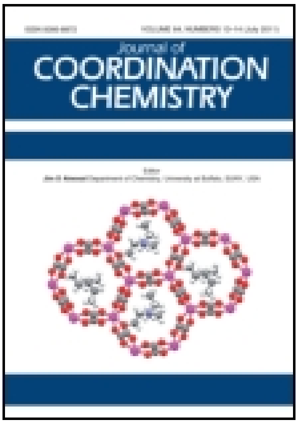

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A family of double-layered octahedral coordination networks built up from divalent metal ions, formate anions, and ethyl carbazate ligands: M $(CHO_2)_2(C_3H_8N_2O_2)$ (M=Co, Zn, Cd)

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A family of double-layered octahedral coordination networks built up from divalent metal ions, formate anions, and ethyl carbazate ligands: $M(CHO_2)_2(C_3H_8N_2O_2)$ ($M = Co, Zn, Cd$)

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The syntheses, structures, and characterization (IR, TGA/DTA, UV/visible spectroscopy) of an isostructural family of layered coordination networks containing divalent metal ions (Co^{2+}, Zn^{2+}, and Cd^{2+}), CHO_2^- formate (ft) anions and neutral $C_3H_8N_2O_2$ ethyl carbazate (ec) ligands of formula $M(ft)_2(ec)$ are described. A manganese-containing compound with the same stoichiometry possibly adopts the same structure. Single-crystal structures of the zinc and cadmium phases show the presence of distorted ZnO_5N and CdO_5N octahedra, in which ec adopts N,O-bidentate coordination, and four monodentate ft anions bridge to adjacent metal ions. This connectivity leads to polymeric sheets built up from double octahedral layers propagating in the (001) plane. The crystal structures are completed by N–H $\cdots$ O and N–H $\cdots$ (O,O) hydrogen bonds. Crystal data: $Zn(CHO_2)_2(C_3H_8N_2O_2)$, $M_r = 259.52$, triclinic, $P\bar{1}$ (No. 2), $a = 8.0848(2)$ Å, $b = 8.7345(1)$ Å, $c = 13.2841(3)$ Å, $\alpha = 74.2839(14)^\circ$, $\beta = 86.7150(12)^\circ$, $\gamma = 89.4713(15)^\circ$, $V = 901.51(3)$ Å^3, $Z = 4$, $R(F) = 0.024$, $wR(F^2) = 0.056$. $Cd(CHO_2)_2(C_3H_8N_2O_2)$, $M_r = 306.55$, triclinic, $P\bar{1}$ (No. 2), $a = 8.4574(2)$ Å, $b = 8.9112(3)$ Å, $c = 13.5119(5)$ Å, $\alpha = 73.101(1)^\circ$, $\beta = 86.366(2)^\circ$, $\gamma = 89.420(2)^\circ$, $V = 972.36(5)$ Å^3, $Z = 4$, $R(F) = 0.022$, $wR(F^2) = 0.053$.

Keywords: Layered coordination network; Formate anion; Bidentate ligand; Crystal structure

1. Introduction

Metal–organic framework solids have attracted much interest due to their structural topologies and potential applications [1–3]. Among the various structures, 2-D (layered) structures have been reported for a number of metal–organic coordination polymers that have been constructed using various carboxylates in the presence of organic blocking ligands [4–6]. Layered compounds have been successfully extended into

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3-D-pillared topologies with tunable pore sizes by replacing terminal ligands by appropriate bridging ligands as pillars [7, 8].

However, coordination polymers using formate anions (HCO_2^-) in combination with neutral chelating ligands are infrequently reported. Formate is the simplest carboxylate and exhibits diverse coordination like other simple carboxylates and also mediates magnetic coupling between paramagnetic metal centers [9, 10]. Some layered framework solids containing bridging formate have been reported [11].

As part of our ongoing studies of network solids constructed from formate in the presence of neutral organic blocking units, we now describe the syntheses, crystal structures, and physical characterization of a new isostructural family of layered coordination polymers, $M(CHO_2)_2(C_3H_8N_2O_2)$ ($M = $ Co, Zn, Cd). A manganese compound may also adopt the same structure.

