Self-Assembly of the Octanuclear Cluster $[Cu_8(OH)_{10}(NH_2(CH_2)_2CH_3)_{12}]^{6+}$ and the One-Dimensional *N*-Propylcarbamate-Linked Coordination Polymer $\{[Cu(O_2CNH(CH_2)_2CH_3)(NH_2(CH_2)_2CH_3)_3](ClO_4)\}_n$**

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Abstract: The reaction of $Cu(ClO_4)_2\cdot 6H_2O$ and *n*-propylamine in methanol gives two high-nuclearity products of well-defined compositions. At amine concentrations greater than seven equivalents compared to copper ion concentration, the system fixes carbon dioxide from air to form the one-dimensional carbamate-bridged coordination polymer, $\{[Cu(\mu_2\text{-}O,O'\text{-}O_2CNH(CH_2)_2CH_3)(NH_2(CH_2)_2CH_3)_3](ClO_4)\}_n$ ($\{\mathbf{1}\text{-}ClO_4\}_n$). Lower relative amine concentrations lead to the self-assembly of an octanuclear copper-amine-hydroxide cluster $[Cu_8(OH)_{10}(NH_2(CH_2)_2CH_3)_{12}]^{6+}$ (**2**). Both compounds exhibit unique structures: $\{\mathbf{1}\text{-}ClO_4\}_n$ is the first μ_2-*O,O'*-mono-*N*-alkylcarbamate-linked coordination polymer and **2** is the largest copper-hydroxide-monodentate amine cluster identified to date. The crystal structures indicate that the size of the *n*-propyl group is probably crucial for directing the formation of these compounds. Magnetic susceptibility studies indicate very weak antiferromagnetic coupling for **1**. The octanuclear cluster **2** displays slightly stronger net antiferromagnetic coupling, despite the presence of a number of Cu-O(H)-Cu angles below the value of about 97° that would normally be expected to yield ferromagnetic coupling.

Keywords: copper · magnetic properties · N ligands · octanuclear complexes · self-assembly

Introduction

In their seminal work of over half a century ago, the Danish chemist Bjerrum and his co-workers described in some detail the aqueous complexation chemistry of Cu^{2+} with simple alkyl amines and ammonia.[1] Using predominantly solution spectroscopic techniques, Bjerrum and co-workers identified the dinuclear diol species $[Cu_2(OH)_2(\text{am(m)ine})_4]^{2+}$ at low amine concentrations and the mononuclear species $[Cu(\text{am(m)ine})_5]^{2+}$ and $[Cu(\text{am(m)ine})_4(OH)]^{+}$ at higher amine concentrations. Between these extremes of concentration, the more familiar $[Cu(\text{am(m)ine})_4]^{2+}$ and $[Cu(\text{am(m)ine})_4(H_2O)_2]^{2+}$ are probably also present.[2] Surprisingly, there is a relative paucity of solid-state data for these simple ammonia and mono-*N*-alkylamine (aquo/hydroxo) complexes. One plausible explanation for this is a difficulty associated with the preparation of single-phase crystalline products; in many cases, mixtures are isolated that contain very closely related compounds, indistinguishable by sight and routine solid-state spectroscopy. In the course of other research, we have had reason to revisit the chemistry of simple copper–amine systems under predominantly nonaqueous conditions and have been surprised to discover chemistry somewhat more complex than that described for the aqueous environment. We report here the formation and isolation of two quite unexpected products generated from simple mixtures of $Cu(ClO_4)_2\cdot 6H_2O$ and *n*-propylamine in methanol. At high amine concentrations, the system fixes carbon dioxide from air to form the one-dimen-

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sional (1D) *N*-propylcarbamate-bridged coordination polymer, $\{[Cu(\mu_2\text{-}O,O'\text{-}O_2CNH(CH_2)_2CH_3)(NH_2(CH_2)_2CH_3)_3](ClO_4)\}_n$ ($\{\mathbf{1}\text{-}ClO_4\}_n$), while lower amine concentrations lead to the self-assembly of an *octanuclear* copper-amine-hydroxide cluster $[Cu_8(OH)_{10}(NH_2(CH_2)_2CH_3)_{12}]^{6+}$ (**2**).

Results and Discussion

Preparation and characterization of $\{\mathbf{1}\text{-}ClO_4\}_n$: Reaction of $Cu(ClO_4)_2{\cdot}6\,H_2O$ with 1–20 equivalents of *n*-propylamine in dry methanol under air gives blue precipitates of variable composition (indicated by powder X-ray diffraction (PXRD) and elemental analyses; the products are effectively indistinguishable by IR spectroscopy). When this reaction is performed with 20 or more equivalents of amine, however, PXRD analysis of the product suggests the presence of only a single phase. Evaporation of this reaction mixture over four days yielded thin, fragile crystals that were shown by single-crystal X-ray diffraction to be the perchlorate salt of the 1D coordination polymer, catena(*n*-propylcarbamato)tripropylaminecopper(II), $\{[Cu(\mu_2\text{-}O,O'\text{-}O_2CNH(CH_2)_2CH_3)(NH_2(CH_2)_2CH_3)_3](ClO_4)\}_n$ ($\{\mathbf{1}\text{-}ClO_4\}_n$).[3] The homogeneity of the bulk product was confirmed by comparison of its PXRD profile with that simulated from the crystal structure of $\{\mathbf{1}\text{-}ClO_4\}_n$. Identical reaction mixtures under an N_2 atmosphere yield only the tetra-primary amine copper(II) complex, $Cu(NH_2(CH_2)_2CH_3)_4(ClO_4)_2$ ($\mathbf{3}\text{-}(ClO_4)_2$),[4] demonstrating that atmospheric CO_2 is required for carboxylation of the primary amine.

