Coordination Complexes with Infinite Lattice Structures: Solvothermal Synthesis and X-Ray Crystal Structures of $K_2M[NC_5H_3(CO_2)_2\text{-}2,3]_2$ (M = Mn, Zn)

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Reaction of MCl_2 (M = Mn, Zn) with 2 equivalents of $K_2[NC_5H_3(CO_2)_2\text{-}2,3]$ in methanol at 200 °C produces the compounds $K_2M[NC_5H_3(CO_2)_2\text{-}2,3]_2$ which are found by X-ray crystallography to have structures based on interpenetrating diamondoid networks.

Superheated solvents allow reactions to be performed in the temperature range intermediate between conventional solutions techniques and solid-state synthesis producing metastable products.[1–3] Additionally, some normally intractable solids can be crystallised,[4] easing characterisation. This technique (mainly using superheated water) has been used extensively to produce zeolites and related oxide[5] and phosphate materials.[6] The use of solvents other than water has further extended the range of compounds available and supercritical amines have recently been used to prepare novel molecular and solid-state sulfides and selenides.[1,2,7–9] The relatively low temperatures needed in these reactions allow systems incorporating organic substituents to be investigated, such as those containing organic phosphonates and arsenates.[3] An enormous variety of acids suitable for use in solvothermal synthesis is available. Hence by using acids with defined geometries it should be possible to exert a high degree of control over crystal architecture. This has already been illustrated by the large variety of network solids based on coordination complexes which have recently been prepared.[10,11] We now report the extension of solvothermal synthesis to compounds containing carboxylates and the preparation of two novel three-dimensional network solids based on simple metal–pyridinedicarboxylate units.

The appropriate metal chloride, 2 equivalents of KOH and 2 equivalents of pyridine-2,3-dicarboxylic acid were placed with 15 ml of methanol in a 23 ml Teflon lined autoclave. After heating at 200 °C for 2 days the autoclave was cooled to room temperature over a period of 3 h and the compounds $K_2M[NC_5H_3(CO_2)_2\text{-}2,3]_2$ (M = Mn, Zn) were formed. The yellow–brown manganese compound can be obtained pure by washing with water but similar treatment of the zinc compound causes decomposition; however, well formed yellow octahedra can be harvested manually. Initially the reactions were performed with excess ligand salt to promote crystallisation but good quality crystals can also be obtained using stoichiometric quantities of reagents.

The two compounds have been characterised by X-ray crystallography and are isostructural with normal bond lengths and angles.† In each case the metal M is coordinated to four ligands in an octahedral geometry. Two ligands chelate *via* the pyridine nitrogen and one of the oxygens of the carboxylate in the 2 position, the two remaining coordination sites are occupied by oxygen atoms from the carboxylate in the 3 position. The nitrogens are *trans* to the monodentate ligands. Bond lengths are between 2.159 and 2.273 Å for manganese and 2.081 and 2.161 Å for zinc. The asymmetric unit contains only one ligand which is coordinated to two identical metal atoms, one in a chelating fashion and the other monodentate. Hence the four ligands around each metal bridge it to four neighbouring identical metals. This results in the formation of a slightly distorted tetrahedron [four sides of 12.840 (12.714) Å and two of 14.041 (13.876) Å for Mn (Zn)] with the original metal atom at the centre (Fig. 1). As each metal atom is bridged to four others in a tetrahedral arrangement a diamondoid network is thus produced. Within each crystal there are two independent interpenetrating diamondoid networks related by a mirror plane (Fig. 2). The metal atoms are chiral with all those within one network being of Λ configuration and the other network is Δ. The distance between metals in the same network is 8.115 Å for Mn and 8.030 Å for Zn whilst the shortest distances to noncontiguous metals are 7.155 and 7.066 Å, respectively. Viewed parallel to the *c* axis the anionic networks appear closely packed but there are rectangular channels parallel to the *a* and *b* axes which contain the potassium ions (Fig. 3). The potassium ions lie to the sides of the channels with irregular coordination environments and distances to oxygen of between 2.6 and 2.9 Å. X-Ray powder diffraction patterns were recorded for precipitates formed in similar reactions performed at room temperature. These differ from those of the above compounds showing that high temperatures are required for their formation. The magnetic behaviour of the manganese compound has been investigated using a SQUID magnetometer in the temperature range 2–300 K at a field of 1 kG (0.1 T). The magnetic moment indicates the presence of five unpaired electrons per metal and the material behaves as a simple paramagnet down to 4 K with no evidence for magnetic coupling.

