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Linear distortion of octahedral metal centres by multiple hydrogen bonds in modular ML_4 systems

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Received (in Columbia, Mo, USA) 24th February 2004, Accepted 4th May 2004
First published as an Advance Article on the web 25th May 2004

A series of compounds of the type $[M(1)_4(H_2O)_2]SO_4{\cdot}2H_2O$ containing a simple urea-based pyridyl ligand have been synthesised and characterised by X-ray crystallography. The enclathrated water exists within discrete linearly stacked cavities and causes significant distortions in the $M–OH_2$ bonds due to the presence of a strongly hydrogen bonded water square.

Supramolecular interactions, particularly hydrogen bonding, within crystalline samples can exert a significant effect on their surrounding environment. Such interactions are being used widely in crystal engineering as supramolecular synthons due to their ubiquitous nature and versatility.[1–3] For example, strong hydrogen bonding can be responsible for lowering of molecular symmetry by 'pulling' the donor and acceptor moieties away from their expected positions.[4] Hydrogen bonds have also been observed to play a role in distorting the geometry of transition metal centres, especially those containing aqua ligands.[5] We now report a remarkable homologous series based on metal complexes of ligand **1** that contains a urea group, known for displaying strongly hydrogen bonded networks including those involving transition metal complexes.[6,7] The ligand is readily synthesised in excellent yield and has previously been used successfully as a component of anion hosts based around both organic and inorganic cores.[8,9]

Upon reaction of **1** with a series of M(II)SO_4 salts in water–methanol solution (50 : 50 v/v) a highly insoluble crystalline solid of formula $[M(\mathbf{1})_4(H_2O)_2]SO_4{\cdot}2H_2O$ (M = Co, Ni, Cu, Zn; **2–5** respectively) is readily formed in all cases, in essentially quantitative yields. The solid-state structures of all four materials (including the Jahn–Teller distorted Cu(II) complex) proved isomorphous and revealed thread-like motifs comprising head-to-tail stacked, cup-shaped *trans*-$M(\mathbf{1})_4(H_2O)_2$ moieties with C_4 symmetry exhibiting a chain of cavities incorporating the two molecules of enclathrated water. The water exerts a significant effect upon the length of the O–M–O axis, producing a linear distortion of the M–O bonds, Fig. 1.†

The urea oxygen atoms all point towards the inside of the cavities, presenting a large electronegative surface. The included water guests are involved in hydrogen bonding networks with both the urea oxygen atoms and the water molecules coordinated to the metal centre. The strands of the $[M(\mathbf{1})_4(H_2O)_2]^{2+}$ unit are arranged in a tetrahedral fashion around the sulfate counter-anions, with each anion binding to urea groups from four separate ligands *via* two NH···O interactions. The water within the cavities forms a distorted, hydrogen bonded square of oxygen atoms between the enclathrated and the coordinated water, Fig. 2. The solvent molecules are further held by hydrogen bonding to the urea oxygen atoms. Both guest water and urea oxygen atoms exhibit twofold disorder suggesting that, in principle, a water octahedron could be accommodated. It is clear that water···water interactions would be repulsive in such a situation, however, and elemental analysis results agree with the dihydrate formulation.

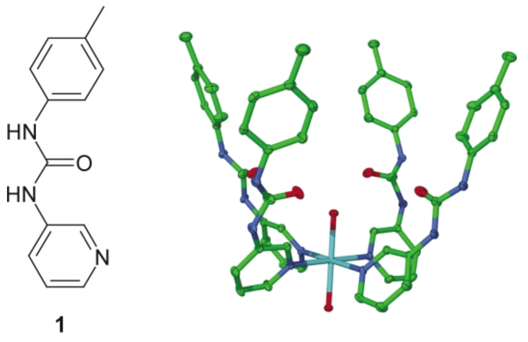

Fig. 1 Cup shaped $[Co(\mathbf{1})_4(H_2O)_2]^{2+}$ unit. Only one disordered urea oxygen shown and hydrogen atoms omitted for clarity.

