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The synthesis and characterization of the cross-packed 1-D coordination polymer $[Co_2(C_2O_4)_2(C_4H_6N_2)_4]\cdot H_2O$ ($C_4H_6N_2$ = 4-methylimidazo)

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The metal–ligand complex $[Co_2(C_2O_4)_2(C_4H_6N_2)_4]\cdot H_2O$ ($C_4H_6N_2$ = 4-methylimidazo) has been hydrothermally synthesised and structurally characterised.

The development of molecular assemblies in crystals is of increasing current interest.[1–4] It gives insight into the chemistry of supramolecular interactions and functional materials since the characterization of crystals as supramolecules holds far greater importance than just a collection of molecular building blocks because the bulk properties of a molecular crystal often deviate from those of its fundamental components.[5–10] Presently, there have been considerable strategies reported on the basis of binding organic spacers and coligands to metal ions toward extended structures, but how to control the arrangement of building blocks in the formation of supramolecular solids is poorly understood.[11–13] Here, we describe the hydrothermal synthesis and characterization of novel compound $[Co_2(C_2O_4)_2(C_4H_6N_2)_4]\cdot H_2O$ **1** constructed on the basis of cross-packed 1-D polymer chains.[†]

Figures 1 and 2 illustrate the molecular structure of compound **1**[‡] and indicate that the structure of this compound consists of 1-D cobalt–oxalate chains with lattice H_2O molecules. In the chain structure, the metal atoms arrange with a zig-zag pattern, and each of them has a distorted octahedral coordination environment consisting of two 4-methylimidazo nitrogen atoms and four oxalate oxygen atoms. In the repeating unit $[Co_2(C_2O_4)_2(C_4H_6N_2)_4]$, two groups of the four 4-methylimidazo ligands bind to metal atoms respectively with only one nitrogen atom such as [N(1), N(3)] and [N(5), N(7)], but exhibit different binding fashions, one is *cis*-conformation, and the other adopts *trans*-conformation.

An interesting point of the structure of compound **1** is that the 4-methylimidazo coligand is asymmetric, and the repeating unit $[Co_2(C_2O_4)_2(C_4H_6N_2)_4]$ is chiral. Because the compound forms monoclinic crystals, space group $P2_1/c$, it contains a conversion centre, and, as a result, the polymeric chains are composed of *meso*-$[Co_2(C_4H_6N_2)_4(C_2O_4)_2]_2$ groups. Along *ab* planes, the polymeric chains are parallel and arranged into a layer. Along the crystallographic *c* axis, the layers pack with an inter-layered distance of 6.83 Å. Since the existence of crystallographic 2_1 screw axis and *c* slide plane, two neighbour layers come with a cross-packed pattern in the crystal (Figure 2).

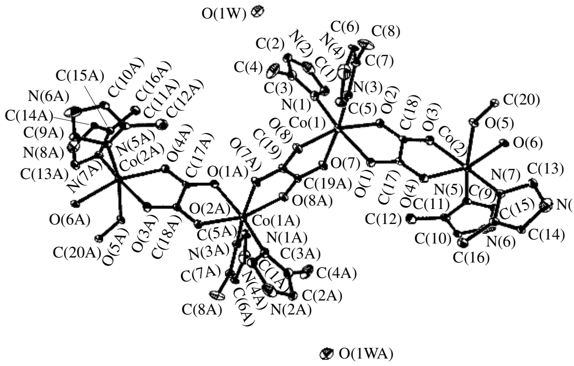

Figure 1 Molecular structure of compound **1** (15% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Co(1)–N(1) 2.085(4), Co(1)–N(3) 2.105(4), Co(1)–O(2) 2.115(3), Co(1)–O(8) 2.120(3), Co(1)–O(1) 2.132(4), Co(1)–O(7) 2.171(3), Co(2)–N(5) 2.085(4), Co(2)–O(4) 2.105(3), Co(2)–N(7) 2.109(4), Co(2)–O(5) 2.145(3), Co(2)–O(6) 2.158(3), Co(2)–O(3) 2.169(4), N(1)–Co(1)–N(3) 96.6(2), N(1)–Co(1)–O(2) 91.6(2), N(3)–Co(1)–O(2) 101.6(2), N(1)–Co(1)–O(8) 98.2(2), N(3)–Co(1)–O(8) 91.6(1), N(3)–Co(1)–O(1) 87.1(2), O(2)–Co(1)–O(1) 78.1(1), O(8)–Co(1)–O(1) 91.4(1), N(1)–Co(1)–O(7) 88.7(2), O(2)–Co(1)–O(7) 89.5(1), O(8)–Co(1)–O(7) 77.1(1), O(1)–Co(1)–O(7) 89.7(1), N(5)–Co(2)–O(4) 104.6(2), N(5)–Co(2)–N(7) 95.4(2), O(4)–Co(2)–N(7) 94.6(2), O(4)–Co(2)–O(5) 89.4(1), N(7)–Co(2)–O(5) 90.5(2), N(5)–Co(2)–O(6) 88.1(1), N(7)–Co(2)–O(6) 95.2(2), O(5)–Co(2)–O(6) 76.8(1), N(5)–Co(2)–O(3) 92.0(2), O(4)–Co(2)–O(3) 77.5(1), O(5)–Co(2)–O(3) 83.9(1), O(6)–Co(2)–O(3) 91.3(1).

