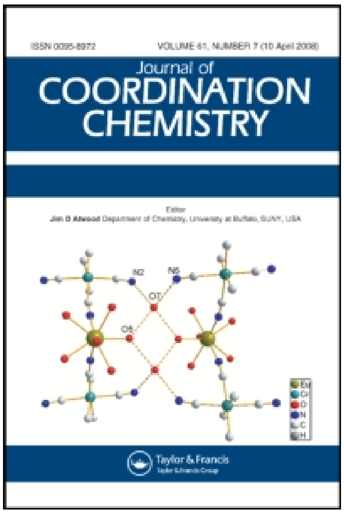

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Yue-Qing Zheng[a]; Hong-Zhen Xie[a]
[a] Municipal Key Laboratory of Solid Materials Chemistry, Institute of Inorganic Chemistry, Ningbo University, Ningbo 315211, P.R. China

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Fumarato-bridged open layers: Syntheses and crystal structures of $M(H_2O)_2L$, with $M = Cu$, Cd and H_2L = fumaric acid

YUE-QING ZHENG* and HONG-ZHEN XIE

Municipal Key Laboratory of Solid Materials Chemistry, Institute of Inorganic Chemistry,
Ningbo University, Ningbo 315211, P.R. China

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Two fumarato-bridged coordination polymers $M(H_2O)_2(C_4H_2O_4)$, with M = Cu (**1**) and Cd (**2**), were prepared and structurally characterized using single-crystal X-ray methods. In **1**, Cu atoms are coordinated by two aqua oxygen atoms at *trans* positions and three oxygen atoms of different fumarate anions to form a square pyramid; two adjacent CuO_5 square pyramids share edges to form Cu_2O_8 dimers. Cd atoms in **2** are coordinated by seven oxygen atoms of two aqua ligands and three different fumarate anions to form a distorted pentagonal bipyramid, with two adjacent pentagonal bipyramids sharing a common edge to form Cd_2O_{12} dimers. Both dimers in **1** and **2** are bridged by fumarato ligands to generate open layers with a (4, 4) topology. Close packing of the layers prevents formation of porous 3D networks. The magnetic behavior of **1** was investigated.

Keywords: Copper; Cadmium; Fumarato complexes; Coordination polymers; Crystal structure; Magnetic properties

1. Introduction

Crystal engineering of coordination polymers is an efficient route to functional materials with a wide range of potentially useful electronic, magnetic, microporous, nonlinear optical and luminescent properties [1,2]. In particular, interest in open-framework coordination polymers has grown steadily to explore materials with related ion exchange and heterogeneous catalysis properties. Use of benzene di-, tri- and polycarboxylic acids is of current interest with respect to rational design and synthesis of nanoporous inorganic–organic hybrid materials [3–6]. By contrast, aliphatic α,ω-dicarboxylates are flexible ligands in terms of their conformational and coordination behavior [7,8]. Construction of coordination polymers based on α,ω-dicarboxylate anions is of current interest in coordination and supramolecular chemistry, with the

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*Corresponding author. Email: zhengcm@nbu.edu.cn

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expectation that the flexibility of dicarboxylato ligands might prevent collapse of structures upon removal of guest molecules and favor modification of guest to host. Growing attention has also been paid to the rational design and synthesis of coordination polymers by use of saturated aliphatic dicarboxylate ligands, but only a few coordination polymers with open 3D networks have been prepared [9–14]. Compared to succinate anions, fumarate anions exhibit less conformational freedom because of the C=C double bond. To the best of our knowledge, few coordination polymers based on the fumarato ligand have been reported [15]. One previous investigation showed that substitution of fumarate for succinate led to retention of a coordination polymer framework [16,17]. In addition, a basic cobalt succinate, $[Co_3(H_2O)_4(OH)_2(C_4H_4O_4)_2] \cdot 6H_2O$, exhibits a porous 3D framework [18] and replacement of succinate by fumarate anions resulted in a similar coordination polymer, $[Co_3(H_2O)_4(OH)_2(C_4H_2O_4)_2] \cdot 2H_2O$ [19], which is isostructural with $[Ni_3(H_2O)_4(OH)_2(C_4H_2O_4)_2] \cdot 2H_2O$, reported by Gulliou and coworkers [20]. Here, we report the syntheses and structural characterization of two new fumarato coordination polymers, $M(H_2O)_2L$ with M = Cu (**1**), Cd (**2**), both of which feature open layer structures.

