1, 2-, 1, 3- and 1, 4-Cyclohexanedicarboxylates of Cd and Mn with chain and layered structures[†]

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A systematic study has been carried out on the three isomeric cyclohexanedicarboxylates (CHDCs) formed by cadmium and manganese with the three isomeric dicarboxylic acids, in the presence or absence of amines. The CHDCs have been prepared under hydrothermal conditions and their structures established by X-ray crystallography. We have been able to isolate two-dimensional layered structures of 1,2-, 1,3- and 1,4-cyclohexanedicarboxylates and chain structures of 1,3- and 1,4-cyclohexanedicarboxylates. The infinite metal–oxygen–metal linkages are observed only in the case of the 1,2-dicarboxylate. In all the three isomeric cyclohexanedicarboxylates, the e,e conformation is most favored, although the 1,4-CHDCs often contain rings in both the e,e and the a,e conformations.

Introduction

Other than the aluminosilicates and phosphates, metal carboxylates constitute a large family of open framework structures.1-18 A variety of metal carboxylates has been studied for their interesting properties such as porosity, sorption, catalysis, non-linear optics, luminescence and magnetism.¹⁹⁻³⁰ In particular, the benzenedicarboxylic acids have been found to be the ideal ligands for designing coordination polymers and open framework structures.^{1-9,13} Cyclohexanedicarboxylic acids would similarly be expected to be useful ligands, considering that they also occur in different conformations. There have, however, been very few metal cyclohexanedicarboxylates (CHDCs) reported in the literature.³¹⁻³⁴ We have been investigating the compounds formed by cadmium and manganese with 1,2-, 1,3- and 1,4-cyclohexanedicarboxylic acids in the presence and absence of organic amines, with a view to examine the structure, conformation as well as dimensionality. In 1,2 derivatives, the equatorial, equatorial (e,e) and the axial, equatorial (a,e) conformers are known as the cis isomers. The axial, axial (a,a) conformer is known as the *trans* isomer. In 1,3 derivatives, the (e,e) and the (a,a) conformers are known as the cis isomers. The (a,e) conformer is known as the trans isomer. In 1.4 derivatives, the (e,e) and the (a,a) conformers are known as the trans isomers. The (a,e) conformer is known as the cis isomer. It is to be noted that the e,e form is most stable in the 1,2-, 1,3and 1,4-CHDCs and the a,a form is least stable. The a,e form is reasonably stable in the 1,4-CHDCs. The present study has enabled us to isolate several isomeric CHDCs of Cd and Mn with chain and layered structures, where the e,e conformation dominates in all except the 1,4-derivatives. In the latter, the a,e conformation also occurs.