2. Experimental

2.1. *Physical measurements*

All reagents were purchased commercially and used without purification. Elemental analyses (C, H, and N) were measured on a Perkin Elmer–240B CHN element analyzer. Metal contents were determined using EDTA complexometric titrations. Hydrazine contents were determined volumetrically using a standard KIO_3 (0.025 M) solution [12]. IR spectra were recorded from 4000 to 400 cm^{-1} on a Shimadzu FTIR 8000 spectrophotometer using a KBr pellet. The UV-Vis spectrum for an aqueous solution of **3** was recorded on a SYSTRONICS 119 spectrometer. Combined thermogravimetric/differential thermal (TGA/DTA) analyses were performed on a Perkin Elmer Pyris Diamond thermal analyzer from room temperature to 850°C under oxygen with a heating rate of 20°C min^{-1}.

2.2. *Synthesis and characterization*

Ethyl carbazate (ec) (0.208 g, 0.002 mol) was added to an aqueous solution (25 mL) of formic acid (85%, 0.1 mL, 0.002 mol) and dissolved. To this solution, the respective metal (Mn, Co, Zn, Cd) formates, dissolved in 50 mL of water, were added. The metal formates were prepared by heating an aqueous solution (10 mL) containing the metal carbonate (e.g., $MnCO_3$, 0.115 g; 0.001 mol) and an excess of formic acid (85%, 1 ml) to dryness. The resulting solutions of pH ~ 4 were concentrated on a water-bath to one-third of their initial volume and left for crystallization at room temperature. After 1 week, crystalline $M(CHO_2)_2(C_3H_8N_2O_2)$ formed [$M = $ Mn (**1**) yield = 85%, Co (**2**) yield = 90%, Zn (**3**) yield = 92%, Cd (**4**) yield = 89%] and were filtered off, washed with ethanol, and dried in air. Products **1** and **2** were polycrystalline and **3** and **4** contained crystals large enough for structure determination. All products are colorless except the cobalt compound, which is pink. When stored in air, the manganese compound turns dark brown, perhaps indicating the oxidation of Mn^{II}. All are slightly soluble in cold water.

IR (KBr disk, cm^{-1}): **1** ν(N–H) 3249, ν(N–N) 1103, ν_{asym}(OCO) 1577, ν_{sym}(OCO) 1370, ν(C=O(ec)) 1690; **2** ν(N–H) 3234, ν(N–N) 1115, ν_{asym}(OCO) 1577, ν_{sym}(OCO) 1372, ν(C=O(ec)) 1695; **3** ν(N–H) 3236, ν(N–N) 1123, ν_{asym}(OCO) 1580, ν_{sym}(OCO) 1386, ν(C=O(ec)) 1698; **4** ν(N–H) 3232, ν(N–N) 1126, ν_{asym}(OCO) 1585, ν_{sym}(OCO) 1375, ν(C=O(ec)) 1696. Elemental analysis (Found, Calcd %): **1** hydrazine (12.50, 12.86), Mn (22.40, 22.07), C (29.12, 28.12), N (10.98, 11.25), H (4.90, 4.82); **2** hydrazine (12.30, 12.65), Co (22.60, 22.30), C (24.12, 23.72), N (11.02, 11.07), H (3.82, 3.95); **3** hydrazine (12.30, 12.34), Zn (24.80, 25.21), C (23.25, 23.13), N (10.02, 10.79), H (4.90, 4.82); **4** hydrazine (10.20, 10.44), Cd (36.60, 36.69), C (19.32, 19.58), N (9.40, 9.14), H (3.02, 3.26).

Powder X-ray diffraction patterns for **2**–**4** are very similar (see supplementary figure S7), indicating that these compounds are isostructural. However, **1** gave a more complex pattern: there appeared to be some degree of peak overlap with **2–4**, but there were also many extra peaks. This may correlate with the color change (decomposition) noted above and we can only tentatively suggest at this stage that the freshly prepared Mn compound is isostructural with its Co, Zn, and Cd congeners, as suggested by its IR and chemical analysis data. Simulations based on the single-crystal structures of **3** and **4** gave satisfactory agreements with the measured patterns.