The crystal structure of $\{\mathbf{1}\text{-}ClO_4\}_n$ contains 1D polymeric chains of copper(II) ions linked by $CH_3CH_2CH_2NHCO_2^-$ groups in a *syn-anti* μ_2-*O*,*O'* coordination mode (Figure 1a). The perchlorate counteranions adopt positions between the polymeric chains, accepting hydrogen bonds from the N−H groups of the coordinated *n*-propylamine ligands (Figure 1b). Each counteranion is surrounded by a set of eight NH_2 groups from two adjacent polymers at the vertices of a monoclinic prism with (N···N) dimensions about 2.9×4.9×6.5 Å (Figure 1c). The anions display orientational disorder within this N−H donor-rich environment. The polymer $\{\mathbf{1}\text{-}ClO_4\}_n$ is of some chemical interest since to the best of our knowledge it is the first example of a carbamate-bridged coordination polymer in which the carbamate moiety is derived from a primary amine (i.e. one H atom remains bound to N). Structurally characterised coordination complexes with mono-*N*-alkylated carbamates are rare in general,[7] the vast majority containing di-*N*-alkylated carbamate moieties.[8] Amongst the dialkylated carbamates, there is only one example of a *polymeric* complex, namely $\{[Ag(\mu_3\text{-}O,O'\text{-}O_2CN(CH_3)_2)]\}_n$, containing *N*,*N'*-dimethylcarbamate in a μ_3-bridging mode.[9]

The formation of carbamate-bridged metal complexes *via* fixing of CO_2 is well known in biology: metalloenzymes such as dinickel(II) urease,[10] dizinc phosphotriesterase[11] and dihydropyrimidinases[12] contain dinuclear sites in which metal(II) ions are bridged by carboxylated lysine, formed by fixing of CO_2. In synthetic metal-containing systems, fixing of CO_2 is relatively common for *secondary* amines,[8] but rather more rare for *primary* amines. Two examples have been reported recently: carboxylation of propylenediamine by CO_2 has been shown to occur in the presence of Fe^{III}, Al^{III} and Ga^{III} complexes of the dinucleating ligand $hpdta^{5-}$ (hpdta = 2-hydroxypropane-1,3-diamine-*N*,*N*,*N'*,*N'*-tetraacetate), and a calixarene-encapsulated di-uranyl site has been

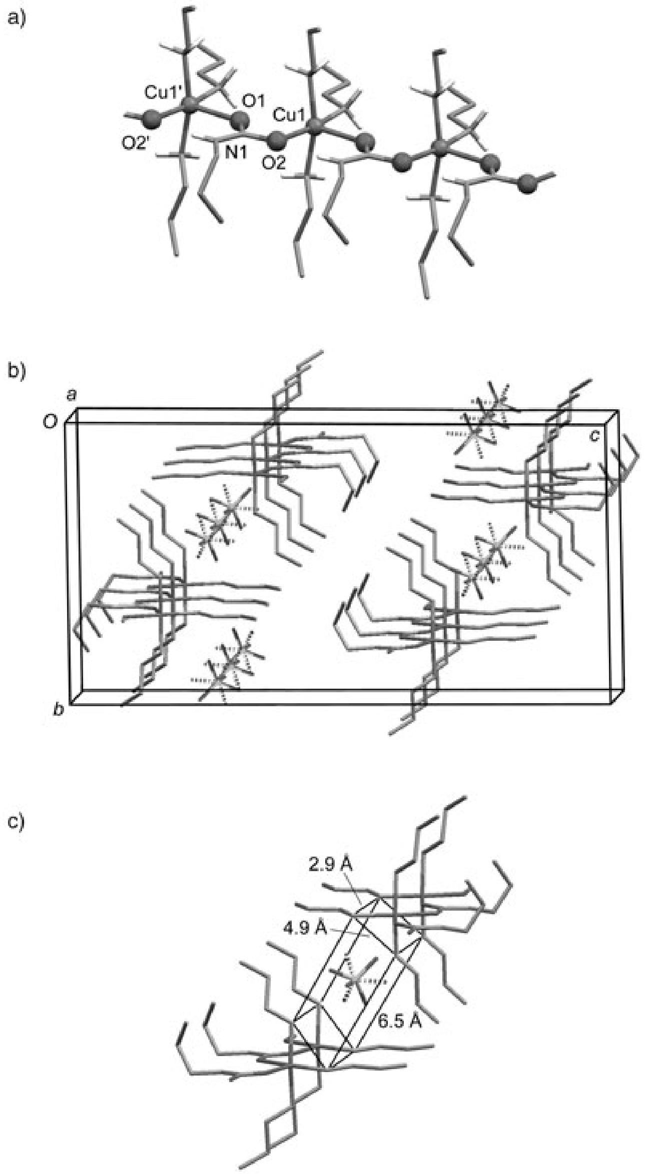

Figure 1. a) Section of the carbamate-bridged polymer in $\{\mathbf{1}\text{-}ClO_4\}_n$ (H atoms bound to C omitted). The Cu1···Cu1' distance within the polymer is 4.867(2) Å. The O atoms of the carbamate occupy one axial coordination site (O1) and one equatorial coordination site (O2) on each square-pyramidal Cu centre; b) view of the structure approximately along the direction of polymer propagation (the crystallographic *a* axis) showing disordered perchlorate anions sited between polymer chains; c) the environment of one perchlorate anion illustrated by the monoclinic prism described in the text. The solid and dashed lines illustrate two orientations modelled for the perchlorate moiety.

shown to trap CO_2-carboxylated *n*-butylamine.[7] The carboxylation of *n*-propylamine in **1** differs from these examples in two respects. Firstly, the existing literature cases[7] involve strongly Lewis acidic and oxophilic M^{III} and M^{VI} cations. Secondly, the formation of **1** proceeds in the absence of any pre-organising dinucleating or macrocylic ligand. The presence of borderline soft metal(II) ions in the present case is more closely comparable to the dimetal sites (Ni, Zn) in metalloenzymes, although the degree to which the formation of the carbamate bridging group is metal-assisted has not yet been established in either the chemical or biological environments.