2. Experimental

2.1. *Physical measurements*

All chemicals of reagent grade were commercially available and used without further purification. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 2400II CHNS/O instrument. IR spectra (KBr pellets) in the range 4000–400 cm^{-1} were recorded using a Shimadzu FTIR-8900 spectrophotometer. Magnetic measurements were performed on polycrystalline samples with a Quantum Design MPMS-7 SQUID magnetometer with an applied field of 10,000 G in the temperature range $5 \leq T(K) \leq 300$. Diamagnetic corrections were estimated from Pascal's constants [21].

2.2. *Syntheses*

2.2.1. $Cu(H_2O)_2(C_4H_2O_4)$, 1. Addition of an aqueous solution of $CuCl_2 \cdot 2H_2O$ (0.43 g, 2.50 mmol) in 4.0 cm^3 of H_2O to 6.0 cm^3 of aqueous 1 M Na_2CO_3 yielded blue $Cu(OH)_{2-2y}(CO_3)_y \cdot zH_2O$, which was separated by centrifugation and washed several times with doubly distilled water until no Cl^- ions were detected in the supernatant. The precipitate was added to a stirred methanolic aqueous solution of 0.29 g (2.50 mmol) of fumaric acid in 50 cm^3 of CH_3OH/H_2O (1 : 1 v/v). The mixture was stirred for 30 min and the blue suspension formed (pH 2.32) was filtered off. The solid was taken up in conc. NH_3/H_2O (1 : 4 v/v) and the resulting dark blue filtrate (pH 14.01) was allowed to stand at room temperature. Slow evaporation over 3 months afforded well-shaped blue crystals. Yield: 40% based on initial $CuCl_2 \cdot 2H_2O$. Anal. Calcd. for $C_4H_6CuO_6$(%): C, 22.49; H, 2.83. Found: C, 22.44; H, 2.84. IR (cm^{-1}): 3330s (sharp), 3127m (broad), 1560s, 1537m (shoulder), 1388vs (doublet), 1274m (sharp), 1213m (doublet), 970m (doublet), 798m (sharp), 686s, 597w.

2.2.2. $Cd(H_2O)_2(C_4H_2O_4)$, 2. Some 3.0 cm^3 of aqueous 1 M Na_2CO_3 was added to an aqueous solution of 0.57 g (2.50 mmol) of $CdCl_2 \cdot 2H_2O$ to produce a white precipitate of $Cd(OH)_{2-2x}(CO_3)_x \cdot yH_2O$, which was centrifuged and washed several times with doubly distilled water until no Cl^- ions were detected in the supernatant. Fresh precipitate was added to a stirred methanolic aqueous solution of 0.29 g (2.50 mmol) of fumaric acid in 50 cm^3 of CH_3OH/H_2O (1 : 1 v/v). The mixture was stirred for 30 min and the suspension formed was filtered off. The filtrate (pH 4.38) was maintained at room temperature and colorless crystals of the product grew by slow evaporation over 2 months. Unfortunately, the yield was so low that no attempt was made at further characterization.

