

**Synthesis and characterisation of double-layered octahedral coordination
polymers built up from divalent metal ions, mixed carboxylate anions, and
ethyl carbazate ligands**

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Abstract

A new family of mixed formate–acetate containing coordination polymers of formulae $M(\text{HCOO})_{2-x}(\text{CH}_3\text{COO})_x(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$ [$M = \text{Mn}$ (**1**), Co (**2**), Zn (**3**) and Cd (**4**)] and $\text{Cd}(\text{CH}_3\text{COO})_2(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$ (**5**) ($\text{C}_3\text{H}_8\text{N}_2\text{O}_2 = \text{ethyl carbazate}$) are described. The compounds have been crystallised from aqueous solution and characterised using elemental analysis, IR and UV/visible spectroscopy, TGA, NMR and PXRD and the single-crystal structures of **1** and **3** have been determined. These isostructural compounds consist of M^{2+} ions coordinated by N,O-chelating ethyl carbazate molecules and four bridging acetate or formate anions (some of which are disordered). The resulting coordination polyhedra for the metal atoms are distorted MO_5N octahedra. The polyhedral connectivity (*via* both formate and acetate bridges) generates double layers propagating in (100) with the topology of a square grid for the metal–metal links. Intra-layer $\text{N–H}\cdots\text{O}$ hydrogen bonds help to establish the structures.

Keywords: layered coordination network; mixed carboxylate; bidentate ligand; crystal structure

Introduction

Metal-organic frameworks (MOFs) have been intensively studied in recent years due to their structural diversity and potential applications in various fields including catalysis, gas storage, magnetism and separation [1–5]. A variety of ligands have been used to synthesise MOFs with different structures: in this context, carboxylate ligands have been particularly effective owing to the diversity of their coordination modes [6–8]. A large number of different carboxylates in combination with various neutral blocking ligands have been hitherto used to synthesis MOFs with different topologies [9–11]. As well as long-chain and aromatic carboxylates, simple anions such as formate and acetate are effective in forming MOFs, where their small size, strong coordinating power and flexible coordination modes lead to distinct structures, which are often layered [12–16].

In terms of our own studies in this area, we have recently described a series of coordination polymers using bridging anionic ligands such as formate and thiocyanate in combination with ethyl carbazate as a chelating, blocking ligand [17, 18]. In continuation of these studies, we now describe the synthesis, characterisation and single-crystal structures of a new series of mixed formate–acetate compounds $M(\text{HCOO})_{2-x}(\text{CH}_3\text{COO})_x(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$ ($M = \text{Mn, Co, Zn}$ and Cd) and $\text{Cd}(\text{CH}_3\text{COO})_2(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$ where $\text{C}_3\text{H}_8\text{N}_2\text{O}_2 = \text{ethyl carbazate}$.

Experimental

Elemental analyses for C, H, and N were carried out using a Perkin Elmer–240B CHN element analyzer. The metal contents were determined using EDTA complexometric titrations after decomposing the complexes with dilute hydrochloric acid. Hydrazine contents were determined by titration using KIO_3 solution [19]. The IR spectra (KBr pellets) were recorded between 4000 and 400 cm^{-1} using a Shimadzu FTIR 8000 spectrophotometer. The

UV/visible spectrum for an aqueous solution of the cobalt compound was recorded on a SYSTRONICS 119 spectrometer and $^1\text{H-NMR}$ spectra were obtained on a Bruker 400/500 MHz instrument. Thermal analyses were performed on a Perkin-Elmer Pyris Diamond and NETZSCH STA 449 F3 Jupiter thermal analyzer under oxygen/nitrogen atmospheres with a heating rate of $20\text{ }^\circ\text{C min}^{-1}$.

Synthesis and Characterisation

$\text{M}(\text{CHO}_2)_{2-x}(\text{C}_2\text{H}_3\text{O}_2)_x(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$ [M = Mn (1), Co (2), Zn (3) and Cd (4)]