Preparation and characterization of 2-$(ClO_4)_6$·$2H_2O$: From a methanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ and *n*-propylamine in 1:6 proportions under air, the cluster **2** crystallises reproducibly as a hydrated perchlorate salt **2**-$(ClO_4)_6 \cdot 2H_2O$. The structure of the octanuclear cation core (Figure 2 and Table 1), elucidated by single-crystal X-ray diffraction,[13] comprises a trinuclear–dinuclear–trinuclear stack topology that approximates a distorted face-sharing double cubane flanked with "wings" on two opposing cube vertices. The $[Cu_8(OH)_{10}(NH_2(CH_2)_2CH_3)_{12}]^{6+}$ cluster is close to centrosymmetric, although its environment in the solid state is not so. Each of the Cu atoms adopt tetragonally distorted octahedral coordination geometries typical of Cu^{2+}. In the central dinuclear unit, $[Cu_2(OH)_2(NH_2(CH_2)_2CH_3)_4]$, both axial sites of Cu4 and Cu5 are occupied by O atoms of trinuclear units, $[Cu_3(OH)_4(NH_2(CH_2)_2CH_3)_4]$. For the central atoms in each trinuclear unit, Cu2 and Cu7, one axial coordination site is occupied by an O atom of a dinuclear unit, and the second is occupied at a somewhat greater distance by an O atom of a lattice water molecule. For the outer Cu atoms of the trinuclear units, two (Cu3 and Cu8) have both axial sites occupied by O atoms of perchlorate anions, whereas two (Cu1 and Cu6) have one axial site occupied by the O atom of a perchlorate anion and one occupied by a lattice water molecule. The lattice water molecule O100 might be considered to provide a loose μ_2-bridge between Cu1 and Cu2. The two perchlorate anions (containing Cl1 and Cl4) sandwiched between the trinuclear units "push apart" the Cu atoms so that the double cubane arrangement is significantly elongated at the Cu1···O6 and Cu6···O5 edges. Indeed, the perchlorate moieties clearly occupy the axial coordination sites of Cu1 and Cu6, so that the cubane edges might be considered to lie in a "second coordination sphere". On account of poor crystal quality, the precision of the structure is relatively low so that the derived bond distances and angles cannot support conclusively the assignment of hydroxide bridges rather than oxo or water bridges. However, charge balance within the structure necessitates that any oxo bridge would require the presence of an accompanying Cu^{3+} cation, whereas any water bridge would require the presence of Cu^{+}, both cases being unlikely.

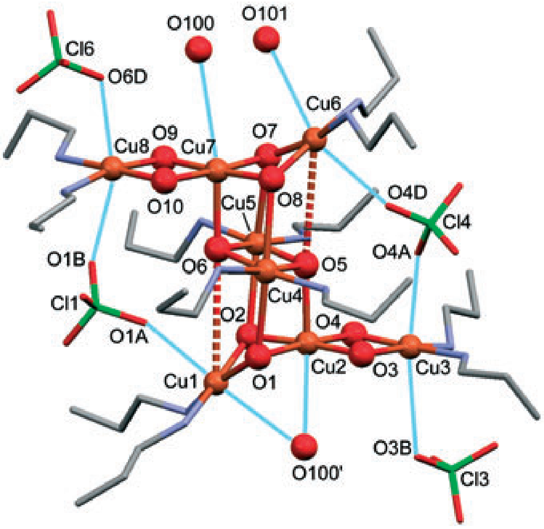

Figure 2. Octanuclear cluster in the crystal structure of **2**-$(ClO_4)_6 \cdot 2H_2O$, showing the complete coordination environments of the Cu atoms. O100 and O101 are lattice water molecules. H atoms and two non-coordinated perchlorate moieties (containing Cl2 and Cl5) are omitted for clarity. Primed atoms are related to unprimed atoms by the symmetry operation: $x, 1.5+y, 0.5+z$.

The characterisation of **2** is significant in several respects. 1) It is by some margin the largest Cu-am(m)ine-(hydr)oxide cluster containing *monodentate* amine ligands that has

Table 1. Selected bond lengths [Å] and angles [°] for **2**-$(ClO_4)_6 \cdot 2H_2O$

Cu1−O1	1.88(2)	Cu5−O2	2.61(2)	Cu1-O1-Cu2	93.8(9)
Cu1−O2	1.94(3)	Cu5−O5	1.96(2)	Cu1-O2-Cu2	92.1(11)
Cu1−O6	3.82(2)	Cu5−O6	1.94(2)	Cu2-O3-Cu3	98.7(11)
Cu2−O1	1.94(2)	Cu5−O7	2.64(2)	Cu2-O4-Cu3	98.0(11)
Cu2−O2	1.93(2)	Cu6−O5	3.68(2)	Cu4-O5-Cu5	99.7(9)
Cu2−O3	1.86(2)	Cu6−O7	1.96(2)	Cu4-O6-Cu5	100.4(9)
Cu2−O4	1.94(2)	Cu6−O8	1.91(2)	Cu6-O7-Cu7	95.6(10)
Cu2−O5	2.24(2)	Cu7−O6	2.28(2)	Cu6-O8-Cu7	97.5(11)
Cu3−O3	1.96(2)	Cu7−O7	1.92(2)	Cu7-O9-Cu8	98.8(12)
Cu3−O4	1.90(2)	Cu7−O8	1.92(2)	Cu7-O10-Cu8	98.8(11)
Cu4−O1	2.55(2)	Cu7−O9	1.92(3)		
Cu4−O5	1.97(2)	Cu7−O10	1.96(2)		
Cu4−O6	1.97(2)	Cu8−O9	1.95(3)		
Cu4−O8	2.61(2)	Cu8−O10	1.90(2)		
Cu1−O100[a]	3.17(4)	Cu6−O101	3.22(5)		
Cu1−O1A	2.76(2)	Cu6−O4D	2.79(1)		
Cu2−O100[a]	3.02(4)	Cu7−O100	3.66(4)		
Cu3−O4A	2.62(2)	Cu8−O1B	3.08(3)		
Cu3−O3B	3.11(2)	Cu8−O6D	2.64(2)		

[a] Symmetry code: $x, 1.5+y, 0.5+z$.