2.3. *Crystal structure determinations*

Intensity data for **3** (colorless lath, $0.42 \times 0.20 \times 0.10\,mm^3$) and **4** (colorless block, $0.36 \times 0.24 \times 0.20\,mm^3$) were collected on a Nonius Kappa CCD diffractometer at 120 K using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Empirical (multi-scan) absorption corrections were applied at the data reduction stage (transmission-factor ranges = 0.393–0.772 and 0.498–0.661 for **3** and **4**, respectively) and the structures were routinely solved in space group $P\bar{1}$ (No. 2) by direct methods with SHELXS97 and the structural models refined against $|F|^2$ by full-matrix non-linear least squares with SHELXL97. All hydrogen atoms were geometrically placed and refined as riding atoms (C–H = 0.95–0.99 Å; N–H = 0.88–0.92 Å) with the constraint $U_{iso}(H) = 1.2U_{eq}$ (carrier) [$1.5U_{eq}$(C) for methyl H atoms] applied. Crystallographic and

Table 1. Crystallographic and data-collection parameters for **3** and **4**.

	3	4
Empirical formula	$C_5H_{10}N_2O_6Zn$	$C_5H_{10}CdN_2O_6$
Formula weight	259.52	306.55
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Unit cell dimensions (Å, °)		
a	8.0848(2)	8.4574(2)
b	8.7345(1)	8.9112(3)
c	13.2841(3)	13.5119(5)
α	74.2839(14)	73.101(1)
β	86.7150(12)	86.366(2)
γ	89.4713(15)	89.420(2)
Volume (Å^3), Z	901.51(3), 4	972.36(5), 4
Calculated density ($g\,cm^{-3}$)	1.912	2.094
$R(F)$	0.024	0.022
$wR(F^2)$	0.056	0.053
Largest difference peak and hole (e Å^{-3})	−0.53 and +0.52	−0.69 and +1.00

data collection parameters are summarized in table 1 and full details are available in the "Supplementary material."

3. Results

3.1. *Physical data*

Elemental analysis data for **1**–**4** are generally in agreement with the proposed compositions. IR spectra for **1**–**4** are similar to each other (supplementary figure S1) and the observed bands were assigned by comparing to the literature data [13]. The formate groups show one asymmetric (around $1570\,\mathrm{cm^{-1}}$) and one symmetric (around $1380\,\mathrm{cm^{-1}}$) stretching vibration. Although the zinc and cadmium crystal structures (*vide infra*) contain two formate anions in their asymmetric units, separate bands for the two anions could not be resolved. However, the difference of $\sim 200\,\mathrm{cm^{-1}}$ between the asymmetric and symmetric stretches clearly shows that the formate ion is bridging bidentate [14]. The spectra also exhibit a band around $1695\,\mathrm{cm^{-1}}$, which is characteristic of the C=O (amide group) stretching frequency of ec. The shift to lower frequency in these metal complexes compared to the free ligand ($1735\,\mathrm{cm^{-1}}$) indicates that the carbonyl oxygen is coordinated to the metal. Besides these, absorptions centered around 3240 and $1120\,\mathrm{cm^{-1}}$ are in accord with N–H and N–N stretching vibrations, respectively, of ec, signifying the coordination of nitrogen to metal.

The electronic spectrum for **2** (supplementary figure S2) shows a broad absorption band with $\lambda_{\max}$ around $19{,}600\,\mathrm{cm^{-1}}$ ($\sim 510\,\mathrm{nm}$, in the green region of the visible spectrum), which can be assigned to the ${}^4T_{1g}(\mathrm{F}) \rightarrow {}^4T_{1g}(\mathrm{P})$ electronic transition for an octahedral $\mathrm{Co^{2+}}$ d^7 system [15].

3.2. *Crystal structures*

$\mathrm{Zn(CHO_2)_2(C_3H_8N_2O_2)}$ (**3**) and $\mathrm{Cd(CHO_2)_2(C_3H_8N_2O_2)}$ (**4**) are isostructural, with small differences in their unit-cell parameters and unit-cell volumes. This description will focus on zinc and note significant differences in the cadmium phase where appropriate. Selected geometrical data for **3** and **4** are given in tables 2 and 3, respectively, and hydrogen-bond parameters are given in tables 4 (Zn) and 5 (Cd).