Ethyl carbazate (ec) (0.208 g, 0.002 mol) was dissolved in an aqueous solution (25 ml) of formic acid (85%, 0.1 ml, 0.002 mol). To these solutions, 0.001 mol of the respective metal (Mn, Co, Zn, Cd) acetate hydrate (for example $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$: 0.245 g), dissolved in 50 ml of water, were added. The resulting solutions of pH ~ 4 were placed on a water-bath and concentrated to about one third of their initial volume. These were then put aside for crystallization at room temperature: after one week, the solid products formed were recovered by filtration, rinsed with ethanol and dried in air. Compounds **2** and **4** formed as powders whereas products **1** and **3** contained single crystals large enough for structure determination. Yields: **1** (78%), **2** (83%), **3** (90%), **4** (86%). IR (KBr disk, cm^{-1}): **1**; $\nu(\text{N-H})$ 3249, $\nu(\text{N-N})$ 1101, $\nu_{\text{asym}}(\text{OCO})$ 1605 + 1575, $\nu_{\text{sym}}(\text{OCO})$ 1452 + 1384, $\nu(\text{C=Oec})$ 1695; **2**; $\nu(\text{N-H})$ 3231, $\nu(\text{N-N})$ 1114, $\nu_{\text{asym}}(\text{OCO})$ 1605 + 1580, $\nu_{\text{sym}}(\text{OCO})$ 1450 + 1370, $\nu(\text{C=Oec})$ 1695; **3**; $\nu(\text{N-H})$ 3236, $\nu(\text{N-N})$ 1120, $\nu_{\text{asym}}(\text{OCO})$ 1619 + 1570, $\nu_{\text{sym}}(\text{OCO})$ 1455 + 1369, $\nu(\text{C=Oec})$ 1700; **4**; $\nu(\text{N-H})$ 3234, $\nu(\text{N-N})$ 1116, $\nu_{\text{asym}}(\text{OCO})$ 1615+ 1576, $\nu_{\text{sym}}(\text{OCO})$ 1460 + 1373, $\nu(\text{C=Oec})$ 1695.

Elemental analysis (found, calc., %): $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_6\text{Mn}$, **1**: Mn (20.60, 20.89), C (26.98, 27.38), N (10.70, 10.65), H (4.52, 4.56); **hydrazine** (12.30, 12.17); $\text{C}_6\text{H}_{12}\text{N}_2\text{O}_6\text{Co}$, **2**: Co (21.80,

22.08), C (27.02, 26.97), N (10.20, 10.49), H (4.82, 4.50); hydrazine (12.30, 11.99); C₆H₁₂N₂O₆Zn, **3**: Zn (24.10, 23.92), C (26.22, 26.34), N (10.13, 10.24), H (4.01, 3.75); hydrazine (11.80, 11.70); C₆H₁₂N₂O₆Cd, **4**: Cd (34.60, 35.08), C (22.86, 22.47), N (9.10, 8.74), H (4.20, 3.75); hydrazine (10.20, 9.99).

¹H-NMR (400 MHz, DMSO, δ in ppm) for **3**: 1.16(t, 3H), 1.83(s, 3H), 4.02(q, 2H), 8.25(s, 1H).

Cd(C₂H₃O₂)₂(C₃H₈N₂O₂) (5**)**

This compound was prepared by replicating the above procedure except that formic acid was replaced by acetic acid. The dark pink solid formed after two weeks was recovered by filtration, washed with alcohol and dried in air. The compound is hygroscopic on exposure to air. Yield: 82%. IR (KBr disk, cm⁻¹): ν(N–H) 3250, ν(N–N) 1202, ν_{asym}(OCO) 1560, ν_{sym}(OCO) 1419, ν(C=O_{ec}) 1693; Elemental analysis (found, calc., %): C₇H₁₄N₂O₆Cd: hydrazine (10.20, 10.44), Cd (33.40, 33.61), C (25.26, 25.14), N (8.10, 8.37), H (3.20, 3.59).

¹H-NMR (500 MHz, DMSO, δ in ppm) for **5**: 1.16(t, 3H), 1.83(s, 3H), 4.02(q, 2H), 4.29(s, 1H).

Crystal structure determinations

Intensity data for **1** (colourless block, 0.48 × 0.40 × 0.36 mm) and **3** (colourless slab, 0.41 × 0.36 × 0.21 mm) were collected at room temperature on a Nonius KappaCCD diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) and empirical absorption corrections were applied during data reduction (transmission-factor ranges = 0.503–0.862 and 0.778–0.928 for **1** and **3**, respectively). The manganese structure was easily solved in space group *P*2₁/*c* (No. 14) by direct methods with SHELXS-97 and the structural model was