been identified to date. A surprisingly small number of these simple compounds are present in the Cambridge Structural Database. Two tetranuclear species exist: $\{[Cu_2(OH)_2(NH_2C_6H_{11})_4](ClO_4)_2\}_2$[14] and $\{[Cu_2(OH)_2(NH_2CH_3)_4]SO_4{\cdot}H_2O\}_2$.[15] In both cases, the authors describe these systems as dinuclear, although further Cu···O contacts of 2.61 Å and 2.40 Å in the two cases, respectively, suggest that a tetranuclear description is more appropriate. Three genuine dinuclear species are also found: in two of these, $[Cu_2(OH)_2(C_5H_7N_3)_4](ClO_4)_2$[16] and $[Cu_2(OH)_2(C_4H_6N_2)_4](ClO_4)_2{\cdot}2H_2O$,[17] perchlorate anions provide an additional bridge across the two Cu atoms, whereas in the third, $[Cu_2(OH)_2(C_4H_5N_3)_4](F_3CSO_3)_2{\cdot}2(C_4H_5N_3)$,[18] triflate anions are bound to each Cu atom in a fifth coordination site. 2) The wing-tipped double cubane arrangement of **2** represents a new topology for multinuclear copper-(hydr)oxo clusters. The most closely related existing copper-hydroxide species with nuclearities higher than four are the heptanuclear vertex-sharing double cubane found in $\{[Cu_3(bipym)_3(OH_2)(\mu_3\text{-}OH)_4]_2Cu\}(NO_3)_6$[19] (bipym = 2,2′-bipyrimidine), $[Cu_7(OH)_6Cl_2(pn)_6(H_2O)_2](C(CN)_3)_4Cl_2$[20] and $\{[Cu_3(Hpz\mathit{t}Bu)_3(\mu_3\text{-}Cl)(\mu_3\text{-}OH)_3]_2Cu\}(Cl)_6$[21] (pn = 1,3-diaminopropane; Hpz*t*Bu = *tert*-butyl-1-pyrazolyl), and the other is the octanuclear ring-shaped molecule $[Cu_8(dmpz)_8(OH)_8]$[22] (dmpz = 3,5-dimethylpyrazol), in which $dmpz^-$ ligands bridge between copper atoms. Several heterometallic Cu-lanthanide-hydroxide species have also been described, each based on a cuboctahedron of 12 Cu^{2+} ions, bridged by 24 OH groups in a μ_3-bridging mode: $[Cu_{12}La_8(OH)_{24}(NO_3)_{22}(MeLH)_{13}(H_2O)_6]^{2+}$ (MeLH = 6-methyl-2-hydroxypyridine) includes La^{3+} ions capping the eight triangular faces of the Cu_{12} cuboctahedron,[23] and $[Cu_{12}Ln_6(OH)_{24}(ClO_4)(pyb)_{12}(H_2O)_{18}]^{17+}$ (pyb = pyridine betaine, Ln = Gd, Y or Nd) includes Ln^{3+} ions capping the six square faces of the Cu_{12} cuboctahedron.[24] We have found no homometallic copper-hydroxide cluster with nuclearity higher than four in the absence of auxillary multidentate ligands. 3) Compound **2** does not contain multidentate ligands, and its formation requires the self-assembly of at least 30 discrete components (12 *n*-propylamine, 10 hydroxide, 8 Cu^{2+} cations, plus counter anions[25]), itself a record for copper-(hydr)oxo clusters. 4) Finally, and perhaps most remarkably, the formation of **2** is reproducible and quite controllable.

Controlled isolation of $\{\mathbf{1}\text{-}ClO_4\}_n$ and $\mathbf{2}\text{-}(ClO_4)_6{\cdot}2H_2O$: Semi-quantitative PXRD analyses were performed for the products of the reactions with Cu^{2+}:*n*-propylamine ratios in the range 1–20 (Figure 3).[26] As mentioned previously, a pure phase of $\{\mathbf{1}\text{-}ClO_4\}_n$ may be obtained at Cu^{2+}:*n*-propylamine ratios of 1:20 and higher. At amine concentrations between 6 and 20 equivalents, the products are a mixture of $\{\mathbf{1}\text{-}ClO_4\}_n$ and $\mathbf{2}\text{-}(ClO_4)_6{\cdot}2H_2O$. A pure phase of $\mathbf{2}\text{-}(ClO_4)_6{\cdot}2H_2O$ is obtained with a Cu^{2+}:*n*-propylamine ratio of 1:6. Reducing the amine concentration below this level leads to increasing precipitation of amorphous $Cu(OH)_2$. The PXRD analyses reveal a relatively narrow window of composition available for production of a pure phase of $\mathbf{2}\text{-}(ClO_4)_6{\cdot}2H_2O$; increasing the Cu^{2+}:*n*-propylamine ratio from 1:6 to 1:7 leads to formation of about 90% of the carbamate $\{\mathbf{1}\text{-}ClO_4\}_n$.

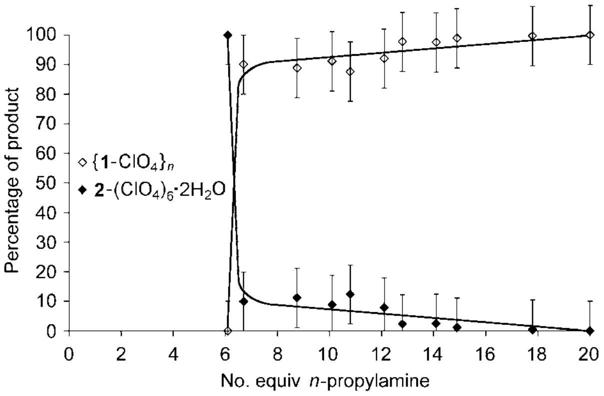

Figure 3. Relative proportions of the carbamate polymer $\{\mathbf{1}\text{-}ClO_4\}_n$ and octanuclear cluster $\mathbf{2}\text{-}(ClO_4)_6{\cdot}2H_2O$ as a function of *n*-propylamine concentration, determined from semi-quantitative PXRD analyses of the bulk solids obtained from the reaction mixtures (see Supporting Information). Error bars are shown at a fixed estimate of ±10% and the solid lines are sketched to provide a guide to the eye. Mixtures of $\mathbf{2}\text{-}(ClO_4)_6{\cdot}2H_2O$ and amorphous $Cu(OH)_2$ are obtained below six equivalents of *n*-propylamine.

