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A Triple-Decker Heptadecanuclear $(Cu^{II})_{15}(Cr^{III})_2$ Complex Assembled from Pentanuclear Metallacrowns

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Reaction of the pentanuclear Cu^{II} metallacrown $[Cu_5(ahpha)_4](ClO_4)\cdot4H_2O$ ($ahpha^{2-}$ is the dianion of 3-amino-3-(hydroximino)propanehydroxamic acid), with $Cr(C_2O_4)_3^{3-}$ led to the formation of a heptadecanuclear complex $\{[Cu_5(ahpha)_4]_3[Cr(C_2O_4)_3]_2\cdot4H_2O\}\cdot8H_2O\cdot\mathbf{1}/3(DMF)$ ($\mathbf{1}\cdot8H_2O\cdot1/3(DMF)$). This compound contains three stacked $Cu_5(ahpha)_4^{2+}$ building blocks, linked by axial bonds between Cu^{2+} ions of one Cu_5 metallacrown and hydroxamate oxygen atoms of the neighboring Cu_5 unit. Two $Cr(C_2O_4)_3^{3-}$ anions are bonded to the two lateral $Cu_5(ahpha)_4^{2+}$ cations through axial Cu–O(oxalate) bonds. The formation of **1** may be considered the first example of metallacrown trimerization caused by anion metathesis. The compound contains 10 × 13 Å voids (about 25 % of crystal volume), filled with solvate water molecules. The magnetic properties ($\chi_M T$ vs. T) could be fitted as the superposition of the magnetism of $3\chi_M T(Cu^{II}_5)$ and $2\chi_M T(Cr^{III})$. Exchange interactions within the Cu^{II}_5 units were fit in the framework of a model based on the Hamiltonian $H(Cu^{II}_5) = -2J_1(S_1{\cdot}S_5 + S_2{\cdot}S_5 + S_3{\cdot}S_5 + S_4{\cdot}S_5) -2J_2(S_1{\cdot}S_2 + S_2{\cdot}S_3 + S_3{\cdot}S_4 + S_4{\cdot}S_1)$, where S_5 represents the central Cu^{2+} ions' spins and the other spin operators correspond to the peripheral Cu^{2+} ions. With other possible interactions taken into account using a molecular field approach, the best fit corresponded to $J_1 = -153(5)\ cm^{-1}$, $J_2 = -71(2)\ cm^{-1}$ and $zJ' = -0.058(4)\ cm^{-1}$.

Introduction

Polynuclear complexes have been attracting attention due to their unique magnetic properties, arising from exchange interactions of paramagnetic metal centers, and to their potential use for formation of magnetic[1] and multifunctional materials.[2] Polynuclear compounds, including heterometallic ones, may be created by self-assembling processes from mononuclear complexes or salts and organic ligands,[3] though the outcomes of such reactions are usually not predictable. Prior assembly of polynuclear particles in one molecule represents a promising route to enhancing the nuclearity of coordination compounds.[4] Such an approach may allow one to study the extent to which the properties of the resulting compound are determined by the properties of its constituent building blocks, which is an important factor for the generation of materials with pre-determined properties. Metallacrown complexes are suitable objects for such studies and because of certain features of their structures, they have several advantages over other polynuclear compounds. Metallacrowns are polynuclear complexes possessing a cyclic structure similar to crown ethers, but with transition metal ions and nitrogen atoms instead of methylene groups.[5] Metal ions in metallacrowns are coordinatively unsaturated (or have readily substituted axial solvent molecules) and the coordination is nearly planar, so that steric hindrances to access by donor atoms of potential ligands are minimal. In addition, metallacrowns are usually characterized by high stability in solution over a range of conditions, such as change of pH,[6] which makes them promising candidates for generation of polynuclear systems by acting as oligomerizable building blocks in the presence of a variety of reagents. Compounds of this class possess exchange interactions among metal ions,[7] which lead to interesting magnetic properties. Additional reasons for interest in such metallacrowns include their potential bioac-

