A new 2D network built from potassium sandwiches {K[Cu$^{II}_3$(bdap)$_3$]$_2$} and {(μ$_{1,3}$-SCN)$_3$Cu^I(NCS)} anions: structure and magnetic behaviour†

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The addition of a solution of excess K(SCN) to an aqueous solution containing Cu(NO$_3$)$_2$·6H$_2$O and 1,3-bis(amino)-2-propanol (bdapH) yields a novel 2D mixed Cu^I–Cu^{II} complex; X-ray diffraction and magnetic studies are reported herein.

Construction of metal-based molecular aggregates is currently of great interest to many research groups, not only in the area of supramolecular chemistry but also in the coordination chemistry field.[1] This may be attributed largely to the potential application of coordination polymers in many areas. Most of the time, the contemporary challenge is to produce new compounds with interesting molecular architectures and magnetic properties.[2] For this, rational synthetic design for the tuning of the solid state structure is important. Typical synthetic routes to create metalloaggregates are the metal-directed self-assembly of multidentate organic compounds that connect two or more metal centres. One of the standard strategies to obtain systems of this type involves the coordination of polytopic ligands containing anchoring N-donor atoms (usually N-pyridinic, but also aliphatic amines) and alkoxo units that are able to act as a bridge between two or three metals. Recently,[3] we have reported that aminated ligands such as 1,3-bis(amino)-2-propanolato (bdap) or 1,3-bis(dimethylamino)-2-propanolato (bdmap) (Scheme 1) can be used to generate high nuclearity derivatives. The aminoalcohol bdapH has three binding sites: two neutral amino groups and one hydroxyl group which can be deprotonated readily to bind to two metal ions. Each metal ion still has several free coordination positions that can be used by means of an appropriate ligand to connect to other similar units and increase the nuclearity of the complex.

In this context, by reacting copper sources with 1,3-bis(amino)-2-propanol and potassium thiocyanate, we wanted to synthesize a

new compound with high nuclearity following our work directed towards the investigation of molecular magnetic systems.[3] However, we unexpectedly obtained small amounts of {[KCu$^{II}_6$(bdap)$_6$(μ$_{1,3}$-SCN)$_3$Cu^I(NCS)](SCN)$_4$}$_n$ (1), an unusual infinite 2D compound as shown by single-crystal X-ray diffraction. We repeated the experiment‡ introducing some changes in the process of the reaction and we were able to isolate the product 1 in high yield. Herein we report the spontaneous self-assembly and crystal structure of compound 1 as well as investigations on its magnetic behaviour.

The structure of 1 is made up of a potassium cation sandwiched between two triangular tricopper(II) units (Fig. 1), connected to six similar adjacent sandwiches by [(μ$_{1,3}$-SCN)$_3$Cu^I(NCS)]$^{3-}$ groups to form an infinite 2D network structure (Fig. 2).§ The positive charge of the {K[Cu$^{II}_3$O$_3$]$_2$[Cu^I(SCN)$_4$]}$^{4+}$ unit is compensated by four free thiocyanate anions.

The Cu(II) atoms in each triangular unit are bridged by the bdap ligand through an oxygen and two nitrogen atoms. The nearest-neighbour Cu···Cu distances vary between 3.294(1) and 3.607(1) Å.
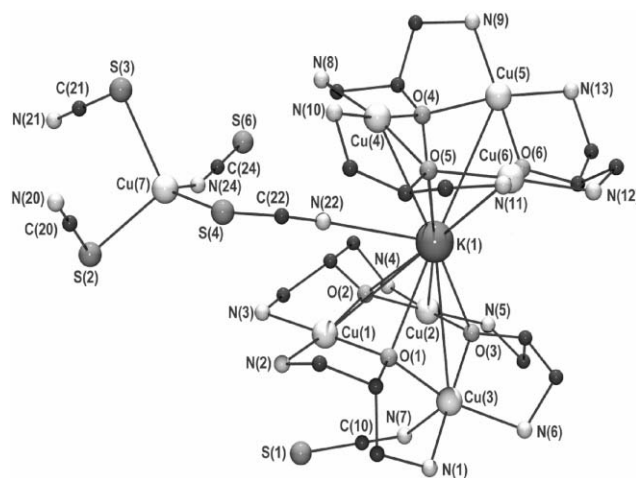

