

# Synthesis, structure, and preliminary magnetic studies of unprecedented hexacopper(II) barrel clusters with spin ground state $S = 3$

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The structure of a discrete hexacopper(II) barrel cluster and that of a coordination polymer formed by a related hexanuclear repeating unit have been determined. The Cu<sup>II</sup> metals of the hexanuclear units are held together by eight chelating L-prolinato type ligands, which in turn provide the eight oxygen donors trapping a sodium ion in the center. The structure of the [Cu<sub>6</sub>Na] unit in the discrete system and in the infinite cluster-chain are essentially the same and both display intra-unit ferromagnetic superexchange. A preliminary magnetic study shows that, for both compounds, the copper centers within the [Cu<sub>6</sub>] unit are ferromagnetically coupled, yielding an  $S = 3$  spin ground state.

## Introduction

The synthesis of heteronuclear and/or polynuclear complexes continues to be an intensive and challenging area of investigation. Among the many interesting aspects of these species are their electrochemical and magnetic properties. On the one hand, recent developments in the field of supramolecular chemistry have shown that small building blocks can lead, through self-assembly processes, to large, well-defined structures, which are held together by non-covalent interactions such as hydrogen bonds<sup>1</sup> and metal–ligand coordination.<sup>2</sup> In this field, coordination supramolecular chemistry has progressed remarkably and important achievements have been made in the design and preparation of multidentate ligands capable of participating in complicated molecular structures upon complexation, in predetermined manners, with transition metals.<sup>3</sup> One of the fruits of this effort is the preparation of several examples of cluster polymers.<sup>4</sup> For example, the chain compound [ $\{Cu_4(L)(OMe)_4(NO_3)_2\}_n$ ] (H<sub>3</sub>L = a molecule containing two β-diketone units and a phenol group that constitutes a symmetric O-pentadentate ligand) is interesting as a potential magnetic material. This compound is formed by the polymerization into one-dimensional chains of [Cu<sup>II</sup><sub>8</sub>] clusters assembled by the dimerization of two ligand-held four-metal atom rows, showing strong magnetic coupling.<sup>5</sup>

In this context, we have explored the possibility of using square planar [Cu<sup>II</sup>(L-prolinato)<sub>2</sub>] complexes as potential building blocks in the formation of more complicated polynuclear arrays. This effort has resulted in the formation of a new cluster polymer with a unique sodium centered hexacopper(II) barrel portion, *catena*-[NaCCu<sub>2</sub>{Cu(hpro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub>]·4H<sub>2</sub>O (**1**) (hpro = 4-hydroxy-L-prolinato).<sup>6</sup> The repeating polynuclear units are connected *via* coordination of the OH groups from two hpro ligands, to Cu<sup>II</sup> ions from two neighbouring units. The full description of the structure of **1** is given here, along with that of the new discrete hexanuclear cluster [NaCCu<sub>2</sub>{Cu(pro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub>CH<sub>3</sub>OH]·H<sub>2</sub>O (**2**) (pro = L-prolinato), formed when the L-proline ligand without hydroxide group was used. The

preliminary magnetic properties of these two related systems are compared.

## Experimental

### Synthesis

All reagents were used as obtained from Waco Pure Chemical Ltd. [Cu(pro)<sub>2</sub>]·2H<sub>2</sub>O was prepared according to a method in the literature.<sup>7</sup> [Cu(hpro)<sub>2</sub>]·2H<sub>2</sub>O was prepared according to a modified version of the method for the preparation of [Cu(pro)<sub>2</sub>]·2H<sub>2</sub>O.

**catena**-[NaCCu<sub>2</sub>{Cu(hpro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub>]·4H<sub>2</sub>O (**1**). Sodium perchlorate (0.140 g, 1 mmol), copper(II) perchlorate hexahydrate (0.742 g, 2 mmol), and [Cu(hpro)<sub>2</sub>]·2H<sub>2</sub>O (1.44 g, 4 mmol) (molar ratio of 1 : 2 : 4) were dissolved in methanol (100 mL). Vapor of Et<sub>2</sub>O was allowed to diffuse into the resulting blue solution and blue crystals of **1** suitable for X-ray crystallography were obtained after a week in quantitative yield. Anal. Calcd (found) for **1**·2H<sub>2</sub>O: C, 24.28 (24.64); H, 3.46 (3.81); N, 5.66 (5.34).

[NaCCu<sub>2</sub>{Cu(pro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub>CH<sub>3</sub>OH]·H<sub>2</sub>O (**2**). *Method 1*. Sodium perchlorate (0.140 g, 1 mmol), copper(II) perchlorate hexahydrate (0.742 g, 2 mmol), and [Cu(pro)<sub>2</sub>]·2H<sub>2</sub>O (1.31 g, 4 mmol) (molar ratio of 1 : 2 : 4) were dissolved in methanol (100 mL). X-ray quality blue square-pyramidal crystals of **2** were obtained in almost quantitative yield from the mixed solution by slowly diffusing ether vapor into it for a few days at room temperature. Anal. Calcd (found) for **2**·H<sub>2</sub>O: C, 26.16 (26.08); H, 3.85 (3.81); N, 5.95 (5.87).

*Method 2*. Complex **2** was also obtained by mixing in methanol (100 mL) sodium perchlorate (0.112 g, 0.8 mmol), copper perchlorate (1.78 g, 4.8 mmol), and L-proline (Hpro) (0.737 g, 6.4 mmol) (ratio of 1 : 6 : 8) and following the same procedure as above. The yield was quantitative.

