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Two succinato-pillared coordination polymer: hydrothermal syntheses, crystal structures and properties of $Mn_5(OH)_2L_4$ and $Cd_3(OH)_2L_2$ with $H_2L{=}HOOC(CH_2)_2COOH$ [☆]

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Abstract

Two succinato-pillared coordination polymers $Mn_5(OH)_2L_4$ **1** and $Cd_3(OH)_2L_2$ **2** were prepared by hydrothermal reactions of succinic acid ($H_2L{=}HOOC(CH_2)_2COOH$) and KOH with the corresponding metal chlorides at 180°C. Within **1**, the adjacent MnO_6 octahedra are edge shared to generate Mn_5O_{22} pentamers, which are interconnected to form 2D manganese oxide layers stabilized by the intralayer gauche succinato groups within the aperture. The manganese oxide layers are pillared by the interlayer *trans* succinato groups to complete 3D framework. The magnetic behavior of **1** obeys Curie–Weiss law $\chi_m(T-\Theta) = 4.46(2)\,cm^3\,mol^{-1}\,K$ with the Weiss constant $\Theta = -67.3(3)\,K$ over the temperature range $5{-}300\,K$. Compound **2** contains CdO_6 octahedra and edge-shared Cd_2O_{10} bi-octahedra. The former CdO_6 octahedra are each surrounded by four Cd_2O_{10} bi-octahedra which in turn are each surrounded by four former CdO_6 octahedra and four neighboring Cd_2O_{10} bi-octahedra, thus resulting in the corrugated cadmium oxide layers. The formed 2D layers are pillared by *trans* succinato groups to constitute 3D coordination polymer. Additionally, thermal decomposition of both title coordination polymers upon heating in a flowing nitrogen atmosphere from room temperature to 800°C is discussed. Crystal data: (1) monoclinic, $P2_1/c$, $Z=2$, $a=9.575(2)\,Å$, $b=9.611(2)\,Å$, $c=12.526(3)\,Å$, $\beta=97.04(2)°$, $V=1144.0(4)\,Å^3$, $R_1=0.0289$ and $wR_2=0.0815$ for 2411 observed reflections ($I\geqslant 2\sigma(I)$) out of 2629 unique reflections; (2) orthorhombic, $Pbca$, $Z=4$, $a=10.679(1)\,Å$, $b=6.873(1)\,Å$, $c=16.996(2)\,Å$, $V=1247.5(3)\,Å^3$, $R_1=0.0234$ and $wR_2=0.0585$ for 1213 observed reflections ($I\geqslant 2\sigma(I)$) out of 1437 unique reflections.

Keywords: Manganese(II); Cadmium(II); Coordination polymer; Hydrothermal syntheses; Crystal structure; Properties

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1. Introduction

The past decade has witnessed an enormous expansion of the research field of coordination polymers based on metal-organic ligand coordination. Coordination polymers with specific topologies display promising properties for potential technological and industrial application as catalysts, hosts in intercalation compounds, and electronic, electrooptical, photooptical, and magnetic materials, and the pillared-layer structure is found to be a representative of porous structural motifs [1].

Currently, rational design and syntheses of coordination polymers using rigid di- and polycarboxylates as bridging spacers are of growing interests [2]. On the other hand, exploitation of conventional saturated α,ω-dicarboxylates as flexible bridging spacers to constitute coordination polymers aroused extensive attentions of many laboratories [3–9]. Among the saturated α,ω-dicarboxylate anions, the succinate ligands are of special interest. To the best of our knowledge, the simultaneous coordination of hydroxide and succinate groups to transition metal atoms tends to form coordination polymers with 3D open framework [10]. Here, we report two succinato-pillared coordination polymer $Mn_5(OH)_2L_4$ **1** and $Cd_3(OH)_2L_2$ **2** ($H_2L{=}HOOC(CH_2)_2COOH$), which are prepared by hydrothermal reactions of

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succinic acid and KOH with the corresponding metal chlorides.

2. Experimental

All chemicals of reagent grade were commercially available and used without further purification. The C and H microanalyses were performed with a Heraeus Rapid-CHNO elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. The magnetic susceptibility of **1** was measured on a powdered sample (53.96 mg) using a SQUID magnetometer (Quantum Design Model MPMS-7) in temperature range $5 \leqslant T(K) \leqslant 300$ with an applied field of 10,000 G. The combined TG/DTA measurements were carried out from room temperature to 800°C on preweighed samples (8.3743 mg **1**, 6.4237 mg **2**) in a flowing nitrogen atmosphere using a Seiko Exstar6000 TG/DTA6300 equipment with a heating rate of 10°C/min.

2.1. Syntheses

2.1.1. $Mn_5(OH)_2(C_4H_4O_4)_4$ 1

A mixture consisting of 0.98 g (5.0 mmol) $MnCl_2 \cdot 4H_2O$, 1.18 g (10.0 mmol) succinic acid, 1.32 g (23.6 mmol) KOH and 20 mL doubly distilled H_2O was loaded in a 50 mL Teflon-lined stainless-steel vessels and heated at 180°C for 5 days. After cooling to room temperature and filtered out, a small amount of incarnadine clumpy aggregates of **1** were handpicked from brownish fine precipitate (yield: less than 5% based on the initial $MnCl_2 \cdot 4H_2O$ input). Since the yield is so low, the synthetic work was repeated to collect sufficient sample for the relevant characterizations. Anal. calc. for $C_{16}H_{18}Mn_5O_{18}$ (%): C, 24.86; H, 2.35. Found: C, 24.69; H, 2.57. IR (cm^{-1}): 3379s (sharp), 2962vw (quartet), 1614 (shoulder), 1551vs, 1506 (shoulder), 1419vs, 1307s, 1275w, 1230w, 1174m, 1055w, 1032m, 978w, 939m, 878w, 822m, 777vw, 756vw, 656s, 546m, 480 m, 444m.