Scheme 1

Fig. 1 View of the asymmetric unit in 1 showing atom labelling scheme. Relevant bond lengths [Å] and angles [°]: Cu(1)···Cu(2) 3.607(1), Cu(1)···Cu(3) 3.480(1), Cu(2)···Cu(3) 3.343(1), Cu(4)···Cu(5) 3.454(1), Cu(4)···Cu(6) 3.598(1), Cu(5)···Cu(6) 3.294(1), Cu(1)–O(1) 1.949(3), Cu(1)–O(2) 1.951(3), Cu(2)–O(3) 1.957(3), Cu(2)–O(2) 1.961(3), Cu(3)–O(1) 2.003(3), Cu(3)–O(3) 1.960(3), Cu(4)–O(4) 1.934(3), Cu(4)–O(5) 1.939(4), Cu(5)–O(4) 1.945(3), Cu(5)–O(6) 1.903(4), Cu(6)–O(5) 1.955(3), Cu(6)–O(6) 1.962(4), Cu(1)–O(1)–Cu(3) 123.4(2), Cu(1)–O(2)–Cu(2) 134.5(2), Cu(2)–O(3)–Cu(3) 117.2(2), Cu(4)–O(4)–Cu(5) 125.9(2), Cu(4)–O(5)–Cu(6) 135.0(2), Cu(5)–O(6)–Cu(6) 117.0(2), Cu(7)–S(2) 2.390(2), Cu(7)–S(3) 2.480(2), Cu(7)–S(4) 2.320(2), Cu(7)–N(24) 1.938(5).
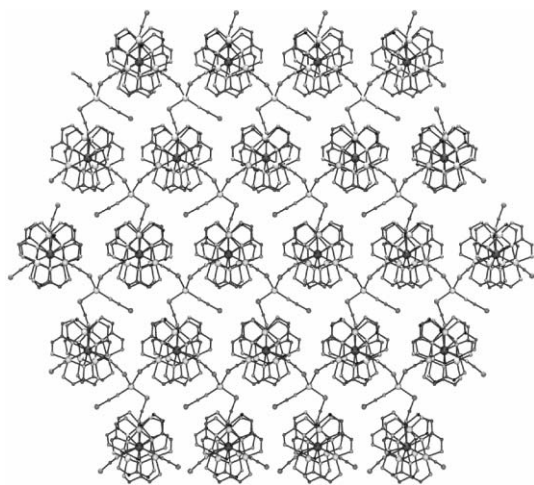
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Fig. 2 View of the infinite *xy* plane of $\{[K(Cu_3O_3)_2]^{7+}\}_n$ connected by $\{[Cu(SCN)_4]^{3-}\}_n$ in **1**. The non bonded thiocyanates are omitted for clarity.

The coordination around the Cu(II) centres is a square-planar environment. In the title compound, one non-bonded thiocyanate nitrogen N(7) is placed near the Cu(3) atom to provide weak axial contacts (Cu(3)–N(7) 2.378(6) Å). As a consequence of this, the coordination polyhedron around the copper atoms Cu(3) is best described as a distorted square pyramid. The Cu–O distances are in the range 1.903(4) to 2.003(3) Å, whereas the Cu–N bond lengths are in the range 1.966(4)–2.027(4) Å. In each of the triangular tricopper units, there are three different Cu–O–Cu angles: 134.5(2) and 135.0(2)°, 123.4(2) and 125.9(2)° and 117.2(2) and 117.0(2)° corresponding to different μ_2-alkoxide oxygen bridges. All these distances should be considered as normal.[3,4]

The most important feature in the crystal packing of **1** is related with the potassium ion, which shows tricapped trigonal prismatic coordination with capping nitrogen atoms in the centre of the three rectangular faces as is shown in Fig. 3. Such an $[O_6N_3]$ environment in the case of the potassium cation is observed for the first time. The K(1)–O_{bdap} distances vary between 2.732(4) and 2.924 Å, while the K(1)–$N_{thiocyanate}$ distances are in the range 2.849(4)–2.971(6) Å, which are comparable to those reported in 78 structures found in the literature, ranging from 2.689 to 3.380 Å and with a mean value of 2.858 Å (CSD Version 5.27, update June 2006).