## Measurements

Crystals for X-ray diffraction measurements were mounted on a glass fiber. Measurements were made on a Rigaku AFC-7R diffractometer using the  $\omega$ - $2\theta$  scan technique to a maximum  $2\theta$  value of  $65^\circ$  with graphite-monochromated Mo  $K\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) radiation at  $23^\circ\text{C}$ . The structure was solved by heavy-atom Patterson methods<sup>8</sup> and expanded using Fourier techniques.<sup>9</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement for compound **1** was based on 7045 observed reflections ( $I > 3.00\sigma(I)$ ,  $2\theta < 59.98$ ) and 1000 variable parameters and converged with unweighted and weighted agreement factors of  $R = 0.060$  and  $R_w = 0.082$ . Four water molecules of crystallization were found in the asymmetric unit. These were considered to be loosely trapped in the lattice because of their extremely large thermal parameters. For compound **2**, it was based on 1838 observed reflections ( $I > 3.00\sigma(I)$ ,  $2\theta < 65.08$ ) and 259 variable parameters and converged (largest parameter shift was 0.06 times its esd) with unweighted and weighted agreement factors of  $R = 0.037$  and  $R_w = 0.051$ . One oxygen atom of water was found in a general position, with 0.25 of occupancy. Consequently, the unit cell was found to contain a total of one water molecule. This water molecule (O13) is next to a disordered full molecule of MeOH (C11 and O12), which is coordinated to Cu (Cu3). The thermal parameters of the former are extremely large, however, it was not possible to obtain a model involving disorder over different positions. The electron density corresponding to C11 was spread over a large area and this was modeled with positional disorder over four positions. This can be the first reason why O13 and C11 are seen in abnormal close proximity ( $1.468 \text{ \AA}$ ). It is possible that the position of methanol is in fact partially occupied by water. This could also help to explain the abnormal proximity of O13 and C11. A model contemplating the presence of only two molecules of water (instead of water and methanol) was considered and provided a slightly less satisfactory fit. No further attempts were made to refine the disorder in this position, since this would not provide crucial, new information, relevant to this work. Given the uncertainty associated with the positions of atoms C11, O12 and O13 (due to disorder and large thermal parameters), no hydrogen atoms were allocated to the molecules corresponding to these atoms (neither refined nor with idealized positions). The absolute configurations of compounds **1** and **2** were calculated according to that of the corresponding proline ligand, the absolute configuration of which was known. In each compound, at the stage of locating all of the atoms except for hydrogen, the comparison of  $R$  factors for the two absolute configurations indicated that the absolute configuration based on hpro or pro was reasonable.

CCDC reference numbers 177586 and 179092.

See <http://www.rsc.org/suppdata/dt/b2/b212494g/> for crystallographic data in CIF or other electronic format.

Ultraviolet-visible (UV-vis) absorption and powder diffuse reflection spectra of the samples were recorded on a Hitachi U-3200 spectrophotometer: a 1 cm quartz cell was used for a solution sample, and a standard Hitachi reflection attachment and magnesium oxide (for the standard and a diluent) were used for a powder sample.

Infrared (IR) absorption spectra were obtained by means of a Horiba FT-300 infrared spectrophotometer with the powder diffuse reflection method using silicon as a matrix.

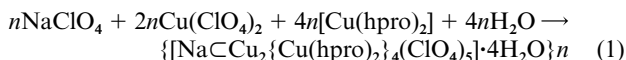
Elemental analysis was performed in house with a Carlo Erba Instruments CHNS-O EA-1108 Elemental Analyzer.

Field cooled measurements of the magnetisation of smoothly powdered microcrystalline samples of **1** (37.13 mg) and **2** (22.35 mg) were performed in the range 300–1.8 K with a Quantum Design MPMS-7XL SQUID magnetometer with an applied field of 1000 G.

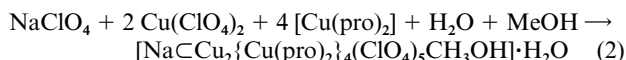
## Results and discussion

### Synthesis

The mixing in methanol of  $\text{NaClO}_4$ ,  $\text{Cu}(\text{ClO}_4)_2$  and  $[\text{Cu}(\text{hpro})_2]$  in the molar ratio 1 : 2 : 4 in the presence of adventitious water produced the coordination polymer *catena*- $[\text{Na}\text{C}\text{Cu}_2\{\text{Cu}(\text{hpro})_2\}_4(\text{ClO}_4)_5]\cdot 4\text{H}_2\text{O}$  (**1**), according to reaction (1).



The structure of this compound (*vide infra*) shows that the complex  $[\text{Cu}(\text{hpro})_2]$  can be successfully used as building block or complex-ligand for the assembly of complicated architectures *via* coordination through the donor atoms that were not bound to Cu in the original mononuclear compound. The stabilization of the cluster is furthered by coordination to  $\text{Na}^+$ . The polymerization is ensured by the dative bonds between the hydroxyl groups of two hpro ligands of one hexanuclear unit and one  $\text{Cu}^{\text{II}}$  ion from each of two neighbouring hexanuclear units. If the reaction is performed by using a L-proline ligand without the hydroxyl group, the discrete complex  $[\text{Na}\text{C}\text{Cu}_2\{\text{Cu}(\text{pro})_2\}_4(\text{ClO}_4)_5\text{CH}_3\text{OH}]\cdot \text{H}_2\text{O}$  (**2**) is obtained [eqn. (2)].



This shows that the supramolecular organization of the unit  $[\text{Cu}_6\text{Na}]$  can be chemically controlled by using the appropriate derivative of the proline ligand. Complex **2** could also be formed from the simple components  $\text{NaClO}_4$ ,  $\text{Cu}(\text{ClO}_4)_2$ , and L-proline (Hpro) in the appropriate molar ratio. This does not preclude the  $[\text{Cu}(\text{pro})_2]$  unit as a building block for the formation of the whole structure, since it may form in solution before the final assembly takes place.

### Description of the structures

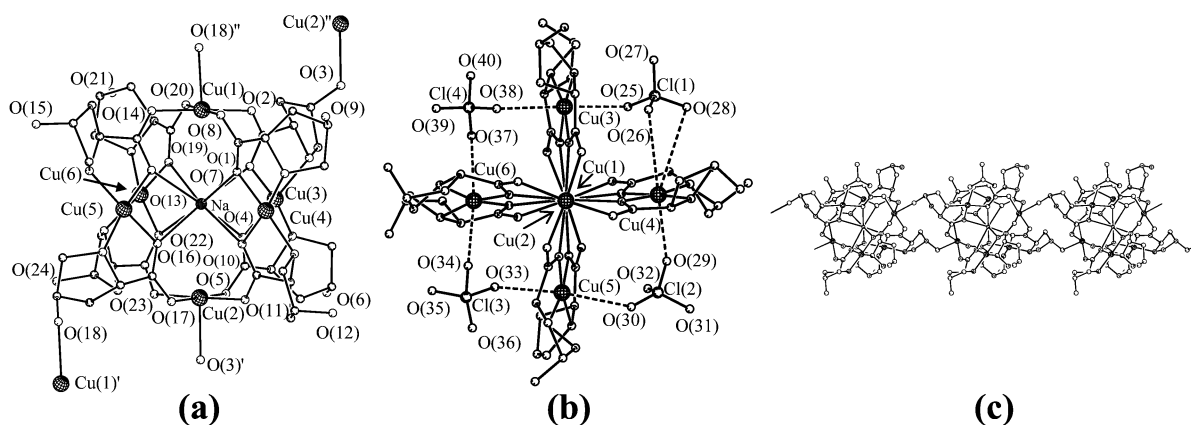
Crystal, data collection and refinement parameters for compounds **1** and **2** are given in Table 1 and selected interatomic distances and bond angles are collected in Tables 2 and 3, respectively.

