

Hydrothermal Synthesis and Characterisation of $M(\text{pdc})\cdot 3\text{H}_2\text{O}$ ($\text{pdc} = 2,5\text{-pyridinedicarboxylate}$); $M = \text{Co}, \text{Ni}, \text{Co}_x\text{Ni}_y$ ($x = 0.4\text{--}0.6, y = 0.6\text{--}0.4$)

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A hydrated coordination polymer is formed by heating the tecton 2,5-pyridinedicarboxylic acid with cobalt(II), nickel(II) or cobalt(II) and nickel(II) acetate in water

The self-assembly of organic molecular building blocks with metal ions into crystalline coordination polymers is giving access to new solid state materials of scientific interest and technological potential. Organic ligands with divergent functional groups and the corresponding metal ions that have been used include polyaromatic acids with alkaline earths,¹ Co^{II} , Ni^{II} and Zn^{II} ,² polyaromatic nitriles with Ag^{I} salts³ and polyaromatic pyridyls with numerous transition metal ions.⁴ Novel structural features include interpenetrating lattice networks which avoids the formation of void volume and some stability to guest or template exchange and desorption/adsorption.^{1,2,5}

Here, we report the hydrothermal synthesis of $M(\text{pdc})\cdot 3\text{H}_2\text{O}$, where $M = \text{Co}^{\text{II}}$, Ni^{II} or a mixture of Co^{II} and Ni^{II} . 2,5-Pyridinedicarboxylic acid and a stoichiometric quantity of $M(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ in water (10 ml) were sealed in a digestion bomb and heated to 180 °C followed by slow cooling. Red crystals of $\text{Co}(\text{pdc})\cdot 3\text{H}_2\text{O}$ and green crystals of $\text{Ni}(\text{pdc})\cdot 3\text{H}_2\text{O}$ were obtained in high yield. By using the ligand and a mixture of Co^{II} and Ni^{II} metal ions in a 2:1:1 ratio a brown microcrystalline material of approximate composition $\text{Co}_x\text{Ni}_y(\text{pdc})\cdot 3\text{H}_2\text{O}$ ($x = 0.5, y = 0.5$) was obtained. X-Ray powder diffraction patterns showed that all three materials were isostructural. Thermal gravimetric analysis showed an endothermic mass loss of 20% between 150 and 260 °C for all three materials corresponding to complete dehydration of the sample. Boiling the reagents in water for 12 h gave the same microcrystalline materials, which was confirmed by powder XRD, but with a much smaller particle size that was unsuitable for X-ray single crystal structure determination.

The structure of $\text{Co}(\text{pdc})\cdot 3\text{H}_2\text{O}$ is shown in Figs. 1–4. The cobalt cations are six-coordinate in a distorted environment arising from coordination by three anions and two water molecules (Fig. 1). Whereas anion A acts as a bidentate ligand forming bonds $\text{Co}-\text{N}$ and $\text{C}-\text{O}(1)$, anions B and C behave as monodentate ligands giving rise to bonds $\text{Co}-\text{O}(3)$ and $\text{Co}-\text{O}(4)$, respectively. The most marked distortion of the octahedral cobalt environment is the bite

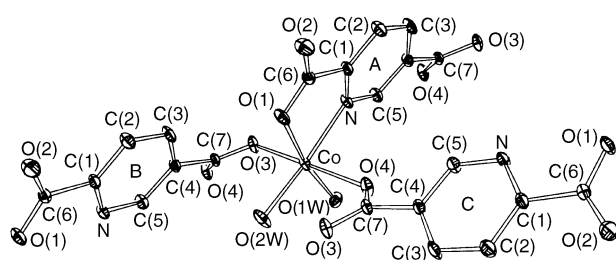


Fig. 1 The cation coordination showing the crystallographic labelling scheme. Non-hydrogen atoms are shown as 40% ellipsoids and hydrogens have been omitted for clarity

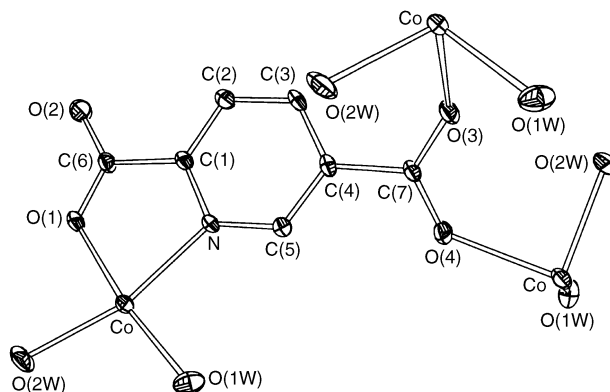


Fig. 2 The coordination of the anions in the manner of Fig. 1

angle of the bidentate ligand A [$\text{O}(1)\text{--Co--N}$ $77.41(12)^\circ$]. Each anion is bonded to three cobalt atoms (Fig. 2). One of these is coordinated in a bidentate manner by nitrogen and $\text{O}(1)$ of the carboxylate group in the 2-position. As a result this carboxylate group, defined by $\text{C}(6)$, $\text{O}(1)$ and $\text{O}(2)$ is essentially coplanar with the pyridine nucleus. The carboxylate group in the 5-position, on the other hand, bridges between the two cobalt centres and is rotated by approximately 32.5° about the $\text{C}(4)\text{--C}(7)$ bond relative to the plane of the pyridine nucleus.