2.1.2. $Cd_3(OH)_2(C_4H_4O_4)_2$ 2

Complex **2** was analogously prepared. The detailed synthetic procedure is as follows. 1.14 g (5.0 mmol) $CdCl_2 \cdot 2.5H_2O$, 1.18 g (10.0 mmol) succinic acid and 1.34 g (23.6 mmol) KOH were added to 20 mL doubly distilled H_2O and stirred vigorously for ca. 30 min. The resulting suspension (pH = 8.82) was then moved to a 50 mL Teflon-lined stainless-steel vessels and heated at 180°C for 15 days. After cooling to room temperature, colorless prismatic crystals of **2** could be separated from fine powder, which was not identified. The yield reaches ca. 20% based on the initial $CdCl_2 \cdot 2.5H_2O$ input. Anal. calc. for $C_8H_{10}Cd_3O_{10}$ (%): C, 15.93; H, 1.67. Found: C, 15.74; H, 1.95. IR (cm^{-1}): 3626s (sharp), 2937vw (quartet), 1558s, 1541w (shoulder) 1418s, 1389s, 1339vw, 1306w, 1273m, 1221m, 1159w, 1065w, 1028m, 959vw, 930w, 810m, 652s (triplet), 505m (sharp), 419w.

2.2. X-ray crystallography

For single-crystal X-ray analyses, a fragment of **1** was cut from incarnadine clumpy aggregate and a single crystal of **2** was selected under a polarizing microscope. They were fixed with epoxy cement on respective fine glass fibers which were then mounted on a Bruker P4 diffractomerter with graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) for cell determination and subsequent data collection. The lattice parameters were refined from the 2ϑ values (10–25°) of 25 carefully centered reflections. The reflection intensities with $2\vartheta_{max} = 55°$ were collected at 293 K using the $\vartheta - 2\vartheta$ scan technique. On the basis of the monitored reflections, the employed single crystals exhibit no detectable decay during the data collection. The data were corrected for Lp and absorption effects. SHELXS-97 and SHELXL-97 programs [11,12] were used for structure solution and refinement. The structures were solved by using direct methods. Subsequent difference Fourier syntheses enabled all non-hydrogen atoms to be located. After several cycles of refinement, all hydrogen atoms of succinato groups were geometrically generated while the hydroxo hydrogen atoms were located from the successive difference Fourier syntheses. Finally, all non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares technique and hydrogen atoms with isotropic displacement parameters. Detailed information about the crystal data and structure determination is summarized in Table 1. Atomic coordinates, equivalent isotropic displacement parameters are listed in Tables 2 and 3. Selected interatomic distances and bond angles are given in Tables 4 and 5. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 205597 ($C_{16}H_{18}Mn_5O_{18}$) and CCDC 205598 ($C_8H_{10}Cd_3O_{10}$). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. $Mn_5(OH)_2(C_4H_4O_4)_4$ 1

Hydrothermal reactions of a suspension (pH = 8.50) of $MnCl_2 \cdot 4H_2O$, succinic acid and KOH in H_2O

Table 1
Summary of crystal data, data collection, structure solution and refinement details for $Mn_5(OH)_2L_4$ **1** and $Cd_3(OH)_2L_2$ **2**

Compounds	**1**	**2**
Empirical formula	$C_{16}H_{18}Mn_5O_{18}$	$C_8H_{10}Cd_3O_{10}$
Formula weight	773.00	603.36
Description	Faintly redish block	Colorless elongated plate
Crystal size (mm)	0.422 × 0.222 × 0.200	0.356 × 0.111 × 0.067
Temperature	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pbca*
Unit-cell dimensions		
a (Å)	9.575(2)	10.679(1)
b (Å)	9.611(2)	6.873(1)
c (Å)	12.526(3)	16.996(2)
β (°)	97.04(2)	
Volume (Å^3)	1144.0(4)	1247.5(3)
Z	2	4
D_{calc} (g cm^{-3})	2.244	3.213
$F(000)$	766	1128
μ (mm^{-1})	2.776	5.119
Absorption correction	Empirical	Empirical
Min. and max. transmission	0.143, 0.170	0.070, 0.126
θ range (deg)	2.14–27.49	2.40–27.50
Refinement method	full–matrix least–squares on F^2	
Reflections collected	3462	1941
Independent reflections (R_{int})	2629 (0.0161)	1437 (0.0166)
Data/restraints/parameters	2411/0/215	1213/0/118
Goodness of fit on F^2	1.231	1.095
R_1, wR_2 $[I \geqslant 2\sigma(I)]$[a]	0.0289, 0.0815	0.0234, 0.0585
R_1, wR_2 (all data)[a]	0.0323, 0.0835	0.0301, 0.0620
Extinction coefficients	0.020(1)	0.0039(2)
A, B values in weighting scheme[b]	0.0484, 0.0000	0.0298, 0.618
$\delta\rho_{max}$, $\delta\rho_{min}$ (e Å^{-3})	0.608, –0.604	0.740, –0.775

[a] $\mathrm{w}R_2 = [\sum \mathrm{w}(F_o^2 - F_c^2)^2 / \sum \mathrm{w}(F_o^2)^2]^{1/2}$.
[b] $\mathrm{w} = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

Table 2
Atomic parameters and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms in $Mn_5(OH)_2L_4$ **1**