*catena*- $[\text{Na}\text{C}\text{Cu}_2\{\text{Cu}(\text{hpro})_2\}_4(\text{ClO}_4)_5]\cdot 4\text{H}_2\text{O}$  (**1**). Fig. 1(a and b) shows the structure of the repeating unit of **1**. In the barrel portion,  $[\text{Na}\text{C}\text{Cu}_2\{\text{Cu}(\text{hpro})_2\}_4]^{5+}$ ,  $\text{Na}^+$  is trapped in the center. The central metal ion is surrounded by eight carboxylate oxygen atoms which link it to the copper atoms of four  $[\text{Cu}(\text{hpro})_2]$  units. These four units provide in turn the square planar environment of two further  $\text{Cu}^{\text{II}}$  centers *via* the other carboxylate oxygen atoms from hpro. The six  $\text{Cu}^{\text{II}}$  centers of this repeating cluster form an octahedron with idealized  $D_{4h}$  symmetry, the sodium ion being therefore approximately octahedrally surrounded by copper. Two hydroxyl groups of hpro are coordinated to the (axial) Cu(1) and Cu(2) centers of two neighboring barrel units, respectively, thereby completing their square pyramidal coordination geometry and providing the link for a chain of clusters as shown in Fig. 1(c). Four of five perchlorate ions lie between the propellers formed by the four  $[\text{Cu}(\text{hpro})_2]$  units as shown in Fig. 1(b). Because of the linkage between  $[\text{Cu}_6]$  units, the barrel structure in **1** is distorted and these four perchlorate ions are, therefore, not symmetrically equivalent. Two oxygen atoms from three of these ions are weakly coordinated to two Cu centers from  $[\text{Cu}(\text{hpro})_2]$  units, occupying the axial positions of their tetragonally elongated octahedral environment. The fourth  $\text{ClO}_4^-$  ion, however, binds to one Cu through two of its oxygen atoms, and to another with one O-donor. The fifth  $\text{ClO}_4^-$  ion is on a general position between the chains. Several water

**Table 1** Experimental data for the X-ray diffraction studies of *catena*-[NaCu<sub>2</sub>{Cu(hpro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub>·4H<sub>2</sub>O (**1**) and [NaCu<sub>2</sub>{Cu(hpro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub>·CH<sub>3</sub>OH]·H<sub>2</sub>O (**2**)

	<b>1</b>	<b>2</b>
Formula	Cu <sub>6</sub> NaCl <sub>5</sub> O <sub>48</sub> N <sub>8</sub> C <sub>40</sub> H <sub>72</sub>	Cu <sub>6</sub> NaCl <sub>5</sub> O <sub>38</sub> N <sub>8</sub> C <sub>41</sub> H <sub>70</sub>
FW/g mol <sup>-1</sup>	2014.56	1864.57
Crystal system	Monoclinic	Tetragonal
Space group	<i>P</i> 2 <sub>1</sub> (#4)	<i>I</i> 4 (#79)
<i>a</i> /Å	11.746(2)	13.708(1)
<i>b</i> /Å	24.872(4)	–
<i>c</i> /Å	13.064(2)	18.078(2)
$\beta$ /°	96.58(1)	–
<i>V</i> /Å <sup>3</sup>	3791.5(9)	3397.1(6)
<i>T</i> /°C	23.0	23.0
<i>Z</i>	2	2
$\mu$ (Mo K $\alpha$ )/cm <sup>-1</sup>	19.41	21.48
Unique data	11284	3177
Unique data with <i>I</i> > 3 $\sigma$ ( <i>I</i> )	7045	1838
<i>R</i> , <i>R</i> <sub>w</sub> <sup>a</sup>	0.060, 0.082	0.037, 0.051

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [(\sum w (|F_o| - |F_c|)^2) / \sum w F_o^2]^{1/2}.$$



**Fig. 1** PLATON representations at 30% probability level of *catena*-[NaCu<sub>2</sub>{Cu(hpro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub>·4H<sub>2</sub>O (**1**). (a) Barrel structure and atom-numbering scheme; (b) projection of the barrel along the direction piercing through Cu(1) and Cu(2); (c) binding of the hexanuclear units within the polymeric chain. Symmetry transformation used to generate equivalent atoms: ' 1 + *x*, *y*, *z*;' -1 + *x*, *y*, *z*.

molecules with very large thermal parameters have been found crystallographically in between the polymer chains.

[NaCu<sub>2</sub>{Cu(pro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub>·CH<sub>3</sub>OH]·H<sub>2</sub>O (**2**). Figs. 2 and 3 show the structure of the discrete cluster **2**. The cluster ion [NaCu<sub>2</sub>{Cu(pro)<sub>2</sub>}<sub>4</sub>]<sup>5+</sup> is essentially the same as the barrel portion of **1**. It shows one Na<sup>+</sup> ion trapped in the center linked to the copper atoms of four [Cu(pro)<sub>2</sub>] units *via* eight oxygen donors from the L-prolinato ligands. As in **1**, these four copper atoms form an octahedron along with two further Cu<sup>II</sup> centers. The symmetry of the [Cu<sub>6</sub>] octahedron, *D*<sub>4h</sub>, is higher than in the cluster polymer **1**. This is because of the linkages between neighboring barrel portions in the polymeric compound. In **2**, the prolinato ligands have no hydroxyl groups and the axial Cu ions [Cu(2) and Cu(3)] are coordinated to a disordered perchlorate ion and a methanol molecule, respectively, thereby completing their square pyramidal coordination geometry. The ClO<sub>4</sub><sup>-</sup> and CH<sub>3</sub>OH ligands lie on a crystallographic *C*<sub>4</sub> axis [Fig. 2(a)]. As in the barrel portion of **1**, four perchlorate ions lie between the propellers formed by the four [Cu(pro)<sub>2</sub>] units of **2**, and in this case are symmetrically equivalent, as shown in Fig. 2(c). Two oxygen atoms from each perchlorate ion are weakly coordinated to the Cu centers of two [Cu(pro)<sub>2</sub>] units, lying on the two long axes of their distorted octahedral geometry. The structural similarity between **1** and **2** is consistent with the resemblance of their respective infrared spectra.