Experimental

All the Cd and Mn CHDCs were synthesized by hydrothermal methods by heating the corresponding homogenized reaction mixture in a 23 ml PTFE-lined bomb at 180 °C (150 °C for VIII) for 72 h under autogenous pressure. The pH of the starting reaction mixture was generally in the range 5-6. The pH after the reaction did not show appreciable change. The products of the hydrothermal reactions were vacuum filtered and dried under ambient conditions. The starting compositions for the different new CHDCs synthesized by us are as follows, I $[Cd(H_2O)_2(C_8H_{10}O_4)]$, $1 \text{ Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O} (0.272 \text{ g}, 1 \text{ mM}) : 1(1,4\text{-CHDC}) (0.176 \text{ g}, 1 \text{ mM})$ 1 mM) : 1 piperidine (0.1 ml, 1 mM) : 278 H₂O (5 ml, 278 mM); II $[Cd(C_8H_{10}O_4)(C_{10}H_8N_2)] \cdot H_2O$, $2Cd(OAc)_2 \cdot 2H_2O$ (0.136 g, 0.5 mM) : 2(1,4-CHDC) (0.088 g, 0.5 mM) : 1(2,2'bipy) (0.04 g, 0.25 mM) : 2 piperidine (0.05 ml, 0.5 mM) : 1111 H_2O (5 ml, 278 mM); III [Cd₃(C₈H₁₀O₄)₃(C₁₂H₈N₂)₂]·4H₂O, $2 Cd(OAc)_2 \cdot 2H_2O$ (0.136 g, 0.5 mM) : 1(1,4-CHDC) (0.088 g, 0.5 mM) : 1 (1,10-phen) (0.0.05 g, 0.25 mM) : 2 NaOH (0.1 ml of 5 M solution, 0.5 mM) : $1111 H_2O$ (5 ml, 278 mM); IV $[Mn_3(C_8H_{10}O_4)_3(C_{12}H_8N_2)_2] \cdot 4H_2O$, $2 MnCl_2 \cdot 4H_2O$ (0.102 g, 0.5 mM) : 1(1,4-CHDC) (0.088 g, 0.5 mM) : 1(1,10-phen) (0.0.05 g, 0.25 mM) : 2 piperidine (0.0.05 ml, 0.5 mM) : 1111 H₂O (5 ml, 278 mM); V [Mn₃(C₈H₁₀O₄)₃(C₁₂H₈N₂)₂]·4H₂O, $2 \text{ Mn}(\text{OAc})_2 \cdot 4 \text{H}_2 \text{O}$ (0.124 g, 0.5 mM) : 1(1,3-CHDC) (0.088 g, 0.5 mM) : 1(1,10-phen) (0.05 g, 0.25 mM) : 2 piperidine (0.0.05 ml, 0.5 mM) : $1111 \text{ H}_2\text{O}$ (5 ml, 278 mM); VI $[Cd(H_2O)_2(C_8H_{10}O_4)] \cdot 2H_2O, 1 Cd(OAc)_2 \cdot 2H_2O (0.272 g, 1 mM) :$ 1 (1,3-CHDC) (0.176 g, 1 mM) : 2 NaOH (0.4 ml of 5 M solution, 2 mM) : 278 H₂O (5 ml, 278 mM). VII [Cd(C₈H₁₀O₄)(C₁₂H₈N₂)], 1 Cd(OAc)₂·2H₂O (0.272 g, 1 mM) : 1(1,3-CHDC) (0.176 g, 1 mM) : 1(1,10-phen) (0.199 g, 1 mM) : 2NaOH (0.4 ml of 5 M solution, 2 mM) : 278 H₂O (5 ml, 278 mM; VIII $[Mn(H_2O)(C_8H_{10}O_4)(C_{12}H_8N_2)], 2 Mn(OAc)_2 \cdot 4H_2O (0.124 g,$ 0.5 mM): 1 (1,3-CHDC) (0.088 g, 0.5 mM): 1 (1,10-phen) (0.05 g, 0.25 mM) : 2 piperidine (0.0.05 ml, 0.5 mM) : 1111 H₂O (5 ml, 278 mM); IX [Cd(C₈H₁₀O₄)], 1 Cd(OAc)₂·2H₂O (0.272 g, 1 mM) : 1 (anhydride of 1,2-CHDC) (0.162 g, 1 mM) : 1 piperidine (0.1 ml, 1 mM) : 278 H₂O (5 ml, 278 mM). Powder XRD patterns of

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[†] Electronic supplementary information (ESI) available: Tables S1–S9: Selected bond distances and angles for I–IX. Fig. S1: Plots of experimental μ_{eff} vs. T and $1/\chi_m$ vs. T of IV, V and VIII. Fig. S2: Photoluminescence spectra of I–IX. See DOI: 10.1039/b512843a

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the products were recorded using Cu-K α radiation (Rich-Seifert, 3000TT). The patterns agreed with those calculated for single-crystal structure determination.

Thermogravimetric analysis (TGA) was carried out (Mettler-Toledo) in oxygen atmosphere (flow rate = 50 ml min⁻¹) in the temperature range 25–900 °C (heating rate = 5 °C min⁻¹). Infra-red (IR) spectroscopic studies have been carried out in the mid-IR region using KBr pellets (Bruker IFS-66v). The spectra show characteristic bands of the carboxylate units. Room temperature photoluminescence spectra of samples were recorded on powdered samples. A Perkin-Elmer spectrometer (LS-55) with a single beam set-up was employed using a xenon lamp (50 watt) as the source and a photo-multiplier tube as the detector. The temperature-dependent magnetic susceptibilities of **IV**, **V** and **VIII** were measured from 5 to 300 K in a constant magnetic field of 0.5 T.

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Ka radiation, $\lambda = 0.71073$ Å) operating at 40 kV and 40 mA. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.³⁵ The structure was solved and refined using the SHELXTL-PLUS suite of program.35 All the hydrogen atoms of the carboxylic acids were located in the difference Fourier maps. For the final refinement the hydrogen atoms on the carboxylic acid were placed geometrically and held in the riding mode. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms except C(53)-C(57) in VII and C(2) in IX, and isotropic thermal parameters for the hydrogen atoms. All the hydrogen atoms were included in the final refinement for I, II, IV, VII, VIII and XI. The hydrogen atoms associated with the water molecules (coordinated or lattice water) of III, V, and VI were

located from the difference Fourier maps, but not stable during refinement, hence these hydrogen atoms are excluded from the final refinement. Details of the structure solution and final refinements for the compounds **I–IX** are given in Tables 1–3. The powder XRD patterns of **I–IX** were recorded and were consistent with the patterns generated from single-crystal structure determination.