Atom	Wyckoff site	x	y	z	U_{eq}
Mn(1)	4*e*	0.37640(3)	0.20803(3)	1.16674(2)	0.0158(1)
Mn(2)	2*b*	$\frac{1}{2}$	0	1	0.0160(1)
Mn(3)	4*e*	0.67504(3)	0.18105(3)	0.84622(2)	0.0158(1)
O(1)	4*e*	0.1605(2)	0.1558(2)	1.1615(1)	0.0276(4)
O(2)	4*e*	0.1353(2)	–0.0742(2)	1.1548(1)	0.0293(4)
C(1)	4*e*	0.0883(2)	0.0465(2)	1.1542(2)	0.0205(4)
C(2)	4*e*	–0.0708(2)	0.0584(3)	1.1444(2)	0.0288(5)
C(3)	4*e*	–0.1274(2)	0.2058(2)	1.1417(2)	0.0241(5)
C(4)	4*e*	–0.2852(2)	0.2042(2)	1.1141(2)	0.0166(4)
O(3)	4*e*	–0.3312(2)	0.1460(2)	1.0260(1)	0.0199(3)
O(4)	4*e*	–0.3657(2)	0.2564(2)	1.1754(1)	0.0184(3)
O(5)	4*e*	0.3457(2)	0.4259(2)	1.1636(1)	0.0260(4)
O(6)	4*e*	0.2409(2)	0.4972(2)	1.1107(2)	0.0322(4)
C(5)	4*e*	0.2628(2)	0.4972(2)	1.0992(2)	0.0180(4)
C(6)	4*e*	0.1866(2)	0.4279(3)	1.0012(2)	0.0239(4)
C(7)	4*e*	0.2824(4)	0.4122(3)	0.9132(2)	0.0424(8)
C(8)	4*e*	0.3720(2)	0.2847(2)	0.9152(2)	0.0179(4)
O(7)	4*e*	0.3692(2)	0.1950(2)	0.9880(1)	0.0193(3)
O(8)	4*e*	0.4466(2)	0.2719(2)	0.8391(1)	0.0208(3)
O(9)	4*e*	0.5513(2)	–0.0037(1)	0.8401(1)	0.0156(3)

Note: U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic parameters and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms in $Cd_3(OH)_2L_2$ **2**

Atom	Wyckoff site	x	y	z	U_{eq}
Cd(1)	8*c*	0.16425(2)	0.01373(3)	0.53428(1)	0.0189(1)
Cd(2)	4*a*	$\frac{1}{2}$	0	$\frac{1}{2}$	0.0191(1)
O(1)	8*c*	0.1101(2)	–0.2969(4)	0.5868(1)	0.0265(5)
O(2)	8*c*	0.2630(3)	–0.4303(4)	0.6571(1)	0.0350(6)
C(1)	8*c*	0.1600(3)	–0.3467(5)	0.6526(2)	0.0216(6)
C(2)	8*c*	0.0893(3)	–0.2965(5)	0.7261(2)	0.0231(7)
C(3)	8*c*	0.1439(4)	–0.3811(6)	0.8012(2)	0.0258(7)
C(4)	8*c*	0.0806(3)	–0.3031(5)	0.8741(2)	0.0228(7)
O(3)	8*c*	0.0682(3)	–0.1244(4)	0.8809(2)	0.0343(6)
O(4)	8*c*	0.0451(2)	–0.4247(4)	0.9263(1)	0.0288(6)
O(5)	8*c*	0.3238(2)	–0.1768(4)	0.4876(1)	0.0213(5)

Note: U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

afforded a small amount of incarnadine clumpy aggregates of $Mn_5(OH)_2(C_4H_4O_4)_4$ **1** in brownish fine precipitate, which was not identified. The filtrate (pH = 5.76) obtained after separation of the precipitate was allowed to stand at room temperature and slow evaporation afforded well-shaped crystals of the triclinic modification of $Mn(H_2O)_4(C_4H_4O_4)$ [13,14] in high yield but no monoclinic modification of $Mn(H_2O)_4(C_4H_4O_4)$ [8a,14]. Both crystal structures of the triclinic and monoclinic modifications of $Mn(H_2O)_4(C_4H_4O_4)$ are similar, consisting of 1D $^1_\infty[Mn(H_2O)_4(C_4H_4O_4)_{2/2}]$ supramolecular chains [8a,13,14].

Single-crystal X-ray analyses show that compound **1** contains three crystallographically different Mn atoms (Mn(1), Mn(2) and Mn(3)), two crystallographically succinate anions and one OH group. The Mn(2) atoms are crystallographically imposed by $\bar{1}$ symmetry. As depicted in Fig. 1, the succinate anions adopt anti and gauche conformations, respectively, with the torsion angles of 171.0(2)° and 87.4(3)° for the carbon chains. As far as the anti-group is concerned, the carboxyl O atoms on one end each monodentately coordinate one Mn atom and those on the other end each bidentately bridge two Mn atoms. The gauche succinate anion chelates one Mn atom through two carboxyl O atoms from different ends to form seven-membered ring with one chelating O atom bonded to the second Mn atom and the non-chelating carboxyl O atoms to one and two

Table 4
Selected interatomic distances (Å) and bond angles (deg) for Mn$_5$(OH)$_2$L$_4$ **1**