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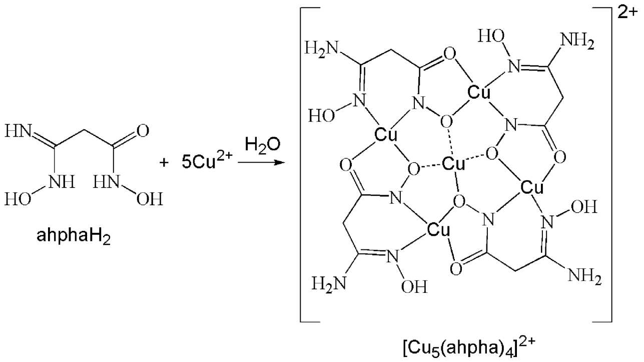
tivity[8] and their ability for selective recognition of cations and anions,[9] which is important for chemical sensors.

The aim of this work was to study the possibility that pentanuclear $Cu_5(ahpha)_4^{2+}$ metallacrowns ($ahpha^{2-}$ is the dianion of 3-amino-3-(hydroximino)propanehydroxamic acid) could be linked by $Cr(C_2O_4)_3^{3-}$ anions and to compare the magnetic properties of the resulting complex containing these several paramagnetic metal ions with the properties of the discrete pentanuclear "building block" $[Cu_5(ahpha)_4]^{2+}$ (Scheme 1), reported previously by Song et al.[10]



Scheme 1. Formation of $[Cu_5(ahpha)_4]^{2+}$; C–N bonds are assigned as single/double based on their lengths found from the X-ray structure.

Tris(oxalato)chromate(III) was chosen as the anionic component for several reasons, including (besides its negative charge) the presence of six oxygen donor atoms potentially capable of bridging Cu^{2+}, its kinetic inertness, the high spin ($S = 3/2$) nature of Cr^{3+} and the fact that Cu^{II}-Cr^{III} complexes are interesting subjects for magnetochemical investigations.[11]

Metathesis of $[Cu_5(ahpha)_4](ClO_4)_2$ into its $Cr(C_2O_4)_3^{3-}$ salt resulted in unexpected trimerization of the pentanuclear block and formation of a $\{Cu_5(ahpha)_4\}_3^{6+}$ cation, "capped" by two tris-oxalatochromates. In this paper we report the synthesis, X-ray structure and magnetic properties of this new heteropolynuclear $Cu^{II}_{15}Cr^{III}_2$ complex, $\{[Cu_5(ahpha)_4]_3[Cr(C_2O_4)_3]_2(H_2O)_4\}\cdot 8H_2O\cdot 1/3(DMF)$ [hereinafter abbreviated as compound **1**$\cdot 8H_2O\cdot 1/3(DMF)$].

Results and Discussion

Molecular and Crystal Structures of Compound 1·14H$_2$O

Complex **1** was obtained by metathesis of perchlorate ions in $[Cu_5(ahpha)_4](ClO_4)_2$ by $Cr(C_2O_4)_3^{3-}$ in a DMF/water solution. The anion change resulted in trimerization of the metallacrown moiety, which is at least partly a consequence of the requirement for charge balance (three cations with charge +2 require two anions with charge –3 for neutral compound formation). To the best of our knowledge, this is the first example of such metallacrown oligomerization, though several "dimers" of planar polynuclear metallacrown cations have previously been reported.[5h,10,12] In compound **1**, $Cr(C_2O_4)_3^{3-}$ does not provide a link between pentanuclear moieties, but one oxalate group in each $Cr(C_2O_4)_3^{3-}$ anion acts as a bridge between Cr^{III} and two Cu^{II} of a single Cu_5 unit.

Though analytical data for an air-dried sample corresponded to composition **1**$\cdot 8H_2O\cdot 1/3(DMF)$, X-ray data for the crystal, taken from the reaction solution, were solved as **1**$\cdot 14H_2O$ (disordered solvent was omitted from the structural model and was corrected for using the SQUEEZE procedure,[13] see Exp. Section for details). Indeed, similar inter-laboratory difficulties with solvents of crystallization have been experienced previously even for compounds with a non-porous structure,[14] and are particularly difficult to avoid in the case of coordination frameworks with substantial voids. As a result, we have had to deal with some compositional variation in regard to the various physical measurements. For instance, the C/H/N analyses varied within 0.3–0.4% due to loss/exchange of DMF/H_2O upon removal of the sample from solution and contact with the atmosphere.