The structure of $\mathrm{Zn(CHO_2)_2(C_3H_8N_2O_2)}$ contains two zinc ions, four formates, and two ecs in the asymmetric unit (figure 1). Both Zn ions adopt somewhat distorted $\mathrm{ZnNO_5}$ octahedral coordination arising, in each case, from an N,O-bidentate ec and four monodentate formates. In each case, the Zn–O bond to ec is noticeably longer than the Zn–O formate bonds. The mean Zn–O separations are 2.145 and 2.212 Å for Zn1 and Zn2, respectively, and the bond-valence sum (BVS) values for Zn1 and Zn2 are 2.08 and 1.96, respectively, [in $\mathrm{Cd(CHO_2)_2(C_3H_8N_2O_2)}$ (figure 2) the mean Cd–O separations for Cd1 and Cd2 are 2.309 Å and 2.310 Å, respectively, and the BVS values are 2.04 and 2.02, respectively]. The bidentate connectivity of ec to zinc in **3** results in five-membered –Zn–N–N–C–O– chelate rings in which the four ligand atoms are almost co-planar (r.m.s. deviation for N1/N2/C5/O9 = 0.020 Å; r.m.s. deviation for N3/N4/C8/

Table 2. Selected bond lengths (Å) and angles (°) for **3**.

Zn1–O8	2.0099(13)	Zn1–O1	2.0854(13)
Zn1–N1	2.1075(15)	Zn1–O4	2.1320(13)
Zn1–O5$^{\mathrm{i}}$	2.1630(13)	Zn1–O9	2.2444(13)
Zn2–O3$^{\mathrm{ii}}$	2.0276(13)	Zn2–O6	2.0827(13)
Zn2–O7	2.1080(13)	Zn2–N3	2.1238(15)
Zn2–O2$^{\mathrm{iii}}$	2.1601(13)	Zn2–O12	2.2410(13)
C1–O2	1.250(2)	C1–O1	1.261(2)
C2–O3	1.240(2)	C2–O4	1.256(2)
C3–O5	1.251(2)	C3–O6	1.257(2)
C4–O8	1.243(2)	C4–O7	1.255(2)
C5–O9	1.225(2)	C5–O10	1.337(2)
C5–N2	1.346(2)	C6–O10	1.458(2)
C6–C7	1.503(3)	N1–N2	1.416(2)
C8–O12	1.232(2)	C8–O11	1.335(2)
C8–N4	1.346(2)	C9–O11	1.466(2)
C9–C10	1.502(3)	N3–N4	1.418(2)
O8–Zn1–O1	96.09(5)	O8–Zn1–N1	172.59(6)
O1–Zn1–N1	91.17(5)	O8–Zn1–O4	81.36(5)
O1–Zn1–O4	92.47(5)	N1–Zn1–O4	96.89(6)
O8–Zn1–O5$^{\mathrm{i}}$	90.51(5)	O1–Zn1–O5$^{\mathrm{i}}$	92.96(5)
N1–Zn1–O5$^{\mathrm{i}}$	90.58(6)	O4–Zn1–O5$^{\mathrm{i}}$	170.66(5)
O8–Zn1–O9	96.95(5)	O1–Zn1–O9	164.96(5)
N1–Zn1–O9	76.05(5)	O4–Zn1–O9	96.88(5)
O5$^{\mathrm{i}}$–Zn1–O9	79.46(5)	O3$^{\mathrm{ii}}$–Zn2–O6	95.86(5)
O3$^{\mathrm{ii}}$–Zn2–O7	81.15(5)	O6–Zn2–O7	93.47(5)
O3$^{\mathrm{ii}}$–Zn2–N3	172.19(6)	O6–Zn2–N3	91.88(5)
O7–Zn2–N3	99.53(6)	O3$^{\mathrm{ii}}$–Zn2–O2$^{\mathrm{iii}}$	90.36(5)
O6–Zn2–O2$^{\mathrm{iii}}$	92.80(5)	O7–Zn2–O2$^{\mathrm{iii}}$	169.92(5)
N3–Zn2–O2$^{\mathrm{iii}}$	88.14(5)	O3$^{\mathrm{ii}}$–Zn2–O12	96.47(5)
O6–Zn2–O12	166.42(5)	O7–Zn2–O12	94.03(5)
N3–Zn2–O12	75.72(5)	O2$^{\mathrm{iii}}$–Zn2–O12	81.46(5)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x, y-1, z$; (iii) $1-x, 1-y, 1-z$.