Mn(1)–O(1)	2.120(2)	Mn(2)–O(7)	2.249(2)	Mn(3)–O(8)	2.347(2)	C(4)–O(4)	1.257(3)
Mn(1)–O(4)$^{\#1}$	2.503(2)	Mn(2)–O(7)$^{\#3}$	2.249(2)	Mn(3)–O(9)	2.131(2)	C(5)–O(5)	1.263(3)
Mn(1)–O(5)	2.114(2)	Mn(2)–O(9)	2.120(2)	C(1)–O(1)	1.255(3)	C(5)–O(6)	1.244(3)
Mn(1)–O(7)	2.236(2)	Mn(2)–O(9)$^{\#3}$	2.120(2)	C(1)–O(2)	1.244(3)	C(5)–C(6)	1.505(3)
Mn(1)–O(8)$^{\#2}$	2.189(2)	Mn(3)–O(2)$^{\#3}$	2.087(2)	C(1)–C(2)	1.517(3)	C(6)–C(7)	1.525(3)
Mn(1)–O(9)$^{\#3}$	2.088(2)	Mn(3)–O(3)$^{\#1}$	2.285(2)	C(2)–C(3)	1.515(3)	C(7)–C(8)	1.494(3)
Mn(2)–O(3)$^{\#1}$	2.135(2)	Mn(3)–O(4)$^{\#5}$	2.211(2)	C(3)–C(4)	1.508(3)	C(8)–O(7)	1.257(2)
Mn(2)–O(3)$^{\#4}$	2.135(2)	Mn(3)–O(6)$^{\#6}$	2.088(2)	C(4)–O(3)	1.267(3)	C(8)–O(8)	1.266(3)
O(1)/Mn(1)/O(4)$^{\#1}$	176.95(6)	O(3)$^{\#4}$/Mn(2)/O(7)$^{\#3}$	82.39(6)	O(4)$^{\#5}$/Mn(3)/O(9)	99.23(6)		
O(1)/Mn(1)/O(5)	95.80(7)	O(3)$^{\#4}$/Mn(2)/O(9)	95.92(6)	O(6)$^{\#6}$/Mn(3)/O(8)	90.18(7)		
O(1)/Mn(1)/O(7)	92.59(7)	O(3)$^{\#4}$/Mn(2)/O(9)$^{\#3}$	84.08(6)	O(6)$^{\#6}$/Mn(3)/O(9)	162.51(7)		
O(1)/Mn(1)/O(8)$^{\#2}$	103.42(7)	O(7)/Mn(2)/O(7)$^{\#3}$	180	O(8)/Mn(3)/O(9)	78.28(6)		
O(1)/Mn(1)/O(9)$^{\#3}$	95.93(6)	O(7)/Mn(2)/O(9)	98.18(5)	O(1)/C(1)/O(2)	125.7(2)		
O(4)$^{\#1}$/Mn(1)/O(5)	87.19(6)	O(7)/Mn(2)/O(9)$^{\#3}$	81.82(5)	O(1)/C(1)/C(2)	118.8(2)		
O(4)$^{\#1}$/Mn(1)/O(7)	87.87(6)	O(7)$^{\mathrm{III}}$/Mn(2)/O(9)	81.82(5)	O(2)/C(1)/C(2)	115.5(2)		
O(4)$^{\#1}$/Mn(1)/O(8)$^{\#2}$	76.05(6)	O(7)$^{\mathrm{III}}$/Mn(2)/O(9)$^{\#3}$	98.18(5)	C(1)/C(2)/C(3)	115.2(2)		
O(4)$^{\#1}$/Mn(1)/O(9)$^{\#3}$	81.13(5)	O(9)/Mn(2)/O(9)$^{\#3}$	180	C(2)/C(3)/C(4)	110.0(2)		
O(5)/Mn(1)/O(7)	92.87(6)	O(2)$^{\#3}$/Mn(3)/O(3)$^{\#1}$	93.51(7)	O(3)/C(4)/C(3)	115.8(2)		
O(5)/Mn(1)/O(8)$^{\#2}$	87.48(6)	O(2)$^{\#3}$/Mn(3)/O(4)$^{\#5}$	100.27(7)	O(4)/C(4)/C(3)	121.9(2)		
O(5)/Mn(1)/O(9)$^{\#3}$	167.69(7)	O(2)$^{\#3}$/Mn(3)/O(6)$^{\#6}$	97.81(7)	O(3)/C(4)/O(4)	122.3(2)		
O(7)/Mn(1)/O(8)$^{\#2}$	163.88(6)	O(2)$^{\#3}$/Mn(3)/O(8)	171.99(7)	O(5)/C(5)/O(6)	123.9(2)		
O(7)/Mn(1)/O(9)$^{\#3}$	82.85(6)	O(2)$^{\#3}$/Mn(3)/O(9)	94.03(7)	O(5)/C(5)/C(6)	119.0(2)		
O(8)$^{\#2}$/Mn(1)/O(9)$^{\#3}$	93.45(6)	O(3)$^{\#1}$/Mn(3)/O(4)$^{\#5}$	166.21(6)	O(6)/C(5)/C(6)	117.0(2)		
O(3)$^{\#1}$/Mn(2)/O(3)$^{\#4}$	180	O(3)$^{\#1}$/Mn(3)/O(6)$^{\#6}$	86.17(7)	C(5)/C(6)/C(7)	111.0(2)		
O(3)$^{\#1}$/Mn(2)/O(7)	82.39(6)	O(3)$^{\#1}$/Mn(3)/O(8)	87.45(6)	C(6)/C(7)/C(8)	117.7(2)		
O(3)$^{\#1}$/Mn(2)/O(7)$^{\#3}$	97.61(6)	O(3)$^{\#1}$/Mn(3)/O(9)	80.27(6)	O(7)/C(8)/C(7)	120.9(2)		
O(3)$^{\#1}$/Mn(2)/O(9)	84.08(6)	O(4)$^{\#5}$/Mn(3)/O(6)$^{\#6}$	91.30(7)	O(8)/C(8)/C(7)	117.3(2)		
O(3)$^{\#1}$/Mn(2)/O(9)$^{\#3}$	95.92(6)	O(4)$^{\#5}$/Mn(3)/O(8)	78.99(6)	O(7)/C(8)/O(8)	122.9(2)		
O(3)$^{\#4}$/Mn(2)/O(7)	97.61(6)						
Hydrogen bonding contacts							
D–H	*d*(D–H)	*d*(H · · · A)	∠(D–H · · · A)	*d*(D–H · · · A)	A		
O(9)–H(5)	0.81	2.07	169	2.873	O(5)$^{\#9}$		

Symmetry codes: #1, $x+1, y, z$; #2, $x, -y+1/2, z+1/2$; #3, $-x+1, -y, -z+2$; #4, $-x, -y, -z+2$; #5, $x+1, -y+1/2, z-1/2$; #6, $-x+1, -y+1, -z+2$; #7, $x-1, y, z$; #8, $x-1, -y+1/2, z+1/2$; #9, $x, -y+1/2, z-1/2$.