The molecule of **1** consists of three $[Cu_5(ahpha)_4]^{2+}$ cations, two $Cr(C_2O_4)_3^{3-}$ anions and four coordinated water molecules (Figures 1 and 2) and was crystallographically solved as a centrosymmetric entity, with the middle Cu_5 unit disordered over two positions {each $[Cu_5(ahpha)_4]^{2+}$ cation is itself not centrosymmetric}. Hereinafter, the $[Cu_5(ahpha)_4]^{2+}$ cations in $[Cu_5(ahpha)_4]_3^{6+}$ are referred to as "middle" (the one located in the center, B in Figure 1) and "lateral" (the remaining two, A and A′ in Figure 1).

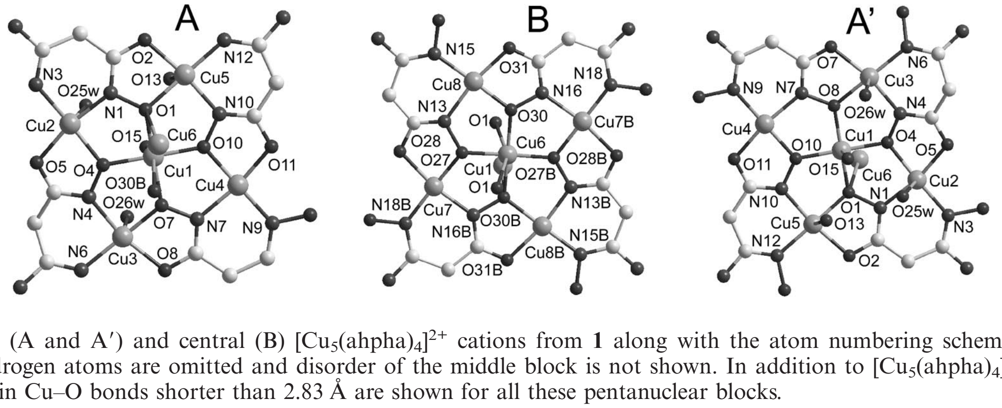


Figure 1. Lateral (A and A′) and central (B) $[Cu_5(ahpha)_4]^{2+}$ cations from **1** along with the atom numbering scheme. For clarity of presentation, hydrogen atoms are omitted and disorder of the middle block is not shown. In addition to $[Cu_5(ahpha)_4]^{2+}$, atoms (Cu^{2+} and O) involved in Cu–O bonds shorter than 2.83 Å are shown for all these pentanuclear blocks.

The structures of all the $[Cu_5(ahpha)_4]^{2+}$ units are generally similar to those observed in discrete non-oligomerized forms of the same cation (structurally characterized as the nitrate salt).[10] In each $[Cu_5(ahpha)_4]^{2+}$ cation five Cu^{2+} ions are bridged by four doubly deprotonated $ahpha^{2-}$ ions. Each $ahpha^{2-}$ binds respectively three Cu^{2+} ions – two "peripheral" ions (located in the Cu_4 metallacrown ring of $[Cu_5(ahpha)_4]^{2+}$) and one "central" ion {located in the center of the $[Cu_5(ahpha)_4]^{2+}$ cation}. The central Cu^{2+} ion in each Cu_5 unit is encapsulated in a cavity formed by four hydroxamate oxygen atoms (square-planar O_4 donor set), while the square-planar N_2O_2 coordination environments of the peripheral Cu^{2+} ions consist of two hydroxamate nitrogens and two oxygen atoms (one carbonyl-O and one hydroxamate-O). Generally, the bond lengths Cu–O and Cu–N in the equatorial plane range from 1.825(8) to 1.986(8) Å, typical of metallacrown complexes (Table S1).[5f–5h,10] The axial Cu–O bonds also differ between the middle and lateral $[Cu_5(ahpha)_4]^{2+}$ units, as described below.