2.3. *X-ray crystallography*

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to the tip of a thin glass fiber, which was then mounted on a Bruker P4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for cell determination and subsequent data collection. Lattice parameters were refined from 2θ values (10–25°) of 25 carefully centered reflections. Reflection intensities up to $2\theta_{max} = 55°$ were collected at 293 K using the θ–2θ scan technique. On the basis of monitored reflections, the crystals exhibited no detectable decay during data collection. Data were corrected for Lp and absorption effects. SHELXS-97 and SHELXL-97 programs [22,23] were used for structure solution and refinement. The structures were solved by direct methods. Subsequent difference Fourier syntheses enabled all nonhydrogen atoms to be located. After several cycles of refinement, all hydrogen atoms of fumarato groups were geometrically generated while the aqua hydrogen atoms were located from successive difference Fourier syntheses. Finally, all nonhydrogen atoms were refined with anisotropic displacement parameters using full-matrix least-squares techniques and hydrogen atoms with isotropic displacement parameters. Detailed information concerning crystal data and structure determination is summarized in table 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in tables 2 and 3. Selected interatomic distances and bond angles are given in tables 4 and 5.

3. Results and discussion

3.1. *Structure description*

In **1** (figure 1), the Cu atom has square pyramidal geometry, where the equatorial plane is defined by two *trans* aqua oxygen atoms and two carboxylato oxygen atoms of different fumarate anions; a carboxylato oxygen atom of a third fumarate anion is situated at the apical position. Two centrosymmetrically related CuO_5 square pyramids are edge-linked to form Cu_2O_8 dimers. Equatorial Cu–O bond lengths lie in the range 1.941 to 1.987 Å and the axial length is 2.345 Å (table 4); the Cu atom is shifted by 0.053(2) Å from the equatorial plane towards the apical carboxylato $O(3)^{\#1}$ ($\#1 = 1-x, 1-y, 2-z$). The Cu–Cu separation of 3.369(1) Å and the acute O(3)–Cu–$O(3)^{\#1}$ angle of 78.2(1)° imply no direct interaction between the metal ions. In **1**, two crystallographically distinct fumarate anions centered at positions 2*a* and 2*c*,

Table 1. Summary of crystal data, data collection, structure solution and refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_4H_6CuO_6$	$C_4H_6CdO_6$
Formula weight	213.63	262.49
Description	Blue prism	Colorless prism
Crystal size (mm)	0.222 × 0.178 × 0.111	0.111 × 0.089 × 0.067
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	8.431(2)	6.760(1)
b (Å)	7.319(2)	7.5469(9)
c (Å)	12.079(2)	7.809(1)
α (°)		68.56(1)
β (°)	106.92(3)	86.54(1)
γ (°)		69.94(1)
Volume (Å^3)	713.1(2)	347.33(9)
Z	4	2
D_{calc} (g cm^{-3})	1.990	2.510
F(000)	428	252
μ (mm^{-1})	3.034	3.124
Absorption correction	Empirical	Empirical
Min. and max. transmission	0.230, 0.390	0.664, 0.802
θ range (°)	2.53–27.48	2.81–27.50
Refinement method	Full-matrix least-squares on F^2	
Reflections collected	2264	1946
Independent reflections (R_{int})	1637 (0.046)	1550 (0.031)
Data/restraints/parameters	1206/0/101	1388/0/101
Goodness of fit on F^2	1.059	1.027
R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0486, 0.1136	0.0247, 0.0540
R_1, wR_2 (all data)[a]	0.0763, 0.1264	0.0298, 0.0561
Extinction coefficient	0.000(1)	0.006(1)
A, B values in weighting scheme[b]	0.0692, 0.2671	0.0197, 0.0000
$\delta\rho_{max}$, $\delta\rho_{min}$ (e Å^{-3})	0.155, −0.524	0.631, −0.563

[a] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

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

Table 2. Final atomic parameters and equivalent isotropic thermal parameters (Å^2) for nonhydrogen atoms in **1**.

