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CRYSTAL STRUCTURES OF A FAMILY OF LAYERED COORDINATION POLYMERS CONTAINING DIVALENT METAL IONS (Mn^{2+}, Co^{2+}, Ni^{2+} AND Zn^{2+}) AND THE 3-AMINO 4-METHYL BENZOATE ION

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The syntheses and crystal structures of the layered coordination polymers $M(C_8H_8NO_2)_2$ [M = Mn (**1**), Co (**2**), Ni (**3**) and Zn (**4**)] are described. These isostructural compounds contain centrosymmetric *trans*-MN_2O_4 octahedra as parts of infinite sheets; the ligand bonds to three adjacent metal ions in μ^3-N,O,O′ mode from both its carboxylate O atoms and its amine N atom. In each case, weak intra-sheet N—H···O and C—H···O hydrogen bonds may help to consolidate the structure. Crystal data: **1**, $C_{16}H_{16}MnN_2O_4$, $M_r = 355.25$, monoclinic, $P2_1/c$ (No. 14), $a = 10.6534(2)$ Å, $b = 4.3990(1)$ Å, $c = 15.5733(5)$ Å, $\beta = 95.1827(10)°$, $V = 726.85(3)$ Å^3, $Z = 2$, $R(F) = 0.026$, $wR(F^2) = 0.067$. **2**, $C_{16}H_{16}CoN_2O_4$, $M_r = 359.24$, monoclinic, $P2_1/c$ (No. 14), $a = 10.6131(10)$ Å, $b = 4.3374(4)$ Å, $c = 15.3556(17)$ Å, $\beta = 95.473(4)°$, $V = 703.65(12)$ Å^3, $Z = 2$, $R(F) = 0.041$, $wR(F^2) = 0.091$. **3**, $C_{16}H_{16}N_2NiO_4$, $M_r = 359.02$, monoclinic, $P2_1/c$ (No. 14), $a = 10.6374(4)$ Å, $b = 4.2964(2)$ Å, $c = 15.2827(8)$ Å, $\beta = 95.9744(14)°$, $V = 694.66(6)$ Å^3, $Z = 2$, $R(F) = 0.028$, $wR(F^2) = 0.070$. **4**, $C_{16}H_{16}N_2O_4Zn$, $M_r = 365.68$, monoclinic, $P2_1/c$ (No. 14), $a = 10.6385(5)$ Å, $b = 4.2967(3)$ Å, $c = 15.2844(8)$ Å, $\beta = 95.941(3)°$, $V = 694.89(7)$ Å^3, $Z = 2$, $R(F) = 0.038$, $wR(F^2) = 0.107$.

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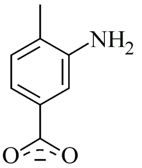
INTRODUCTION

The benzoate anion, $C_7H_5O_2^-$, is a very familiar ligand in coordination chemistry, with over 1200 crystal structures reported in the Cambridge Database (version 5.31 with updates to 19 February 2014) [1] for first-row transition metals. Its bonding modes include monodentate-O, chelating-O,O′, bridging μ^2-O,O′ and combined chelating and bridging modes. Amine derivatives of benzoic acid provide further structural variety, in which the —NH_2 group can form hydrogen bonds to nearby acceptor atoms and/or bond to another metal ion (as a bridging ligand), but these have been much less studied: the Cambridge Database shows 13, 9 and 60 crystal structures for the *ortho*, *meta* and *para* amino benzoate isomers, respectively, in combination with first-row transition metals.

As part of our investigations in this area, we now describe the hydrothermal syntheses and crystal structures of the family of isostructural layered coordination networks $M(C_8H_8NO_2)_2$ [M = Mn (**1**), Co (**2**), Ni (**3**) and Zn(**4**)], where $C_8H_8NO_2^-$ is the 3-amino 4-methyl benzoate anion:



So far as we are aware, the only previously-reported example of this ligand incorporated into a coordination compound is in $Eu_2(C_8H_8NO_2)_6(H_2O)_4 \cdot 2H_2O$ [2], which contains square-anti-prismatic EuO_8 polyhedra and bridging (μ^2-O,O′) and chelating O,O′-bonded $C_8H_8NO_2^-$ anions as parts of an isolated binuclear cluster: the crystal packing is consolidated by an extensive array of N—H···O and O—H···O hydrogen bonds.

