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Characterization of a well resolved supramolecular ice-like $(H_2O)_{10}$ cluster in the solid state†

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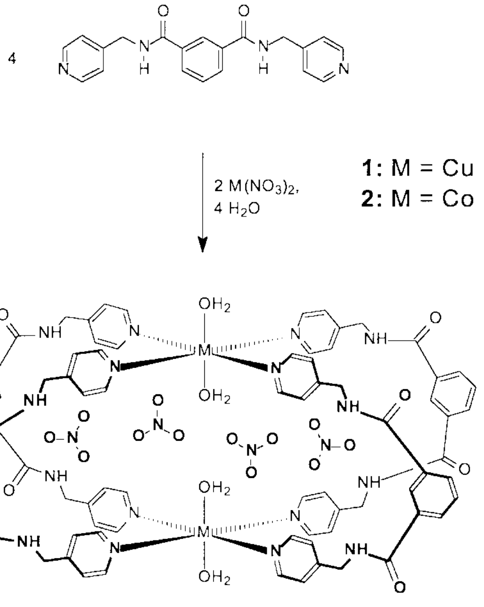
The conformation of a previously observed ice-like water cluster in the solid state proves to be robust to geometric changes in its surroundings and the hydrogen bonded arrangement is finally revealed in detail.

Water clusters can play an important role in the stabilization of supramolecular systems both in solution and in the solid state and there is clearly a need for a better understanding of how such aggregates influence the overall structure of their surroundings.[1–5] In this context, we recently characterized a solid-state structure of a $[Cu_2(H_2O)_4L_4]\cdot nH_2O$ complex **1** (Scheme 1) featuring an $(H_2O)_{10}$ cluster with an ice I_c-like arrangement of the water molecules.[6] At the time, owing to inherently poor crystal quality and the lack of low temperature X-ray data collection capability, the structure was only modestly resolved and several important points remained to be addressed. First, although the positions of the water molecules constituting the decameric cluster were determined unequivocally, the water hydrogen atoms were never located. While an ordered arrangement of these hydrogen atoms was inferred from the discontinuous nature of the cluster (in contrast to the disordered hydrogen arrangement in the continuous ice lattice[7]), we were not able to verify this conjecture experimentally. Second, disorder of the contents of the macrocyclic cage, coupled with poor resolution, precluded us from determining the composition of the interior of the cage with sufficient certainty. Third, it was not known to what extent the geometry of the water cluster would be affected by relatively small changes in the overall geometry of the system (*e.g.* substitution of Cu by Ni or Co). We now present a new, well resolved low-temperature crystal structure that addresses all of the above issues satisfactorily.



Scheme 1

Since the metal ion of the Cu^{2+} complex exhibits Jahn–Teller distortion along the M···M vector that also passes through the center of the water cluster, we decided to introduce a slight geometric change to the system by substituting cobalt for copper. Crystals of **2** were grown as previously described[6] and the sngle crystal X-ray structure‡ is discussed below. While the cage complex in **2** is remarkably similar to that of **1**, the extended structures of the two systems are slightly different as evidenced by the unit cell information given in Table 1.

Both structures consist of linear arrays of the dinuclear cage complex (aligned parallel to the M···M axis) with the water cluster effectively acting as an exo-bidentate bridging ligand. Each of these arrays is surrounded by four identical arrays that are offset by half a structural unit along the M···M vector. This staggered arrangement of the globular cage molecules results in the formation of relatively large voids which are occupied by the decameric water clusters.

Fig. 1 shows selected portions of the two structures overlaid in order to illustrate the major differences between them. In the structure of **1**, successive cages are related to one another by $\bar{4}$ site symmetry and, accordingly, the orientation of the ligand amide groups alternates from one cage to the next within each strand. However, successive cages in **2** are related to one another by a simple unit cell translation and all the ligand arms therefore have the same orientation within a linear strand. Note that the cage complexes of **1** and **2** shown at bottom are almost identical in geometry with their M···M distances differing by only 0.441 Å [Cu···Cu 9.582(7) Å, Co···Co 9.141(4) Å].

Fig. 2 shows the arrangement of the water cluster in **2**. The distance across the decamer from O(1W) to O(4W) is 6.287(4) Å (*cf.* 6.35 Å in ice I_c)[7] while the corresponding distance in **1** is 5.65 Å [average of two unique distances: 5.779(7) and 5.512(7) Å]. This difference of about 0.6 Å in the length of the water cluster along the M···M vector is attributed to the longer M–O coordination bond in the Cu complex (average Cu–O 2.33 Å, average Co–O 2.10 Å). This clearly demonstrates that the flexibility of its internal hydrogen bonds allows the cluster to adjust its geometry in response to small changes in its environment and that the overall ice-like conformation is quite robust to such changes. All of the water hydrogen atoms were

Table 1 Unit cell parameters for $[M_2L_4(H_2O)_4](NO_3)_4\cdot 16H_2O$

	1	2
M	Cu^{2+}	Co^{2+}
T/°C	20	−100
Crystal system	Tetragonal	Monoclinic
Space group	$I4_1/a$	$C2/c$
Unit cell dimensions		
a/Å	21.9265(8)	21.886(1)
b/Å	21.9265(8)	19.623(1)
c/Å	39.754(2)	22.170(1)
β/°	—	90.886(1)

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† Electronic supplementary information (ESI) available: thermal ellipsoid plots and labeling schemes for **2**. See http://www.rsc.org/suppdata/cc/b0/b001862g/

located in difference electron density maps and the hydrogen bonded arrangement is indeed as inferred in our report of the structure of complex **1** (see .cif file for distances and angles relating to hydrogen bonds). The water cluster is situated on a two-fold rotation axis passing through O(1W) and O(4W) and only half of the remaining water molecules are crystallographically unique. O(1W) donates hydrogen bonds to O(9W) which in turn donates to O(8W) and O(10W). Similarly, O(4W) donates to O(7W) which also donates to O(8W) and O(10W). O(8W) and O(10W) each donates a hydrogen bond to a nitrate oxygen atom as well as to an amide oxygen atom from a cage complex of a neighboring strand. With the exception of O(7W) and O(9W), all water hydrogen atoms participate in the formation of four relatively strong hydrogen bonds. The closest non-covalent approach of any atoms to O(7W) and O(9W) are by the amide nitrogen atoms N(8B) and N(8A) of neighboring strands at distances of 3.549(4) and 3.357(4) Å, respectively. These distances are too long to be considered appreciably strong hydrogen bonds and are due to steric effects that inhibit a closer approach.