We propose a route of combining simple ligands to afford polymeric structures. In the tested system, the ligands may be $C_2O_4^{2-}$, N-ligands or H_2O, but the first is obviously the pre-

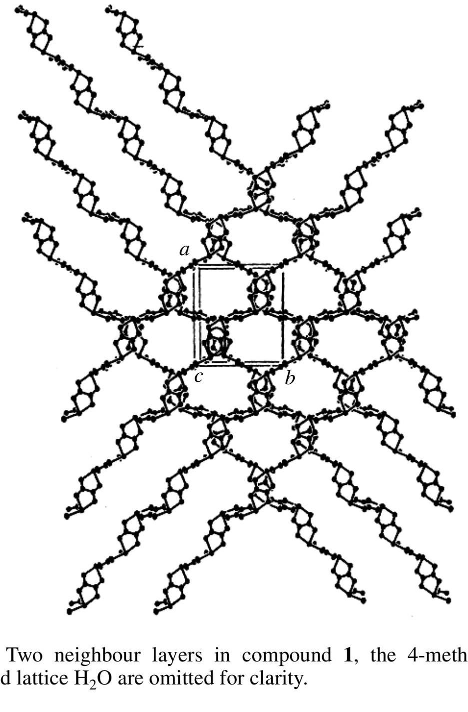

Figure 2 Two neighbour layers in compound **1**, the 4-methylimidazo ligands and lattice H_2O are omitted for clarity.

[†] *Synthesis of compound* **1**. A mixture of $CoCl_2\cdot 6H_2O$ (2.3 g), methylimidazole (0.40 g), $Na_2C_2O_4$ (2.10 g) and H_2O (25 ml) was heated at 160 °C for 3 days in a sealed 30 ml Teflon-lined reactor steel vessels under autogeneous pressure. After the reaction, the mixture was slowly cooled to room temperature, and red crystals were obtained (38% yield based on Co). IR (KBr, ν/cm^{-1}): 3174 (s), 1679 (s), 1604 (s), 1490 (s), 1433 (s), 1359 (m), 1316 (s), 1289 (s), 1158 (m), 1125 (s), 1010 (s), 931 (m), 870 (s), 793 (s), 772 (s), 752 (s), 676 (s), 488 (s). Found (%): C, 37.31; H, 3.95; N, 17.58; Co, 19.01. Calc. for $C_{20}H_{18}Co_2N_8O_9$ (%): C, 37.51; H, 4.09; N, 17.50; Co, 18.41.

[‡] *X-ray structure determination of compound* **1**. $C_{20}H_{18}Co_2N_8O_9$, monoclinic, space group $P2_1/c$, a = 13.943(6), b = 11.954(3), c = 17.049(4) Å, β = 104.06(2)°, V = 2756.5(15) Å^3, Z = 4, M = 640.35, d_{calc} = 1.543 g cm^{-3}, μ = 1.256 mm^{-1}, crystal size: 0.52×0.36×0.30 mm. The crystal was examined on an Enraf-Nonius CAD4 (MoKα graphite monochromator, λ = 0.71073 Å) instrument using the ω-2θ scan technique. A total of 6272 reflections ($1.51 < \theta < 25.02$) were collected, of which 4854 unique reflections were used. The structure was solved and refined to R = 0.0522 for 4854 reflections with $I > 2\sigma(I)$ using SHELXL program. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2002. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/121.

ferred candidate to Co^{II} ions. The other two may only occupy the remaining coordination sites of each metal ion. Although they are similar as monodentate ligands, however, the organic N-ligands favour less soluble products by forming fewer hydrogen bonds in the crystal lattice. The final result illustrates this possibility. For the synthesis of compound **1**, we chose hydrothermal conditions for effectively increasing the solubility of starting reactants and the lability of aqua ligands. Since controlling the arrangement of building blocks in the crystal engineering of new solids is incompletely understood, the successful assembly of this compound may provide with useful knowledge for the designing of new advanced materials.

The thermogravimetric analysis of compound **1** reveals that this compound loses lattice water at 95–140 °C. At higher temperatures, the weight of the phase remained unchanged up to 300 °C, then, the compound gradually decomposed at temperatures up to 540 °C.

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