MATERIALS AND METHODS

Synthesis of 1. A mixture of 99 mg (0.5 mmol) of $MnCl_2 \cdot 4H_2O$ and 227 mg (1.5 mmol) of 3-amino 4-methyl benzoic acid (HL) were added to 1.5 ml of 1 M KOH with stirring. The resulting mixture was heated to 200°C in a 23 ml Teflon-lined autoclave for 15 hours. The autoclave was then removed from the oven and cooled to room temperature over several hours. The crystalline product was purified by sonication (3×20 s) in water (20 ml), followed by decanting of the cloudy supernatant liquors. Finally, colourless plates of **1** were manually isolated from the other unidentified products and rinsed with water and dried. Elemental analysis (%): observed (calc.) for $C_{16}H_{16}MnN_2O_4$: C 54.05 (54.01); H 4.50 (4.48).

Synthesis of 2. The same procedure as for **1** was followed, except that 128 mg (0.5 mmol) of $Co(acac)_2$, 151 mg (1.0 mmol) of HL and 1.0 ml of 1 M KOH were used. The separated product consisted of dark pink slabs of **2**. Elemental analysis (%): observed (calc.) for $C_{16}H_{16}CoN_2O_4$: C 53.45 (53.44); H 4.45 (4.45).

Synthesis of 3. The same procedure as for **1** was followed, except that 238 mg (1.0 mmol) of $NiCl_2 \cdot 6H_2O$, 302 mg (2.0 mmol) of HL and 2.0 ml of 1 M KOH were used and the autoclave was heated to 150 °C for 15 hours. The separated product consisted of green plates of **3**. Elemental analysis (%): observed (calc.) for $C_{16}H_{16}N_2NiO_4$: C 53.47 (53.46); H 4.45 (4.44).

Synthesis of 4. The same procedure as for **1** was followed, except that 100 mg (0.55 mmol) of $Zn(OAc)_2$, 226 mg (1.5 mmol) of HL and 1.5 ml of 1 M KOH were used. The separated product for **4** consisted of colourless plates. Elemental analysis (%): observed (calc.) for $C_{16}H_{16}N_2O_4Zn$: C 52.50 (52.49); H 4.38 (4.37).

Crystallographic studies. The intensity data for **1**—**4** were collected using a Nonius KappaCCD diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, $T = -93$ °C). For **1**, a colourless slab of dimensions 0.28×0.10×0.02 mm was chosen for data collection; for **2**, dark-pink plate, 0.23×0.21×0.01 mm; for **3**, green slab, 0.28×0.10×0.02 mm; for **4**, colourless slab, 0.23×0.07×0.02 mm. Empirical (multi-scan) absorption corrections were applied with SADABS [3] at the data-reduction stage: for **1**, the transmission-factor range was 0.781—0.982, with equivalent values of 0.763—0.988, 0.692—0.972 and 0.684—0.965, for **2**, **3** and **4**, respectively.

The manganese structure was easily solved by direct methods using SHELXS-97 in space group $P2_1/c$ (No. 14) and the atomic model was developed and refined against $|F|^2$ with SHELXL-97 [4]. One the basis of their unit-cells, the other structures were evidently isostructural with the manganese compound, and the Mn atomic model was used (with appropriate metal substitution) as the starting model for the other structures. The N-bonded H atoms were found in a difference map, relocated to idealised positions (N—H = 0.92 Å) and refined as riding atoms with $U_{iso}(H) = 1.2U_{eq}(N)$. The