The hydrogen bonding environment within the cavities is cause for an exceptional linear distortion of the O–M–O axis in all cases studied. In order to better interact with the included solvent molecules the coordinated water on the 'bottom' of the bowl units is pulled further away from the metal centre. This results in the two $M–OH_2$ lengths differing considerably, Table 1. A CSD search reveals that it is indeed the lower oxygen atom that is being pulled down into the cavity rather than the upper M–O bond becoming contracted (by a comparison with mean M–O bonds for the metals involved).[10] The hydrogen bond length to the 'lower' coordinated water molecules is significantly shorter than that to the 'upper' water indicating that it is the relative strengths of these interactions responsible for the distorted nature of the O–M–O axis. The Cu(II) structure displays the most marked difference in bond lengths between the two M–O bonds, presumably due to its Jahn–Teller distortion and consequent weak axial M–O bonds. The strength of the hydrogen bonding is telling in that these interactions between the complex and the included solvent are responsible for holding the infinite stacks together with the aid of π–π interactions between the tolyl ring of one molecule with the pyridinium ring on the one above.

TGA studies on the cobalt complex **2** show that no solvent loss occurs until approximately 140 °C when water is lost in three sharp, distinct steps (136, 146 and 153 °C) attributable to initial loss of enclathrated water followed by aqua ligands. The solvent water is

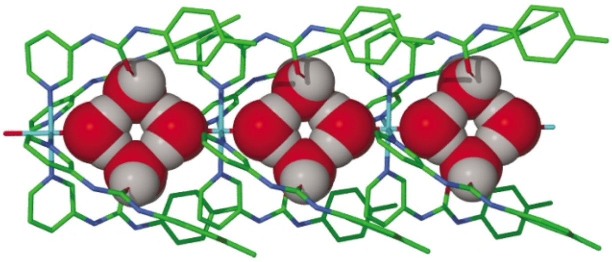

Fig. 2 Part of an infinite strand of ML_4 units showing the way in which the chain is held together in $[Co(\mathbf{1})_4(H_2O)_2]SO_4{\cdot}2H_2O$.

Table 1 $M–OH_2$ bond lengths in complexes **2–5**

	M–O(1)/Å[a]	M–O(2)/Å[a]	Δ M–O/Å
Co	2.074(3)	2.128(3)	0.055
Ni	2.077(4)	2.121(4)	0.044
Cu	2.282(3)	2.458(4)	0.176
Zn	2.126(3)	2.188(3)	0.062

[a] O(1) refers to the 'upper' oxygen atom as in Fig. 1.

DOI: 10.1039/b402884h

strongly held within the structure, as evidenced by the lack of exchange with D_2O when left for 5 days, as monitored by IR measurements and lack of crystal decomposition upon heating at 80 °C for up to one week. Compound **2** additionally shows a very sharp weight loss at 158 °C corresponding to loss of one of the four ureido pyridyl ligands. Decomposition with loss of the remaining ligands occurs in a series of much less well defined stages above 200 °C. In contrast, the Cu(II) complex **4** shows a single broad water loss step with onset 147 °C followed by a single decomposition step with onset 240 °C. While the weaker axial Cu–OH_2 bonds in **4** result in loss of the separate weight loss stages, dehydration occurs, if anything, less readily indicating that the water is strongly held within the stack cavity.