CCDC reference numbers 283059–283067.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512843a

Results and discussion

We have been able to synthesize the cadmium derivatives of all the three isomeric cyclohexanedicarboxylic acids and the manganese derivatives of the 1,3- and 1,4-cyclohexanedicarboxylic acids. In the case of the 1,3- and 1,4-CHDCs, we have found both onedimensional chain and two-dimensional layered structures. We have isolated only a layered Cd 1,2-CHDC. The conformation of the cyclohexanedicarboxylate acid in the different metal derivatives is an important aspect of the study. In the 1,4-CHDCs, the e,e conformer (trans structure) is the most stable form, while the a,a conformer (trans structure) is the least stable form because of the 1,3-diaxial hindrance. The stability of the a,e conformer (cis structure) falls in between the a.a and e.e forms. In the 1.3-CHDCs, the e,e conformer (cis structure) is more stable than the a,a conformer (cis structure) and the a,e conformer (trans structure) is chiral. In the 1,2-CHDCs, the e,e conformer (trans structure) is most stable. In what follows, we discuss the structures of the Cd and Mn CHDCs along with their conformations.

1,4-Cyclohexanedicarboxylates

The cadmium 1,4-cyclohexanedicarboxylate $[Cd(H_2O)_2(C_8H_{10}-O_4)]$, **I**, is a one-dimensional chain structure consisting of octahedral CdO₆ units connected by the carboxylate groups (Fig. 1),

Table 1 Crystal data and structure refinement parameters for 1,4-CHDCs I, II and III

	I	П	ш
Empirical formula	$C_8H_{14}CdO_6$	$C_{18}H_{20}CdN_2O_5$	$C_{48}H_{54}Cd_3N_4O_{16}$
$M_{\rm r}$	318.59	456.76	1280.15
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>C</i> 2/ <i>c</i> (no. 15)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>P</i> 1̄ (no. 2)
a/Å	11.5724(3)	17.3563(4)	8.9419(2)
b/Å	5.4816(2)	11.8464(3)	11.9987(3)
c/Å	16.7944(4)	18.3098(5)	12.4863(2)
$a/^{\circ}$	90	90	102.4650(10)
β/°	102.941(2)	97.1720(10)	91.7580(10)
y/°	90	90	111.7710(10)
$V/Å^3$	1038.30(5)	3735.22(16)	1205.70(5)
Ζ	4	8	1
$D_{\rm c}/{\rm g~cm^{-3}}$	2.038	1.624	1.763
μ/mm^{-1}	2.110	1.200	1.387
Total data collected	2104	7651	5149
Unique data	753	2676	3440
Observed data $[I > 2\sigma(I)]$	735	2438	3118
$R_{ m merg}$	0.0376	0.0304	0.0179
<i>R</i> indexes $[I > 2\sigma(I)]$	$R_1 = 0.0357;^a w R_2 = 0.901^b$	$R_1 = 0.0300;^a w R_2 = 0.0805^b$	$R_1 = 0.0210^a; wR_2 = 0.553^b$
R indexes (all data)	$R_1 = 0.03704;^a w R_2 = 0.913^b$	$R_1 = 0.0327;^a w R_2 = 0.0827^b$	$R_1 = 0.0232^a; wR_2 = 0.0561^b$

^{*a*} $R_1 = \sum ||F_o|| - |F_c|| / \sum |F_o||$, ^{*b*} $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o^2, 0) + 2(F_c)^2] / 3$, where a = 0.545 and b = 4.8788 for I, a = 0.0394 and b = 10.4253 for II, and a = 0.0321 and b = 0.0 for III.