Compounds with diamondoid networks are of current interest because they frequently crystallise in the polar space groups necessary for the presence of physical properties such as second-order optical properties.[12] This approach represents a potential route to robust materials with useful solid-state

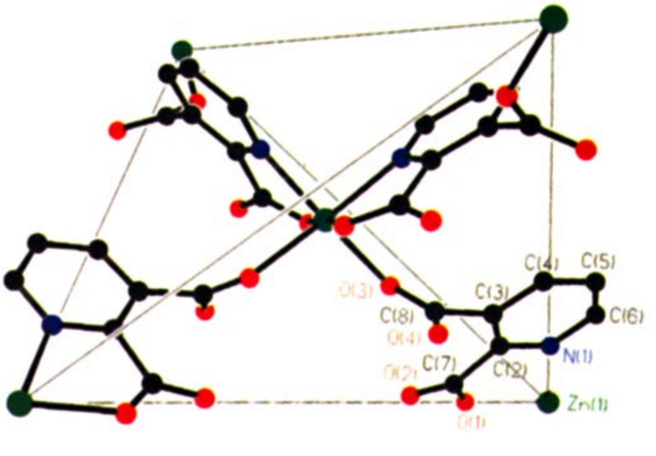

Fig. 1 View of a small part of $K_2M[NC_5H_3(CO_2)_2\text{-}2,3]_2$ (M = Mn or Zn) illustrating the tetrahedral arrangement of four metal atoms around the central one

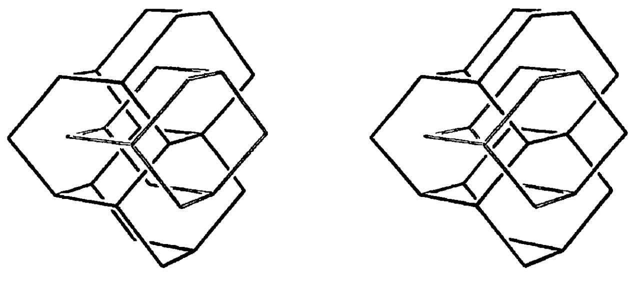

Fig. 2 Stereoscopic view of the interpenetrating networks formed by the metal atoms, each vertex corresponds to one Mn or Zn atom