The controlled isolation of $\mathbf{2}\text{-}(ClO_4)_6{\cdot}2H_2O$ is perhaps somewhat surprising given the vast number of possible products that might be envisaged from combining primary *n*-alkylamines and hydroxide ions with Cu^{2+} in multinuclear clusters. Indeed, this complexity is likely to be one contributor to the paucity of pure phases of simple copper (hydroxide) amines that was alluded to previously. One approach often employed to impart some degree of synthetic control in such systems is the incorporation of multidentate chelating ligands that cap and thereby block uncontrolled formation of polymeric metal (hydr)oxides. In the formation of **2**, the key factor appears to be something different. Inspection of the gross crystal structure highlights one notable feature: interactions between the charged and hydrophobic regions of the clusters are segregated (Figure 4). The clusters themselves lie in columns running along the crystallographic *c* axis, with the trinuclear and dinuclear moieties of the clusters lying in the perpendicular planes (110) and ($\bar{2}20$). The perchlorate anions also lie exclusively in these planes, so that the charged regions of the structure form a channel-type (4^4) network that appears square in projection along the channel direction. The water molecules included within the lattice lie close to the charged regions (loosely coordinated to Cu atoms and also hydrogen-bonded to each other and to the perchlorate moieties) so that the channels are occupied exclusively by the hydrophobic *n*-propyl chains. Clearly, the dimensions of the *n*-propyl chain are significant: shorter alkyl chains would leave voids within such a structure, whereas longer chains would disrupt the network formed by the clusters and the perchlorate moieties. This suggests that the thermodynamic stability associated with the crystal lattice controls the formation and crystallisation of $\mathbf{2}\text{-}(ClO_4)_6{\cdot}2H_2O$, and that the stabilisation of **2** is specific to *n*-propylamine ligands. It is possible that systematic ex-

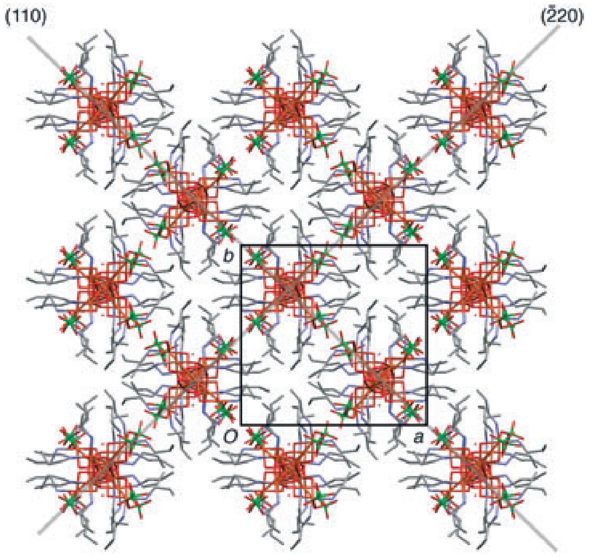

Figure 4. Projection of the crystal structure of **2**-$(ClO_4)_6{\cdot}2H_2O$ along the *c* direction (approximately along the stacking direction of the double cubane units), highlighting segregation of the interactions between the charged components and the hydrophobic *n*-propyl chains (H atoms omitted for clarity). The charged components form a (4^4) square network in the (110) and ($\bar{2}$20) planes and the *n*-propyl chains lie in channels between them.

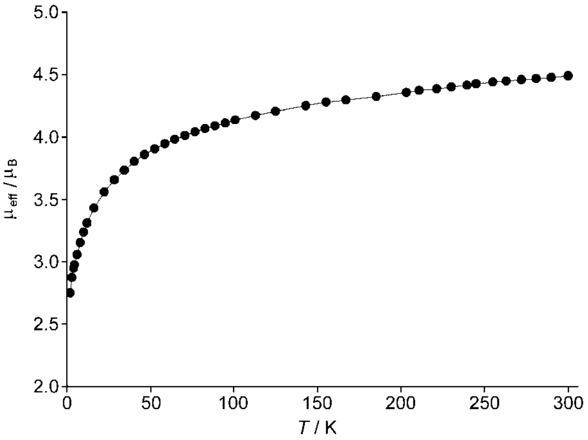

Figure 5. A plot of μ_{eff} per Cu_8 versus temperature for **2**-$(ClO_4)_6{\cdot}2H_2O$ in a field of 1 T. The solid line is not calculated, but provides a guide to the eye.

ploitation of other *n*-alkyl amines and metal hydr(oxo) systems may provide an elegant means to the controlled formation of other novel multinuclear clusters, although our attempts to prepare *characterisable* analogues of **2** using other *n*-alkylamines have been unsuccessful to date.

Magnetic properties of 1 and 2: The O atoms of the bridging carbamate groups in $\{$**1**-$ClO_4\}_n$ occupy one axial coordination site (O1) and one equatorial coordination site (O2) on each square-pyramidal Cu centre; thus, they interact with orthogonal *d* orbitals on adjacent Cu^{II} ions in the 1D chain (Figure 1a). This arrangement has been predicted to provide a ferromagnetic superexchange pathway,[27] and intrachain ferromagnetic coupling has indeed been observed previously in the structurally similar carbonate-bridged polymer $\{[Cu(\mu\text{-}O,O'\text{-}CO_3)(4\text{-aminopyridine})_2]H_2O\}_n$.[28] Magnetic measurements for $\{$**1**-$ClO_4\}_n$, however, indicate only very weak antiferromagnetic interactions (see Supporting Information). The magnetic moment per Cu remains constant at 1.85 μ_B between 300 and 25 K, then decreases to reach 1.57 μ_B at 2 K. The intrachain Cu···Cu distance in **1** is large (ca. 4.9 Å) and the four-bond superexchange pathway of the −O−C−O− bridge is probably too long for significant magnetic coupling. Alternatively, it is possible that the weak antiferromagnetic interaction could also be inter-chain in its origin and that this may conceal any weaker intra-chain ferromagnetism.