O12 = 0.013 Å) and the metals are significantly displaced from their mean planes by 0.509(3) Å (Zn1) and 0.558(3) Å (Zn2). All formates bridge two adjacent zincs (one Zn1 and one Zn2), resulting in a polymeric, layered network of Zn–O–C–O–Zn links that propagates parallel to (001). In terms of metal coordination polyhedral, double octahedral layers result (figures 3 and 4) with the ethyl side chains of the ec ligands projecting into the inter-layer regions.

The structure of **3** is consolidated by N–H $\cdots$ O and bifurcated N–H $\cdots$ (O,O) hydrogen bonds, which are both intra- and inter-layer. Topologically, in terms of metal–metal connectivity, a highly puckered square network arises (figure 5), in which the Zn $\cdots$ Zn separations range between 5.1 Å and 5.9 Å.

3.3. *Thermal study*

The thermal stability and reactivity of **1**–**4** were studied using simultaneous TG-DTA (figures S3–S6). Complexes **1** and **4** are stable to ~165°C and 180°C, respectively,

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

Cd1–O8	2.2353(16)	Cd1–O1	2.2786(17)
Cd1–O4	2.2830(17)	Cd1–N1	2.3016(19)
Cd1–O5^{i}	2.3497(16)	Cd1–O9	2.3961(16)
Cd2–O3^{ii}	2.2494(16)	Cd2–O6	2.2752(17)
Cd2–O7	2.2775(16)	Cd2–N3	2.3091(19)
Cd2–O2^{iii}	2.3523(16)	Cd2–O12	2.3958(16)
C1–O2	1.246(3)	C1–O1	1.255(3)
C2–O3	1.236(3)	C2–O4	1.260(3)
C3–O5	1.245(3)	C3–O6	1.258(3)
C4–O8	1.240(3)	C4–O7	1.254(3)
C5–O9	1.227(3)	C5–O10	1.339(3)
C5–N2	1.341(3)	C6–O10	1.455(3)
C6–C7	1.502(4)	N1–N2	1.414(3)
C8–O12	1.231(3)	C8–O11	1.332(3)
C8–N4	1.344(3)	C9–O11	1.467(3)
C9–C10	1.497(4)	N3–N4	1.417(3)
O8–Cd1–O1	94.99(6)	O8–Cd1–O4	79.20(6)
O1–Cd1–O4	92.33(6)	O8–Cd1–N1	168.81(7)
O1–Cd1–N1	95.16(6)	O4–Cd1–N1	105.07(6)
O8–Cd1–O5^{i}	87.22(6)	O1–Cd1–O5^{i}	91.61(6)
O4–Cd1–O5^{i}	166.14(6)	N1–Cd1–O5^{i}	87.79(6)
O8–Cd1–O9	98.00(6)	O1–Cd1–O9	162.21(6)
O4–Cd1–O9	101.98(6)	N1–Cd1–O9	71.10(6)
O5^{i}–Cd1–O9	76.99(6)	O3^{ii}–Cd2–O6	93.86(6)
O3^{ii}–Cd2–O7	77.97(6)	O6–Cd2–O7	94.43(6)
O3^{ii}–Cd2–N3	167.58(7)	O6–Cd2–N3	95.70(7)
O7–Cd2–N3	109.09(6)	O3^{ii}–Cd2–O2^{iii}	87.07(6)
O6–Cd2–O2^{iii}	91.86(6)	O7–Cd2–O2^{iii}	164.12(6)
N3–Cd2–O2^{iii}	84.72(6)	O3^{ii}–Cd2–O12	98.27(6)
O6–Cd2–O12	164.19(6)	O7–Cd2–O12	97.97(6)
N3–Cd2–O12	71.00(6)	O2^{iii}–Cd2–O12	78.74(6)

Symmetry codes: (i) $-x$, $1-y$, $1-z$; (ii) x, $y-1$, z; (iii) $1-x$, $1-y$, $1-z$.

Table 4. Hydrogen bonds (Å and °) for **3**.