It is also interesting to notice the presence of the $[(\mu_{1,3}$-$SCN)_3Cu^I(NCS)]^{3-}$ anion in **1**. To the best of our knowledge, this anion has never been reported before (Fig. 1). The Cu(7) atom
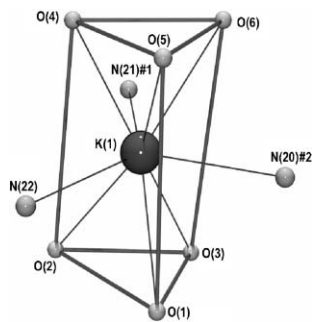

Fig. 3 Tricapped trigonal prismatic arrangement of oxygen and nitrogen atoms coordinated to potassium in **1** (#1: $-x + 1$, $y - 1/2$, z; #2: $-x$, $y - 1/2$, z).

shows a distorted tetrahedral environment, novelly, due to the coordination mode of the thiocyanate ligands, and shows three Cu–S bond lengths with distances of 2.320(2), 2.390(2) and 2.480(2) Å and one Cu–N bond length of 1.938 (5) Å. The Cu–S distances are close to those reported in the polymeric compound $\{[C_5H_6N][Cu_2(SCN)_3]\}_n$ (which lie in the range 2.319(3)–2.493(4) Å),[5] but are larger than those observed in the $[H_2L]_2[Cu(SCN)_3]$ compound (varying from 2.24(2) to 2.34(3) Å).[6]

The magnetic behaviour of **1** is shown in Fig. 4 as a plot of $\chi_M T$ *vs. T*. $\chi_M T$ shows a value of 1.769 cm^3 K mol^{-1} for each $[Cu_6^{II}Cu^I]$ unit at room temperature, which is smaller than the expected for six uncoupled $S = 1/2$ ions with $g = 2.0$ (2.25 cm^3 K mol^{-1}). On cooling, $\chi_M T$ decreases quickly showing a plateau from *ca.* 40 K with a $\chi_M T$ value of 0.837 cm^3 K mol^{-1}, corresponding to two isolated $S = 1/2$ ground states with $g = 2.11$. This behaviour indicates a strong antiferromagnetic interaction between Cu^{II} centres in each triangular entity. At very low temperature, $\chi_M T$ decreases slightly to 0.742 cm^3 K mol^{-1} due to weak antiferro-magnetic intertrimer interactions.

The magnetization measurements at 2 K up to an external field of 5 T show the saturation of complex **1** tending to 1.98 $N\beta$ for each $[Cu_6^{II}–Cu^I]$ unit (Fig. 4).

Taking into account the compound topology, which magnetically is that of a trinuclear compound, we can count three exchange pathways, grouped in three different averaged exchange parameters J_1, J_2, and J_3 corresponding to the different alkoxo bridges of the bdap ligands. In light of the well known linear correlation between the exchange coupling constant J and the Cu–O–Cu angle (θ) in divalent copper complexes bridged by hydroxide,[7–10] and alkoxide,[11,12] oxygen atoms, and taking into account the different Cu–O–Cu bond angle values of 134.5(2)°, 123.4(2)° and 117.2(2)°, the $|J_1|$ value should be greater than $|J_2|$ which should be greater than $|J_3|$, corresponding to the angles Cu(1)–O(2)–Cu(2), Cu(1)–O(1)–Cu(3) and Cu(2)–O(3)–Cu(3), respectively. The mean Cu–O–Cu bond angles in the $[Cu_3–O_3]$ cores are summarized in Fig. 4.

As a first approach we have analysed the experimental data as the coupling constant case $J_1 = J_2$ (named $J_{1,2}$) > J_3. From the
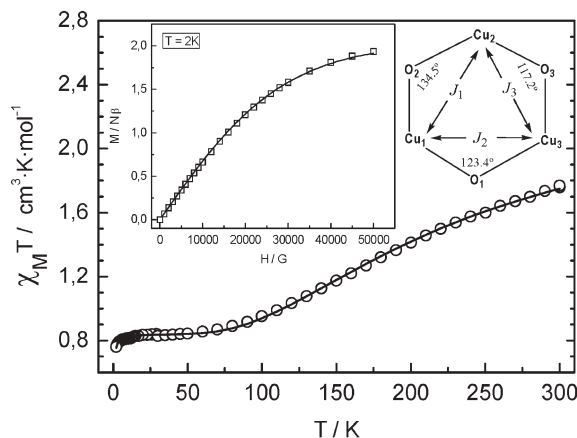