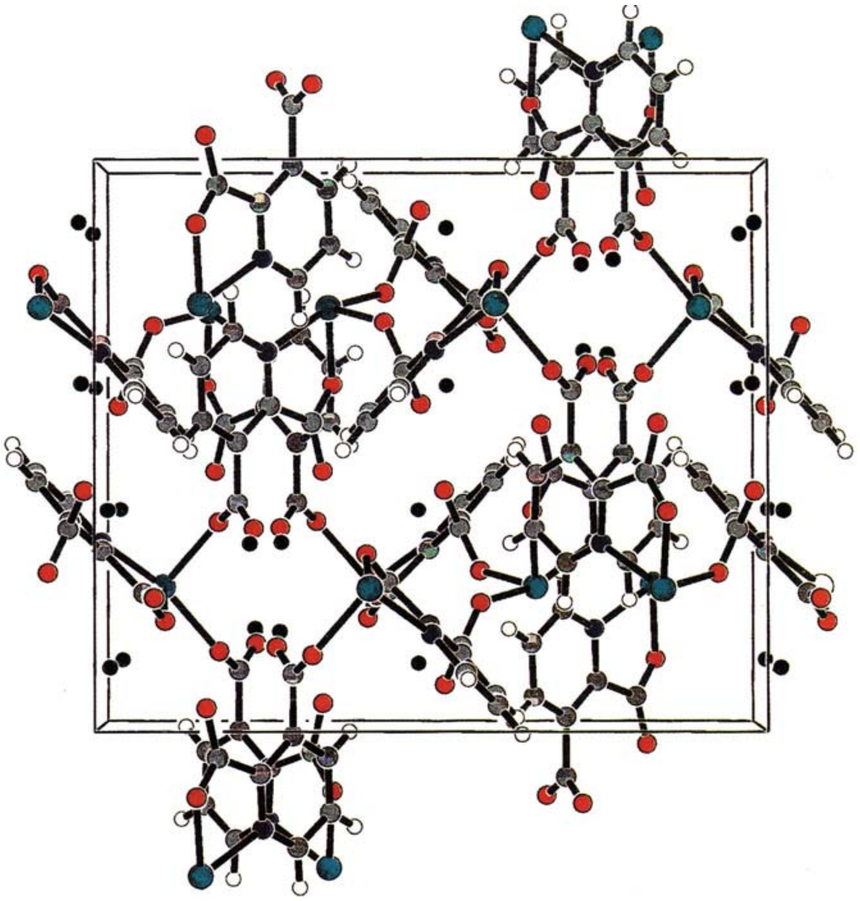

Fig. 3 View of $K_2M[NC_5H_3(CO_2)_2\text{-}2,3]_2$ parallel to the *a* axis. Mn/Zn (green), N (blue), O (red), H (hollow), C (grey), K (black).

properties. Clearly there are many other metal–ligand combinations for which this technique will work, some of these are currently under investigation.

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Footnote

† *Crystal data* for $C_{14}H_6K_2MnN_2O_8$, M = 463.34, tetragonal, space group $I4_1/a$, (no. 88), a = 14.049(7), c = 16.284(2) Å, U = 3214(1) Å^3, Z = 8, D_c = 1.91 g cm^{-3}, μ(Cu-Kα) = 118.25 cm^{-1}, $F(000)$ = 1848.0. The crystal was mounted on a glass fibre. 1154 independent reflections were collected at 298 K on a Rigaku AFC7S diffractometer, ω–2θ scan method, $5 \leqslant 2\theta \leqslant 120°$, graphite-monochromated Cu-Kα radiation (λ = 1.541 78 Å) with 890 observed [$I > 3.00\ \sigma(I)$] and corrected for Lorentz and polarisation factors. An empirical absorption correction was applied (transmission factors 0.87–1.00, yellow plate, dimensions 0.25 × 0.14 × 0.25 mm). The structure was solved by direct methods,[13] and the non-hydrogen atoms refined anisotropically. The hydrogen atoms were idealised. Refinement of 124 parameters by full-matrix least squares gave R = 0.041, R_w = 0.038 [$w^{-1} = \sigma^2(F_o)$]. The maximum residual electron density in the final ΔF map was 1.45 e Å^{-3} and the maximum shift/error in the final refinement cycle was 0.01

Crystal data for $C_{14}H_6K_2N_2O_8Zn$. M = 473.79, tetragonal, space group $I4_1/a$ (no. 88), a = 13.876(8), c = 16.173(1) Å, U = 3114(1) Å^3, Z = 8, D_c = 2.02 g cm^{-3}, μ(Cu-Kα) = 74.93 cm^{-1}, $F(000)$ = 1888.0. The crystal was mounted on a glass fibre. 1325 independent reflections were collected at 298 K on a Rigaku AFC7S diffractometer, ω–2θ scan method, $5 \leqslant 2\theta \leqslant 120°$, graphite-monochromated Cu-Kα radiation (λ = 1.541 78 Å) with 1105 observed [$I > 3.00\ \sigma(I)$] and corrected for Lorentz and polarisation factors. An empirical absorption correction was applied (transmission factors 0.64–1.00, yellow octahedron, dimensions 0.22 × 0.24 × 0.32 mm). The structure was solved by direct methods,[13] and the non-hydrogen atoms refined anisotropically. The hydrogen atoms were idealised. Refinement of 124 parameters by full-matrix least squares gave R = 0.32, R_w = 0.033 [$w^{-1} = \sigma^2(F_o)$]. The maximum residual electron density in the final ΔF map was 0.34 e Å^{-3} and the maximum shift/error in the final refinement cycle was 0.04.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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