Table 2 Crystal data and structure refinement parameters for 1,4- and 1,3-CHDCs IV, V and VI

	IV	V	VI
Empirical formula	$C_{48}H_{54}Mn_3N_4O_{16}$	$C_{48}H_{54}Mn_3N_4O_{16}$	$C_8H_{16}CdO_7$
M_r	1107.77	1107.77	336.61
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 1̄ (no. 2)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>Pccn</i> (no. 56)
a/Å	8.8827(15)	8.5210(4)	13.1510
b/Å	11.856(2)	21.5643(10)	20.4388(4)
c/Å	12.321(2)	26.7853(12)	8.5602(2)
a/°	76.791(2)	90	90
β/°	87.930(3)	91.0070(10)	90
y/°	68.309(2)	90	90
$V/Å^3$	1172.1(3)	4921.0(4)	2300.81(7)
Ζ	1	4	8
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.569	1.495	1.943
u/mm^{-1}	0.874	0.833	1.916
Total data collected	13718	10308	8944
Unique data	5463	3546	1654
Observed data $[I > 2\sigma(I)]$	4366	2749	1479
R _{merg}	0.0281	0.0418	0.0329
<i>R</i> indexes $[I > 2\sigma(I)]$	$R_1 = 0.0384;^a w R_2 = 0.0907^b$	$R_1 = 0.05777;^a w R_2 = 0.1542^b$	$R_1 = 0.0309;^a w R_2 = 0.0670^b$
R indexes (all data)	$R_1 = 0.0519^a$; $wR_2 = 0.0954^b$	$R_1 = 0.0779^a$; $wR_2 = 0.1694^b$	$R_1 = 0.0373;^a w R_2 = 0.0705^b$

 ${}^{a}R_{1} = \sum ||F_{\circ}|| - ||F_{\circ}|| / \sum ||F_{\circ}|| \cdot {}^{b}wR_{2} = \{\sum [w(F_{\circ}^{2} - F_{\circ}^{2})^{2}] / \sum [w(F_{\circ}^{2})^{2}] \}^{1/2}; w = 1/[\sigma^{2}(F_{\circ})^{2} + (aP)^{2} + bP], P = [\max.(F_{\circ}^{2}, 0) + 2(F_{\circ})^{2}] / 3, \text{ where } a = 0.0505 \text{ and } b = 0.0 \text{ for } \mathbf{IV}, a = 0.0845 \text{ and } b = 16.1649 \text{ for } \mathbf{V}, \text{ and } a = 0.0185 \text{ and } b = 7.0434 \text{ for } \mathbf{IV}.$

Table 3 Crystal data and structure refinement parameters for 1,3- and 1,2-CHDCs VII, VIII and IX

	VII	VIII	IX
Empirical formula	$C_{40}H_{36}Cd_2N_4O_8$	$C_{40}H_{40}Mn_2N_4O_{10}$	$C_8H_{10}CdO_4$
M _r	925.53	846.64	282.56
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)
a/Å	11.6099(2)	9.8431(5)	27.349(7)
b/Å	17.0455(2)	17.6527(9)	4.9842(12)
c/Å	18.5687(2)	11.6066(5)	12.627(3)
β/°	104.8900	104.0900(10)	96.163(4)
$V/Å^3$	3551.29(8)	1956.06(16)	1711.3(7)
Ζ	4	2	8
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.731	1.437	2.193
μ/mm^{-1}	1.259	0.708	2.528
Total data collected	14758	8107	4868
Unique data	5076	2804	1994
Observed data $[I > 2\sigma(I)]$	4509	2282	1575
R _{merg}	0.0416	0.0326	0.040
<i>R</i> indexes $[I > 2\sigma(I)]$	$R_1 = 0.0500;^a w R_2 = 0.1336^b$	$R_1 = 0.0718;^a w R_2 = 0.1430^b$	$R_1 = 0.0843;^a w R_2 = 0.2058^b$
R indexes (all data)	$R_1 = 0.0556;^a w R_2 = 0.1375^b$	$R_1 = 0.0889;^a w R_2 = 0.1504^b$	$R_1 = 0.1004;^a w R_2 = 0.2136^b$

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|$. ${}^{b}wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}$; $w = 1/[\sigma^{2}(F_{o})^{2} + (aP)^{2} + bP]$, P = [n 0.0665 and b = 13.3409 for VII, a = 0.0271 and b = 4.6127 for VIII, and a = 0.1345 and b = 0.0 for IX.

with the asymmetric unit containing eight non-hydrogen atoms. The cadmium atom sits on the twofold axis, on an inversion center, 4e. This cadmium atom is in a distorted octahedral environment (CdO₆) with the Cd–O bond distances in the 2.295(4)–2.404(4) Å range. Two of the oxygens in the CdO₆ polyhedron are from the coordinated water molecules and the remaining four oxygens are from two different carboxyl groups with (11) connectivity.³⁶ The polyhedra are connected to each other by the dicarboxylates with (1111) connectivity,³⁶ resulting in a one-dimensional infinite zigzag chain. The cyclohexane ring lies about an inversion center. The two carboxylate groups are in equatorial position (e,e), the torsional angle (θ) between the two being 180°. The structure is stabilized by inter chain hydrogen bonding interaction between the water

molecules and the carboxylate oxygen (H · · · O 1.85(3)–1.90 (3) Å, O · · · O 2.708(3)–2.731(2) Å and $\angle O$ –H · · · O 168(2)–173(2)°).