The magnetic moment of the octanuclear cluster **2** per Cu_8 decreases gradually from 4.49 μ_B ($\chi T = 2.52\ cm^3\,mol^{-1}\,K$) at 300 K to reach 2.75 μ_B at 2 K with the moment still decreasing rapidly (Figure 5). This is indicative of net antiferromagnetic coupling. There is no field dependence in μ_{eff} at all temperatures for $H = 20$, 100, 1000 and 10000 Oe thus ruling out any long-range effects or field dependent Zeeman mixing of levels.[29] Eight uncoupled $S = \frac{1}{2}$ Cu^{II} centres would lead to $\mu_{eff} = 4.89\ \mu_B$ ($g = 2.0$) at 300 K and thus the coupling is weak. There is no levelling off in the magnetic moment (or χT) at low temperatures which would indicate an isolated coupled ground state. This is also borne out in the magnetisation *versus* field data (at 2, 3, 4, 5.5, 10 and 20 K) which show a linear dependence of *M* at 20 K and gradual curvature at temperatures down to 2 K, without saturation being achieved in the highest field of 5 T (Figure 6). The *M* value of 2.38 $N\mu_B$ in the 5 T field at 2 K is possibly indicative of an $S = 1$ ground state. The magnetisation data are generally in agreement with weak antiferromagnetic coupling, probably with low lying *S* levels being close in energy. From the structural details of the bridging interactions (Figure 2 and Table 1), the full exchange calculations would require a 256 matrix. This could conceivably be re-

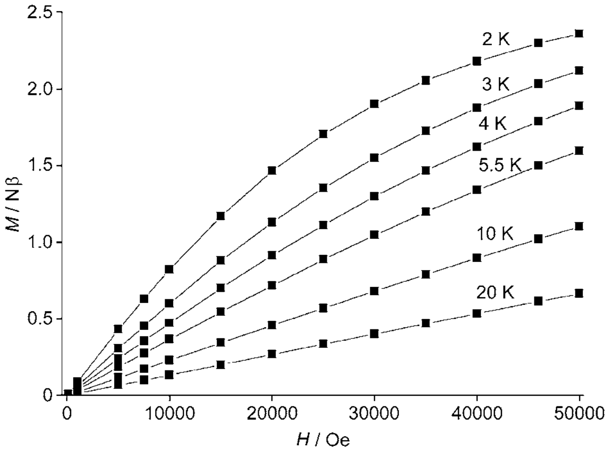

Figure 6. Plots of magnetisation per Cu_8 *vs.* applied field for **2**-$(ClO_4)_6{\cdot}2H_2O$. The solid lines provide a guide to the eye.

duced to a four-J model assuming, for instance, $J_{12}=J_{23}=J_{67}=J_{78}=J_A$; $J_{13}=J_{68}=J_B$; $J_{24}=J_{25}=J_{47}=J_{57}=J_C$; $J_{45}=J_D$ with all other Js equal to zero. These assumptions are limited, however. Past experience with $Cu_2(OH)_2$ dimers,[27] for example, suggests that the dihedral angles of about 40° and 30° formed across the O1···O2 and O7···O8 edges, respectively, will lead to different (less negative) J values compared to the almost planar Cu–O(H)–Cu pathways across O3···O4 and O9···O10. The Cu–O(H)–Cu bond angles—available only to limited precision from the crystal structure of **2**-$(ClO_4)_6{\cdot}2H_2O$—vary from 92.1(11)° to 100.4(9)°, close to the angle of about 97.5° expected for changeover from antiferromagnetic to ferromagnetic coupling in planar dihydroxo-bridged systems.[30] Out-of-plane pathways such as J_C will also play some part. Full treatment of such a complex problem would require numerical analyses using irreducible tensor operator methods[31] or density functional theory/broken symmetry techniques;[32] we have not undertaken these studies to date.

Conclusions

The results described here demonstrate that "simple" reactions of Cu^{2+} with monodentate amines can lead to a multitude of feasible products, including not only the well-known binary compounds and dimeric diols reported 50 years ago by Bjerrum and co-workers, but also higher-nuclearity hydroxo-bridged clusters, and products derived from fixing of CO_2 (i.e. carbamates and carbonates). The composition profiles obtained *via* PXRD analyses indicate that the composition window available for isolating products such as **2**-$(ClO_4)_6{\cdot}2H_2O$ can be extremely narrow. Given this observation, together with the more or less identical colours of the Cu:amine complexes and lack of salient spectroscopic signatures, it is not surprising that these more complex multinuclear structures have not been discovered earlier. It might reasonably be concluded that related species can potentially be formed for most copper-am(m)ine systems, and that these have rarely been recognised.

Experimental Section

Synthetic procedure: **Caution**: *while we have not experienced any difficulties, perchlorate salts of metallo-organic complexes are potentially explosive and should be handled with care in small quantities.*

$\{[Cu(O_2CNH(CH_2)_2CH_3)(NH_2(CH_2)_2CH_3)_3](ClO_4)\}_n$, $\{$1-$(ClO_4)\}_n$: With vigorous stirring, *n*-propylamine (4.6 mL, 55.9 mmol) was added dropwise to $Cu(ClO_4)_2{\cdot}6H_2O$ (1.034 g, 2.79 mmol) dissolved in methanol (10 mL) in an open flask until the pH reached about 11.3 to give a dark blue solution. On standing in the open flask at room temperature blue needles suitable for single-crystal X-ray diffraction appeared over several days. On evaporation to dryness, the homogeneity of the bulk sample was confirmed by powder X-ray diffraction (PXRD) analysis. Elemental analysis calcd (%) for $\{$**1**-$ClO_4\}_n$, $C_{13}H_{35}ClCuN_4O_6$: C 35.30, H 7.97, N 12.67; found: C 34.59, H 7.75, N 12.13.

$[Cu_8(OH)_{10}(NH_2(CH_2)_2CH_3)_{12}](ClO_4)_6{\cdot}2H_2O$, 2-$(ClO_4)_6{\cdot}2H_2O$: With vigorous stirring, *n*-propylamine (1.5 mL, 18.6 mmol) was added dropwise to $Cu(ClO_4)_2{\cdot}6H_2O$ (1.150 g, 3.1 mmol) dissolved in methanol (10 mL) in an open flask until the pH reached about 9.9–10 to give a dark blue solution. On standing in the open flask at room temperature, violet-tinged plates suitable for single-crystal X-ray diffraction appeared over several days. On evaporation to dryness, the homogeneity of the bulk sample was confirmed by PXRD analysis. Elemental analysis calcd (%) for **2**-$(ClO_4)_6{\cdot}2H_2O$, $C_{36}H_{122}Cl_6Cu_8N_{12}O_{36}$: C 21.40, H 6.08, N 8.32; found: C 21.68, H 5.88, N 8.22.