Atom	x/a	y/b	z/c	U_{eq}
Cu	0.41363(6)	0.46083(8)	0.85771(4)	0.0216(2)
O(1)	0.3030(4)	0.4286(5)	0.5954(3)	0.0344(9)
O(2)	0.1970(4)	0.4650(5)	0.7421(3)	0.0319(8)
O(3)	0.6410(4)	0.4748(5)	0.9668(3)	0.0258(7)
O(4)	0.7581(4)	0.4444(5)	0.8259(3)	0.0341(9)
O(5)	0.4320(4)	0.7197(5)	0.8287(3)	0.0388(9)
O(6)	0.4010(5)	0.1951(6)	0.8804(3)	0.045(1)
C(1)	0.1856(6)	0.4576(7)	0.6356(4)	0.025(1)
C(2)	0.0152(6)	0.4918(7)	0.5557(4)	0.027(1)
C(3)	0.7671(5)	0.4670(7)	0.9275(4)	0.0217(9)
C(4)	0.9310(5)	0.4975(6)	1.10146(4)	0.022(1)

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

Table 3. Final atomic parameters and equivalent isotropic thermal parameters (Å^2) for nonhydrogen atoms in **2**.

Atom	x/a	y/b	z/c	U_{eq}
Cd	0.14673(4)	0.81722(3)	0.88937(3)	0.0209(1)
O(1)	0.2748(5)	0.8729(4)	0.5770(3)	0.0314(6)
O(2)	0.3237(4)	0.5657(4)	0.7788(3)	0.0285(6)
O(3)	−0.0103(5)	0.8437(3)	1.1594(3)	0.0303(6)
O(4)	0.1430(5)	0.5300(4)	1.1824(3)	0.0283(6)
O(5)	0.4561(5)	0.8139(4)	0.9982(4)	0.0321(6)
O(6)	−0.1781(4)	0.8501(4)	0.7764(3)	0.0265(5)
C(1)	0.3480(5)	0.6829(5)	0.6223(4)	0.0212(6)
C(2)	0.4623(6)	0.5978(5)	0.4847(4)	0.0232(7)
C(3)	0.0373(5)	0.6562(5)	1.2496(4)	0.0172(6)
C(4)	−0.0341(6)	0.5943(5)	1.4399(4)	0.0212(7)

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

Table 4. Selected interatomic distances (Å) and bond angles (°) for **1**.

Cu–O(2)	1.950(3)	C(1)–O(1)	1.241(6)	C(3)–O(4)	1.222(5)
Cu–O(3)	1.987(3)	C(1)–O(2)	1.263(6)	C(3)–C(4)	1.487(6)
Cu–O(3)$^{\#1}$	2.345(3)	C(1)–C(2)	1.500(6)	C(4)–C(4)$^{\#3}$	1.311(9)
Cu–O(5)	1.941(4)	C(2)–C(2)$^{\#2}$	1.301(1)	Cu–Cu$^{\#1}$	3.369(1)
Cu–O(6)	1.971(4)	C(3)–O(3)	1.285(5)		
O(2)–Cu–O(3)	174.6(1)	O(5)–Cu–O(3)	87.6(1)	Cu–O(3)–Cu$^{\#1}$	101.8(1)
O(2)–Cu–O(3)$^{\#1}$	104.8(1)	O(5)–Cu–O(3)$^{\#1}$	90.8(2)	O(1)–C(1)–O(2)	124.9(4)
O(2)–Cu–O(6)	92.2(2)	O(5)–Cu–O(6)	176.8(2)	O(4)–C(3)–O(3)	124.0(4)
O(3)–Cu–O(3)$^{\#1}$	78.2(1)	O(6)–Cu–O(3)	92.3(2)		
O(5)–Cu–O(2)	87.9(1)	O(6)–Cu–O(3)$^{\#1}$	92.3(1)		
Hydrogen-bonding contacts					
D–H	*d*(D–H)	*d*(H–A)	∠(D–H–A)	*d*(D–H–A)	A
O(5)–H(5A)	0.85	1.85	153	2.642	O(1)$^{\#5}$
O(5)–H(5B)	0.87	1.85	153	2.649	O(4)$^{\#5}$
O(6)–H(6A)	0.83	2.27	162	3.071	O(4)$^{\#6}$
O(6)–H(5B)	0.87	2.22	169	3.082	O(1)$^{\#7}$