D–H···A	D–H	H···A	D···A	D–H···A
N1–H1A···O7^{ii}	0.92	2.34	3.162(2)	148
N1–H1A···O3	0.92	2.15	2.892(2)	137
N1–H1B···O1^{iii}	0.92	2.03	2.924(2)	162
N2–H2A···O2^{iii}	0.88	2.37	2.909(2)	120
N3–H3A···O5^{i}	0.92	2.65	3.217(2)	120
N3–H3B···O4	0.92	2.29	3.132(2)	152
N3–H3B···O8	0.92	2.20	2.914(2)	134
N4–H4A···O5^{i}	0.88	2.42	2.969(2)	121

Symmetry codes: (i) $1-x$, $1-y$, $1-z$; (ii) x, $1+y$, z; (iii) $-x$, $2+y$, $1-z$.

whereas **2** and **3** are stable to above 200°C (supplementary table S1). For all the compounds, the observed weight loss in the first decomposition step corresponds to the loss of ec. DTA shows an endothermic peak for this decomposition. On further heating, the metal formates, thus formed, yield the respective metal oxides of general formula *M*O except **4**, which gave cadmium metal as an end product at 280°C. This latter result

Table 5. Hydrogen bonds (Å and °) for **4**.

D–H $\cdots$ A	D–H	H $\cdots$ A	D $\cdots$ A	D–H $\cdots$ A
N1–H1A $\cdots$ O7^{ii}	0.92	2.14	3.004(3)	155
N1–H1A $\cdots$ O3	0.92	2.38	3.015(2)	126
N1–H1B $\cdots$ O1^{iii}	0.92	2.00	2.899(3)	166
N2–H2A $\cdots$ O2^{iii}	0.88	2.35	2.915(3)	122
N3–H3A $\cdots$ O5^{i}	0.92	2.65	3.208(2)	120
N3–H3B $\cdots$ O4	0.92	2.10	2.982(3)	159
N3–H3B $\cdots$ O8	0.92	2.46	3.048(2)	122
N4–H4A $\cdots$ O5^{i}	0.88	2.40	2.969(3)	122

Symmetry codes: (i) $1-x$, $1-y$, $1-z$; (ii) x, $1+y$, z; (iii) $-x$, $2+y$, $1-z$.

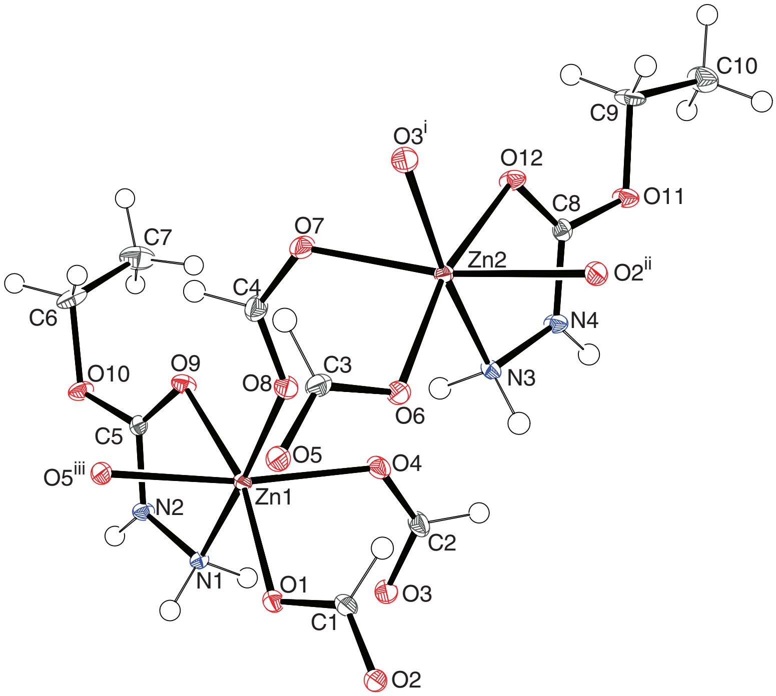

Figure 1. The asymmetric unit of **3** expanded to show full coordination spheres of zinc (50% displacement ellipsoids for the non-hydrogen atoms). Symmetry codes: (i) x, $y-1$, z; (ii) $1-x$, $1-y$, $1-z$; (iii) $-x$, $1-y$, $1-z$.

is somewhat surprising for TGA carried out under oxygen, but it is possible that the decomposing hydrazine residue of the ec moiety has served as a reducing agent. The calculated weight loss values for the decomposition pathway $M(CHO_2)_2(C_3H_8N_2O_2) \rightarrow M(CHO_2)_2 \rightarrow MO$ (or M for Cd) are in satisfactory agreement with the observed weight losses (Supplementary material). DTA shows that the decompositions of metal formates are exothermic.