Table 1

Key Crystallographic Data for **1**—**4**

Parameter	**1**	**2**	**3**	**4**
Emp. Formula	$C_{16}H_{16}MnN_2O_4$	$C_{16}H_{16}CoN_2O_4$	$C_{16}H_{16}N_2NiO_4$	$C_{16}H_{16}N_2O_4Zn$
MW	355.25	359.24	359.02	365.68
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	10.6534(2)	10.6131(10)	10.6374(4)	10.6385(5)
b, Å	4.3990(1)	4.3374(4)	4.2964(2)	4.2967(3)
c, Å	15.5733(5)	15.3556(17)	15.2827(8)	15.2844(8)
β, deg.	95.1827(10)	95.473(4)	95.9744(14)	95.941(3)
V, Å^3	726.85(3)	703.65(12)	694.66 (6)	694.89(7)
Z	2	2	2	2
ρ_{calc}, g/cm^{-3}	1.623	1.696	1.716	1.748
μ, mm^{-1}	0.931	1.243	1.420	1.791
Data collected	4844	3505	5099	3561
Unique data	1423	1223	1580	1214
R_{Int}	0.032	0.069	0.043	0.037
$R(F)$	0.026	0.041	0.028	0.038
$wR(F^2)$	0.067	0.091	0.070	0.107
CCDC code*	984541	984542	984543	984544

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* Full crystallographic data for these structures including atom positions and geometrical parameters can be accessed at: http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx by citing the code number shown.

C-bonded H atoms were geometrically placed and modelled as riding atoms with C—H = 0.95—0.98 Å and U_{iso}(H) = $1.2U_{\text{eq}}$(C) or $1.5U_{\text{eq}}$(methyl C). The methyl groups were allowed to rotate, but not to tip, to best fit the electron density. The structures were analysed with PLATON [5] and the molecular graphics were generated with ORTEP-3 [6] and ATOMS [7]. Crystal data for **1**—**4** are summarized in Table 1.

RESULTS

Crystal structures. These four compounds are isostructural and we will describe the manganese structure, (**1**), in detail and compare the cobalt (**2**), nickel (**3**) and zinc (**4**) phases where significant differences arise. The asymmetric unit of **1** contains a Mn^{2+} ion located on an inversion centre and one anionic $C_8H_8NO_2^-$ ligand deprotonated at the carboxylate group (Fig. 1). The carboxylate group of the ligand is slightly rotated from the plane of the aromatic ring, by 13.51(18)° for **1**, 16.0(4)° for **2**, 17.02(19)° for **3** and 17.2(4)° for **4**. The carboxylate bonds lengths (Table 2) indicate substantial electronic delocalisation in each case such that the C7—O1 and C7—O2 bond lengths are almost equal. The O1—C7—O2 bond angles are tightly clustered