$[Cu(NH_2(CH_2)_2CH_3)_4](ClO_4)_2$, 3-$(ClO_4)_2$: With vigorous stirring under N_2, *n*-propylamine (4.6 mL, 55.9 mmol) was added dropwise to $Cu(ClO_4)_2.6H_2O$ (1.034 g, 2.79 mmol) dissolved in methanol (10 mL) until the pH reached about 11.3 to give a dark blue solution. On standing at room temperature, violet crystals of **3**-$(ClO_4)_2$ appeared over several days. On evaporation to dryness, the homogeneity of the bulk sample was confirmed by PXRD analysis. Elemental analysis calcd (%) for **3**-$(ClO_4)_2$, $C_{12}H_{36}Cl_2CuN_4O_8$: C 28.89, H 7.27, N 11.23; found: C 28.04, H 7.04, N 10.67.

Magnetic measurements: These were made using a Quantum Design MPMS 5 Squid magnetometer, in a field of 1 T, with the sample (ca. 20 mg) contained in gel capsule fixed to the end of the sample rod. The field was calibrated by use of a standard palladium sample obtained from Quantum Design and checked by use of chemical calibrants such as $CuSO_4{\cdot}5H_2O$. Diamagnetic corrections for the ligands were calculated from Pascal's constants. The field-dependent magnetisation data were obtained using fields of 0–5 T.

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[1] B. V. Agarwala, L. Ilcheva, J. Bjerrum, *Acta Chem. Scand. Ser. A* **1980**, *34*, 725–731; J. Bjerrum, C. G. Lamm, *Acta Chem. Scand.* **1950**, *4*, 997–1004.

[2] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Pergamon Press, **1994**, p. 1383.

[3] a) Crystal data for $\{$**1**-$ClO_4\}_n$: $C_{13}H_{35}ClCuN_4O_6$, $M_r=442.44$, monoclinic, space group $P2_1/c$, $a=4.867(2)$, $b=29.028(9)$, $c=15.164(5)$ Å, $\beta=90.08(2)°$, $V=2142(1)$ Å^3, $Z=4$, $\rho_{calcd}=1.372$ Mg m^{-3}, $\mu(Mo_{K\alpha})=1.177$ mm^{-1}. Data were collected at 120(2) K on a Siemens SMART CCD diffractometer. Of 4646 reflections measured, 2508 were unique ($R_{int}=0.154$) and 1197 were observed $[I>2\sigma(I)]$. The crystal was twinned and refined using the twin law (100, 0–10, 00–1), final batch scale factor 0.29(1). Refinement was performed against F^2. The final $wR2=0.1904$ (all data), $R1\,[F^2>2\sigma(F^2)]=0.0867$, and goodness-of-fit on F^2, $S=0.93$. The structure is of relatively low precision. b) CCDC-239610 ($\{$**1**-$ClO_4\}_n$), CCDC-239612 (**3**-$(ClO_4)_2$) and CCDC-239611 (**2**-$(ClO_4)_6{\cdot}2H_2O$) contain the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/products/csd/request/(or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336033 or deposit@ccdc.cam.ac.uk).

[4] Crystal data for **3**-$(ClO_4)_2$: $C_{12}H_{36}Cl_2CuN_4O_8$, $M_r=498.91$, triclinic, space group $P\bar{1}$, $a=7.3334(8)$, $b=7.9920(9)$, $c=10.327(1)$ Å, $\alpha=86.184(2)$, $\beta=86.552(2)$, $\gamma=63.313(2)°$, $V=539.3(1)$ Å^3, $Z=1$, $\rho_{calcd}=1.536$ Mg m^{-3}, $\mu(Mo_{K\alpha})=1.304$ mm^{-1}. Data were collected at 120(2) K on a Siemens SMART CCD diffractometer. Of 2535 reflections measured, 1825 were unique ($R_{int}=0.050$) and 1691 were observed $[I>3\sigma(I)]$. Refinement was performed against F. The final $R1=0.027$, $wR2=0.036$ $[I>3\sigma(I)]$.[3b] Surprisingly, only two other structures of tetra-monodentate primary amine copper(II) complexes are present in the Cambridge Structural Database, one containing methylamine[5] and one containing cyclohexylamine.[6]

[5] O. A. Babich, V. N. Kokozei, V. A. Pavlenko, *Russ. J. Inorg. Chem.* **1996**, *41*, 74–77.

[6] J. Gouteron, S. Jeannin, Y. Jeannin, J. Livage, C. Sanchez, *Inorg. Chem.* **1984**, *23*, 3387–3393.

[7] W. Schmitt, C. E. Anson, R. Sessoli, M. van Veen, A. K. Powell, *J. Inorg. Biochem.* **2002**, *91*, 173–189; W. Schmitt, P. A. Jordan, R. K. Henderson, G. R. Moore, C. E. Anson and A. K. Powell, *Coord. Chem. Rev.* **2002**, *228*, 115–126; B. Masci and P. Thuéry, *Supramol. Chem.* **2003**, 15, 101–108.

[8] See for example: M. H. Chisholm, F. A. Cotton, M. W. Extine, B. R. Stults, *Inorg. Chem.* **1977**, *16*, 603–611; M. H. Chisholm, F. A. Cotton, M. W. Extine, D. C. Rideout, *Inorg. Chem.* **1978**, *17*, 3536–3540; F. Calderazzo, D. B. Dell'Amico, G. Pelizzi, *Gazz. Chim. Ital.* **1985**, *115*, 145–146; F. Calderazzo, U. Englert, A. Guarini, F. Marchetti, G. Pampaloni, A. Segre, G. Tripepi, *Chem. Eur. J.* **1996**, *2*, 412–419; U. Abram, D. B. Dell'Amico, F. Calderazzo, C. D. Porta, U. Englert, F. Marchetti and A. Merigo, *Chem. Commun.* **1999**, 2053; M. T. Caudle, R. A. Nieman and V. G. Young Jr., *Inorg.Chem.* **2001**, *40*, 1571–1575.