The cadmium 1,4-cyclohexanedicarboxylate $[Cd(C_8H_{10}O_4)-(C_{10}H_8N_2)]\cdot H_2O$, **II**, is a two-dimensional layer structure (Fig. 2), formed by the connectivity of $Cd_2N_4O_8$ dimers and the carboxylate groups. The asymmetric unit of **II** contains 27 non-hydrogen atoms. The cadmium atom is in a distorted pentagonal bipyramidal environment (CdN₂O₅) with the Cd–O bond distances in the 2.269(3)–2.624(3) Å range and Cd–N bond distances are 2.342(3) and 2.349(3) Å. The two nitrogens of the CdN₂O₅ polyhedron are from the terminal 2,2'-bipy molecule and the oxygens are from three different carboxylic acid groups with (11) or (21) connectivity.³⁶ Two such polyhedra form an edge-sharing dimer



Fig. 1 (a) Structure of $[Cd(H_2O)_2(C_8H_{10}O_4)]$, I and (b) the packing arrangement in I, viewed along the *a* axis.



Fig. 2 (a) Structure of $[Cd(C_8H_{10}O_4)(C_{10}H_8N_2)] \cdot H_2O$, **II** and (b) view of the layered structure of **II** along the *b* axis.

by sharing the μ_2 oxygen atom from a tridentate carboxylate (21). These dimers are connected to four other dimers by four acid molecules of two types with (2111) connectivity.³⁶ Two of the carboxylate groups are in equatorial position (e,e), with a torsional angle (θ) of 7.83(4)° between the two carboxyl groups. The other is the (e,e) conformation with $\theta = 168.61(4)^\circ$. The 2,2'-bipy rings projects on both the sides of the layer and the structure is stabilized by interlayer $\pi - \pi$ interaction (3.663(4) Å, 3.77(5)°) between the adjacent bipy molecules, besides hydrogen bonding between the lattice water molecules and the carboxylate oxygens (H · · · O 1.8(2) Å, O · · · O 2.834(6) Å and $\angle O - H \cdots O 164^{\circ}$).

The cadmium 1,4-cyclohexanedicarboxylate, $[Cd_3(C_8H_{10}O_4)_3-$ (C12H8N2)2]·4H2O, III, is a two-dimensional layer structure consisting of one-dimensional infinite chains made up of trinuclear $Cd_3N_4O_{12}$ units connected by the carboxylate groups (Fig. 3). The asymmetric unit contains 36 non-hydrogen atoms. Two Cd atoms are in crystallographically independent sites with Cd(1) in an octahedral environment (CdO₆) and Cd(2) is in a distorted pentagonal bipyramidal environment (CdN₂O₅). The Cd(1) atom sits on the twofold axis, on an inversion center, 1b. The Cd-O bond distances are in the 2.240(2)–2.602(3) Å range and the Cd–N bond distances are 2.331(2) and 2.377(2) Å. The oxygens of the $Cd(1)O_6$ polyhedron are from six different carboxyl groups with either (11) or (21) connectivity.³⁶ The two nitrogens of the $Cd(2)N_2O_5$ polyhedron are from the terminal 1,10-phen molecule and the five oxygens are from three different carboxyl groups with either (11) or (21) connectivity.³⁶ The Cd(1)O₆ polyhedron is connected to two different $Cd(2)N_2O_5$ polyhedra by sharing the edges to form a trinuclear $Cd_3N_4O_{12}$ unit. Four of the μ_2 oxygen atoms from four tridentate carboxylates (21) connect the three polyhedra. The trinuclear unit gets connected to two other similar units by four different carboxylates (2121) on either side giving rise to an infinite one-dimensional chain structure. Between the two carboxylate groups with (2121) connectivity,³⁶ one is in axial position and the other is in equatorial position (a,e) and the torsional angle between the two carboxyl groups is 5.84(3)°. The infinite onedimensional chains are connected with each other resulting in



Fig. 3 (a) Structure of $[Cd_3(C_8H_{10}O_4)_3(C_{12}H_8N_2)_2]\cdot 4H_2O$, **III** viewed along the *a* axis and (b) structure of **III** viewed along the *c* axis (the rings in 1,10-phen molecules are not shown).

the infinite two-dimensional layer structure. The two carboxylate groups in the connecting acid with (1111) connectivity³⁶ are in equatorial position (e,e) with a torsional angle of 180°. The lattice water molecules are between the layers and hydrogen bonded to the carboxylate oxygens. The structure is stabilized by interlayer π - π interaction (3.43(1) Å, 0.4°) between the 1,10-phen molecules.