developed and refined against $|F|^2$ with SHELXL-97 [20]. The O2/C2/C3 side chain of the ec ligand is disordered over two orientations; atom C6 is part of a partially occupied acetate ion and atoms C5, O5 and O6 correspond to overlapped formate and acetate ions (*vide infra*): the site occupancies of these groups of atoms were refined (constrained to sum to unity in each case). All the H atoms were geometrically placed and refined as riding atoms (C–H = 0.96–0.97 Å; N–H = 0.86–0.90 Å) with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ or $1.5U_{\text{eq}}(\text{methyl C})$ applied. The similar monoclinic unit cells indicated that **1** and **3** are isostructural and the atom positions from **1** (with Zn replacing Mn) were used as the starting model for **3**, with the same disorder model applied: a slightly different refined formate to acetate ratio resulted. Key crystallographic and data collection parameters are summarised in Table 1 and full details are available in the supplementary materials (cif files).

Results and discussions

Synthesis

The elemental analysis data for **1–4** are in reasonable agreement with the proposed chemical compositions of these compounds. When freshly prepared, all these phases are colourless except **2**, which is pale pink. When stored in air, the manganese compound transforms to a dark brown solid after a week, which was also observed for its formate analogue [17], whereas compounds **3** and **5** transform to pale blue and pink colours, respectively. Compounds **1–4** are slightly soluble in cold water whereas compound **5** is readily soluble in water. We have already reported [17] a family of compounds of general formula $\text{M}(\text{HCOO})_2(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$ (M = Mn, Co, Zn and Cd), which were prepared by reacting the respective metal formate with an aqueous mixture of ec and formic acid. By adapting the same procedure, except with metal acetates replacing formic acid, we could isolate the new

family of compounds, $M(\text{HCOO})_{2-x}(\text{CH}_3\text{COO})_x(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$, reported here. Interestingly, our attempt to prepare the analogous ‘pure acetate’ compounds of putative formula $M(\text{CH}_3\text{COO})_2(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$ was not successful except with cadmium, which resulted in a hygroscopic, light pink solid.

Spectroscopic data

The IR spectra for **1–5** are similar to each other and band assignments were made by comparison to literature data [17]. Except for compound **5**, two distinct asymmetric (between 1615–1570 cm^{-1}) and symmetric (between 1450–1369 cm^{-1}) carboxylate stretching vibrations could be assigned for compounds **1–4**, which we ascribe to the presence of both formate and acetate ligands. For compound **5**, the asymmetric and symmetric acetate-carboxylate vibrations are observed at 1560 and 1419 cm^{-1} , respectively. The frequency differences of $\leq 200 \text{ cm}^{-1}$ between the asymmetric and symmetric stretches indicate that the both the formate and acetate ions are coordinated as bridging bidentate (μ^2) ligands. All the spectra exhibit a band occurring around 1700 cm^{-1} , which is characteristic of the C=O (amide group) stretching frequency of ethyl carbazate: the shift to lower frequency in these metal complexes compared to the free ligand (1735 cm^{-1}) strongly suggest that the carbonyl O atom is coordinated to the metal, as conformed by the crystal structures. Besides these, absorptions centred around 3240 (for **5**, 3250) cm^{-1} and 1120 (for **5**, 1201) cm^{-1} are in accordance with N–H and N–N stretching vibrations, respectively, of ethyl carbazate, which signify the coordination of the terminal nitrogen atom to the metal atom.

The UV/visible spectrum for **2** shows a broad absorption band with $\lambda_{\text{max}} = 19600 \text{ cm}^{-1}$ (~510 nm), which can be assigned to the usual ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ transition for an octahedral $\text{Co}^{2+} d^7$ system [21].

The proton NMR spectra of **3** and **5**, recorded as representative examples, show a triplet around 1.16 ppm for $-\text{CH}_2-\text{CH}_3$ and a quartet at 4.06 ppm for $-\text{OCH}_2-\text{CH}_3$ groups. For both **3** and **5**, the spectra show a broad singlet at 4.23 ppm, which can be assigned to the NH_2 protons. In the spectrum of compound **3**, two peaks (s, 8.25 ppm for HCOO^- and s, 1.83 ppm for CH_3COO^-) are observed. However in **5**, a singlet at 1.83 ppm is observed due to the presence of just acetate ions.