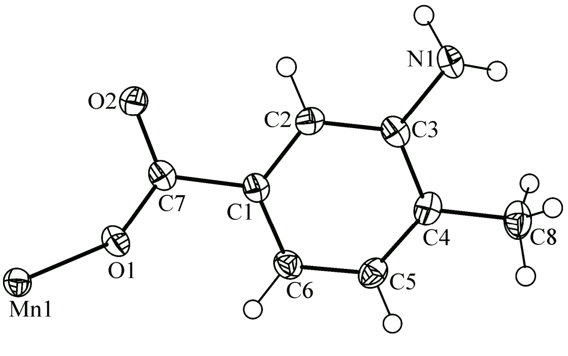

Fig. 1. The asymmetric unit of **1** showing 50 % displacement ellipsoids

Table 2

Significant Bond Lengths (Å) *and Angles* (deg.) *in* **1**—**4**

Bond	**1**	**2**	**3**	**4**	Angle	**1**	**2**	**3**	**4**
M—O1	2.1621(11)	2.070(2)	2.0716(12)	2.071(2)	O1—C7—O2	124.00(15)	123.9(3)	125.22(16)	125.2(3)
M—O2^{i}	2.1673(11)	2.091(2)	2.0801(12)	2.078(2)	O1—C7—C1	117.95(14)	118.5(3)	117.18(15)	117.4(3)
M—N1^{ii}	2.3436(13)	2.223(3)	2.1525(15)	2.154(3)	O2—C7—C1	118.05(14)	117.6(3)	117.60(15)	117.4(3)
C7—O1	1.265(2)	1.271(4)	1.264(2)	1.259(4)	C7—O1—M	124.55(10)	125.7(2)	124.83(11)	125.0(2)
C7—O2	1.263(2)	1.271(5)	1.259(2)	1.259(4)	C7—O2—M^{iii}	128.38(10)	128.8(2)	128.46(11)	128.8(2)
C3—N1	1.431(2)	1.435(5)	1.435(2)	1.436(4)	C3—N1—M^{iv}	119.78(10)	121.3(2)	124.83(11)	121.6(2)
C1—C7	1.502(2)	1.501(5)	1.507(2)	1.511(5)					

Symmetry codes: ^{i} x, $1+y$, z; ^{ii} x, $1/2-y$, $1/2+z$; ^{iii} x, $-1+y$, z; ^{iv} $1-x$, $-1/2+y$, $1/2-z$.

around 125°. For each structure, the C7—O1—M bond angle is some 3° smaller than the C7—O2—M bond angle.

The C3—N1 and C1—C7 bond lengths are statistically indistinguishable in these four compounds. It is notable that the amine N atom shows a small but quite consistent displacement from the mean plane of its attached ring, by –0.100(3) Å, –0.111(5) Å, –0.101(3) Å and –0.097(5) Å for **1**, **2**, **3** and **4**, respectively, whereas the methyl carbon atom (C8) is consistently displaced in an opposite sense, by 0.072(3) Å for **1**, 0.086(6) Å for **2**, 0.095(3) Å for **3** and 0.103(6) Å for **4**.

Extended structures. In each case, the ligand bonds to a symmetry-equivalent metal ion from both of its carboxylate O atoms and also from its amine N atom (Fig. 2), *i.e.* in μ^3-N,O,O′ mode. With respect to the C7/O1/O2 carboxylate group, one of the metal ions (bonded to O1) is displaced in a ″downwards″ sense [by –1.564(5) Å for **1**, –1.503(9) Å for **2**, –1.496(5) Å for **3** and –1.496(9) Å for **4**] and the other (bonded to O2) is displaced ″upwards″ [by 1.078(6) Å, 0.998(12) Å, 0.989(6) Å and 0.977(12) Å for **1**, **2**, **3** and **4**, respectively], with respect to the CO_2^- plane. This ligand bonding mode generates a centrosymmetric *trans*-MN_2O_4 octahedron for each metal ion: the M—N bond lengths are the longest in each case and the MnN_2O_4 octahedron in particular has a quite significant tetragonal elongation of some 0.18 Å.

Key metrical data for the metal polyhedra are as follows: for **1**, the MN_2O_4 octahedron has a volume of 14.59 Å^3 and the angular variance of the *cis* X—M—Y (X, Y = N, O) bond angles is 7.9°^{2} [8]. Equivalent data for **2**: 12.77 Å^3 and 11.6°^{2}; for **3**: 12.29 Å^3 and 15.5°^{2}; for **4**: 12.29 Å^3 and 15.4°^{2}, respectively. The trend in octahedral volumes is consistent with the decreasing size of the metal ions from $Mn^{2+} \rightarrow Zn^{2+}$ [9] and there also appears to be a trend in the angular variances to increase slightly as the metal ions become smaller: however, it should be noted that all these variances are very small and the octahedra are essentially regular. Bond-valence sum (BVS) calculations using the Brown—Altermatt formalism [10] for the metal ions are reasonably consistent with their divalent character, yielding values of 1.98, 1.83, 1.87 and 2.09 for **1**, **2**, **3** and **4**, respectively (expected value = 2.00).

