Three-dimensional coordination networks from tricyanomelamine and Co^{II}, Ni^{II}, Cu^{II} and Cd^{II}

Brendan F. Abrahams, Simon J. Egan, Bernard F. Hoskins and Richard Robson*

School of Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia

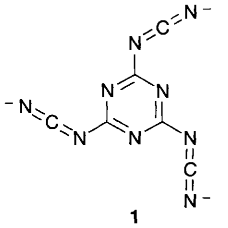
Crystals of composition [M(Htcmel)]·$3H_2O$ (M = Co, Ni, Cu, Cd; H_3tcmel = tricyanomelamine) contain sheets of hydrogen-bonded pairs of essentially planar ligands cemented together by metal centres to give a three-dimensional coordination network.

New materials with useful properties (*e.g.* catalytic, electronic) may be afforded by infinite networks constructed from building blocks of various connectivities and geometries. In principle three-connecting building blocks provide access to a wide range of three-dimensional nets some of which exist only hypothetically in that real chemical examples are unknown.[1] We began our exploration of the coordination polymers of three-connecting ligands with one of the simplest we could envisage, namely, the tricyanomethanide ion, $C(CN)_3^-$.[2] This affords interpenetrating corrugated hexagonal polymeric sheets with Ag^I,[3] interpenetrating rutile-related nets with a range of octahedral metal centres[2] and numerous other three-dimensional coordination networks.[4] The larger three-connector 2,4,6-tris-(4-pyridyl)-1,3,5-triazine provides a number of unprecedented and highly symmetrical, cubic three-dimensional networks.[5,4] Moore and coworkers, using the three-connecting ligand 1,3,5-tris(4-ethynylbenzonitrile)benzene have recently reported an interesting hinged three-dimensional coordination network with Ag^I which has the $ThSi_2$ topology,[6] a net designated by Wells as (10,3)-b.[1]

We are now extending our exploratory work to the potentially three-connecting ligand **1**, tcmel^{3-}, derived from tricyanomelamine (H_3tcmel). The $-NCN^-$ group is potentially capable of binding one, two or three metal centres and is isoelectronic with the cyanate ion which has a rich coordination chemistry. Attractive features of **1** with regard to studies of derived coordination networks are its ready availability, its great thermal stability (the sodium salt is generated at 500 °C!), its potentially strong metal-binding capacity and, in particular, its relationship to the dicyanoquinodiimine ligands which give stable radical anions and form coordination polymers with metal-like electrical conductivity.[7]

Crystals of [M(Htcmel)]·$3H_2O$ (M = Co, Ni, Cu, Cd), obtained by slow diffusion of aqueous Na_3(tcmel) solutions into ethanolic solutions of the metal nitrate in the presence of HBF_4 have been examined by single-crystal X-ray diffraction.† All four derivatives have essentially the same structure.

All ligands are equivalent, the C/N skeleton being only slightly deformed from planarity. Each ligand is attached to four metals as shown in Fig. 1. As can be seen in Fig. 1 the metal–nitrogen bonds are considerably inclined to the general ligand plane. All metal centres are equivalent, being essentially octahedral with four nitrogen donor atoms and two *cis* water ligands. In the case of the Cu derivative the metal environment is markedly distorted, the bond to a ligand 'elbow' nitrogen, in particular, being elongated [2.628(3) Å]. Eight-membered rings consisting of two metals bridged by two cyanamide NCN units are present. Extensive delocalisation within the ligand is indicated by the fact that for all four compounds all C–N bond distances are < 1.38 Å.



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The ligands appear in essentially coplanar hydrogen-bonded pairs which, in turn, are arranged in infinite two-dimensional sheets in which all triazine rings are close to coplanar (Fig. 2); the connectivity, however, is not two- but three-dimensional, as described below. The metal centres directly coordinated to one sheet of ligands are located in pairs on both sides of the sheet as is apparent in Fig. 2. Parallel sheets of ligands are cemented together by pairs of metal centres located between the sheets. The links between sheets are illustrated in Fig. 1 in which a pair of metals bind together two ligands clearly belonging to adjacent sheets. Thus every metal is coordinated by two nitrogen atoms from each of the two sheets between which it is sandwiched.

Hydrogen bonds have been extensively employed in crystal engineering[8–10] and in particular hydrogen bonds to melamine or melamine derivatives related to those observed here have been used by Mingos and coworkers in the construction of transition-metal containing extended networks.[11]

From a topological viewpoint both metal and ligand may be considered as four-connectors (taking into account only coordinate bond connections) which link together to form a three-dimensional net related to that of the felspars.[12]

Obtaining coordination polymers in the form of crystals large enough for single crystal diffraction studies is proving more difficult for the tcmel^{3-} ligand than for Htcmel^{2-} but the pursuit of this objective is continuing.