The connectivity within a polymeric layer of cations and anions is shown in Fig. 3. First alternating cobalt cations and anions form chains in the direction of a using $\text{Co}\text{--O}(1)$, $\text{N}\text{--O}$ bidentate and $\text{Co}\text{--O}(3)$ monodentate links. $\text{Co}\text{--O}(4)$ bonds link the chains in the direction of b and also result

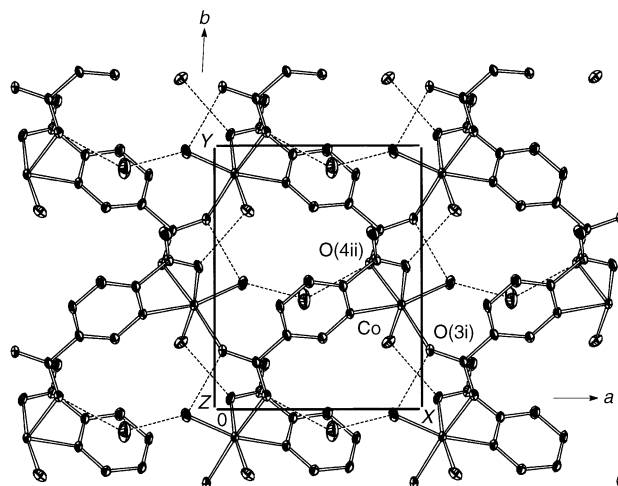


Fig. 3 A polymeric layer. The view down c and z is in the range 0.49–1.01 Å. Ellipsoids are shown at the 40% probability level and dashed lines indicate hydrogen bonded $\text{O}\cdots\text{O}$ contacts less than 2.85 Å

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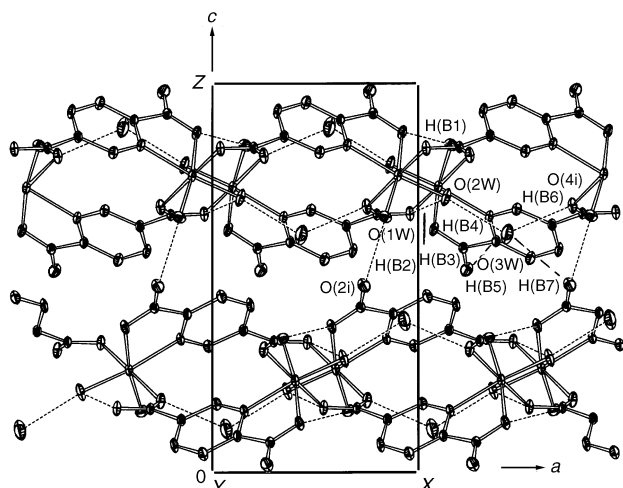


Fig. 4 The cell viewed along b which runs down into the page. Ellipsoids are shown at the 40% probability level and dashed lines indicate hydrogen bonded O...O contacts less than 2.85 Å

in the bridging nature of the 5-position [C(7), O(3), O(4)] carboxylate group of the anion.

Some of the inter- and intra-layer hydrogen bonds are shown in Fig. 4. The water molecules [O(1W) and O(2W)] not only complete the coordination of cobalt but also participate in hydrogen bond formation. Both water molecules form hydrogen bonds within a polymeric layer of cations and anions. In addition there is a contact O(1W)...O(2ⁱ) between layers and a contact O(2W)...O(3W) to a third molecule of water. This water molecule forms further weak hydrogen bonds with the polymeric layers.

The formation of the mixed cobalt–nickel coordination polymer is worthy of further discussion; Co^{II} and Ni^{II} are of similar size and since the two form isostructural coordination polymers we anticipated that a mixed lattice might form. This is indeed the case when both metal ions are used together. Microanalysis showed that the ratio of Co:Ni was approximately 1:1. Examination by optical microscopy showed that the material was homogenous and was not a mixture of separate green and red crystals. Ten individual single crystals were examined by transmission electron microscopy (TEM) which confirmed that each crystal contained both cobalt and nickel but the quantity of each metal ion varied from between 40 and 60%. To the best of our knowledge this is the first example of a mixed metal ion coordination polymer prepared by hydrothermal synthesis.

We are currently exploring hydrothermal synthesis with a ligand and a mixture of metal ions followed by TEM analysis of individual crystals as a combinatorial approach to the discovery of new ligand:mixed metal-ion coordination polymers.

Experimental

Crystal Data for Co(pdc)·3H₂O.— $F(000) = 564$, orthorhombic, $a = 7.350(7)$, $b = 9.405(10)$, $c = 13.954(13)$ Å, $V = 964.6(16)$ Å³, space group $P2_12_12_1$, $Z = 4$, $D_o = 1.915$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.079$ mm⁻¹. The experimental data were collected at 298 K on a Nicolet P3 diffractometer with Mo-K α radiation ($\lambda = 0.71069$ Å) and refined using Nicolet P3 software. The structure was solved by direct methods and refined by full matrix least squares on F^2 . Final R indices [$I > 2\sigma(I)$] $R_1 = 0.0426$, $wR_2 = 0.1010$, for all data $R_1 = 0.0467$ and $wR_2 = 0.1038$. The estimated standard deviations for the geometrical parameters involving non-hydrogen atoms lie within the following ranges: bond lengths 0.003–0.005 Å; bond angles 0.12–0.4°.

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Techniques used: IR, X-ray crystallography, powder diffraction, thermal gravimetric analysis, transmission electron microscopy (JEOL 2000EX with link AN10/85S X-ray analyser).

References: 13

Figs: 8

Tables: 10 (crystal data and structure refinement, atomic coordinates and U_{eq} values, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, torsion angles, hydrogen bonds, selected least squares planes and deviations)

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