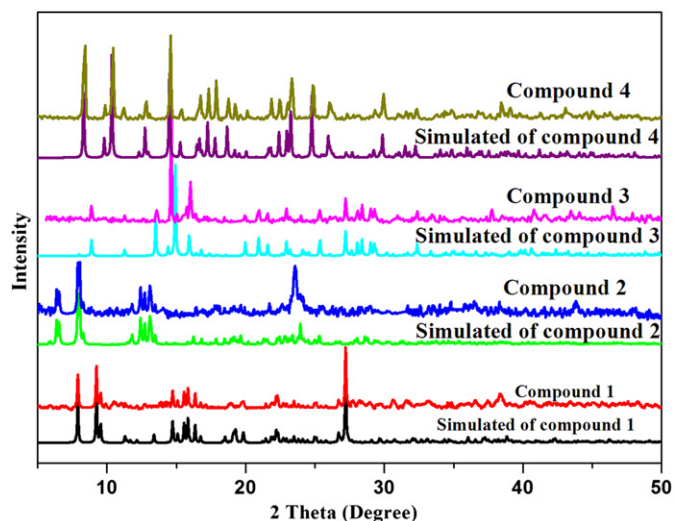


Fig. 9. Experimental and simulated powder XRD patterns of **1–4**.

with the simulated powder patterns obtained from the single crystal data. As depicted in Fig. 9, the basic features of the PXRD patterns resemble the simulated single crystal data, indicating that the bulk product obtained is homogenous.

3.4. Thermo-gravimetric analyses (TGA)

Thermogravimetric analysis studies of complex **1–4** are performed in an air atmosphere from room temperature to 800 °C at a heating rate of 10 °C/min (Fig. 10). For **1**, the first weight loss of 7.50% (calcd: 7.60%) from room temperature to 90 °C corresponds to the loss of six water molecules per formula unit $\{[\text{Cd}(\text{H}_2\text{dtpc})(\text{phen})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{dtpc}) \cdot 4\text{H}_2\text{O}\}_2$, the second weight loss of 5.99% (calcd: 6.32%) from 91 to 196 °C corresponds to the loss of five water molecules per formula unit, remaining one water molecule was slowly lost from 196 to 295 °C, and then further slowly lose weight with increasing temperature. For **2**, the first weight loss of 4.84% (calcd: 5.05%) from room temperature to 124 °C corresponds to the loss of five water molecules per formula unit $[\text{Cd}_3(\text{dtpc})_2(\text{phen})_5] \cdot 13\text{H}_2\text{O}$, the second weight loss of 4.90% (calcd: 5.05%) from 124 to 245 °C corresponds to the loss of five water molecules per formula unit, remaining three water

molecules were slowly lost from 245 to 287 °C, and then further slowly lose weight with increasing temperature. For **3**, the first weight loss of 16.20% (calcd: 16.77%) from room temperature to 246 °C corresponds to the loss of twelve water molecules per formula unit $[\text{Cd}(\text{Hdtpc})(\text{H}_2\text{O})_3]_4$, and then further slowly lose weight with increasing temperature. For **4**, The first weight loss of 3.95% (calcd: 3.72%) corresponds to one guest water molecule per formula unit $\{[\text{Cd}(\text{Hdtpc})(\text{phen})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}$ from room temperature to 220 °C. A sharp drop of weight is observed after 300 °C, indicating the collapse of the complex framework.

3.5. Fluorescent properties

The emission spectrum of compounds **1–4** in the solid state at room temperature is depicted in Fig. 11. The intense photoluminescence with an emission maximum at ca. 425 nm upon excitation at 370 nm is observed for **1**, strong emission band at 530 ($\lambda_{\text{ex}}=400$ nm) for **2** and 382 ($\lambda_{\text{ex}}=320$ nm) for **3**, two emission bands at 387 and 403 ($\lambda_{\text{ex}}=330$ nm) for **4**. Since free H_3dtpc ligands exhibit photoluminescence emission at 363 nm, and free phen ligands exhibit emission at 362 and 381 nm, the emission bands of **1**, **2** may be assigned to ligand-to-metal charge transition, red-shift is observed as compared with the emission spectrum for the orotate and phen ligands [23,24]. The emission band of **3** may be assigned to the photoluminescence emission of Cd(II)

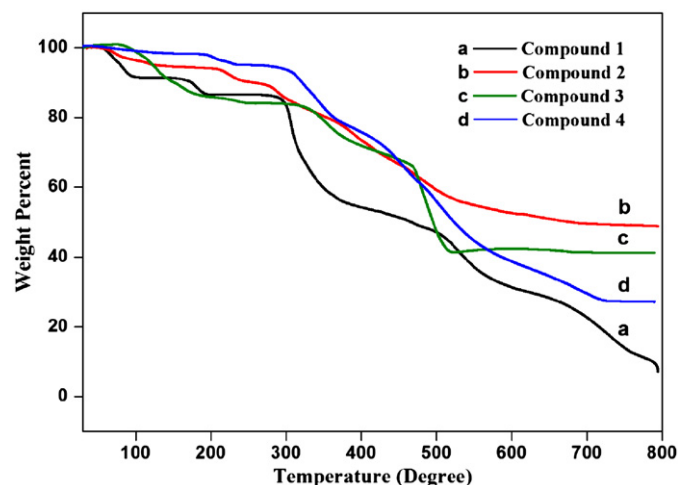


Fig. 10. TGA curves of **1–4**.

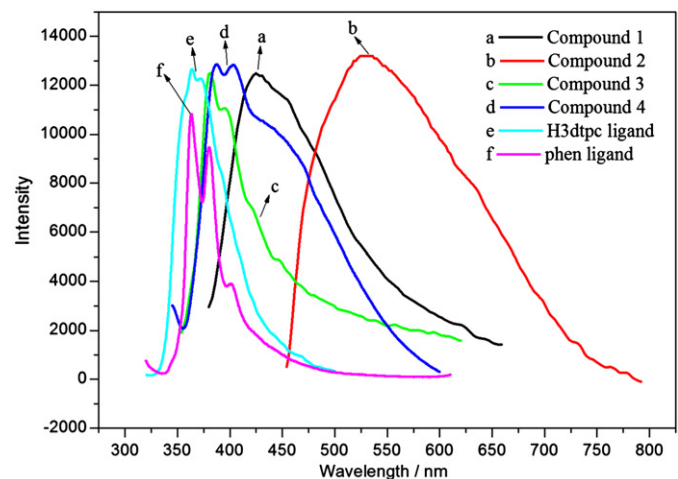


Fig. 11. Solid-state emission spectra of **1–4** at room temperature.

ions, the emission band at 387 of **4** can be attributed to the phen ligand donation and the band of 403 may be attributed to ligand-to-metal charge transition [23,24].

4. Conclusion

In summary, four new cadmium compounds have been prepared from orotic acid under different crystallization systems. Compounds **1–3** are di-, tri- and tetranuclear clusters, respectively, and **4** have one-dimensional chain structure. The orotate ligands display various connection modes and high stability in information of compounds **1–4** under the different reaction conditions. The strong photoluminescence emissions have been observed in compounds **1–4**, which afford valuable information for the generation of photoluminescence materials.

Supporting Information Available

X-ray Crystallographic data for compounds **1–4** in CIF form. CCDC 788606–788609 contains the crystallographic data for the paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2011.05.031](https://doi.org/10.1016/j.jssc.2011.05.031).

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