Table 5
Selected interatomic distances (Å) and bond angles (deg) for Cd$_3$(OH)$_2$L$_2$ **2**

Cd(1)–O(1)	2.385(3)	Cd(1)–O(5)$^{\#1}$	2.274(2)	Cd(2)–O(5)	2.249(2)	C(2)–C(3)	1.519(5)
Cd(1)–O(2)$^{\#1}$	2.261(2)	Cd(2)–O(1)$^{\#1}$	2.347(2)	Cd(2)–O(5)$^{\#7}$	2.249(2)	C(3)–C(4)	1.510(5)
Cd(1)–O(4)$^{\#2}$	2.316(2)	Cd(2)–O(1)$^{\#4}$	2.347(2)	C(1)–O(1)	1.285(4)	C(4)–O(3)	1.240(4)
Cd(1)–O(4)$^{\#3}$	2.372(2)	Cd(2)–O(3)$^{\#5}$	2.315(2)	C(1)–O(2)	1.243(4)	C(4)–O(4)	1.277(4)
Cd(1)–O(5)	2.291(2)	Cd(2)–O(3)$^{\#6}$	2.315(2)	C(1)–C(2)	1.500(4)		
O(1)/Cd(1)/O(2)$^{\#1}$	83.68(9)	O(5)/Cd(1)/O(5)$^{\#1}$	111.85(7)	O(3)$^{\#6}$/Cd(2)/O(5)$^{\#7}$	81.64(9)		
O(1)/Cd(1)/O(4)$^{\#2}$	85.82(9)	O(1)$^{\#1}$/Cd(2)/O(1)$^{\#4}$	180	O(5)/Cd(2)/O(5)$^{\#7}$	180		
O(1)/Cd(1)/O(4)$^{\#3}$	79.95(9)	O(1)$^{\#1}$/Cd(2)/O(3)$^{\#5}$	99.93(9)	O(1)/C(1)/O(2)	122.9(3)		
O(1)/Cd(1)/O(5)	78.37(8)	O(1)$^{\#1}$/Cd(2)/O(3)$^{\#6}$	80.07(9)	O(1)/C(1)/C(2)	117.1(3)		
O(1)/Cd(1)/O(5)$^{\#1}$	168.96(8)	O(1)$^{\#1}$/Cd(2)/O(5)	87.78(9)	O(2)/C(1)/C(2)	120.0(3)		
O(2)$^{\#1}$/Cd(1)/O(4)$^{\#2}$	164.97(9)	O(1)$^{\#1}$/Cd(2)/O(5)$^{\#7}$	92.22(9)	C(1)/C(2)/C(3)	114.8(3)		
O(2)$^{\#1}$/Cd(1)/O(4)$^{\#3}$	91.87(9)	O(1)$^{\#4}$/Cd(2)/O(3)$^{\#5}$	80.07(7)	C(2)/C(3)/C(4)	112.4(3)		
O(2)$^{\#1}$/Cd(1)/O(5)	99.3(1)	O(1)$^{\#4}$/Cd(2)/O(3)$^{\#6}$	99.93(9)	O(3)/C(4)/C(3)	118.4(3)		
O(2)$^{\#1}$/Cd(1)/O(5)$^{\#1}$	98.27(9)	O(1)$^{\#4}$/Cd(2)/O(5)	92.22(9)	O(4)/C(4)/C(3)	118.1(3)		
O(4)$^{\#2}$/Cd(1)/O(4)$^{\#3}$	75.70(9)	O(1)$^{\#4}$/Cd(2)/O(5)$^{\#7}$	87.78(9)	O(3)/C(4)/O(3)	123.5(3)		
O(4)$^{\#2}$/Cd(1)/O(5)	89.04(8)	O(3)$^{\#5}$/Cd(2)/O(3)$^{\#6}$	180	Cd(1)/O(5)/Cd(1)$^{\#8}$	117.1(1)		
O(4)$^{\#2}$/Cd(1)/O(5)$^{\#1}$	90.07(9)	O(3)$^{\#5}$/Cd(2)/O(5)	81.64(9)	Cd(1)/O(5)/Cd(2)	106.3(1)		
O(4)$^{\#3}$/Cd(1)/O(5)	154.28(9)	O(3)$^{\#5}$/Cd(2)/O(5)$^{\#7}$	98.36(9)	Cd(1)$^{\#8}$/O(5)/Cd(2)	115.2(1)		
O(4)$^{\#3}$/Cd(1)/O(5)$^{\#1}$	89.11(9)	O(3)$^{\#6}$/Cd(2)/O(5)	98.36(9)				

Symmetry codes: #1, $-x+1/2, y+1/2, z$; #2, $x, -y-1/2, z-1/2$; #3, $-x, y+1/2, -z+3/2$; #4, $x+1/2, -y-1/2, -z+1$; #5, $-x+1/2, -y, z-1/2$; #6, $x+1/2, y, -z+3/2$; #7, $-x+1, -y, -z+1$; #8, $x-1/2, -y-1/2, -z+1$; #9, $x, -y-1/2, z+1/2$; #10, $-x, y-1/2, -z+3/2$; #11, $-x+1/2, -y, z+1/2$; #12, $-x+1/2, -y-1/2, -z+1$.

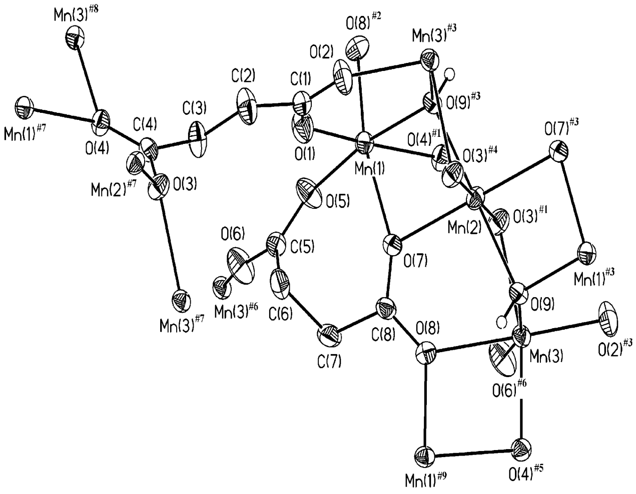

Fig. 1. Ortep view of the coordination modes of both *trans* and gauche succinato ligands and the atomic labelling for **1**. The displacement ellipsoids are drawn at 60% probability level (symmetry codes: see Table 4).