It is not uncommon for crystal packing effects to distort the coordination environment of a transition metal centre, although such distortions most often occur in more than one dimension and are combined with a deformation of the octahedral angles around the metal. A CSD search for Co, Ni, Cu and Zn centres with all octahedral angles constrained to 90 ± 2° showed that the vast majority of structures have equal M–O lengths, Fig. 3. The only notable exceptions being three copper(II)-containing systems in which the aqua ligands are influenced by interactions with neighbouring molecules[11–13] and a cobalt(II) system in which enclathrated water draws aqua ligands away from the metal in a similar manner to that observed in this work.[14,15] There are no examples of distorted nickel or zinc systems previously reported within this range. When the angle constraint is relaxed to within 3°, more systems display a bond length distortion along with more distorted angles. Aqua ligands on lanthanides have also been shown to exhibit linear axial distortions upon interaction with enclathrated water with key consequences for the understanding of water exchange in the application of such systems as MRI contrast agents.[16]

This series of structures represents the most linear distortion of these metal centres observed in the solid state and highlights the importance of hydrogen bonding as an interaction, able to affect strong metal–ligand bonds.

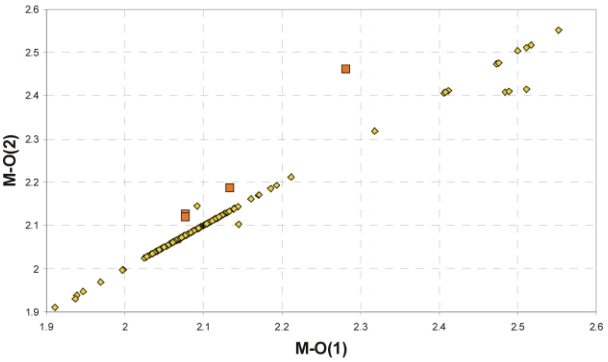

Fig. 3 M–O(1) *vs.* M–O(2) distances in octahedral systems with angles constrained to 90 ± 2°. Data from this work shown as red squares.

We thank the EPSRC for a studentship (DRT) and for the X-ray crystallography service in Southampton.

Notes and references

† Crystal data: for compound **2**. $C_{52}H_{60}CoN_{12}O_{12}S$, M = 1136.11, tetragonal, a = 18.070(3), c = 8.0756(16) Å, U = 2636.9(7) Å^3, T = 173(2)K, space group $P4/n$ (no. 85), Z = 2, μ(Mo–Kα) = 0.440mm^{-1}, 4642 reflections measured, 3007 unique (R_{int} = 0.0345) which were used in all calculations. The final $R1$ and $wR2$ were 0.0424 and 0.0996 [$I > 2\sigma(I)$]. For compound **3**. $C_{52}H_{60}N_{12}NiO_{12}S$, M = 1135.89, tetragonal, a = 18.028(3), c = 8.1143(16) Å, U = 2637.3(7) Å^3, T = 120(2)K, space group $P4/n$ (no. 85), Z = 2, μ(Mo–Kα) = 0.483mm^{-1}, 4131 reflections measured, 2540 unique (Rint = 0.0564) which were used in all calculations. The final $R1$ and $wR2$ were 0.0404 and 0.0830 [$I > 2\sigma(I)$]. For compound **4**. $C_{52}H_{60}CuN_{12}O_{12}S$, M = 1140.72, tetragonal, a = 17.846(3), c = 8.3019(17) Å, U = 2644.0(8) Å^3, T = 120(2)K, space group $P4/n$ (no. 85), Z = 2, μ(Mo–Kα) = 0.527mm^{-1}, 4682 reflections measured, 3021 unique (Rint = 0.0326) which were used in all calculations. The final $R1$ and $wR2$ were 0.0470 and 0.1097 [$I > 2\sigma(I)$]. For compound **5**. $C_{52}H_{60}N_{12}O_{12}SZn$, M = 1142.55, tetragonal, a = 18.0760(5), c = 8.1208(3) Å, U = 2653.41(14) Å^3, T = 120(2)K, space group $P4/n$ (no. 85), Z = 2, μ(Mo–Kα) = 0.577mm^{-1}, 4859 reflections measured, 3034 unique (Rint = 0.0428) which were used in all calculations. The final $R1$ and $wR2$ were 0.0406 and 0.0811 [$I > 2\sigma(I)$]. CCDC 233240–233243. See http://www.rsc.org/suppdata/cc/b4/b402884h/ for crystallographic data in .cif or other electronic format.

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