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

respectively, display normal bond lengths and angles [15,20,24]. The former fumarate anion functions as a bismonodentate ligand to bridge Cu$_2$O$_8$ dimers in the [101] direction, while each carboxylate group of the latter monoatomically bridges two Cu atoms in the [100] direction. Thus, 2D open layers are formed parallel to (010) with 28-membered rhombic apertures (*ca* 8.4 × 12.6 Å), showing a (4, 4) topology (figure 2). Along the *b* axis, the layers are stacked in such a way that Cu$_2$O$_8$ dimers are located above the centers of the rhombic apertures of adjacent layers and the aqua ligands donate hydrogen atoms to uncoordinated carboxylate oxygen atoms of neighboring layers to form relatively strong [*d*(O–O) = 2.642, 2.649 Å, table 4] and weak hydrogen bonds [*d*(O–O) = 3.071, 3.082 Å, table 4].

Two Cu(II) succinates of composition Cu(C$_4$H$_4$O$_4$) · 2H$_2$O [25] and Cu(H$_2$O)(C$_4$H$_4$O$_4$) [26] have been reported previously; succinato ligands in both assume the *gauche* conformation. In the former, paddle-wheel dicopper units are doubly bridged by bis-bidentate succinato ligands to generate ribbon-like infinite chains [25].

Table 5. Selected interatomic distances (Å) and bond angles (°) for **2**.

Cd–O(1)	2.474(3)	Cd–O(5)	2.293(3)	C(2)–(2)$^{\#2}$	1.318(7)
Cd–O(2)	2.301(2)	Cd–O(6)	2.315(3)	C(3)–O(3)	1.261(4)
Cd–O(3)	2.347(2)	C(1)–O(1)	1.261(4)	C(3)–O(4)	1.243(4)
Cd–O(3)$^{\#1}$	2.292(2)	C(1)–O(2)	1.260(4)	C(3)–C(4)	1.490(4)
Cd–O(4)	2.518(2)	C(1)–C(2)	1.493(4)	C(4)–C(4)$^{\#3}$	1.321(7)
O(1)–Cd–O(4)	139.75(8)	O(3)$^{\#1}$–Cd–O(3)	73.31(9)	O(6)–Cd–O(1)	89.67(9)
O(2)–Cd–O(1)	54.67(8)	O(3)$^{\#1}$–Cd–O(4)	126.28(8)	O(6)–Cd–O(3)	88.1(1)
O(2)–Cd–O(3)	138.06(8)	O(3)$^{\#1}$–Cd–O(5)	87.5(1)	O(6)–Cd–O(4)	92.61(9)
O(2)–Cd–O(4)	85.08(8)	O(3)$^{\#1}$–Cd–O(6)	87.51(1)	O(1)–C(1)–C(2)	118.6(3)
O(2)–Cd–O(6)	92.37(9)	O(5)–Cd–O(1)	90.9(1)	O(2)–C(1)–O(1)	121.4(3)
O(3)–Cd–O(1)	167.15(8)	O(5)–Cd–O(2)	92.0(1)	O(2)–C(1)–C(2)	120.1(3)
O(3)–Cd–O(4)	53.03(8)	O(5)–Cd–O(3)	90.3(1)	O(4)–C(3)–O(3)	120.8(4)
O(3)$^{\#1}$–Cd–O(1)	93.96(8)	O(5)–Cd–O(4)	90.16(9)	O(4)–C(3)–C(4)	122.1(3)
O(3)$^{\#1}$–Cd–O(2)	148.62(8)	O(5)–Cd–O(6)	174.99(8)	C(4)$^{\#3}$–C(4)–C(3)	123.3(4)

Hydrogen-bonding contacts

D–H	d(D–H)	d(H–A)	$\angle$DHA	d(D–H–A)	A
O(5)–H(5A)	0.87	2.13	160	2.965	O(6)$^{\#5}$
O(5)–H(5B)	0.84	1.85	171	2.683	O(2)$^{\#6}$
O(6)–(H6A)	0.88	1.85	177	2.735	O(1)$^{\#7}$
O(6)–H(6B)	0.87	1.84	167	2.694	O(4)$^{\#8}$