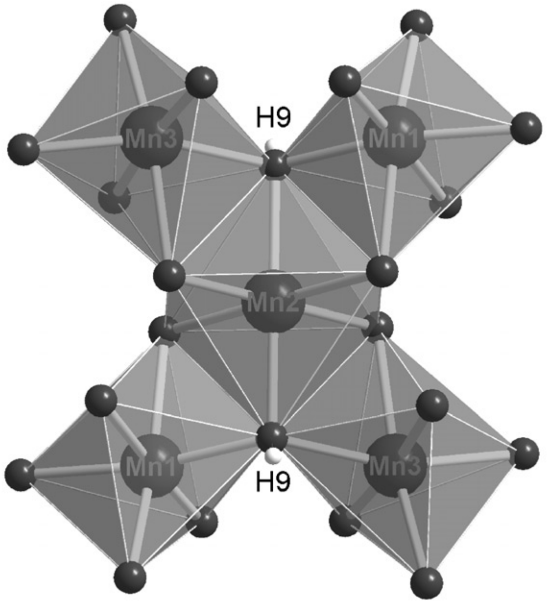

Fig. 2. Edge-shared Mn_5O_{22} pentamer in **1**.

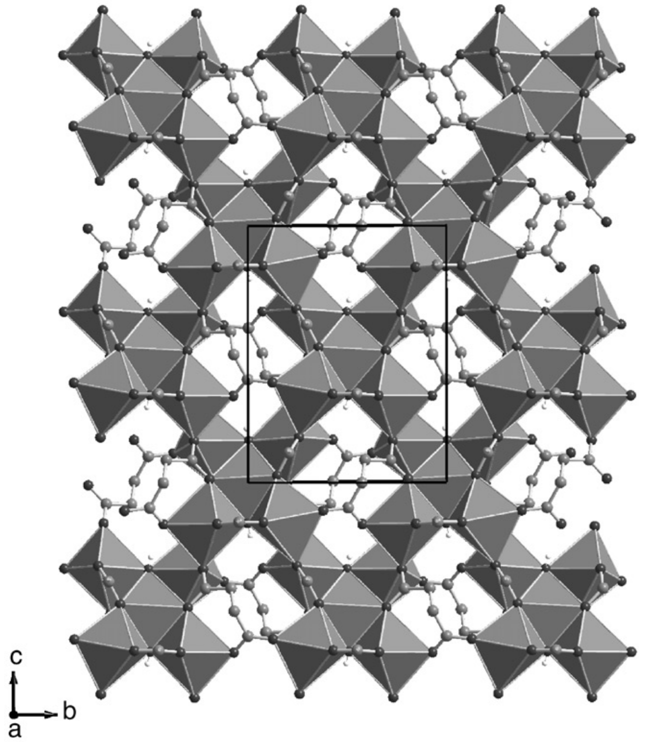

Fig. 3. 2D manganese oxide layer generated from edge-sharing Mn_5O_{22} pentamers with the intralayer gauche succinato ligands within apertures.

Mn atoms, respectively. All succinate anions exhibit the typical bonding values (Table 4). All Mn atoms are each in distorted octahedral MnO_6 coordination. Six O atoms about the Mn(1) atom belong to one hydroxide group, two anti-succinate groups and two gauche succinate groups and those around the Mn(3) atom to one hydroxide group, two gauche succinate groups and three anti-dicarboxylate anions, whereas the O atoms coordinating Mn(2) atom come from two hydroxide groups, two anti-succinate groups and two gauche succinate groups. The Mn–O bond distances fall in the region 2.114–2.503, 2.120–2.249, and 2.087–2.347 Å for Mn(1), Mn(2), and Mn(3), respectively. The cisoid O–Mn–O bond angles around Mn(1), Mn(2), and Mn(3) are within the range 76.05–95.90°, 81.82–98.18°, and 78.99–99.23°, respectively, and the transoid O–Mn–O bond angles around Mn(1) and Mn(3) in the region 163.88–176.95° and 162.51–171.99°, respectively, while the transoid O–Mn–O bond angles at Mn(2) are equal to 180° due to the crystallographically symmetric imposition. Through two couple opposite oxygen–oxygen edges, the Mn(2)O_6 octahedron is connected to two Mn(1)O_6 octahedra and two Mn(3)O_6 octahedra, forming edge-shared Mn_5O_{22} pentamer with all Mn atoms in an exact plane (Fig. 2). The pentamers are further interconnected via two couple remote opposite oxygen–oxygen edges with four neighbors to generate Mn oxide layers parallel to (100) with the chelating gauche succinato groups residing on both sides of the pseudo rhomboid apertures (Fig. 3). The resulting layers are pillared by the anti-succinato ligands to complete 3D coordination polymer (Fig. 4).