In cluster-polymer **1**, the average Cu–O and Cu–N bond distances within the [Cu(pro)<sub>2</sub>] unit are 1.942 and 2.006 Å, respectively. They are slightly longer than the corresponding average distances of cluster **2**: Cu–O = 1.933 Å and Cu–N =

1.994 Å. The mean Na–O distance in **1** (2.563 Å) is also slightly longer than that in **2** (2.546 Å). Reflecting this, the size of the octahedron formed by six copper atoms in **1** is slightly larger than that of **2**: the average diagonal lengths are 7.085 and 7.035 Å, for the octahedra of **1** and **2**, respectively. The remaining Cu···Cu distances are also slightly longer in **1** than in **2**. However, in **1**, the mean Cu–O<sub>eq</sub> bond distances of the unique Cu centers (1.951 Å) are shorter than in **2** (1.961 Å). In **1**, two hydroxyl groups from hpro are coordinated to the (axial) Cu(1) and Cu(2) centers of two neighboring barrel units with an average bond distance of Cu–O<sub>OH</sub> = 2.312 Å. The bond distances for the corresponding axial positions in **2** are Cu–O = 2.22 Å (CH<sub>3</sub>OH) and Cu–O = 2.39 Å (perchlorate).

The structure of the [Cu<sub>6</sub>] unit in discrete barrel cluster and that in the cluster polymer appear stable in a solution since the UV-vis spectra of the solutions exactly reproduce these from the powder diffuse reflection.

An important question to elucidate in order to understand the self-assembly process leading to **1** and **2**, is whether the [Cu<sub>2</sub>{Cu(chelate)<sub>2</sub>}<sub>4</sub>]<sup>4+</sup> (chelate = hpro or pro) cage is rigid enough to bind Na<sup>+</sup> selectively, or other cations can be trapped in its central cavity. Thus, the reaction described by eqn. (2) was repeated in the presence of excess Li<sup>+</sup> and/or K<sup>+</sup>. In all cases, only the Na<sup>+</sup>-cluster (**2**) could be crystallized. This result implies that Li<sup>+</sup> is too small to be accommodated in the cluster whereas K<sup>+</sup> is too large: the ionic radii (8-coordination) of Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> are 1.06, 1.32 and 1.65 Å, respectively.<sup>10</sup> On the other hand, however, a certain degree of flexibility is allowed since the analogous reaction using Ag<sup>+</sup> (ionic radius = 1.41 Å) instead of Na<sup>+</sup> leads to the silver version of **2**, *i.e.* [AgCu<sub>2</sub>-

**Table 2** Selected interatomic distances (Å) for compounds **1** and **2**<sup>a</sup>

Complex 1			
Cu(1)–O(18)''	2.306(8)	Cu(5)–O(33)	2.73(2)
Cu(1)–O(2)	1.975(7)	Cu(6)–O(34)	2.67(3)
Cu(1)–O(8)	1.904(8)	Cu(6)–O(37)	2.77(1)
Cu(1)–O(14)	1.944(7)	Na–O(1)	2.535(8)
Cu(1)–O(20)	1.988(8)	Na–O(4)	2.608(9)
Cu(2)–O(3)'	2.318(7)	Na–O(7)	2.579(9)
Cu(2)–O(5)	1.998(7)	Na–O(10)	2.511(9)
Cu(2)–O(11)	1.918(7)	Na–O(13)	2.592(9)
Cu(2)–O(17)	1.908(7)	Na–O(16)	2.536(8)
Cu(2)–O(23)	1.975(7)	Na–O(19)	2.553(9)
Cu(3)–N(1)	2.007(7)	Na–O(22)	2.586(9)
Cu(3)–N(2)	2.058(9)	Cu(1) ⋯ Cu(3)	5.070(2)
Cu(4)–N(3)	1.978(9)	Cu(1) ⋯ Cu(4)	4.932(2)
Cu(4)–N(4)	1.987(9)	Cu(1) ⋯ Cu(5)	4.970(2)
Cu(5)–N(5)	1.977(8)	Cu(1) ⋯ Cu(6)	4.993(2)
Cu(5)–N(6)	1.986(8)	Cu(2) ⋯ Cu(3)	4.977(2)
Cu(6)–N(7)	2.022(10)	Cu(2) ⋯ Cu(4)	5.053(2)
Cu(6)–N(8)	2.031(10)	Cu(2) ⋯ Cu(5)	4.993(2)
Cu(3)–O(1)	1.918(7)	Cu(2) ⋯ Cu(6)	4.980(2)
Cu(3)–O(4)	1.944(6)	Cu(1) ⋯ Cu(2)	6.998(2)
Cu(4)–O(7)	1.944(7)	Cu(3) ⋯ Cu(5)	7.147(2)
Cu(4)–O(10)	1.992(7)	Cu(4) ⋯ Cu(6)	7.111(2)
Cu(5)–O(13)	1.939(7)	Cu(3) ⋯ Cu(4)	4.954(2)
Cu(5)–O(16)	1.967(7)	Cu(3) ⋯ Cu(6)	5.023(2)
Cu(6)–O(19)	1.909(8)	Cu(4) ⋯ Cu(5)	5.283(2)
Cu(6)–O(22)	1.930(7)	Cu(5) ⋯ Cu(6)	4.903(2)
Cu(3)–O(25)	2.57(2)	Na ⋯ Cu(1)	3.511(5)
Cu(3)–O(38)	2.70(1)	Na ⋯ Cu(2)	3.487(5)
Cu(4)–O(29)	2.57(2)	Na ⋯ Cu(3)	3.570(5)
Cu(4)–O(26)	3.51(4)	Na ⋯ Cu(4)	3.572(5)
Cu(4)–O(28)	3.58(2)	Na ⋯ Cu(5)	3.579(5)
Cu(5)–O(30)	2.77(3)	Na ⋯ Cu(6)	3.541(5)

Complex 2			
Cu(2)–O(9)	2.39(1)	Na–O(3)	2.543(6)
Cu(2)–O(2)	1.955(5)	Cu(1) ⋯ Cu(2)	4.953(1)
Cu(3)–O(12)	2.22(1)	Cu(1) ⋯ Cu(3)	4.995(1)
Cu(3)–O(4)	1.967(4)	Cu(2) ⋯ Cu(3)	7.011(1)
Cu(1)–N(1)	1.995(5)	Cu(1) ⋯ Cu(1)''	7.058(1)
Cu(1)–N(2)	1.992(5)	Cu(1) ⋯ Cu(1)''	4.9906(8)
Cu(1)–O(1)	1.926(4)	Cu(1) ⋯ Cu(1)'	4.9906(7)
Cu(1)–O(3)	1.940(4)	Na ⋯ Cu(2)	3.490(7)
Cu(1)–O(5)	2.721(9)	Na ⋯ Cu(3)	3.521(7)
Cu(1)–O(6)'	2.78(1)	Na ⋯ Cu(1)	3.5289(6)
Na–O(1)	2.549(5)		

<sup>a</sup> Symmetry transformation used to generate equivalent atoms: see Fig. 1 and 2.

