Rational Design of Open-Framework Coordination Solids − Synthesis and Structure of $[Co_5(OH)_2\{1,2,4,5\text{-}(O_2C)_4C_6H_2\}_2(H_2O)_4]\cdot xH_2O$

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A strategy for preparing open-framework coordination solids by hydrothermal synthesis has been developed and tested by the synthesis of a new porous cobalt carboxylate which can be dehydrated by heating to give a material with coordinatively unsaturated metal ions.

A number of groups are developing methods for synthesising open framework materials incorporating transition metals. These strategies include methods which aim to modify premade materials[1−8] as well as ones designed to construct the framework with the transition metal already incorporated.[9−19] Amongst the first class are syntheses in which the transition metal is substituted into a preformed zeolite,[1−3] or a metal complex is encapsulated within zeolite channels (ship-in-a-bottle catalysts)[4−7] and chemical modification of mesoporous (e.g. MCM-41) materials.[8] The second class includes the synthesis of molybdenum and vanadium phosphates,[9,10] zeolite-like cobalt (alumino) phosphate networks[11] and metal-organic coordination frameworks.[12−20] It is hoped that these materials will have the stability of zeolites with enhanced catalytic activity.

Our recent synthesis[20] of $[Co_3(OH)_2(C_4O_4)\cdot 3H_2O]$ has shown that microporous transition-metal-containing species can be produced based on metal hydroxide structural members joined together by anionic ligands. These materials can be viewed as being made up from assemblies of tubes with rectangular or diamond-shaped cross sections in which the ligands are the walls of the tube and the metal hydroxide chains form the corners. From the isolation of this material we postulated that the formation of open framework materials could be encouraged by a number a factors and we have now illustrated the usefulness of this theory by the preparation of the title compounds.

The factors which are important in the rational synthesis of open framework coordination solids relate to both the types of structural members (i.e. ligands) which can be used and also the way in which the voids can be stabilised during synthesis. The ligand should be capable of forming part of the metal hydroxide backbone and it should have a central portion which will act as part of the channel wall (Figure 1). Therefore we should be able to control the dimensions of the channel by choosing ligands with different distances between the donor groups. The channel structure can be stabilised by filling the lacunae with water molecules held in place by hydrogen bonds, particularly to bridging hydroxide ligands but also to coordinated water. The formation of species containing bridging hydroxide ligands is therefore encouraged by the use of high pH conditions for these reactions.

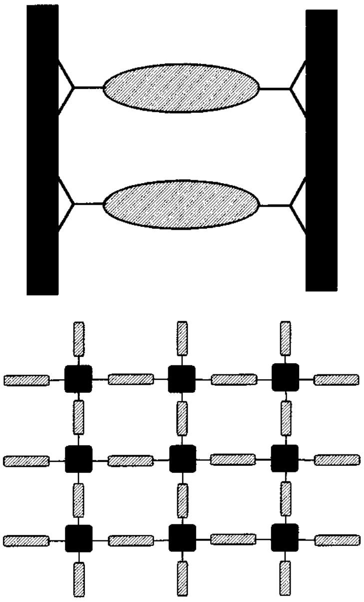

Figure 1. Schematic view of the construction of open-framework materials; black areas represent metal-oxo strips, shaded areas represent ligand “spacer” regions

The structure[21] (Figure 2) of the title compound is built around a $Co_5(\mu_3\text{-}OH)_2$ “bow-tie” cluster in which two metal triangles have a common vertex. Each triangle has a μ_3-OH at its centre and is held together by 1,3-bridging carboxylates around the periphery in a manner similar to the well-known $[M_3(O)(O_2CR)_6L_3]$ compounds. The two carboxylate functions responsible for the Co(1)−Co(2) and

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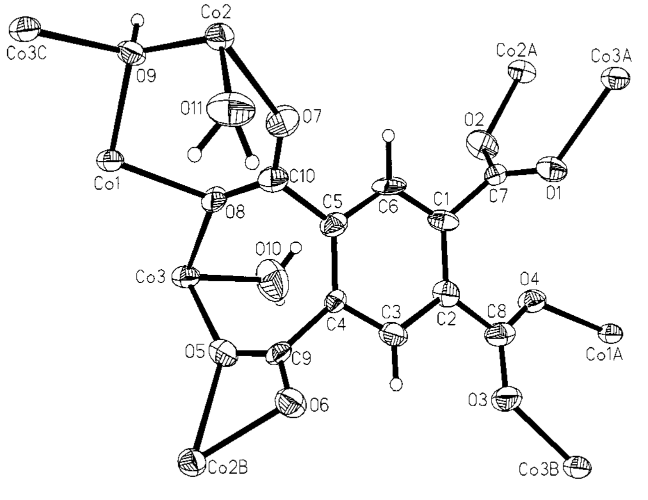