Thermal analysis

TGA for compound **5** was performed under a nitrogen atmosphere whereas all other compounds were studied in an oxygen atmosphere. Compound **2** is stable up to 215 °C on heating whereas compounds **1**, **3**, **4** and **5** start to decompose below 200 °C. In general, the thermal behaviour of these five compounds is similar to those of the already reported formate complexes [17]. The observed (calculated) percentage weight losses are 40.5 (39.6) for **1**, 39.5 (39.0) for **2**, 38.5 (38.0) for **3**, 31.5 (32.5) for **4** and 30.5 (31.1) for **5** for the first decomposition step for all the compounds, which is due to the loss of ethyl carbazate to result in the respective metal-carboxylate intermediates. DTA shows an endothermic peak for this decomposition in each case. The intermediates from **1–4** further decompose to yield the respective metal oxides as final residues: total percentage mass losses are 70.5 (73.0) for **1**, 71.5 (71.9) for **2**, 70.5 (70.2) for **3** and 69.5 (59.9) for **4**. The DTA traces show an exothermic peak for the formation of these oxides. Conversely, the cadmium carboxylate intermediate from compound **5** decomposes in an endothermic fashion as shown by DTA to results in cadmium metal [observed = 62.5, calculated = 61.6) as end residue. The metal-oxide/metal formation temperatures for compounds **1**, **2**, and **4** are found to be relatively low (below 400 °C) compared to **3** and **5** (above 600 °C).

Powder diffraction

X-ray powder diffraction data for **1–4** were collected on a Bruker AXS D8 Advance Diffractometer using Cu K α radiation: the resulting similar powder patterns (see supplementary materials) strongly suggest that **1–4** are isostructural.

Crystal structures

Although they have slightly different refined formate to acetate ratios, Mn(CHO₂)_{1.689}(C₂H₃O₂)_{0.311}(C₃H₈N₂O₂) (**1**) and Zn(CHO₂)_{1.839}(C₂H₃O₂)_{0.161}(C₃H₈N₂O₂) (**3**) crystallise in the same space group and with almost the same unit-cells and may be regarded as being isostructural. This description will focus on the manganese phase and note significant differences in the zinc phase where appropriate. Selected geometrical data (including hydrogen bonds) for **1** and **3** are given in Tables 2 and 3, respectively.

The asymmetric unit of **1** contains one manganese ion, one formate anion (C4/O3/O4), one disordered (overlapped) formate (C5/O5/O) + acetate (C5/C6/O5/O6) ion in a 0.689 (15):0.311 (15) ratio and one ethyl carbazate ligand (Figure 1). When symmetry-generated species are considered, the metal ion adopts a somewhat distorted MnNO₅ octahedral coordination geometry (angular variance [22] = 61.5^{o2}) arising from an N,O-bidentate ec ligand and four bridging-monodentate formate/acetate ions. The disordered formate/acetate ions are orientated in a *cis* arrangement with respect to the metal ion. The Mn1–O1 bond to the ec ligand is noticeably longer than the charge-assisted Mn–O formate/acetate bonds: the mean Mn–O separation is 2.187 Å. In **3**, the angular variance for the ZnO₅N octahedron is 48.5^{o2} indicating rather less angular distortion and the mean Zn–O separation is 2.110 Å.

The bidentate connectivity of the ec ligand to the metal atom in **1** results in a five-membered –Mn1–N1–N2–C1–O1– chelate ring [bite angle = 72.13 (8)°] in which the four ligand atoms are almost co-planar (r.m.s. deviation for N1/N2/C1/O1 = 0.008 Å) and the metal atom is significantly displaced from their mean plane by 0.500 (8) Å to result in an envelope conformation. The side-chain of the ec ligand is disordered over two orientations in a 0.573 (8):0.427 (8) ratio. Equivalent data for the zinc phase are: chelate bite angle = 75.33 (7)°; r.m.s. deviation = 0.010 Å; metal-ion displacement = 0.519 (5) Å and disorder ratio = 0.583 (10):0.417 (10).

In both phases, all the formate/acetate ions bridge a pair of metal ions: the C4 (formate) species generate [010] chains and the C5 (disordered formate/acetate) ions generate [001] chains. Together, these lead to a polymeric, layered network of M–O–C–O–M (M = Mn or Zn) links that propagates parallel to (100). In terms of metal coordination polyhedra, double octahedral layers result (Figure 3), with the ethyl side chains of the ec ligands projecting into the inter-layer regions. Topologically, in terms of metal–metal connectivity, a highly puckered square network arises (Figure 4), in which the Mn···Mn separations are 5.3432 (6) Å and 5.9891 (7) Å [equivalent data for the Zn···Zn separations in **3** = 5.2117 (5) Å and 5.8609 (5) Å]. The extended structures are consolidated by N–H···O and bifurcated N–H···(O,O) hydrogen bonds arising from the hydrazine moiety of the ethyl carbazate ligand (Tables 2 and 3), all of which are intra-layer, with almost no differences apparent between **1** and **3**.