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

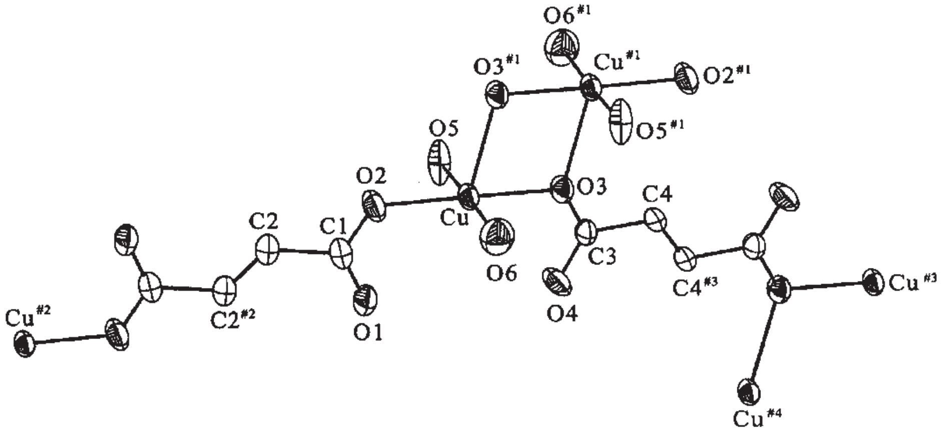

Figure 1. ORTEP view of the coordination environment around Cu with the atom labeling scheme for **1** (displacement ellipsoids are drawn at the 45% probability level).

Succinato ligands in the latter complex bond one Cu atom through two distal carboxylate oxygen atoms and nonchelating carboxylate oxygen atoms interconnect square pyramidally coordinated Cu centers into infinite layers [26]. The *gauche* conformation clearly yields different layer structures to the one reported here.

As shown in figure 3, Cd atoms in **2** are coordinated by seven oxygen atoms of two aqua ligands and three different fumarate anions to form significantly distorted CdO_7 pentagonal bipyramids with aqua oxygen atoms at the apical positions. The equatorial Cd–O bond distances fall in the range 2.292 to 2.518 Å and axial Cd–O bond distances

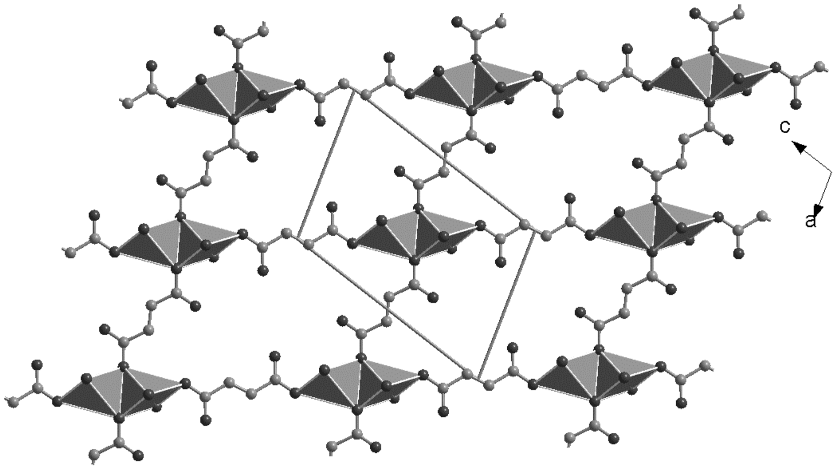

Figure 2. The open 2D layer in **1**.