{Cu(pro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub>CH<sub>3</sub>OH]·H<sub>2</sub>O, as shown by X-ray diffraction data.<sup>11</sup> Another interesting result is the fact that the Na<sup>+</sup>-cluster **2** is again the only compound that crystallizes in the presence of excess Ca<sup>2+</sup>, La<sup>3+</sup> or Lu<sup>3+</sup>, which have ionic radii (1.26, 1.4 and 1.2 respectively)<sup>10</sup> similar to that of Na<sup>+</sup>. This outcome is interpreted in terms of the lack of a suitable way to arrange efficiently the various charged species of the system when the central cation has a charge different than +1. In the complex [NaCCu<sub>2</sub>{Cu(pro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>5</sub>CH<sub>3</sub>OH]·H<sub>2</sub>O (**2**), four of its five perchlorate anions fit perfectly in between the propellers of the cage, where they coordinate to copper. The fifth ClO<sub>4</sub><sup>−</sup> group also acts as a ligand but it is bound to one of the two axial Cu<sup>II</sup> ions of the [Cu<sub>6</sub>] octahedron, thereby giving place to a linear succession of alternating positive and negative species, namely (ClO<sub>4</sub>)<sup>−</sup> and [NaCCu<sub>2</sub>{Cu(pro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>4</sub>CH<sub>3</sub>OH]<sup>+</sup>, along the crystallographic C<sub>4</sub> axis [see Fig. 2(a) and Fig. 3]. Increasing the charge of the central unit would require the presence of a larger number of anions, which would disrupt the organization in the crystal lattice observed in **2**. A noteworthy result supporting this hypothesis is the preliminary structural determination of the compound [CaCCu<sub>2</sub>{Cu(pro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>4</sub>(SO<sub>4</sub>)CH<sub>3</sub>OH]·H<sub>2</sub>O obtained from a reaction similar to that of

**Table 3** Selected bond angles (°) for compounds **1** and **2**<sup>a</sup>

Complex 1			
O(2)–Cu(1)–O(8)	89.9(3)	O(19)–Cu(6)–N(7)	86.3(4)
O(2)–Cu(1)–O(18)''	96.2(3)	O(19)–Cu(6)–N(8)	167.7(4)
O(2)–Cu(1)–O(20)	85.9(3)	O(22)–Cu(6)–N(7)	167.8(3)
O(8)–Cu(1)–O(14)	94.3(4)	O(22)–Cu(6)–N(8)	85.1(3)
O(8)–Cu(1)–O(18)''	91.3(3)	N(7)–Cu(6)–N(8)	100.9(4)
O(14)–Cu(1)–O(18)	86.6(3)	O(25)–Cu(3)–O(38)	175.5(4)
O(14)–Cu(1)–O(20)	89.9(4)	O(29)–Cu(4)–O(26)	157.3(7)
O(18)''–Cu(1)–O(20)	89.9(3)	O(29)–Cu(4)–O(28)	154.3(6)
O(2)–Cu(1)–O(14)	174.9(3)	O(33)–Cu(5)–O(30)	170.0(10)
O(8)–Cu(1)–O(20)	175.7(4)	O(34)–Cu(6)–O(37)	172.1(7)
O(3)′–Cu(2)–O(5)	85.0(3)	O(1)–Na–O(4)	63.3(2)
O(3)′–Cu(2)–O(11)	91.7(3)	O(1)–Na–O(7)	72.8(3)
O(3)′–Cu(2)–O(17)	94.6(3)	O(1)–Na–O(10)	97.7(3)
O(3)′–Cu(2)–O(23)	89.3(3)	O(1)–Na–O(13)	117.9(3)
O(5)–Cu(2)–O(11)	89.5(3)	O(1)–Na–O(16)	174.3(3)
O(5)–Cu(2)–O(23)	87.3(3)	O(1)–Na–O(19)	73.8(3)
O(11)–Cu(2)–O(17)	94.4(3)	O(1)–Na–O(22)	112.5(3)
O(17)–Cu(2)–O(23)	88.8(3)	O(7)–Na–O(7)	113.0(3)
O(5)–Cu(2)–O(17)	176.1(3)	O(4)–Na–O(10)	73.8(3)
O(11)–Cu(2)–O(23)	176.5(3)	O(4)–Na–O(13)	169.2(3)
O(1)–Cu(3)–O(4)	88.6(3)	O(4)–Na–O(16)	116.0(3)
O(1)–Cu(3)–N(1)	86.5(3)	O(4)–Na–O(19)	98.0(3)
O(1)–Cu(3)–N(2)	168.5(3)	O(4)–Na–O(22)	73.5(3)
O(4)–Cu(3)–N(1)	173.1(3)	O(7)–Na–O(10)	64.7(3)
O(4)–Cu(3)–N(2)	84.5(3)	O(7)–Na–O(13)	76.8(3)
N(1)–Cu(3)–N(2)	101.0(3)	O(7)–Na–O(16)	103.0(3)
O(7)–Cu(4)–O(10)	87.5(3)	O(7)–Na–O(19)	115.6(3)
O(7)–Cu(4)–N(3)	86.3(3)	O(7)–Na–O(22)	173.3(3)
O(7)–Cu(4)–N(4)	170.7(4)	O(10)–Na–O(13)	115.8(3)
O(10)–Cu(4)–N(3)	173.4(3)	O(10)–Na–O(16)	76.9(3)
O(10)–Cu(4)–N(4)	84.2(3)	O(10)–Na–O(19)	170.4(3)
N(3)–Cu(4)–N(4)	102.2(4)	O(10)–Na–O(22)	117.3(3)
O(13)–Cu(5)–O(16)	88.1(3)	O(13)–Na–O(16)	63.9(2)
O(13)–Cu(5)–N(5)	85.5(3)	O(13)–Na–O(19)	72.8(3)
O(13)–Cu(5)–N(6)	171.2(3)	O(13)–Na–O(22)	96.9(3)
O(16)–Cu(5)–N(5)	169.8(3)	O(16)–Na–O(19)	111.8(3)
O(16)–Cu(5)–N(6)	85.9(3)	O(16)–Na–O(22)	71.9(3)
N(5)–Cu(5)–N(6)	101.3(3)	O(19)–Na–O(22)	63.7(3)
O(19)–Cu(6)–O(22)	89.9(3)		