Summary

A new family of mixed-ligand, layered, coordination networks of formula $M(\text{HCOO})_2\text{-}_x(\text{CH}_3\text{COO})_x(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$ have been prepared and characterised to complement the $M(\text{HCOO})_2(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$ family reported earlier [17]. It may be noted that no disorder is

found in the structure of the pure formate containing compounds. However, replacing one of the formate anions by slightly bulkier acetate anion, reported herein, resulted in the disordered structures. Our attempts to prepare pure acetate-containing compounds resulted in a hygroscopic compound only with the larger cadmium atom. It seems that subtle features are involved when different alkyl carbazates combine with metal ions and different carboxylate anions and we are continuing our studies of such systems.

Supplementary materials

IR spectra of **1** and **5**, UV/visible spectrum of **2**, TGA/DTA traces for **1–5**, X-ray powder patterns for **1–4**. Full details of the crystal structures of **1** (CCDC 1484593) and **3** (CCDC 1484594) in cif format are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, or e-mail deposit@ccdc.cam.ac.uk.

References

1. A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkovand, F. Verpoort, Metal-organic frameworks: versatile heterogeneous catalysts for efficient catalytic organic transformations, *Chem. Soc. Rev.*, 44 (2015) 6804-6849.
2. A. G. Wong-Foy, A. J. Matzger, O. M. Yaghi, Exceptional H₂ Saturation Uptake in Microporous Metal–Organic Frameworks, *J. Am. Chem. Soc.*, 128 (2006) 3494-3495.
3. S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, Impact of Preparation and Handling on the Hydrogen Storage Properties of Zn₄O(1,4-benzenedicarboxylate)₃ (MOF-5), *J. Am. Chem. Soc.*, 129 (2007) 14176-14177.

4. C. M. Nagaraja, R. Halder, T. K. Maji, C. N. R. Rao, Chiral Porous Metal–Organic Frameworks of Co(II) and Ni(II): Synthesis, Structure, Magnetic Properties, and CO₂ Uptake, *Cryst. Growth Des.*, 12 (2012) 975-981.
5. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae, J. R. Long, Carbon dioxide capture in metal-organic frameworks, *Chem. Rev.*, 112 (2012) 724-781.
6. X. Wang, Y.-B. Zhang, H. Huang, J.-P. Zhang, X.-M. Chen, Microwave-Assisted Solvothermal Synthesis of a Dynamic Porous Metal-Carboxylate Framework, *Cryst. Growth Des.*, 8 (2008) 4559-4563.
7. C.-H. Lee, J.-Y. Wu, G.-H. Lee, S.-M. Peng, J.-C. Jiang, K.-L. Lu, Correlation of Mesh Size of Metal–Carboxylate Layer with Degree of Interpenetration in Pillared-Layer Frameworks, *Cryst. Growth Des.*, 14 (2014) 5608-5618.
8. I.-H. Park, K. Kim, S. S. Lee, J. J. Vittal, An Unusual Interweaving in a 3-Fold Interpenetrated Pillared-Layer Zn(II) Coordination Polymer with a Long Spacer Ligand, *Cryst. Growth Des.*, 12 (2012) 3397-3401
9. Y.-Y. Lin, Y.-B. Zhang, J.-P. Zhang, X.-M. Chen, Pillaring Zn-Triazolate Layers with Flexible Aliphatic Dicarboxylates into Three-Dimensional Metal–Organic Frameworks, *Cryst. Growth Des.*, 8 (2008) 3673-3679.
10. L.-S. Long, X.-M. Chen, M.-L. Tong, Z.-G. Sun, Y.-P. Ren, R.-B. Huang, L.-S. Zheng, A unique open inorganic–organic framework with alternate hexa- and penta-coordinate cobalt(II) sites. Synthesis, crystal structure and magnetic properties of [Co₃(C₄H₄O₄)_{2.5}(OH)]_n·0.5nH₂O, *J. Chem. Soc., Dalton Trans.*, (2001) 2888-2890.
11. A. Pichon, C. M. Fierro, M. Nieuwenhuyzen, S. L. James, A pillared-grid MOF with large pores based on the Cu₂(O₂CR)₄ paddle-wheel, *CrystEngComm*, 9 (2007) 449-451.

