

[Co(NH₃)₆]₃[Cu₄(OH)(CO₃)₈]·2H₂O – a new carbonato-copper(II) anion stabilized by extensive hydrogen bonding†

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Addition of Co(NH₃)₆³⁺ to aqueous solutions of Cu^{II} in excess carbonate promotes the assembly of a new highly charged carbonato-copper(II) anion, [Cu₄(OH)(CO₃)₈]⁹⁻, which contains an unusual μ₄ hydroxo-bridged square Cu₄ arrangement, stabilised in the crystal by no less than forty hydrogen bonds (< 3 Å) to hexammine cations.

Since Werner's time the carbonate ion has played a significant role in the development of coordination chemistry. It displays a rich variety of interactions with metal ions, acting as a monodentate, bidentate and bridging ligand and affording mononuclear, oligonuclear and polynuclear arrangements.¹ Despite the depth and breadth of this earlier work, we believe that many opportunities still remain for the discovery of significant new types of carbonate-based chemistry. We are exploring how various potentially hydrogen-bonding cations with high symmetry influence or control the structures adopted by anionic carbonato-metal species. We have found, for example, that the guanidinium cation alone induces polymeric [Cu^{II}(CO₃)₂]²⁻_n species to adopt a diamond topology whereas the same framework components in the same proportions adopt a sodalite topology when the guanidinium cation is used in concert with certain other cations.² Here we report that the symmetrical hydrogen-bonding cation Co(NH₃)₆³⁺ exerts a dramatically different effect upon the structure adopted by anionic carbonato-cupric species.

Addition of an aqueous solution of Co(NH₃)₆Cl₃ to a solution of cupric nitrate in excess aqueous K₂CO₃–KHCO₃ at room temperature affords green crystals of composition [Co(NH₃)₆]₃[Cu₄(OH)(CO₃)₈]·2H₂O‡ whose structure was determined by single crystal X-ray diffraction.§ The components of the highly charged 9- anion are arranged as in **1** with four equivalent copper centres at the corners of a square and pairs of carbonate bridges along the four edges of the square. Details of the structure of the anion can be seen in Fig. 1. Close to the centre of the Cu₄ square a

hydroxo species is located on a 4-fold axis disordered over two sites on opposite sides of the Cu₄ plane. As can be seen in Fig. 1, the carbonate unit (all equivalent) is asymmetric in that the two coordinated oxygen centres are displaced from the Cu₄ plane to different extents and also in that whilst one copper is located close to the CO₃ plane the other is significantly out of plane. Individual anions therefore are chiral. The two coordinated oxygen atoms of carbonate are each disordered over two sites so as to produce crystallographic mirror symmetry. Enantiomeric pairs of anions are superimposed in the crystallographic solution generating a site of 4/*mmm* symmetry at the centre of the Cu₄ square. The Cu^{II} centre is 5-coordinate with a geometry intermediate between square pyramidal and trigonal bipyramidal. The somewhat elongated Cu–OH bond, of length 2.239(3) Å, occupies the apical position if the system is viewed as square pyramidal and occupies an equatorial position if it is viewed as trigonal bipyramidal. Other Cu–O bonds have lengths in the “normal” range for Cu^{II} (1.965(7) – 1.980(6) Å).

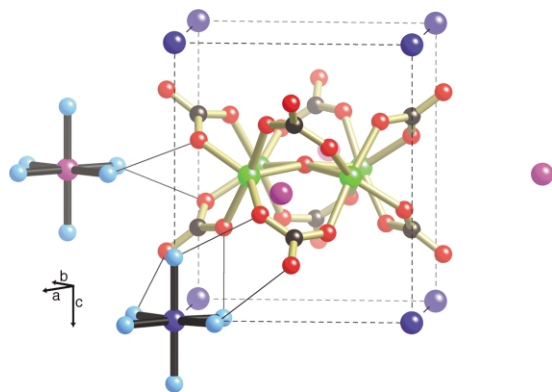
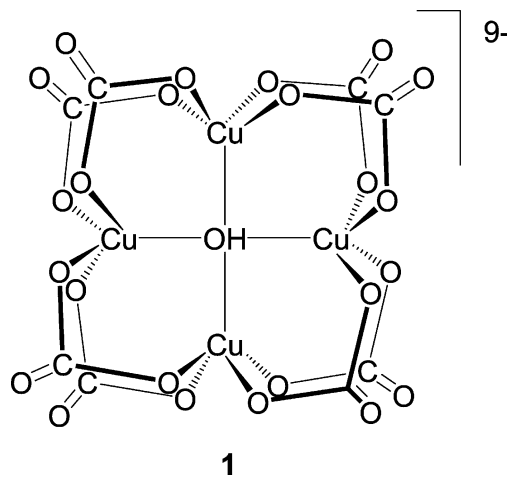