[9] R. Alessio, D. B. Dell'Amico, F. Calderazzo, U. Englert, A. Guarini, L. Labella, P. Strasser, *Helv. Chim. Acta* **1998**, *81*, 219–230.

[10] E. Jabri, M. B. Carr, R. P. Hausinger, P. A. Karplus, *Science* **1995**, *268*, 998–1004.

[11] M. M. Benning, S.-B. Hong, F. M. Raushel, H. M. Holden, *J. Biol. Chem.* **2000**, *275*, 30556–30560.

[12] J. B. Thoden, G. N. Phillips, Jr., T. M. Neal, F. M. Raushel, H. M. Holden, *Biochemistry* **2001**, *40*, 6989–6997; J. Abendroth, K. Niefind, O. May, M. Siemann, C. Syldatk, D. Schomburg, *Biochemistry* **2002**, *41*, 8589–8597.

[13] Crystal data for **2**-$(ClO_4)_6 \cdot 2H_2O$: $C_{36}H_{122}Cl_6Cu_8N_{12}O_{36}$, $M_r = 2020.48$, monoclinic, space group $P2_1/c$, $a = 18.356(4)$, $b = 17.824(4)$, $c = 24.071(5)$ Å, $\beta = 91.40(3)°$, $V = 7873(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.705$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 2.408$ mm^{-1}. Data were collected at 120(2) K on a Siemens SMART CCD diffractometer. Of 35482 reflections measured, 9576 were unique ($R_{int} = 0.285$) and 4634 were observed $[I > 2\sigma(I)]$. The data are relatively weak and were truncated at a maximum resolution of 0.95 Å. The resulting structure is of low precision. Refinement was performed against F^2. Restraints were applied to the geometries of the perchlorate anions and *n*-propylamine chains. Only the Cl atoms of the perchlorate moieties and the Cu and O atoms of the cation were refined anisotropically, the remaining atoms being refined with isotropic displacement parameters. The final $wR2 = 0.4682$ (all data), $R1$ $[F^2 > 2\sigma(F^2)] = 0.1607$, and goodness-of-fit on F^2, $S = 1.06$.[3b] Although the structure may be considered to be of relatively low quality, the fact that it has been determined at all is a testament to the progress of chemical crystallography, in particular dramatic improvements in X-ray diffraction instrumentation.

[14] M. F. Charlot, S. Jeannin, Y. Jeannin, O Kahn, J. Lucrece-Abaul, J. Martin-Frere, *Inorg. Chem.* **1979**, *18*, 1675–1681.

[15] Y. Iitaka, K. Shimizu, T. Kwan, *Acta Crystallogr.* **1966**, *22*, 803–811.

[16] S. Amani Komaei, G. A. van Albada, J. G. Haasnoot, H. Kooijman, A. L. Spek, J. Reedijk, *Inorg. Chim. Acta* **1999**, *286*, 24–29.

[17] G. J. M. Ivarsson, *Acta Chem. Scand. Ser. A* **1979**, *33*, 323–328; A. Bencini, D. Gatteschi, C. Zanchini, *Inorg. Chem.* **1985**, *24*, 700–703.

[18] G. A. van Albada, I. Mutikainen, W. J. J. Smeets, A. L. Spek, U. Turpeinen, J. Reedijk, *Inorg. Chim. Acta* **2002**, *327*, 134–139.

[19] J. A. Real, G. D. Munno, R. Chiappetta, M. Julve, F. Lloret, Y. Journaux, J.-C. Colin, G. Blondin, *Angew. Chem.* **1994**, *106*, 1223–1225; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1184–1186.

[20] S. Triki, F. Thétiot, J. Sala Pala, S. Golhen, J. M. Clemente-Juan, C. J. Gómez-García, E. Coronado, *Chem. Commun.* **2001**, 2172–2173.

[21] X. Liu, J. A. McAllister, M. P. De Miranda, B. J. Whitaker, C. A. Kilner, M. Thornton-Pett, M. A. Halcrow, *Angew. Chem.* **2002**, *114*, 782–784; *Angew. Chem. Int. Ed.* **2002**, *41*, 756–758.

[22] G. A. Ardizzoia, M. A. Angaroni, G. La Monica, F. Cariati, S. Cenini, M. Moret, N. Maschiocchi, *Inorg. Chem.* **1991**, *30*, 4347–4353.

[23] A. J. Blake, R. O. Gould, P. E. Y. Milne, R. E. P. Winpenny, *J. Chem. Soc. Chem. Commun.* **1991**, 1453–1455.

[24] X. M. Chen, S. M. J. Aubin, Y. L. Wu, Y. S. Yang, T. C. W. Mak, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 9600–9601.

[25] The counter anions are likely to be crucial for maintaining the integrity of the structure, so that they might reasonably be included in the count of the number of assembled components. This would bring the total to 36.

[26] Full details of these PXRD measurements are available as Supporting Information.

[27] O. Kahn, Molecular Magnetism, VCH, New York, **1993**.

[28] J. Sertucha, A. Luque, O. Castillo, P. Roman, F. Lloret and M. Julve, *Inorg. Chem. Commun.* **1999**, **2**, 14–16.

[29] P. E. Kruger, G. D. Fallon, B. Moubaraki, K. J. Berry, K. S. Murray, *Inorg. Chem.* **1995**, *34*, 4808–4814.

[30] V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, W. E. Hatfield, *Inorg. Chem.* **1976**, *15*, 2107–2110.

[31] J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, B. S. Tsukerblat, *J. Comput. Chem.* **2001**, *22*, 985–991; M. Murugesu, P. King, R. Clérac, C. E. Anson, A. K. Powell, *Chem. Commun.* **2004**, 740–741.

[32] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, *J. Am. Chem. Soc.* **1997**, *119*, 1297–1303.

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