Figure 2. View of the ligand with all the metal atoms coordinated to it; selected bond lengths: Co1−O4 2.065(6), Co1−O9 2.085(5), Co1−O8 2.133(6), Co2−O9 2.013(6), Co2−O11 2.065(7), Co2−O2 2.076(6), Co2−O7 2.108(6), Co2−O6 2.136(6), Co2−O5 2.361(6), Co3−O3 2.016(6), Co3−O5 2.070(7), Co3−O1 2.083(6), Co3−O9 2.098(6), Co3−O8 2.132(5), Co3−O10 2.202(7) Å; selected bond angles: O4−Co1−O9 88.0(2), O4−Co1−O9′ 92.0(2), O4−Co1−O8 90.4(2), O4−Co1−O8′ 89.6(2), O9−Co1−O8′ 99.0(2), O9−Co1−O8 81.0(2), O9−Co2−O11 117.0(3), O9−Co2−O2 99.0(3), O11−Co2−O2 85.9(3), O9−Co2−O7 96.5(3), O11−Co2−O7 85.2(3), O2−Co2−O7 164.4(3), O9−Co2−O6 143.4(2), O11−Co2−O6 99.5(3), O2−Co2−O6 85.4(2), O7−Co2−O6 83.4(2), O9−Co2−O5 86.2(2), O11−Co2−O5 156.8(3), O2−Co2−O5 89.6(2), O7−Co2−O5 93.5(2), O6−Co2−O5 57.4(2), O3−Co3−O5 170.1(3), O3−Co3−O1 97.5(3), O5−Co3−O1 89.0(3), O3−Co3−O9 89.6(3), O5−Co3−O9 97.3(2), O1−Co3−O9 95.8(2), O3−Co3−O8 89.7(3), O5−Co3−O8 84.4(2), O1−Co3−O8 172.0(2), O9−Co3−O8 80.7(2), O3−Co3−O10 81.1(3), O5−Co3−O10 92.3(3), O1−Co3−O10 82.9(3), O9−Co3−O10 170.3(3), O8−Co3−O10 101.8(2), Co3−O5−Co2 143.2(3), Co3−O8−Co1 94.4(2), Co2−O9−Co1 118.5(3), Co2−O9−Co3 117.1(3), Co1−O9−Co3 96.9(2)°

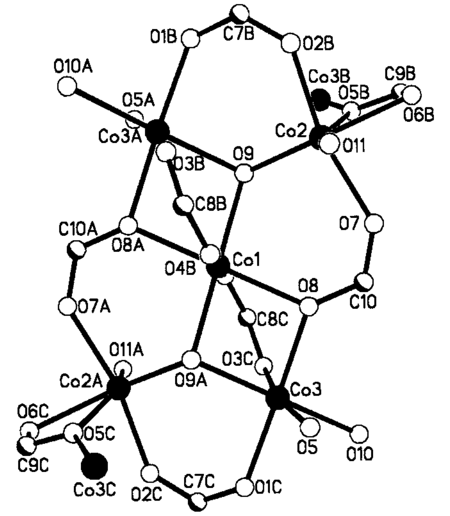

Figure 3. One of the $CO_5(OH)_2$ clusters with associated carboxylate groups; cobalt atoms from neighbouring clusters (Co3B and Co3C) have also been included

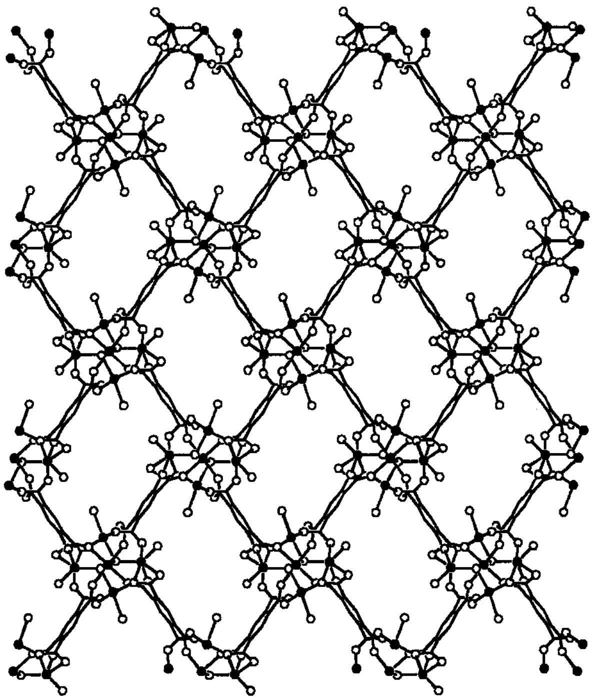

Figure 4. Packing diagram parallel to [100] with the non-coordinated water molecules omitted