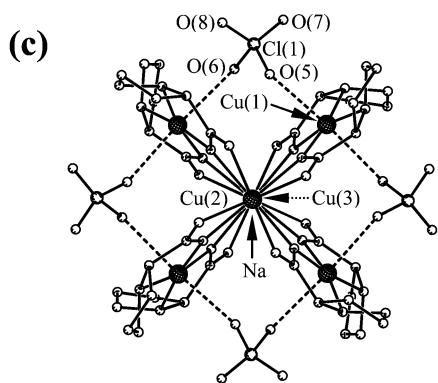
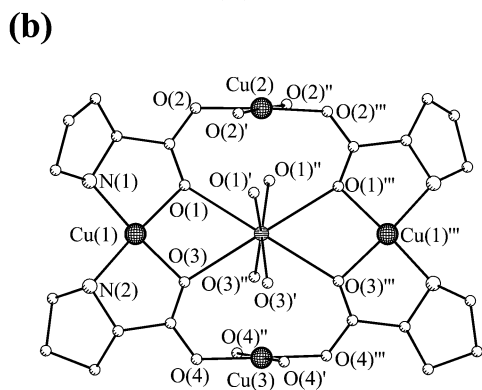
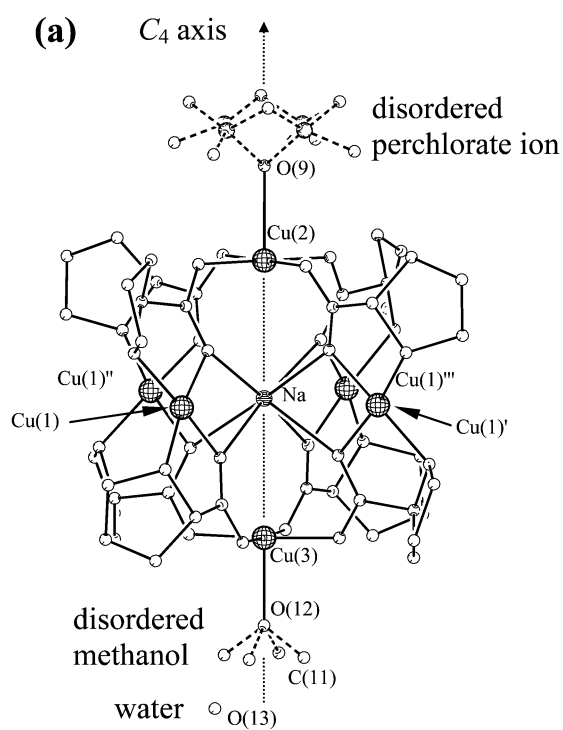
  

Complex 2			
O(2)–Cu(2)–O(2)''	89.999(1)	N(1)–Cu(1)–N(2)	99.6(2)
O(2)–Cu(2)–O(9)	90.2(1)	O(5)–Cu(1)–O(6)'	173.4(4)
O(2)–Cu(2)–O(2)'''	179.6(3)	O(1)–Na–O(1)'''	116.1(3)
O(4)–Cu(3)–O(4)''	89.968(7)	O(1)–Na–O(1)''	73.7(1)
O(4)–Cu(3)–O(12)	91.4(1)	O(1)–Na–O(1)'	73.7(1)
O(4)–Cu(3)–O(4)'''	177.3(2)	O(1)–Na–O(3)	64.5(1)
O(1)–Cu(1)–O(3)	89.3(1)	O(1)–Na–O(3)'''	171.2(1)
O(1)–Cu(1)–N(1)	86.2(2)	O(1)–Na–O(3)''	114.1(1)
O(1)–Cu(1)–N(2)	172.3(2)	O(1)–Na–O(3)'	98.6(1)
O(1)–Cu(1)–O(5)	79.0(2)	O(3)–Na–O(3)'''	116.4(3)
O(1)–Cu(1)–O(6)'	94.6(4)	O(3)–Na–O(3)''	73.9(1)
O(3)–Cu(1)–N(1)	169.1(2)	O(3)–Na–O(3)'	73.9(1)
O(3)–Cu(1)–N(2)	85.9(2)		

<sup>a</sup> Symmetry transformation used to generate equivalent atoms: see Fig. 1 and 2.

eqn. (1), using CaSO<sub>4</sub> instead of NaClO<sub>4</sub>.<sup>11</sup> In this complex, the SO<sub>4</sub><sup>2−</sup> anions occupy the same position as the fifth ClO<sub>4</sub><sup>−</sup> group of **2** and therefore, the alternative succession of positive and negative charges (this time [CaCCu<sub>2</sub>{Cu(pro)<sub>2</sub>}<sub>4</sub>(ClO<sub>4</sub>)<sub>4</sub>CH<sub>3</sub>OH]<sup>2+</sup> and SO<sub>4</sub><sup>2−</sup>, respectively) is preserved in this new compound. The cage trapping a suitable M<sup>2+</sup> cation in the center (Ca<sup>2+</sup>) can thus be observed.