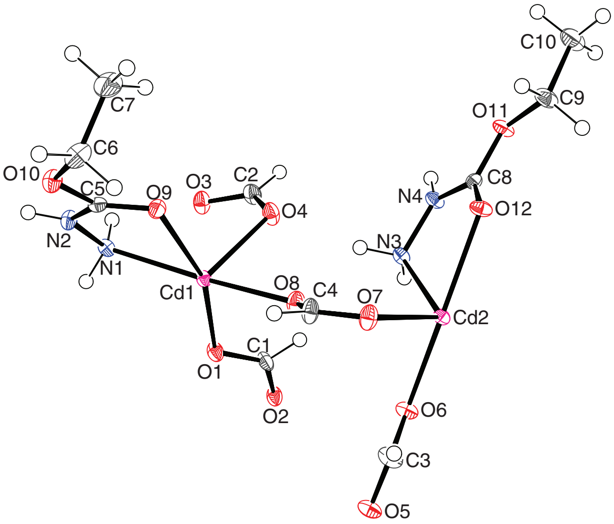

Figure 2. The asymmetric unit of **4** showing 50% displacement ellipsoids for the non-hydrogen atoms.

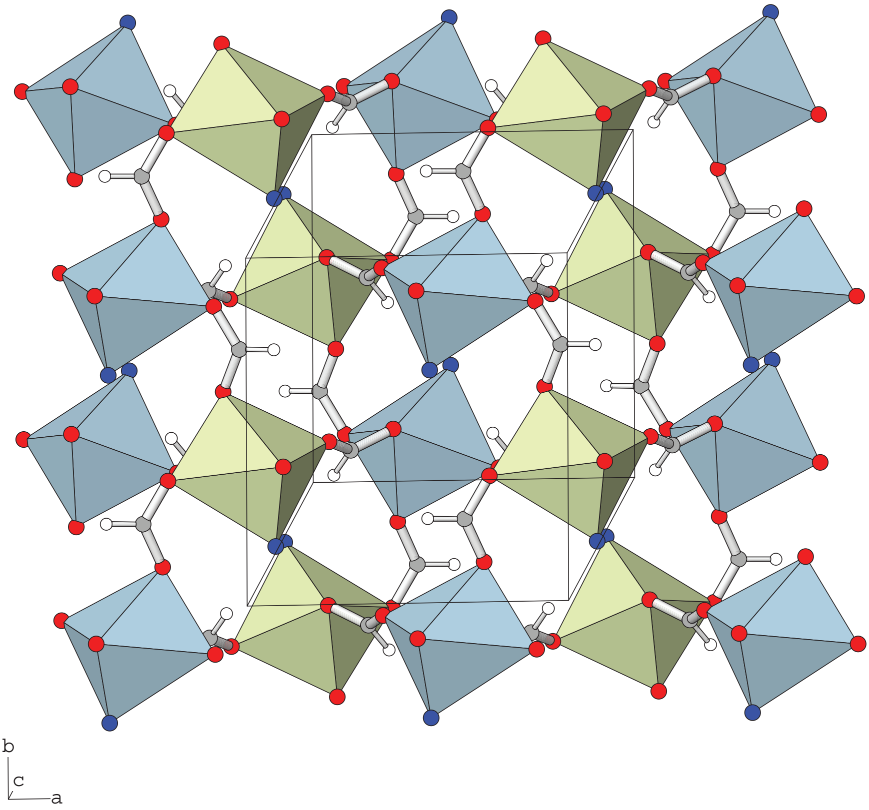

Figure 3. Polyhedral view, approximately down [001], of **3** showing the linkage of Zn1-centered and Zn2-centered octahedra. In the on-line version of the journal, these are colored green and blue, respectively.

