J. Chem. Research (S),
1998, 240–241
J. Chem. Research (M),
1998, 1001–1013

Hydrothermal Synthesis of Co(pdc)$\cdot$2H_2O (pdc = 3,5-Pyridinedicarboxylate). A Two-dimensional Coordination Polymer

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A hydrated coordination polymer is formed by heating the tecton 3,5-pyridinedicarboxylic acid (H_2pdc) with cobalt(II) acetate.

Metal-ion directed assembly of organic molecular building blocks known as tectons is giving access to new open framework solid-state materials with fascinating technological potential and scientific interest.[1] Supramolecular chemistry has frequently centered on the synthesis of hosts with convergent functional groups to form binding cavities which mimic enzyme active sites and can show *homogeneous* catalytic activity.[2] The synthesis of 1D, 2D and 3D coordination polymers, which are structurally analogous to important minerals such as quartz and zeolites,[3] and have the potential for *heterogeneous* catalysis, requires rigid tectons which possess divergent functional groups. Methods for the assembly of crystalline lattices from organic tectons and metal ions which may show stability to guest or template desorption/adsorption are of considerable current interest.

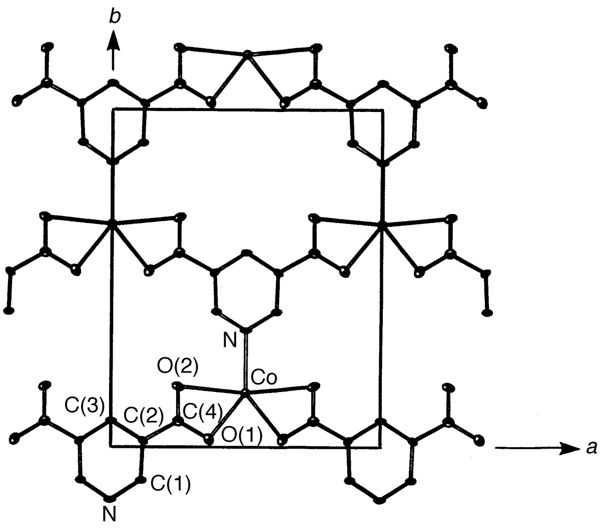

Fig. 1 A view down *c* of the cation/anion layer with *z*/*c* close to 1/4 for all atoms shown. The water molecules and hydrogen atoms have been omitted for clarity. Atoms are shown as 40% probability ellipsoids

Here we report the hydrothermal synthesis and X-ray single-crystal structure characterisation of Co(pdc)$\cdot H_2O$. 3,5-Pyridinedicarboxylic acid (100 mg) and a stoichiometric quantity of $Co(OAc)_2 \cdot 4H_2O$ in water (10 ml) were heated to 180 °C and allowed to cool slowly. Pink crystals of Co(pdc)$\cdot 2H_2O$ were obtained in 90% yield which are insoluble in boiling water. Hydrothermal synthesis is essential to obtain good quality crystals. If the same quantities of reagents are refluxed in water (200 ml) for 2 h complete dissolution does not occur but a pink microcrystalline material identical with the above material does slowly form. The structure shown in Fig. 1 consists of infinite layers of alternating Co^{II} cations and 3,5-pyridinedicarboxylate dianions. Each cobalt ion is seven-coordinate and is coordinated by two identical bidentate carboxylate groups, one pyridine nitrogen and two water molecules. The Co^{II} ions coordinate to the pdc tectons along the crystallographic *a* axis with Co—O(1) and Co—O(2) bond lengths of 2.157(4) and 2.432(4) Å respectively. Although the Co—O(2) bond length is quite long it is shorter than the estimated cobalt–oxygen van der Waals distance of 2.562 Å. This is calculated as the sum of the Co single bond metallic radius of 1.161 Å and the van der Waals radius of an oxygen atom of 1.400 Å.[5] The carboxylate anions form a dihedral angle of 13.3(7)° to the pyridine ring. The pyridine nitrogens coordinate to each cobalt ion along the crystallographic *b* axis forming a Co—N distance of 2.206(7) Å. Hence in the *ab* plane the structure consists of a 2D coordination polymer. The layers are not chemically bonded together in the *c* axis direction but are interleaved with water molecules coordinated to each cobalt ion with a cobalt–oxygen bond length of 2.072(4) Å. The hydrogen atoms of the water molecules form interlayer hydrogen bonds to the carboxylate groups. Adjacent 2D layers are related by crystallographic centres of symmetry with parallel pyridine rings stacked 3.7 Å apart in a zigzag arrangement almost on top of each other along the *c* axis. The zigzag arrangement of pyridine rings occurs parallel to the *b* axis. The half thickness of an aromatic ring is 1.85 Å[6] so the pyridine rings are stacked at the optimum van der Waals distance. The layers are neutral, interleaved with water molecules and might be easily cleaved apart. In this respect the compound