Fig. 1 The structure of the [Cu₄(OH)(CO₃)₈]⁹⁻ anion and the arrangement of the two types of neighbouring Co(NH₃)₆³⁺ ions, namely, type A (blue) at the corners of a tetragonally elongated cube and type B (pink) at the corners of a square coplanar with the Cu₄ square. Thin black lines represent hydrogen bonds. Hydrogen atoms have been omitted for clarity.

† Electronic supplementary information (ESI) available: preparative details. See <http://www.rsc.org/suppdata/cc/b3/b316925a/>

There are two types of Co(NH₃)₆³⁺ cations in the structure represented in Fig. 1 by blue (type A Co) and pink (type B Co) spheres. Associated with each anion are eight type A cations located at the corners of a tetragonally elongated cube and four type B cations located at the corners of a square in an “equatorial belt” coplanar with the Cu₄ square. Type A cations each form two pairs of hydrogen bonds (< 3 Å) to the central anion as is shown in detail for the lower left cation only (for clarity) in Fig. 1. The type B cations each form one pair of hydrogen bonds to the anion. Thus, each type A cation forms 16 hydrogen bonds to the four anions surrounding it, each type B cation forms 8 hydrogen bonds to the four anions surrounding it and each anion is bound to cations by no less than 40 hydrogen bonds!

Fig. 2 shows (in simplified form with carbonates omitted) the unit cell for the structure which indicates more clearly how the components are arranged. Thus the type A cations can be seen to be arranged in a linear fashion parallel to the tetragonal *c* direction. The separation between A-type Co centres in these stacks (8.594 Å) is half the *c* cell length. Type B cations alternate with anions also in a linear fashion parallel to the columns of A-type cations. Two water molecules per anion are located on the 4-fold axis (that passes

through the hydroxo unit) at sites between the anions and the B-type cations as shown in Fig. 2.

The structure of $[\text{Cu}_4(\text{OH})(\text{CO}_3)_8]^{9-}$ is reminiscent of the archetypal "basic chromic acetate structure"³ seen in ions of composition $[\text{M}^{\text{III}}_3(\text{O})(\text{CH}_3\text{CO}_2)_6(\text{H}_2\text{O})_3]^+$ in which three metal centres at the corners of an equilateral triangle with an oxide ion at the centre are linked along the three edges of the triangle by pairs of acetate bridges, $\text{M}-(\text{O}-\text{C}(\text{CH}_3)_2-\text{O})_2-\text{M}$, just as the metal centres in $[\text{Cu}_4(\text{OH})(\text{CO}_3)_8]^{9-}$ are linked along the four edges of the square of copper centres by pairs of carbonate bridges, $\text{Cu}-(\text{O}-\text{CO}-\text{O})_2-\text{Cu}$. The environment of the hydroxo ligand which is equidistant from the four copper centres is unusual because this anion, possessing only three lone pairs of electrons, is predisposed to form at most three dative bonds to metals. A similar μ_4 hydroxo species was reported in a complex of a tetranucleating macrocyclic ligand in which the organisation or order built into the ligand imposed a square arrangement on four nickel centres, which in turn imposed the unusual environment on the central hydroxo group.⁴ In the case of $[\text{Cu}_4(\text{OH})(\text{CO}_3)_8]^{9-}$ it appears that it is the order imposed by the highly complementary set of multiple hydrogen bonds between the hexammine cations and the carbonate ligands (no less than forty