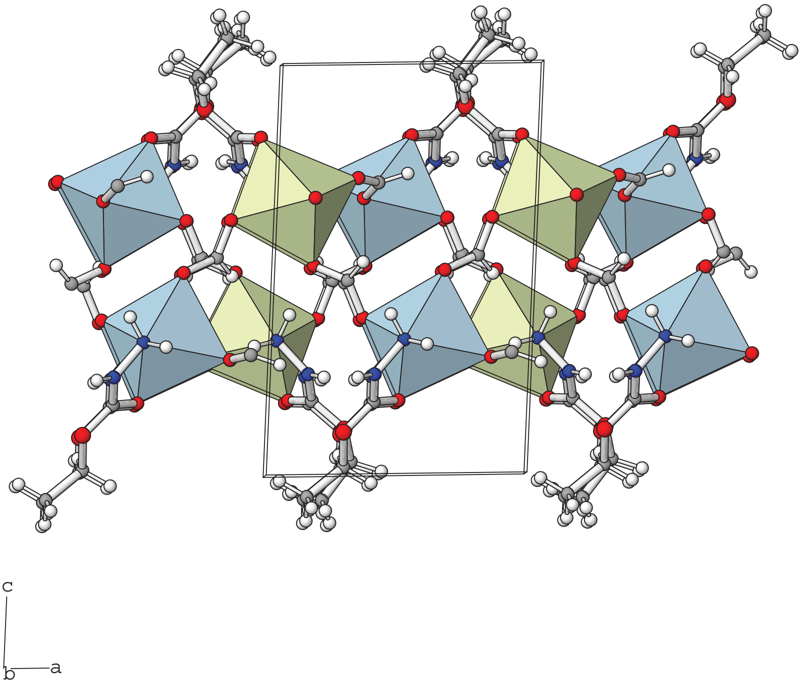

Figure 4. Polyhedral view looking side-on to the double octahedral layers in **3** showing the linkage. In the on-line version of the journal, the Zn1-centered and Zn2-centered octahedra are colored green and blue, respectively.

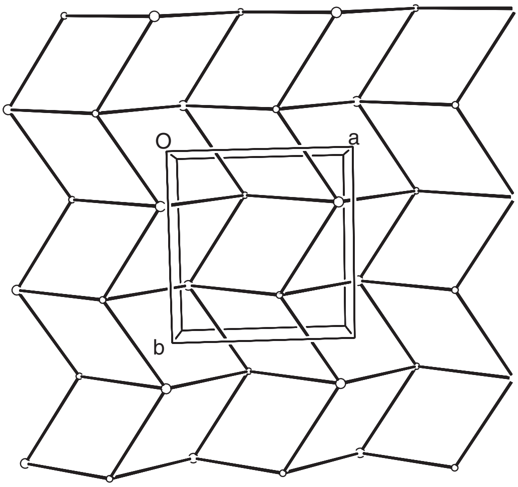

Figure 5. Topological connectivity of the zinc nodes in **3** showing the resulting distorted square grid.

4. Discussion

A family of new layered coordination networks of formula M(ft)$_2$(ec) have been prepared and characterized, and are the first compounds to contain the pairing of formate ions and ec ligands. A few metal complexes containing ec have been prepared, including $Ni(C_3H_8N_2O_2)_3 \cdot 2Cl$ [16] and the isostructural series $M(C_3H_8N_2O_2)_3 \cdot 2NO_3$ [$M = $ Mn [17], Co [18], Ni [19], and Zn [20]]. In all these cases, isolated molecular $[M(ec)_3]^{2+}$ accompanied by counter ions occur. Conversely, formate ions have long been recognized as suitable building blocks for coordination networks. In combination with Zn^{2+}, they are invariably monodentate and bridging, as in $Ba_2Zn(CHO_2)_6(H_2O)_4$ [21] and $(C_2H_8N) \cdot Zn(CHO_2)_3$ [22]. With Cd^{2+}, bridging formate ions have also been seen in a number of structures, for example $NaCd(CHO_2)_3$ [23], but the larger size of the cadmium ion also allows the $[CHO_2]^-$ to act as a bridging/chelating species, as in $Cd(CHO_2)_2$ [24]. These results suggest that the combination of chelating carbazates with bridging anions such as formate is an effective combination to generate new types of coordination networks and we are now studying such systems.

Supplementary material

IR spectra of **1**–**4**, UV-Vis spectrum of **2**, TGA/DTA traces for **1**–**4**, X-ray powder patterns for **1**–**4**, full weight-loss data for **1**–**4**. Full details of the crystal structures of **3** (CCDC No. 771658) and **4** (CCDC No. 771657) in cif format are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; or Email deposit@ccdc.cam.ac.uk.

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