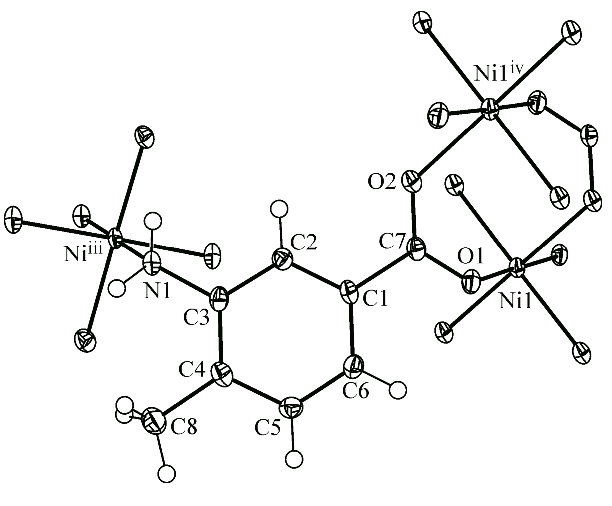

Fig. 2. Coordination environment of the ligand in **3**, showing its μ^3 N,O,O′-bonding mode and the formation of $Ni_2C_2O_4$ loops. For symmetry codes, see Table 2

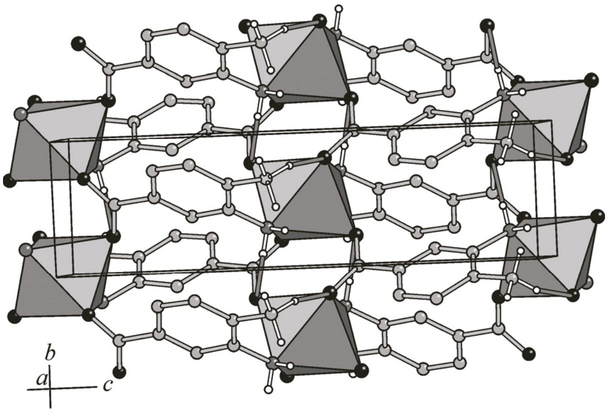

Fig. 3. Fragment of a (100) sheet in the structure of **2** showing the *trans*-CoN_2O_4 octahedra in polyhedral representation. The hydrogen atoms of the benzene ring are omitted for clarity

In the crystal, the bridging ligand generates infinite (001) sheets (Fig. 3). These sheets can be decomposed to [010] chains of octahedra linked by the bridging (μ^2) carboxylate groups, with connectivity in [001] *via* the ligand N atoms. Each crystal structure features one N—H···O hydrogen bond and one C—H···O interaction (Table 3), with very similar geometrical parameters for **1**—**4**. The length of the N—H···O bond suggests that it is weak: it forms a link between the amide group attached to one metal ion and the O atom of the carboxylate ion of the octahedron displaced in the *b* direction. The C—H···O interaction links to an O atom *cis* to the bonded N atom of the amine group. Both these bonds are intra-sheet links.

The packing in the crystal (Fig. 4) could be described as ″dense,″ and there are no identifiable channels or voids that might lead to sorption behaviour. There appear to be no directional inter-sheet interactions beyond normal van der Waals′ contacts.