We have also prepared a manganese derivative of 1,4cyclohexanedicarboxylic acid, $[Mn_3(C_8H_{10}O_4)_3(C_{12}H_8N_2)_2]$ ·4H₂O, **IV**, where all the Mn(II) ions are six coordinated. **IV** has a twodimensional structure similar to that of **III** (see Fig. 4). The Mn–O bond distances in **IV** are in the 2.121(2)–2.371(2) Å range and the Mn–N bond distances are 2.247(2) and 2.299(2) Å. Here the a,e conformer is with (2111) connectivity³⁶ whereas it is (2121) in **III**. At 300 K, the μ_{eff} of Mn in **IV** is 3.35 μ_{B} , larger than the expected 3.13 μ_{B} for a magnetically isolated Mn(II) ions in the trinuclear model. The magnetic susceptibility, χ_m , fitted to the Curie–Weiss law, gave a Weiss temperature, θ , of –25.7 K for **IV**, which indicates weak antiferromagnetic interaction between the Mn(II) centres.



Fig. 4 (a) Structure of $[Mn_3(C_8H_{10}O_4)_3(C_{12}H_8N_2)_2]\cdot 4H_2O$, **IV** viewed along the *a* axis and (b) the layered structure of **IV** (the rings in 1,10-phen molecules are not shown).

1,3-Cyclohexanedicarboxylates

The manganese 1,3-cyclohexanedicarboxylate, $[Mn_3(C_8H_{10}O_4)_3-(C_{12}H_8N_2)_2]$ - $4H_2O$, V, has an infinite one-dimensional chain structure consisting of the trinuclear $Mn_3N_4O_{12}$ unit connected by the carboxylate groups (Fig. 5), with the asymmetric unit containing 36 non-hydrogen atoms. Two of the Mn atoms are in two crystallographically independent sites with Mn(1) in an octahedral environment (MnO₆) and Mn(2) in a distorted octahedral (MnN₂O₄) environment. The Mn(1) atom sits on the twofold axis, on an inversion center, 4e. The Mn–O bond distances are in the 2.141(6)–2.424(4) Å range and the Mn–N



Fig. 5 (a) Structure of $[Mn_3(C_8H_{10}O_4)_3(C_{12}H_8N_2)_2]\cdot 4H_2O$, V, viewed along the *a* axis and (b) structure of V, viewed along the *b* axis.

bond distances are 2.245(5) and 2.255(5) Å. The six oxygens of the $Mn(1)O_6$ polyhedron are from six different carboxyl with (11) or (21) connectivity.³⁶ The two nitrogens of the $Mn(2)N_2O_4$ polyhedron are from the terminal 1,10-phen molecule and the oxygens are from three different carboxyl groups with (11) or (21) connectivity.³⁶ The $Mn(1)O_6$ polyhedron is connected to two different Mn(2)N₂O₄ polyhedra by the sharing of two corners, thus forming the trinuclear $Mn_3N_4O_{12}$ unit. Two μ_2 oxygen atoms from two tridentate carboxylate (21) connect the three polyhedra. The trinuclear unit gets connected to two other similar units by six different carboxylates (2111) on either side resulting in the infinite one-dimensional chain structure. The connecting acid units are in two conformations with one having the two carboxylates in equatorial position (e,e) (torsional angle, 1.05°) and other acid unit appearing to have a flattened chair conformation due to the disorder. The lattice water molecules are between the chains and are hydrogen bonded to the carboxylate oxygens. The structure is stabilized by interchain π - π interaction (3.6 Å, 0°) between the 1,10-phen molecules. At 300 K, the μ_{eff} of Mn in V is 3.59 μ_{B} , larger than the expected 3.13 $\mu_{\rm B}$ for a magnetically isolated Mn(II) ions in the trinuclear model (similar to that for IV). Up to 300 K, the magnetic susceptibility, χ_m , would be fitted to the Curie–Weiss law, with a θ of -18.2 K, which indicates weak antiferromagnetic interaction between the Mn(II) centres.