Co(2)−Co(3) bridges lie close to the Co_3 plane whilst the third, Co(1)−Co(3), lies perpendicular to it. There is a further 1,1-carboxylate bridge between Co(1) and Co(3) which is common to the two fused triangles. The different types of bridging between metal atoms leads to triangles which are close to isosceles. The two edges with only OCO bridges are similar in length whereas the edge with two single-atom bridges is significantly shorter. The three crystallographically distinct metal atoms within each triangle have significantly different coordination environments. The ligand lacks any symmetry, two carboxylates on one side are 1,3-bridging and the other two acid groups together bridge four metals in a more complex arrangement. The Co_5 units are joined to adjacent clusters by four 1,1-carboxylate bridges to form a metal hydroxide-carboxylate backbone (Figure 3) running along the crystallographic *a* axis. The metal hydroxide-carboxylate rods are connected to one another by the ligand to form channels with an approximately rectangular cross-section (Figure 4). The dimensions of the rectangle are defined by the crystallographic *b* and *c* axes i.e. 16.5 × 14.6 Å. Allowing for the van der Waals radius of carbon this gives maximum dimensions of the channel of approximately 13 × 11 Å. A calculation using the PLATON[22] suite of programs shows that the framework occupies only 54.4% of the volume of the unit cell and therefore 45.6% is available for occupation by water. This compares with a free volume of 36.6% for $[Co_3(OH)_2(C_4O_4)_2 \cdot 3H_2O]$ showing that the use of larger spacer ligands not only leads to larger cavities but also to a cavity occupying a greater proportion of the material's volume. There is significant encroachment of the metal backbone into the channels, particularly for the water ligands O(10) and O(11), which hydrogen bond to some of the water molecules within the channels. There are five crystallographically distinct sites within the channels giving a maximum of 10 equivalents of water for each Co_5 unit. At room temperature the thermal parameters of the oxygen atoms suggest that most of these sites are not fully occupied. Refinement of the X-ray data was most successful using a model which has 7.5 molecules of lattice water per Co_5 unit giving a total of 11.5 molecules of water (coordinated plus uncoordinated) per formula unit. This is in reasonable agreement with calculations using the "Squeeze" subroutine in PLATON which gives a value of 171 electrons per unit cell which corresponds to 8.5 molecules of lattice water and a total of 12.5 molecules per formula unit.

TGA studies show a gradual loss of 18% of the original mass from just above room temperature to 130 °C corresponding to 10.8 mol of water per formula unit. This suggests loss of at least half of the coordinated water, producing coordinatively unsaturated cobalt ions lining the channels which are then available as catalytic sites. The change in coordination number of cobalt is confirmed by a distinct colour change from red to blue on dehydration. The dehydrated material does not give good powder diffraction patterns showing that crystallinity is lost; however the connectivity of the lattice is maintained. When the compound is re-exposed to the atmosphere the colour change is reversed very rapidly to give a material with an IR spectrum identical to the original material and an X-ray powder diffraction pattern consistent with the single crystal structure.

In conclusion we have shown that this is a sound strategy for preparing open-framework solids and we are now applying it to other systems.

Experimental Section

Sodium hydroxide (100 mg, 2.5 mmol) was dissolved in H_2O (6 mL). A 4 mL portion of this solution was added to a solution of $CoCl_2{\cdot}6H_2O$ (250 mg, 1.9 mmol) in H_2O (2 mL) to give a blue precipitate of cobalt hydroxide. Solid 1,2,4,5-$(HO_2C)_4C_6H_2$ (100 mg, 0.4 mmol) was added to the remaining 2 mL of alkali solution. The two slurries were combined to give a molar ratio metal:ligand:base of 8:3:19 and a pH of 8.5. The mixture was placed in a 23 mL Teflon-lined autoclave and heated to 190 °C for 48 hours. The reaction vessel was cooled over a period of 4 hours and the product isolated by filtration and purified by repeated cycles of treatment of an aqueous slurry in an ultrasonic bath followed by decanting.

$[Co_5(OH)_2\{1,2,4,5\text{-}(O_2C)_4C_6H_2\}_2(H_2O)_4]{\cdot}xH_2O$ was obtained as red needles in a yield of 85 mg (39% based on ligand). − $C_{20}H_{34}Co_5O_{32}$: calcd. C 22.2, H 3.2; found C 21.7, H 2.7. Isostructural materials containing nickel (green microcrystalline powder) and zinc (colourless crystals) may also be prepared in the same way.

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[20] S. O. H. Gutschke, M. Molinier, A. K. Powell, P. T. Wood, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 991−992.

[21] *Crystal data for* $C_{20}H_{46}Co_5O_{32}$, $M = 1032.06$, monoclinic, $P2_1/n$, $a = 7.452(4)$, $b = 16.472(6)$, $c = 14.586(5)$ Å, $\beta = 95.46(4)$ °, $V = 1782(1)$ Å^3, $Z = 2$, $D_c = 1.923$ g cm^{-3}, F(000) = 1032, $\mu = 2.385$ mm^{-1}, $T = 293(2)$ K, crystal dimensions 0.15 × 0.08 × 0.07 mm. Data were collected on a Rigaku R-axis IIC image plate diffractometer equipped with a rotating anode X-ray source using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). 5352 independent reflections were scaled using the Denzo-Scalepack suite of programs to give 2801 which were unique ($R_{int} = 0.089$). The structure was solved by direct methods and refined using full-matrix least-squares on F^2 to give $R1 = 0.0572$ for $F > 4\sigma(F)$ and $wR2 = 0.1582$, $S = 0.926$ for all data.
Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157236. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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