12. Y.-P. Xia, Y.-W. Li, D.-C. Li, Y.-C. Du, Q.-X. Yao, J.-M. Dou, A new pillared-layer 3D coordination polymer involving in situ generated formate, *J. Mol. Struct.*, 1081 (2015) 362-365.
13. R. Baggioa, D. Stoilovab, G. Pollaa, G. Leyvaa, M. T. Garland, Double formates $\text{Ba}_2\text{M}(\text{HCOO})_6(\text{H}_2\text{O})_4$ (M=Co, Ni, Cu, Zn): crystal structures and hydrogen bonding systems, *J. Mol. Struct.*, 697 (2004) 173-180.
14. O. Sengupta, B. Gole, P. S. Mukherjee, A formate bridged Ni(II) sheet and its 3D analogue in presence of a linear organic linker: Synthesis, crystal structure and magnetic properties, *Polyhedron*, 29 (2010) 2952.
15. W. Huang, D. Hu, S. Gou, S. Chantrapromma, H.-K. Fun, Y. Xu, Q. Meng, Two formate bridging coordination polymers containing dinuclear zinc(II) macrocyclic components, *Inorg. Chim. Acta*, 342 (2003) 9-15.
16. (a) A. V. Prosvirin, H. Zhao, K. R. Dunbar, A Mn(III) chain derived from Mn_{12} -acetate that exhibits both glauber dynamics and antiferromagnetic ordering regimes, *Inorg. Chim. Acta*, 389 (2012) 118-121.
- (b) C. C. Stoumpos, E. Diamantopoulou, C.P. Raptopoulou, A. Terzis, S.P. Perlepes, N. Lalioti, A two-dimensional manganese(II) coordination polymer containing 1-hydroxybenzotriazolate and acetate bridging ligands: Preparation, structural characterization and magnetic study, *Inorg. Chim. Acta*, 361 (2008) 3638-3645.
17. K. Srinivasan, S. Govindarajan, W. T .A. Harrison, A family of double-layered octahedral coordination networks built up from divalent metal ions, formate anions, and ethyl carbazate ligands: $\text{M}(\text{CHO}_2)_2(\text{C}_3\text{H}_8\text{N}_2\text{O}_2)$ (M = Co, Zn, Cd), *J. Coord. Chem.*, 64 (2011) 3541-3550.

18. K. Srinivasan, A. Kathiresan, S. Govindarajan, W. T .A. Harrison. A family of double-layered coordination polymers containing Cd^{2+} , N,O-chelating ligands, and bridging SCN^- and Cl^- , *J. Coord. Chem.*, 67 (2014) 857-869.
19. G. H. Jeffery, J. Bassett, J. Mendham, R.C. Denney. *Vogel's Textbook of Quantitative Chemical Analysis*, 5th Edn, p. 402. Longman Scientific and Technical Publishers, London (1986).
20. G. M. Sheldrick, A short history of SHELX, *Acta Cryst.*, A64 (2008) 112-122.
21. A. Beghidja, R. Welter, P. Rabu, G. Rogez, Synthesis, structure and magnetic properties of a new family of chiral metal(II) citramalates, *Inorg. Chim. Acta*, 360 (2007) 1111-1120.
22. K. Robinson, G. V. Gibbs, P. H. Ribbe, *Science* (Washington DC), Quadratic elongation: a quantitative measure of distortion in coordination polyhedra, 172 (1971) , 567-570.

Figure captions

Figure 1: the asymmetric unit of **1** (40% displacement ellipsoids) expanded to show all the bonded ligands. Just one orientation of the ethyl carbazate side chain is shown and in terms of the disordered (overlapped) C5/C6/O5/O6 formate/acetate anions, one is shown as a formate ion and one as an acetate ion. Symmetry codes: (i) $1-x, y-1/2, 1/2-z$; (ii) $x, 3/2-y, z-1/2$.

Figure 2: the asymmetric unit of **3** (50% displacement ellipsoids) expanded to show all the bonded ligands. Just one orientation of the ethyl carbazate side chain is shown and the disordered (overlapped) C5/C6/O5/O6 formate/acetate anions are both shown as acetate ions. Symmetry codes: (i) $1-x, y-1/2, 1/2-z$; (ii) $x, 3/2-y, z-1/2$.

Figure 3: the packing in **1** viewed down [001]: the MnO₅N octahedra are shown in polyhedral representation.

Figure 4: the topological linkage of the metal nodes in **1** viewed down (100).