The cadmium 1,3-cyclohexanedicarboxylate, $[Cd(H_2O)_2-(C_8H_{10}O_4)]\cdot H_2O$, VI, has a two-dimensional layer structure (Fig. 6) formed by the connectivity between Cd_2O_{13} dimers and the carboxylate groups. The asymmetric unit of VI contains 17 non-hydrogen atoms. The cadmium atom is in a distorted pentagonal bipyramidal environment (CdO₇) with Cd–O bond distances in the 2.258(4)–2.607(4) Å range. The seven oxygens of the CdO₆ polyhedron are from two coordinated water molecules and four different carboxylic acid groups with (2111) connectivity.³⁶ Each



Fig. 6 Structure of $[Cd(H_2O)_2(C_8H_{10}O_4)]\cdot H_2O$, **VI**, viewed along the *b* axis.

CdO₇ polyhedron shares an edge with another CdO₇ polyhedron forming the Cd₂O₁₃ dimer. The dimers are connected with four other dimers by a carboxylate group with (11) connectivity,³⁶ forming the infinite two-dimensional network. The cyclohexane rings project on both the sides of the layer. Both the carboxylate groups of the 1,3-cyclohexanedicarboxylate are in equatorial position (e,e) with a torsional angle of 6.11°. The two lattice water molecules are between the layers forming four-membered water clusters (Fig. 7). The O···O distances between the water molecules are in the 2.03(1)–2.59(1) range. The short O···O distance (2.03 Å) is due to the higher thermal parameter of the oxygen atoms (O100 and O200 with 0.5 occupancy factor). The O···O angles are 83.04(2) and 92.57(2)°. The adjustant clusters are twisted with respect to each other by 55.01(3)° and separated by a distance of 2.59(4) Å.



Fig. 7 (a) The packing arrangement in $[Cd(H_2O)_2(C_8H_{10}O_4)]\cdot H_2O$, VI and (b) the view of the water clusters in VI. The water molecules are connected by the dotted lines.

The TGA curve of **VI** shows two weight losses. The first weight loss of 16.93% around 120 °C and the second weight loss of 49.26% around 380 °C match well with the loss of water molecules, and the cyclohexanedicarboxylate (calc. 16.04% and 50.50% respectively).

The cadmium 1,3-cyclohexanedicarboxylate $[Cd(C_8H_{10}O_4)-$ (C₁₂H₈N₂)], VII, is also a two-dimensional layer structure consisting of an infinite two-dimensional network formed by the connectivity of $Cd_2N_4O_8$ dimers and carboxylate groups (Fig. 8). The asymmetric unit contains 54 non-hydrogen atoms. The cadmium atom is in a distorted pentagonal bipyramidal environment (CdN_2O_5) with Cd–O bond distances in the 2.233(5)–2.702(5) Å range and Cd-N bond distances in the 2.362(4)-2.405(4) Å range. The two nitrogens of the CdN₂O₅ polyhedron are from the terminal 1,10-phen molecule and the oxygens are from three different carboxyl groups with (11) or (21) connectivity.³⁶ Two such polyhedra form an edge-sharing dimer by sharing the μ_2 oxygen atom from a tridentate carboxylate (21). The dimers get connected with four other dimers by the acid units of two types. In one type, two of the carboxylate groups are in equatorial position (e,e) with a torsional angle of $7.83(2)^{\circ}$. The other acid molecule appears as though they have a flattened chair conformation due to the disorder. The 1,10-phen rings project on both the sides of



Fig. 8 (a) Structure of $[Cd(C_8H_{10}O_4)(C_{12}H_8N_2)]$,**VII** and (b) packing arrangement of in **VI**, viewed along the *a* axis.

the layer. The structure is stabilized by intralayer π - π interaction (3.546(4) Å, 7.19(1)°) between the 1,10-phen molecules.