Fig. 5 illustrates the thermal behavior of $Mn_5(OH)_2(C_4H_4O_4)_4$ **1**. The compound is found to be stable below 345°C, from which on the investigated sample decomposes in two continuous endothermic steps centered at 393°C and 438°C, respectively. At 475°C, the observed weight loss reaches 34.5% close to the calculated value of 35.49% for one mole of H_2O, four moles of C_2H_4, two moles of CO_2 and two moles of CO molecules per

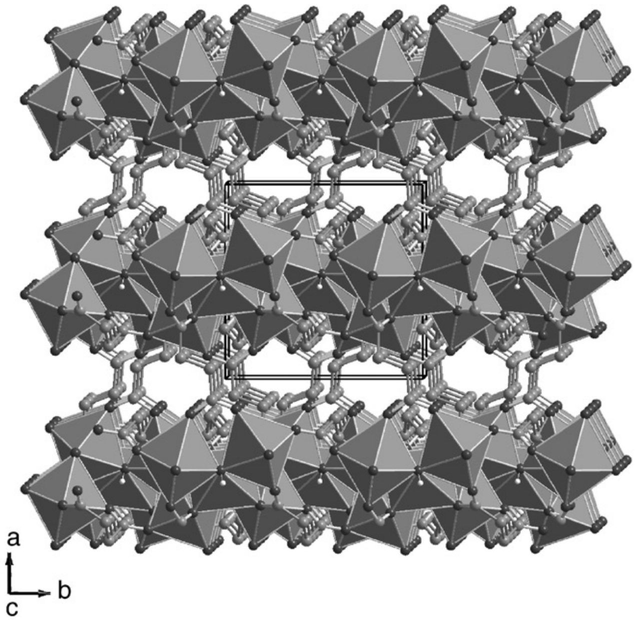

Fig. 4. 2D manganese oxide layers are pillared by interlayer *trans* succinato ligands in **1**.

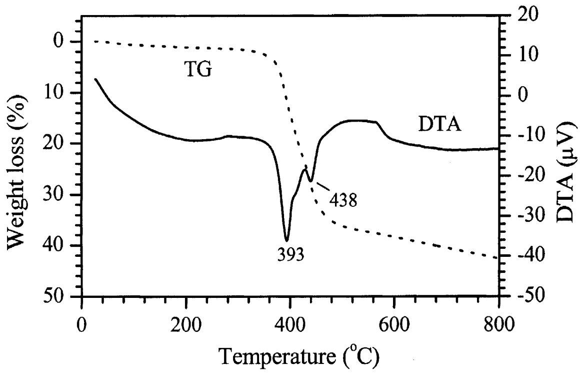

Fig. 5. TG-DTA curves for **1** upon heating in nitrogen stream from room temperature to 800°C.

formula unit. On further heating, the sample gradually loses weight and the additional weight loss of 8.1% at 800°C corresponds to the calculated value of 7.25% for two moles of CO molecules.

Fig. 6 demonstrates the temperature dependence of the inverse susceptibilities (χ_m^{-1}) and effective magnetic moments (μ_{eff}) of **1**, where the χ_m is the magnetic susceptibility per molar Mn^{2+} ion and the effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_m T)^{1/2}$. Over the temperature range 5–300 K, the Mn(II) coordination polymer is paramagnetic, obeying the Curie–Weiss law $\chi_m(T-\Theta) = 4.46(2)\,cm^3\,mol^{-1}\,K$ with the Weiss constant $\Theta = -67.3(3)\,K$. Slightly less than the spin-only value (5.92 B.M.) for the octahedrally coordinated high-spin Mn(II) compound [15], the effective magnetic moment is 5.36 μ_B at room temperature and decreases to 1.55 μ_B at 5 K.

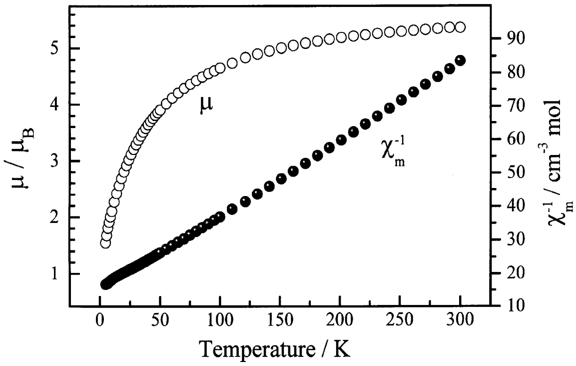

Fig. 6. The χ_m^{-1} vs. T plot of **1** (χ_m^{-1} being the inverse magnetic susceptibility per Mn^{2+} ion).

3.2. *$Cd_3(OH)_2(C_4H_4O_4)_2$* **2**

2 was obtained from hydrothermal reaction of $CdCl_2 \cdot 2.5H_2O$, succinic acid and KOH in H_2O. After reaction, the pH value of the filtrate is 6.3, significantly lower than the pH value of 8.82 of the initial charged suspension. Here, it should be noted that after submission of the initial version of this manuscript and under guidance of one refree we have found that Rao and co-workers, in a very recent issue of inorganic chemistry, had reported crystal structure of **2**, which was obtained by hydrothermal reaction of $CdCl_2$, succinic acid in the presence of piperidine in a mixture of H_2O, *n*-butanol and diazabicyclo[2,2,2]octane at 150°C for 78 h [16].

The X-ray structure analyses show no significant difference between our present results and those by Rao and co-workers. Within coordination polymer **2** exist two crystallographically distinct Cd atoms (Cd(1) and Cd(2)), one hydroxide group and one succinate anion adopting anti-conformation. Both carboxylate group of the succinate anion functions similarly with one carboxyl O atom monodentately coordinating one Cd atom and the other one bidentately bridging two metal atoms (Fig. 7). As expected, the C–O bonds to the bidentate O atoms are significantly longer than those to the monodentate one (Table 5). Contrary to both known Cd succinate compounds $Cd(H_2O)_2(C_4H_4O_4)$ [8b] and $[Cd(H_2O)_2(C_4H_4O_4)] \cdot 0.5H_2O$ [17], where Cd atoms are each in pentagonal bipyramidal environments, the metal atoms in the present cadmium coordination polymer reside in the distorted octahedral CdO_6 geometries, each of which is defined by two hydroxide O atoms and four carboxyl O atoms of different succinato ligands. Both hydroxide O atoms occupy the cis and trans positions around Cd(1) and Cd(2) atoms, respectively (Fig. 7). The Cd–O bond distances for Cd(1) vary from 2.274 to 2.385 Å and those for Cd(2) from 2.249 to 2.347 Å. The cisoid O–Cd–O bond angles fall in the region 75.70–99.3, 80.07–99.93° for Cd(1) and Cd(2), respectively. The axes through the Cd(1) exhibit considerable