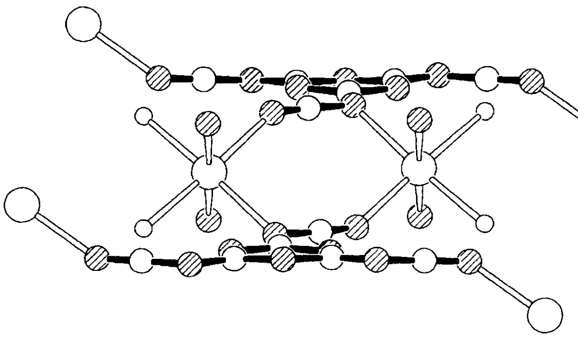

Fig. 1 The ligand and metal environments (Cd derivative). Circles in order of decreasing radius represent metal, C/N (N atoms hatched) and O respectively. For all three different side-arms in all four different metal derivatives (Co, Ni, Cu, Cd) the terminal CN bond lengths fall in the range 1.14–1.17 Å, the cyanamide carbon to 'elbow' nitrogen bond lengths in the range 1.30–1.32 Å and the ring carbon to 'elbow' nitrogen bond lengths in the range 1.32–1.37 Å.

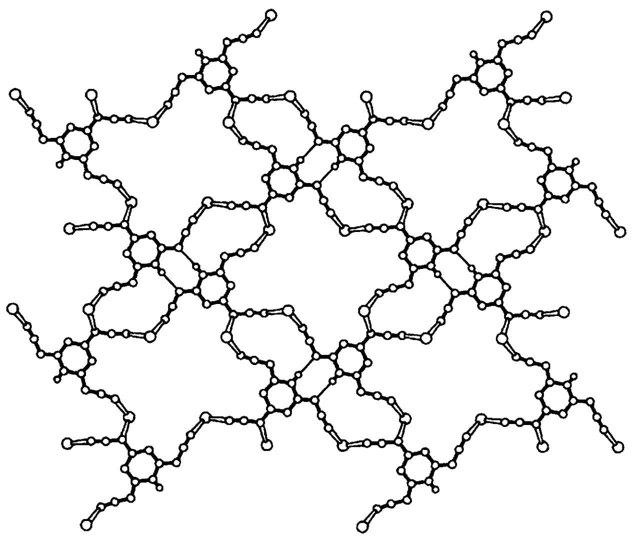

Fig. 2 A single sheet of ligands and the metal centres (Cd here, larger circles) directly coordinated thereto. Fine connections represent NH···N hydrogen bonds [N···N, 2.909(6) for Co, 2.899(6) for Ni, 2.909(4) for Cu and 2.923(4) Å for Cd].

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Footnote

† The copper derivative was dried in air for elemental analysis. Found: C, 22.6; H, 1.9; N, 39.5; Cu, 20.0. Calc. for [Cu(Htcmel)]·3H_2O, $C_6H_7CuN_9O_3$: C, 22.7; H, 2.2; N, 39.8; Cu, 20.1%. Intensity data were collected on an Enraf-Nonius CAD4-MachS diffractometer employing the ω–2θ scan technique, absorption corrections were applied (SHELX-76). Structures were solved using heavy-atom methods (SHELXS-86) and refined using a full-matrix least-squares refinement procedure (SHELXL-93).

Crystal data for [M^{II}Htcmel]·3H_2O, (M = Co, Ni, Cu, Cd respectively): $C_6H_7MN_9O_3$; *M* = 312.11, 311.87, 316.73, 365.59; monoclinic, *C*2/*c*, *a* = 19.084(3), 18.971(5), 18.608(5), 19.588(4) Å; *b* = 16.756(2), 16.667(4), 16.946(5), 17.095(3) Å; *c* = 6.940(1), 6.946(1), 6.942(2), 7.073(2) Å; β = 98.40(1), 98.14(2), 99.10(3), 97.44(3)°; *U* = 2195.4(5), 2174.1(8), 2161.5(11), 2348.5(9) Å^3; *F*(000) = 1256, 1264, 1272, 1424; *Z* = 8; Cu-Kα radiation for M = Co, Mo-Kα radiation for M = Ni, Cu, Cd; μ = 12.54 (Cu-Kα), 1.809, 2.046, 1.883 (Mo-Kα) mm^{-1}; $2\theta_{max}$ = 75.0, 27.5, 27.5, 27.5°; unique reflections 2089, 2587, 2481, 2688; observed reflections [$I > 2\sigma(I)$] 1427, 1710, 1960, 2244; *R*1 = 0.0514, 0.0552, 0.0400, 0.0342; *wR*2 (on F^2) = 0.1391, 0.1209, 0.0978, 0.0940; 173 refined parameters. The hydrogen atom of the Htcmel ligand was located in difference maps.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/35.

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