Fig. 4 Plot of observed $\chi_M T$ *vs.* T and $M/N\beta$ *vs.* H (inset, left) of **1**. Solid line represents the best theoretical fit obtained by using the Hamiltonian in eqn (3) (see text). Schematic diagram (inset, right) representing the exchange interactions with significant bridge angle parameters in the $[Cu_3–O_3]$ core in **1**.

above considerations, the $J_{1,2}$ coupling constant should be only assumed as indicative of the J superexchange range of values, and the real J values should be $J_1 > J_2 > J_3$, which corresponds to an nonsymmetrical triangular array of local $S = 1/2$.

For the approximation with $J_{1,2}$ different to J_3 and taking into account the behaviour of $\chi_M T$ at low temperature, experimental data have been fitted to the eqn (1)

$$\chi_M = N\beta^2 g^2 (f(J,T)/kT - zJ'f(J,T)) \qquad (1)$$

in which zJ' is the intertrimer exchange parameter and $f(J,T) = 1/4\{1 + \exp[(J_{1,2} - J_3)/kT] + 10\exp(3J_{1,2}/2kT)\}/\{1 + \exp[(J_{1,2} - J_3)/kT] + 2\exp(3J_{1,2}/2kT)\}$. In this case, the energy values can be obtained using the Kambe method[13] from the Hamiltonian:

$$H = -J_{1,2}(S_1 S_2 + S_1 S_3) - J_3(S_2 S_3) \qquad (2)$$

The best fit parameters obtained from eqn (1) by minimizing the R factor, $R = \Sigma(\chi_M T^{calc} - \chi_M T^{obs})^2/\Sigma(\chi_M T^{obs})^2$, were $J_{1,2} = -276.6$ cm^{-1}, $J_3 = -34.6$ cm^{-1}, $g = 2.12$, $zJ' = -0.25(5)$ cm^{-1}, and $R = 2.1 \times 10^{-4}$. The low J_3 value is in good agreement with the alkoxo superexchange pathway that relates Cu(2) with Cu(3).

For the case of three different J values, an analytical expression is not available and the eigenvalues for the spin states were performed by means of the computer program CLUMAG[14] using the Hamiltonian:

$$H = -J_1(S_1 S_3) - J_2(S_1 S_2) - J_3(S_2 S_3) \qquad (3)$$

Calculations performed from eqn (3), give the following coupling constant values: $J_1 = -264.6$ cm^{-1}, $J_2 = -67.1$ cm^{-1}, and $J_3 = -29.9$ cm^{-1} for $g = 2.12$ and $zJ' = -0.25$ cm^{-1}. The J values are in good agreement with the structural parameters and may be unambiguously assigned as J_1 to the Cu(1)···Cu(2), J_2 to the Cu(1)···Cu(3) and J_3 to the Cu(2)···Cu(3) interactions.

In conclusion, the synthesis of inorganic materials by using the dinuclear block [Cu$_2$(bdap)]$^{3+}$ and alkali metal ions seems to be a good strategy to obtain new compounds with interesting molecular architectures and magnetic properties. In this context, a new two-dimensional compound containing the [K(Cu$_3$bdap$_3$)$_2$] and [($\mu_{1,3}$-SCN)$_3$Cu^I(NCS)] blocks has been prepared and its magnetic properties has been analysed. The system does not behave as a 2D magnet, and the intramolecular magnetic interactions between the copper(II) ions, mediated by the alkoxo bridge of the bdap ligand, were found to be antiferromagnetic.

Most importantly, this work reveals a new environment of the potassium cation, being in a tricapped trigonal prism [O$_6$N$_3$]. It should be emphasized that the sandwich-like cation [K(Cu$_3$O$_3$)$_2$]$^{7+}$ shown in **1** can be compared perfectly to the well-known alkali crown ether sandwich complexes. Also this work reveals the presence of the new [($\mu_{1,3}$-SCN)$_3$Cu^I(NCS)] anionic unit, showing a coordination mode different to the habitual one in the tetrathiocyanatometallates.

The manner in which infinite stacking assemblies are achieved in **1** may serve as a useful model for the design of functional molecular assemblies with other alkali metals in order to establish the influence of the encapsulated alkali metal ion on the properties of the core, such research efforts are being conducted in our laboratory.

Notes and references

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