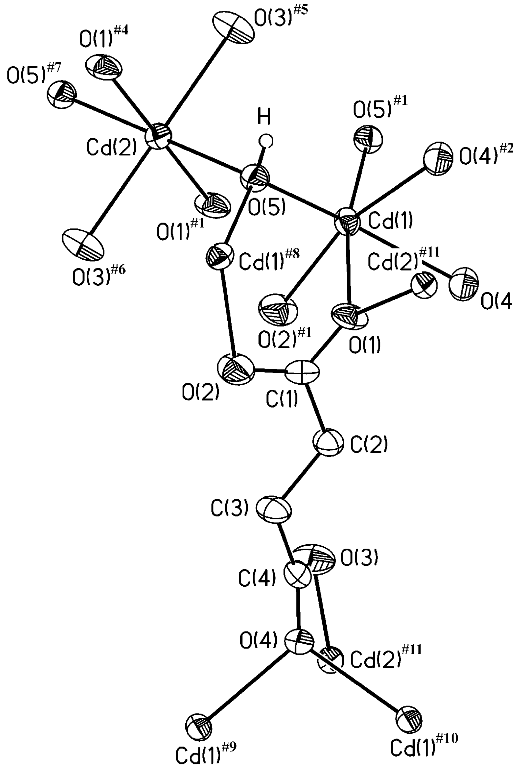

Fig. 7. Ortep view of the coordination mode of succinato ligand and the atomic labelling for **2**. The displacement ellipsoids are drawn at 60% probability level (symmetry codes: see Table 5).

deviation from linerarity while the transoid O–Cd–O bond angles for Cd(2) are equal to 180° due to the crystallographically imposed $\bar{1}$ symmetry. Two coordination polyhedra with Cd(1) centers are edge shared to form Cd_2O_{10} bioctahedron. One octahedron with Cd(2) center is surrounded by six octahedra from four bioctahedra and each bioctahedra is in turn surrounded by four $Cd(2)O_6$ octahedra at the corners of one rhombus and four $Cd(1)O_6$ octahedra of different bioctahedra, thus giving 2D cadmium oxide layers extending infinitely parallel to (001) (Fig. 8). The formed corrugated Cd oxide layers are pillared by the succinato ligands into 3D framework illustrated in Fig. 8.

The thermal behavior of the title Cd(II) compound is demonstrated in Fig. 9. The sample starts decomposition at 270°C in a flowing nitrogen atmosphere. Over the temperature range 270–420°C, two endothermic peaks at 375°C and 395°C are observed and the observed weight loss of 36.2% corresponds well to the value of 36.36% calculated for 1 mol H_2O, 2 mol C_2H_4, 2 mol CO_2 and 2 mol CO molecules per formula unit. The observed weight losses over the temperature range 420–600°C and 600–800°C are 36.9% and 14.6%, respectively, which may be due to sublimation and decomposition of the initially formed CdO, but reasonable interpretation is unfortunately impossible at present.

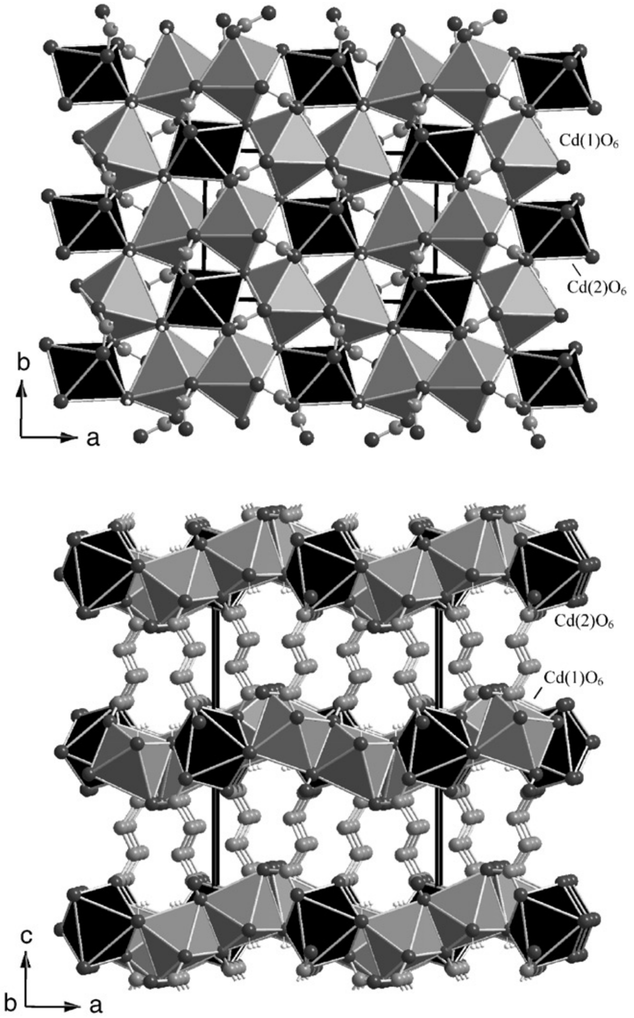

Fig. 8. (Top) the cadmium oxide layer; (Bottom) the 2D cadmium oxide layers are pillared by succinato ligands in **2**.

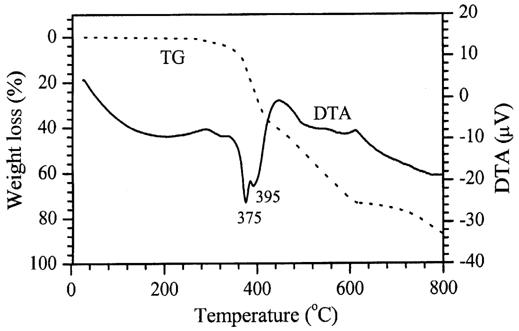

Fig. 9. TG-DTA curves for **2** upon heating in nitrogen stream from room temperature to 800°C.

Acknowledgments

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