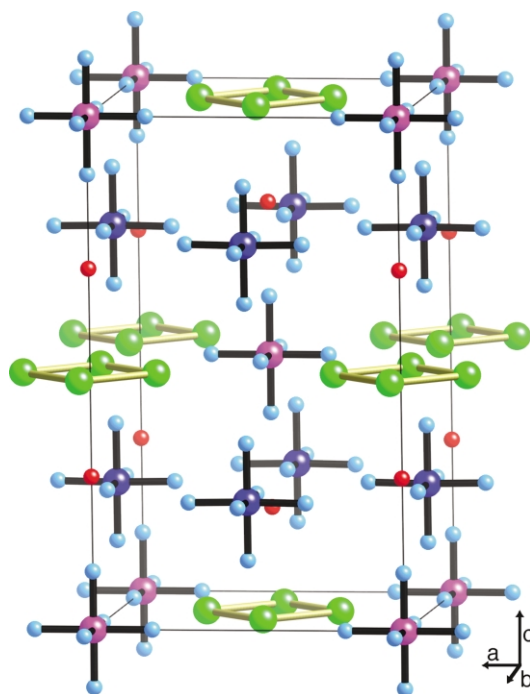


Fig. 2 A schematic representation of the tetragonal unit cell for $[\text{Co}(\text{NH}_3)_6]_3[\text{Cu}_4(\text{OH})(\text{CO}_3)_8] \cdot 2\text{H}_2\text{O}$ showing two types of columns running parallel to the tetragonal c axis. The Cu centres in the anion are represented in green and the carbonate and hydroxide units have been omitted for clarity. One type of column consists of type A $\text{Co}(\text{NH}_3)_6^{3+}$ cations and the other contains the following components in the order: type B cation – lattice water (red) – anion – water – type B cation *etc.*

hydrogen bonds per anion) that strongly favours a square arrangement of four copper centres, which in turn imposes the unusual μ_4 environment on the central hydroxo group.

It is interesting to consider whether a certain equilibrium concentration (presumably at the most minute) of $[\text{Cu}_4(\text{OH})(\text{CO}_3)_8]^{9-}$ exists in the solution and this is simply sequestered by the growing crystal or whether the anion is constructed from its components on the surfaces of the growing crystal. There can be little doubt that the recently reported² diamond-like $[\text{Cu}(\text{CO}_3)_2]^{2-}_n$ network, formed when the guanidinium ion is used as the hydrogen-bonding cationic template, is constructed from its components at the surfaces of the growing crystal. The fact that $[\text{Cu}_4(\text{OH})(\text{CO}_3)_8]^{9-}$ has not been previously reported despite its components being so common and also the fact that it is so highly charged suggest that hydrogen bonding to the hexammine cations in the crystal provides crucial stabilisation and that the anion most likely is constructed from its components as the crystal grows, rather than existing pre-formed in solution.

In our view the generation of significant new structures from simple materials under simple conditions should be an important objective in modern synthetic chemistry; the combination reported here is extremely simple – Cu^{II} , carbonate and $\text{Co}(\text{NH}_3)_6^{3+}$ in aqueous solution at room temperature.

We note that the eight-membered rings formed by the pairs of hydrogen bonds between the carbonate units and the *cis* ammine ligands in the present example are closely similar to those formed between the carbonate bridges and the guanidinium N–H groups in the sodalite-like infinite networks reported recently.² In conclusion, it is clear that the composition and symmetry of hydrogen-bonding counter cations play a crucial, but at this stage unpredictable, role in the structures adopted by anionic carbonate-metal assemblies within the crystal.

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Notes and references

‡ Preparative details are available as ESI. Anal. calcd. for $\text{C}_8\text{H}_{59}\text{Co}_3\text{Cu}_4\text{N}_{18}\text{O}_{27}$: C 7.6; H 4.7; N 19.8; Cu 20.0. Found: C 7.5; H 4.5; N 19.2; Cu 19.7%.

§ Crystal data: $\text{C}_8\text{H}_{59}\text{Co}_3\text{Cu}_4\text{N}_{18}\text{O}_{27}$, $M = 1270.68$, tetragonal, $a = 10.4090(6)$, $c = 17.188(2)$ Å, $U = 1862.3(3)$ Å³, $T = 293$ K, space group $I4/mmm$ (no. 139), $Z = 2$, $\mu(\text{Mo}-K) = 3.663$ mm⁻¹, 5828 reflections measured, 664 unique ($R_{\text{int}} = 0.0406$) which were used in all calculations. The final values for $wR2$ (all data) and $R1$ [$I > 2\sigma(I)$] were 0.1441 and 0.0486 respectively. Crystal structure solved and refined using SHELX-97.⁵ CCDC 228199. See <http://www.rsc.org/suppdata/cc/b3/b316925a/> for crystallographic data in .cif or other electronic format.

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