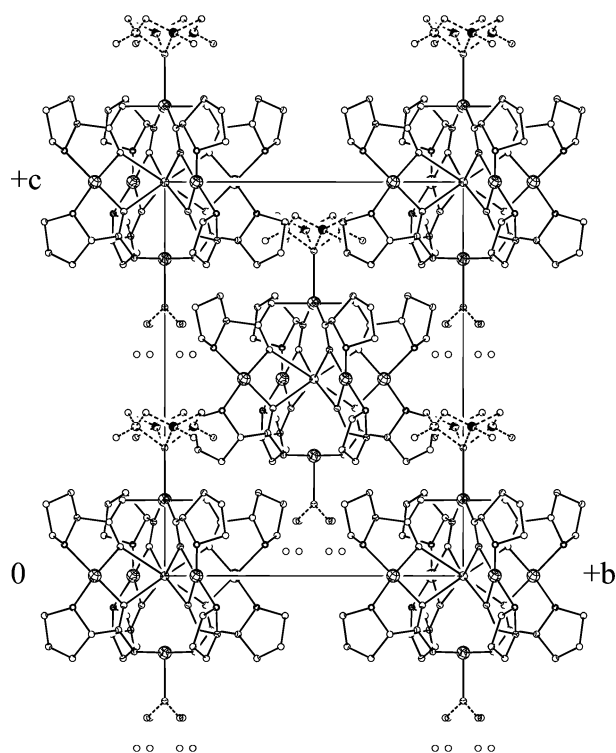
The experimental work described above has provided food for discussion about two important questions to be considered regarding the process of self-assembly of complicated chemical architectures. The first is the decisive role played by the specific geometrical requirements of the various components. The second is the necessity for a suitable way of accommodating the different species of the assembly during their supramolecular arrangement into a superior structure, such as a crystal lattice.



**Fig. 2** PLATON representation at 30% probability level of  $[\text{NaCu}_2\{\text{Cu}(\text{pro})_2\}_4(\text{ClO}_4)_5\text{CH}_3\text{OH}]\cdot\text{H}_2\text{O}$  (**2**): (a) barrel structure; (b) atom-numbering scheme; (c) projection of the barrel along the  $C_4$  axis. Symmetry transformation used to generate equivalent atoms: '  $y, -x, z$ ; ''  $-y, x, z$ ; '''  $-x, -y, z$ .

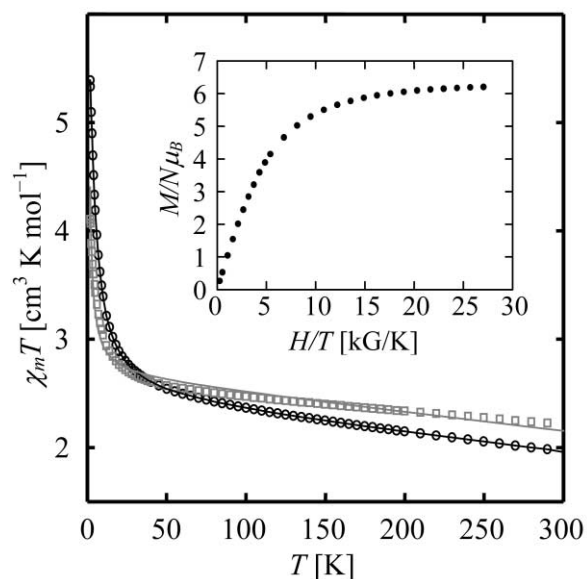
### Magnetochemistry

In a previous communication<sup>6</sup> we have reported on the ferromagnetic exchange between  $\text{Cu}^{\text{II}}$  centers exhibited by the cluster polymer *catena*- $[\text{NaCu}_2\{\text{Cu}(\text{hpro})_2\}_4(\text{ClO}_4)_5\text{CH}_3\text{OH}]\cdot\text{H}_2\text{O}$  (**1**). The synthesis of the complex  $[\text{NaCu}_2\{\text{Cu}(\text{pro})_2\}_4(\text{ClO}_4)_5\text{CH}_3\text{OH}]\cdot\text{H}_2\text{O}$  (**2**) afforded the possibility to study how the magnetic



**Fig. 3** Crystal packing of **2**.

behavior of the  $[\text{Cu}_6]$  unit in the discrete cluster compares to when it is found as part of a cluster polymer. To this end, bulk magnetization data were collected from microcrystalline samples of compounds **1** and **2**, in the 1.8–300 K temperature range under a constant magnetic field of 1000 G. In Fig. 4 are plots of the experimental data in the form of  $\chi_m T$  vs.  $T$  per  $[\text{Cu}_6]$  unit, where  $\chi_m$  is the molar magnetic susceptibility, as calculated without correcting for the diamagnetic contribution of the compounds. Both sets of data are very similar, showing a slight monotonic increase of the product  $\chi_m T$  upon cooling over most of the temperature range, followed by a much sharper increase below *ca.* 30 K. The behavior at the higher temperature regime is consistent with a system of six magnetically independent  $\text{Cu}^{\text{II}}$  centers, affected in form of a small negative slope by the diamagnetic response of the sample. Indeed, at 300 K, the



**Fig. 4** Plot of experimental  $\chi_m T$  vs.  $T$  for compounds **1** (circles) and **2** (squares). The solid lines are fits to the experimental values (see text for details). In the inset are  $M/N\mu_B$  vs.  $H/T$  plots for **1** (circles) indicating the spin ground state,  $S_T = 3$ .

paramagnetic molar susceptibilities,  $\chi_m'$ , obtained by correcting the experimental values for the diamagnetic contribution (*vide infra*) are for **1/2**, 2.55/2.72 cm<sup>3</sup> K mol<sup>-1</sup> (please note the **1/2** format), close to the value calculated for six non-interacting  $S = 1/2$  centers with  $g = 2.1$  (2.48 cm<sup>3</sup> K mol<sup>-1</sup>). The abrupt increase at low temperature (up to  $\chi_m' = 5.39/4.11$  cm<sup>3</sup> K mol<sup>-1</sup>) is indicative of weak ferromagnetic coupling between the paramagnetic centers of the [Cu<sub>6</sub>] unit.

In order to obtain a better description of these exchange-coupled systems, a magnetic susceptibility theoretical equation,  $\chi_m = f(T)$ , was fit to the experimental data. In this function, the experimental susceptibility,  $\chi_m$ , was modeled with both, a paramagnetic and a diamagnetic contribution, *i.e.*  $\chi_m = \chi_m(\text{dia}) + \chi_m'$ . The (constant) value of  $\chi_m(\text{dia})$  was optimized during the fitting procedure, whereas a function for  $\chi_m'$  was obtained from the Van Vleck equation<sup>12</sup> as derived by use of the spin energies arising from the following Heisenberg Spin-Hamiltonian [eqn. (3)].