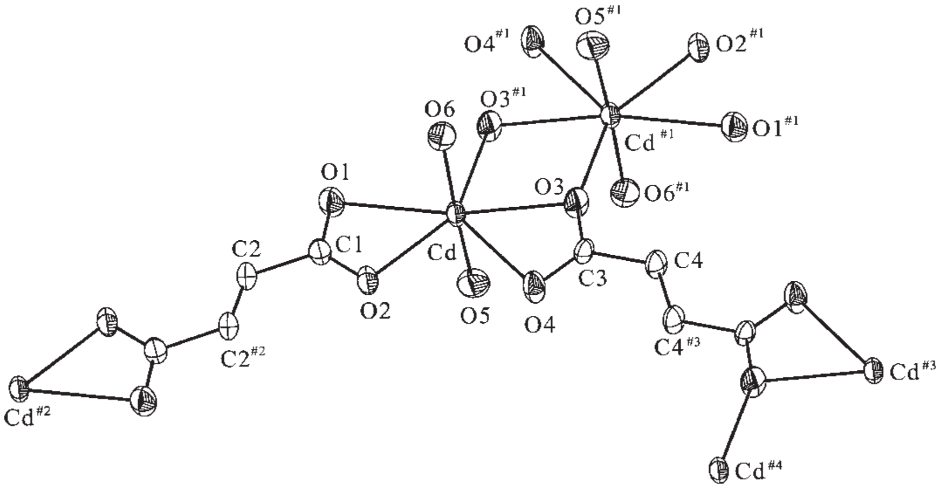

Figure 3. ORTEP view of the coordination environment around Cd with the atom labeling scheme for **2** (displacement ellipsoids are drawn at the 45% probability level).

are 2.293 and 2.315 Å (table 5). The principal axis of the coordination polyhedron with axial O–Cd–O angle 175.0(1)° exhibits a slight deviation from linearity. Two adjacent CdO_7 pentagonal bipyramids are edge-shared to form Cd_2O_7 dimers with a Cd–Cd distance of 3.7214(7) Å. Two crystallographically different fumarate anions are centered at $1h$ and $1g$, respectively. The former acts as a bis-chelating ligand to bridge dimers in the $[1\bar{1}\bar{1}]$ direction and the latter interlinks four Cd atoms of two Cd_2O_7 dimers in the [110] direction so that each carboxylate group chelates one Cd atom with one chelating oxygen atom bonding to the second Cd atom (figure 3). As a result, 2D, grid-like (4, 4)

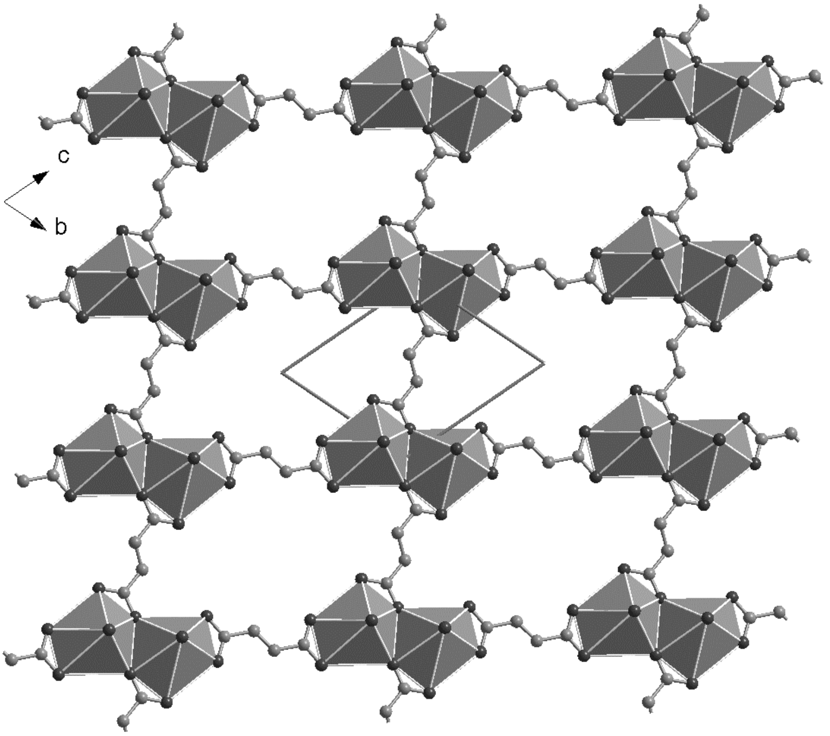

Figure 4. The open 2D layer in **2**.

layers are generated parallel to (101) with 28-membered apertures (*ca* 8.7 × 12.9 Å) (figure 4). Along the [101] direction, the 2D layers are assembled by interlayer hydrogen bonding [d(O–O) = 2.683–2.965 Å, table 5] and the Cd_2O_7 dimers of one layer are situated above the centers of the apertures of neighboring layers.