We have also obtained a zero-dimensional 1,3-cyclohexanedicarboxylate, [Mn(H₂O)(C₈H₁₀O₄)(C₁₂H₈N₂)], VIII, containing 28 non-hydrogen atoms in the asymmetric unit. The Mn atom here is in a distorted octahedral environment (MnN₂O₄) with Mn-O bond distances in the 2.097(4)-2.264(5) Å range and the Mn-N bond distances are 2.244(5) and 2.265(5) Å. The two nitrogens of the MnN₂O₄ polyhedron are from the terminal 1,10-phen molecule. The oxygens are from one terminal coordinated water and the three remaining oxygens are from two different carboxylic acid groups with (11) or (10) connectivity.³⁶ Two such polyhedra form a dimer (Fig. 9) with two dicarboxylates (1110 connectivity), where the two carboxylate groups are in equatorial position (e,e) with a torsional angle of $4.16(2)^{\circ}$. The structure is stabilized by intermolecular π - π interaction (3.89(1)Å, 0.56°) between the 1,10phen molecules and intermolecular $CH \cdots \pi$ interaction between cyclohexane and 1,10-phen rings (3.24(1) Å, 5.83°). At 300 K, the $\mu_{\rm eff}$ of Mn in VIII is 4.18 $\mu_{\rm B}$, larger than the expected 3.84 $\mu_{\rm B}$ for a magnetically isolated Mn(II) ions in the model. Up to 300 K, the magnetic susceptibility, χ_m , could be fitted to the Curie–Weiss law, with a θ of -1.5 K. The small θ value suggests that compound is essentially paramagnetic with little or no antiferromagnetic interaction between the Mn ions.



Fig. 9 (a) Structure of $[Mn(H_2O)(C_8H_{10}O_4)(C_{12}H_8N_2)]$, **VIII** and (b) packing arrangement in **VIII** viewed along the *a* axis.

1,2-Cyclohexanedicarboxylate

The cadmium 1,2-cyclohexanedicarboxylate, $[Cd(C_8H_{10}O_4)]$, **IX**, is a two dimensional layered structure consisting of a twodimensional metal–oxygen–metal network grafted by the carboxylate groups (Fig. 10). The asymmetric unit contains 13 non-hydrogen atoms. The Cd atom is in a distorted octahedral environment with Cd–O bond distances in the 2.227(7)–2.413(6) Å range. The six oxygens of CdO₆ polyhedron are from five different carboxyl groups with (2121) connectivity.³⁶ Each CdO₆ polyhedron sharing its edge with another CdO₆ octahedron to form a edge-shared Cd₂O₁₁ dimer. These dimers are connected with four other dimers by sharing the corners, thus forming the infinite two-dimensional metal–oxygen–metal network, grafted with the carboxylate groups. The cyclohexane rings in **IX** project on both the sides of the layer. Both of the carboxylate groups of the 1,2-cyclohexanedicarboxylate are in equatorial position (e,e) with a torsional angle of 60.59(1)°.



Fig. 10 (a) Structure of $[Cd(C_8H_{10}O_4)]$,IX along the *b* axis and (b) structure of IX, showing the infinite M–O–M linkage.

Conclusions

We have successfully prepared 1,4-, 1,3- and 1,2-CHDCs of cadmium besides 1,4- and 1,3-CHDCs of manganese. In the case of 1,4-CHDCs, we find only the e,e conformation in the onedimensional compound, and a coexistence of the e,e and a,e conformations in the layered compounds formed by Cd and Mn. Only the e,e conformation (*cis* structure) occurs in the 1,3-CHDCs of Cd and Mn. However, some of the 1,3-compounds also contain the CHDC in a flattened chair conformation due to the disorder. The Cd 1,2-CHDC also has e,e conformation. Another aspect of interest is the formation of the metal–oxygen–metal infinite The four-membered ring in **VIII** is reminiscent of the four-membered secondary building unit in open framework phosphates.³⁹⁻⁴² Whether the four-membered dicarboxylate **VIII** can transform to chain, layered and three-dimensional structures is to be explored. It is noteworthy that the zero- and one-dimensional metal carboxylates have been found to transform to two- and three-dimensional structures recently.^{38,43,44}

All the CHDCs, I–IX, exhibit characteristic photoluminescence (PL) spectra while excited at 268 nm. The parent acids themselves show luminescence bands in the 350–385 nm region, while the aromatic amines show a emission band around 450 nm. The main PL band maxima of the Cd CHDCs are as follows: I, 460 nm, II, 422 nm, III, 389 nm, VI, 422 nm, VII, 390 nm, IX, 460 nm. The main PL band maxima of all the Mn CHDCs (IV, V and VIII) were at 422 nm. The Cd and Mn CHDCs exhibit a bathochromic shift with respect to the acids and a hypsochromic shift with respect to the acids and a hypsochromic shift with respect to the all the ligand to the metal ion increases the rigidity, thereby reducing the loss of energy by radiationless decay of the intraligand emission excited state.

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