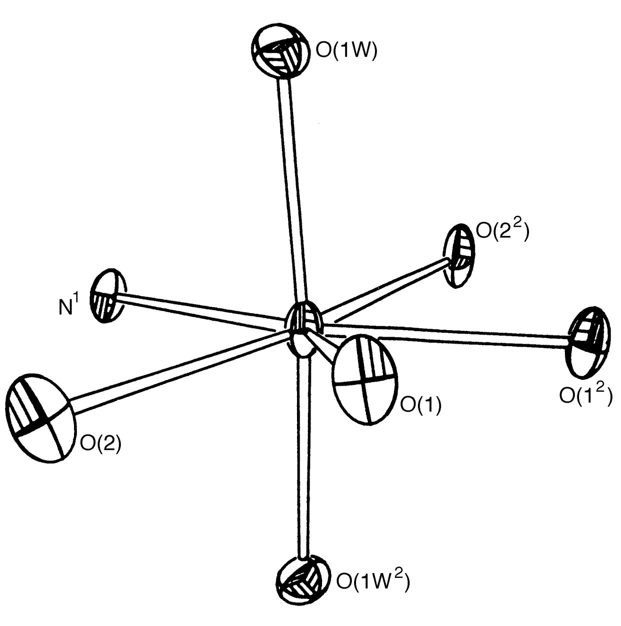

Fig. 2 The coordination of Co. Atoms are shown as 40% probability ellipsoids

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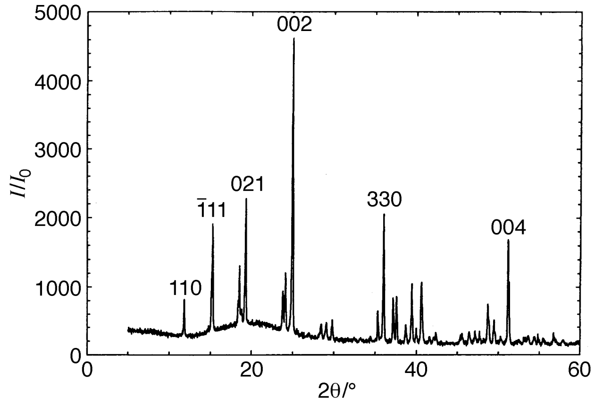

Fig. 3A Powder diffraction pattern for Co(pdc)·$2H_2O$

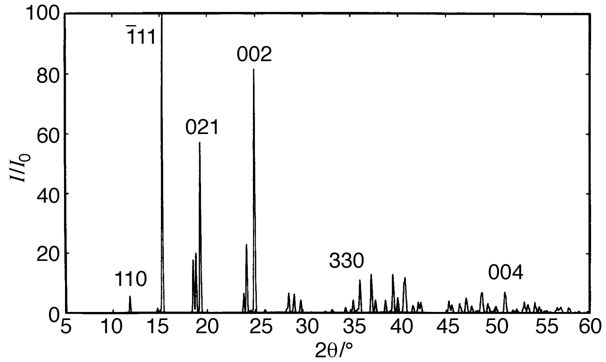

Fig. 3D Calculated powder diffraction pattern for Co(pdc)·$2H_2O$

can be described as an 'organic clay' crudely resembling the inorganic layer silicates.[7] This analogy is supported by the plate-like morphology of the crystals and the observation of preferred orientation in its experimental X-ray powder diffraction pattern (Fig. 3A) as compared with the calculated pattern (Fig. 3D). This is compatible with ready cleavage of the crystals parallel to the planes of cobalt cations and pdc anions which in turn are parallel to the 001 planes. In the original hydrated compound, as explained above, the distance between adjacent cation/anion layers is determined by the van der Waals thickness of the aromatic rings of the pdc anions and cannot be reduced further upon the loss of water.

Further studies on crystalline lattices formed from larger tectonic building blocks are in progress.

Techniques used: IR, X-ray crystallography, powder diffraction, thermal gravimetric analysis

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Figs: 3

Tables: 6 (crystal data and structure refinement, atomic coordinates and U_{eq} values, interatomic distances and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters)

Received, 4th July 1997; Accepted, 22nd December 1997
Paper E/7/04747I

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