$$H = -2J(S_1 + S_2)(S_3 + S_4 + S_5 + S_6) \quad (3)$$

In the above Hamiltonian,  $S_i$  are the spin operators of each Cu<sup>II</sup> center (thus,  $S_i = 1/2$ ) and for both compounds, the numbering scheme used is the same as in Fig. 1. In this model it is therefore assumed that the only significant spin-spin interaction in both systems is the coupling between the axial Cu<sup>II</sup> centers (Cu1 and Cu2) and the equatorial Cu<sup>II</sup> ions of the hexanuclear unit. Given the idealized symmetry of this unit (*ca.*  $D_{4h}$ ), all such interactions are considered equivalent and therefore, described by a unique exchange parameter,  $J$ . Under these conditions, the Spin-Hamiltonian describing **1** and **2** can be solved by use of the Kambe vector coupling method,<sup>13</sup> which originates a total of 20 spin states ranging spin values from 0 to 3 with energies given by eqn. (4). For this, the transformations of spin angular momentum operators in eqn. (5), (6) and (7) have been taken into account.

$$E(S_T, S_A, S_B) = -J[S_T(S_T + 1) - S_A(S_A + 1) - S_B(S_B + 1)] \quad (4)$$

$$S_A = S_1 + S_2 \quad (5)$$

$$S_B = S_3 + S_4 + S_5 + S_6 \quad (6)$$

$$S_T = S_A + S_B \quad (7)$$

Given the ferromagnetic nature of the coupling, the use of this model implies that compounds **1** and **2** are formed by magnetically independent [Cu<sub>6</sub>] units with spin ground state  $S_T = 3$ , corresponding to the (3,1,2) state in the ( $S_T, S_A, S_B$ ) notation, and a triply degenerate first excited state of  $S = 2$ , (2,1,1),  $2J$  cm<sup>-1</sup> higher in energy. The best least-squares fit to the experimental data (Fig. 4, solid lines) was obtained with the following parameters (in the **1/2** format):  $\chi_m(\text{dia}) = 1.98/1.72$  (10<sup>-3</sup> cm<sup>3</sup> mol<sup>-1</sup>),  $g = 2.11/2.17$  and  $J = 1.39/0.56$  (cm<sup>-1</sup>). A ground state  $S_T = 3$  was therefore assigned to both compounds. Attempts to fit the data by including a term  $zJ'$  for inter-cluster interactions<sup>14</sup> ( $z$  is the number of neighbouring clusters and  $J'$  is the inter-cluster coupling constant) gave place to negligible values of  $zJ'$  and larger errors, which indicates that the Cu<sub>6</sub> clusters are quasi-isolated from each other magnetically, even in the polymer **1**. Consistent with the assignment of an  $S_T = 3$  ground state were the variable field magnetization data obtained from the chain complex **1** at 1.9 K, in the 0.5–50 kG range. In the inset of Fig. 4 is a plot of the experimental data (corrected for diamagnetism) in the form of  $M/N\mu_B$  (reduced magnetisation) *vs.*  $H/T$ . The reduced magnetization grows with increasing field to reach saturation at a value near 6.2, which is very close to the saturation value expected for an  $S = 3$  state with  $g = 2.11$  (6.3).

Ferromagnetic exchange between Cu<sup>II</sup> centers is much more rare than antiferromagnetic coupling. This is because the latter is comparatively stronger than the former and it dominates the exchange when mechanisms for both types of interaction coexist. In a few cases, however, the spin delocalization mechanism for the exchange vanishes because the symmetry of the system causes the orthogonality between the magnetic orbitals. In such situation, spin polarization, leading to parallel alignment of spins might be the only mechanism left for the coupling, resulting in ferromagnetism. In complexes **1** and **2**, the magnetic orbitals are the  $d_{x^2-y^2}$  orbitals of the Cu<sup>II</sup> centers, since they all display tetragonally elongated coordination geometry. As a result of the geometry of the [Cu<sub>6</sub>] unit, the magnetic orbitals of all the adjacent Cu<sup>II</sup> centers are perpendicular to each other. Thus, the Cu centers in axial position of the [Cu<sub>6</sub>] polyhedron, Cu(1) and Cu(2), have their magnetic orbitals perpendicular to these of the equatorial Cu ions, and so do the equatorial Cu centers that are mutually in *cis* position. This clearly favours the orthogonality between magnetic orbitals from paramagnetic metal ions that are likely to interact. This is consistent with the presence of weak ferromagnetic exchange within clusters **1** and **2**.

Compounds **1** and **2** are among the few Cu<sup>II</sup> polynuclear aggregates with spin ground state  $S > 1$ . Outstanding examples are the complexes [Cu<sub>6</sub>(bpy)<sub>10</sub>(μ-CO<sub>3</sub>)<sub>2</sub>(μ-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>6</sub>·4H<sub>2</sub>O (bpy = 2,2'-bipyridine;  $S_T = 3$ ),<sup>15</sup> [Cu<sub>7</sub>(OH)<sub>8</sub>(bpym)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>6+</sup> (bpym = 2,2'-bipyrimidine;  $S_T = 7/2$ ),<sup>16</sup> or [Cu<sub>9</sub>(2poap-H)<sub>6</sub>](NO<sub>3</sub>)<sub>12</sub>·9H<sub>2</sub>O (2poap is a flexible polynucleating ligand containing diazines, pyridyl and hydroxyl groups;  $S_T = 7/2$ ).<sup>17</sup> The prospect of extending the self assembly processes presented here to nuclei of higher susceptibility is very attractive and the opportunity to reproduce the synthesis including more highly charged species as central cations might prove very interesting from the theoretical point of view.

## Conclusions

In this paper, the high-yield preparations of a discrete cluster and a coordination polymer containing a [Na<sup>I</sup>Cu<sup>II</sup>]<sub>6</sub> structural unit have been reported. Both compounds have resulted from the self-assembly of four square planar complex-ligands of the type [Cu(pro)<sub>2</sub>] with the metal acceptors Cu<sup>II</sup> and Na<sup>I</sup>. The polymerization of the heterometallic unit into 1D-chains has been achieved by using a derivative of the L-prolinato ligand possessing an additional hydroxyl group. This function ensures the linking between the [Na<sup>I</sup>Cu<sup>II</sup>]<sub>6</sub> clusters *via* coordination to the axial Cu<sup>II</sup> centers. Bulk magnetization studies have shown that the individual spin moments within the hexacopper units are ferromagnetically coupled as a result of the orthogonality between interacting magnetic orbitals. This yields an  $S = 3$  ground state for the [Cu<sub>6</sub>] moieties, which in both compounds are magnetically isolated from each other. The new coordination aggregates presented here are among the very few examples of Cu<sup>II</sup> clusters with an  $S > 1$  spin ground state. This highlights the feasibility of a stepwise approach for the preparation of interesting magnetic materials using preformed building blocks.<sup>18</sup>

## Acknowledgements

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