Two layered Cd succinates $Cd(H_2O)_2(C_4H_4O_4)$ [13b] and $[Cd_2(H_2O)_4(C_4H_4O_4)_2]\cdot H_2O$ [27] have been reported in the literature. The layered structure of the present Cd fumarate differs significantly from that observed in $Cd(H_2O)_2(C_4H_4O_4)$, where the Cd atoms are bis-chelated by *gauche* succinato ligands to form infinite chains and 2D layers are generated by Cd–carboxylate bonds [13b]. However, the open layer in the present fumarate is similar to that reported for $[Cd_2(H_2O)_4(C_4H_4O_4)_2]\cdot H_2O$. This results from the similarity of the coordination modes of the fumarate anions to the *anti* conformations of the succinate anions in $[Cd_2(H_2O)_4(C_4H_4O_4)_2]\cdot H_2O$ [27]. Close-packing of the open layers in both the present Cu and Cd compounds prevents the formation of 3D porous frameworks.

3.2. *Magnetic properties of 1*

Figure 5 shows the temperature dependence of both the magnetic susceptibility (χ_m) and the inverse susceptibility (χ_m^{-1}) of **1**, where the χ_m is the magnetic susceptibility per mol of Cu^{2+} ion. Over the temperature range 5–300 K, the Cu(II) coordination polymer is paramagnetic, obeying the Curie–Weiss law $\chi_m(T-\theta) = 0.48(2)\,cm^3\,mol^{-1}\,K$, with the Weiss constant $\theta = -1.2(3)$ K, indicative of overall antiferromagnetic coupling between

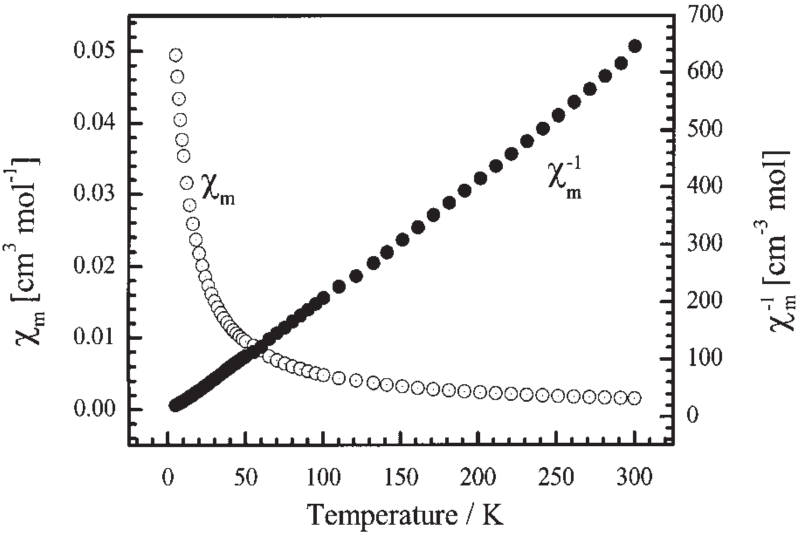

Figure 5. Plots of χ_m *vs* T and χ_m^{-1} *vs* T for **1** (χ_m is the magnetic susceptibility per mol of Cu^{2+} ion).

Cu^{2+} ions. At room temperature, the effective magnetic moment of 1.90 μ_B is slightly larger than the spin-only value (1.73 μ_B) for the free Cu^{2+} ion [21].

Supplementary data

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 257630 ($C_4H_6CuO_6$) and CCDC 257631 ($C_4H_6CdO_6$). 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).

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