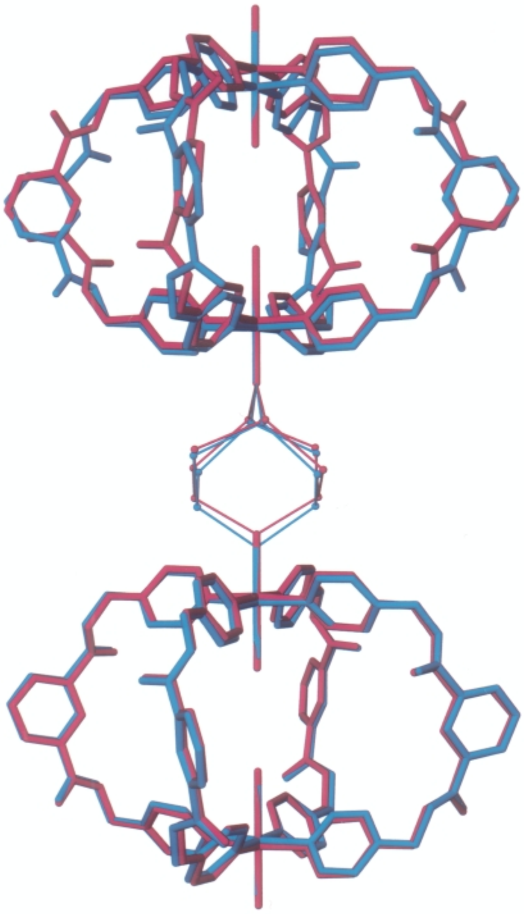

Fig. 1 Overlay of structures **1** (red) and **2** (blue) showing two cage complexes linked by an $(H_2O)_{10}$ water cluster.

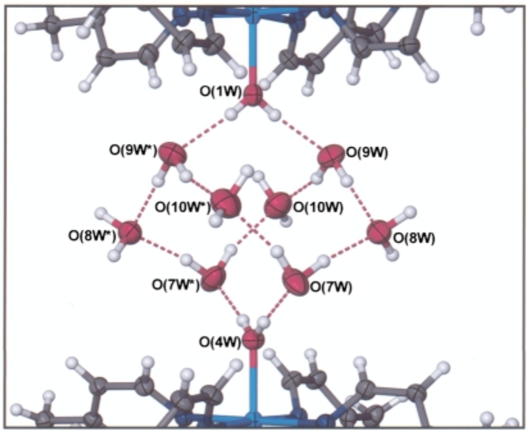

Fig. 2 Thermal ellipsoid (50% probability) plot of the water cluster in **2**. Asterisks within atom labels denote symmetry equivalent atoms.

The structure of **1** had not been determined with sufficiently high resolution to reveal with certainty the contents of the cage complex. Although **1** was modeled with six water molecules in the cage, it was thought that at least another two water molecules resided within the arms of the ligand. However, the low-temperature structural determination of **2** shows unequivocally that the interior of the cage complex does indeed consist of four nitrate anions and six water molecules. Two of the latter are coordinated to the metal cations and form hydrogen bonded contacts with the remaining four water molecules which, in turn, hydrogen bond to the nitrate oxygen atoms and this intricate hydrogen bonded arrangement imparts a high degree of rigidity to the cage interior.

We are grateful for funding from the National Science Foundation.

Notes and references

‡ *Crystal data* for **2**: $C_{80}H_{104}Co_2N_{20}O_{36}$: M = 2039.69, dark blue prismatic crystal, 0.30 × 0.30 × 0.20 mm, monoclinic space group $C2/c$ (no. 15), a = 21.8855(11), b = 19.6232(10), c = 22.1697(11) Å, β = 90.886(1), Z = 4, V = 9519.9(8) Å^3, D_c = 1.423 g cm^{-3}, Bruker SMART CCD diffractometer, Mo-Kα radiation, λ = 0.7107 Å, T = −100 °C, $2\theta_{max}$ = 54.3°, 29439 reflections collected, 10498 unique (R_{int} = 0.0330). The structure was solved and refined using the programs SHELXS-97 and SHELXL-97 respectively.[8] The program X-Seed[9] was used as an interface for the SHELX programs, and to prepare the figures. Final GOF = 1.071, $R1$ = 0.0673, $wR2$ = 0.1857, R indices based on 7050 reflections with $I > 2\sigma(I)$ (refinement on F^2), 691 parameters, L_p and absorption corrections applied, μ = 0.444 mm^{-1}. All non-hydrogen atoms were refined anisotropically with the exception of those belonging to the minor component of a disordered nitrate anion. Hydrogen atoms on the ligand were placed using standard geometric models and with thermal parameters riding on those of their parent atoms. Water hydrogen atoms were located in difference electron density maps and refined with nominal geometric restraints. CCDC 182/1590. See http://www.rsc.org/suppdata/cc/b0/b001862g/ for crystallograpic files in .cif format.

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