CONCLUSIONS

The syntheses and crystal structures of the $M(C_8H_8NO_2)_2$ (M = Mn, Co, Ni, Zn) family of isostructural layered coordination polymers have been described. The small differences in their crystal structures correlate with the different sizes of the divalent metal ions involved. The μ^3 N,O,O′-bonding mode of the ligand in these structures is different to that seen in $Eu_2(C_8H_8NO_2)_6(H_2O)_4\cdot 2H_2O$, where both bridging μ^2-O,O′ and chelating O,O′ bonding modes are seen [2]. In terms of related ligands, a handful of crystal structures containing the 3-amino benzoate anion ($C_7H_6NO_2^-$) and the transition metal ions studied here have been described: $Zn(C_7H_6NO_2)(C_{10}H_8N_2)_2\cdot ClO_4\cdot H_2O$ ($C_{10}H_8N_2$ = 2,2′-bipyridine) [11] contains isolated complex ions, as does $Zn(C_7H_6NO_2)_2(C_{12}H_8N_2)_2\cdot H_2O$ ($C_{12}H_8N_2$ = = 1,10-phenanthroline) [12], with the 3-amino benzoate anion chelating to the metal from its O atoms in both cases. In $Zn(C_7H_6NO_2)_2\cdot H_2O$ [13] however, a three-dimensional coordination network is formed, with the ligand showing μ^2-N,O coordination. In $Zn_2(C_7H_6NO_2)_2(C_{10}H_8N_2)_2Cl_2$ [14], the μ^2-O,O′ 3-amino benzoate anion bridges between the zinc ions to generate a centrosymmetric dimer. In the cobalt complex $Co(C_7H_6NO_2)_2(C_6H_6N_2O)_2(H_2O)_2$ ($C_6H_6N_2O$ = nicotinamide) [15], the manga-

Table 3

Hydrogen-Bond Parameters (Å, deg.) for **1**—**4**

1					**2**				
N1—H1···O2^{i}	0.92	2.29	3.0712(19)	142	N1—H1···O2^{i}	0.92	2.30	3.089(4)	143
C8—H8A···O1^{ii}	0.98	2.47	3.385(2)	156	C8—H8A···O1^{ii}	0.98	2.46	3.339(5)	149
3					**4**				
N1—H1···O2^{i}	0.92	2.27	3.062(2)	144	N1—H1···O2^{i}	0.92	2.27	3.062(4)	144
C8—H8A···O1^{ii}	0.98	2.42	3.298(2)	149	C8—H8A···O1^{ii}	0.98	2.42	3.303(5)	149

The four values refer to the D—H, H···A and D···A separations (Å) and the D—H···A angle (°), respectively. Symmetry codes: ^{i} 1–*x*, *y*–1/2, 1/2–*z*; ^{ii} *x*, 1/2–*y*, *z*–1/2.

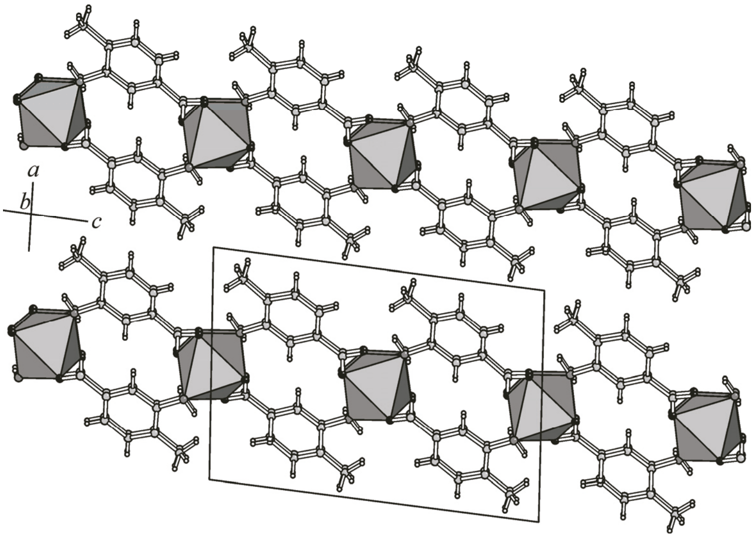

Fig. 4. The packing in **2** viewed down [010] showing the (100) polyhedral sheets

nese complex $Mn(C_7H_6NO_2)(C_{12}H_8N_2)_2(H_2O)\cdot(C_7H_6NO_2)\cdot4.5H_2O$ [16] and the copper complex $Cu(C_7H_6NO_2)_2(C_2H_8N_2)_2$ ($C_2H_8N_2$ = ethylenediamine) [17] the 3-amino benzoate ions bond to the respective metals in monodenate-O fashion: all these are isolated mononuclear complexes. It is interesting that none of these compounds feature the ″saturated″ μ^3-N,O,O′ ligand bonding mode seen in the title compounds.

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