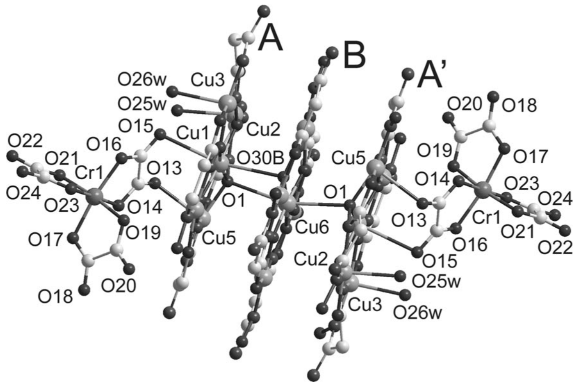


Figure 2. Side view of the molecular fragment of **1**. Only one of the disordered middle $[Cu_5(ahpha)_4]^{2+}$ units is shown and slight disorder of the oxalate ions is also omitted. Note that the Cu6–O1′ bond lengths between the middle and lateral $[Cu_5(ahpha)_4]^{2+}$ cations are not equivalent for the two disordered middle $[Cu_5(ahpha)_4]^{2+}$ units. Hydrogen atoms are omitted for clarity; only Cu–O contacts shorter than 2.83 Å between middle and lateral $Cu_5(ahpha)_4{}^{2+}$ metallacrowns are shown. Symmetry equivalent positions are: x, y, z; $-x, y, -z + 1/2$; $x + 1/2, y + 1/2, z$; $-x + 1/2, y + 1/2, -z + 1/2$; $-x, -y, -z$; $x, -y, z - 1/2$; $-x + 1/2, -y + 1/2, -z$; $x + 1/2, -y + 1/2, z - 1/2$.

The distances between the central and peripheral Cu^{2+} ions lie in the range 3.2184(7) – 3.3096(7) Å, and the distances between neighboring peripheral Cu^{2+} ions are between 4.5649(8) and 4.6660(7) Å, again typical of copper(II) metallacrowns.[5f–5h,10] In both the middle and lateral $[Cu_5(ahpha)_4]^{2+}$ units, the peripheral Cu^{2+} ions are almost coplanar [the largest deviation of any Cu^{2+} ion from the Cu_4 mean plane does not exceed 0.033(1) Å], while for the lateral and middle metallacrowns respectively, the central Cu^{2+} ions lie 0.2354(5) Å and 0.069(1) Å away from the $Cu(peripheral)_4$ mean planes.

The Middle $[Cu_5(ahpha)_4]^{2+}$ Cation in the $\{Cu_5(ahpha)_4\}_3{}^{6+}$ "Sandwich" (B in Figure 1)

In addition to the above-mentioned donor atoms in the coordination spheres of the Cu^{2+} ions, there are two oxygen atoms in axial positions of the middle Cu_5's central Cu6 ion [Cu6–O1′ 2.696(4) Å and Cu6–O1′′ 2.821(4) Å]. Thus, the coordination of this central Cu^{2+} is tetragonally elongated CuO_6 octahedral, where the axial positions are occupied by oxygen atoms from hydroxamate groups of two lateral $[Cu_5(ahpha)_4]^{2+}$ cations. The rest of the Cu^{2+} ions in the middle metallacrown entity exhibit distorted square-planar coordination with CuN_2O_2 chromophores.

Lateral $[Cu_5(ahpha)_4]^{2+}$ Cations in the $\{Cu_5(ahpha)_4\}_3{}^{6+}$ "Sandwich" (A and A′ in Figure 1)

Though the molecule of 1 was refined as a centrosymmetric entity, the environments of the Cu^{2+} ions in the two terminal $Cu_5(ahpha)_4{}^{2+}$ are not identical, if one considers them in relationship to a single disordered middle $Cu_5(ahpha)_4{}^{2+}$ cation position. The central Cu^{2+} ion of one of the lateral $[Cu_5(ahpha)_4]^{2+}$ units possesses a distorted octahedral environment with two oxygen atoms in axial positions: a hydroxamate O-atom from the middle $[Cu_5(ahpha)_4]^{2+}$ unit [Cu1′–O30B, 2.821(7) Å] and an O-atom from a chromium-bound oxalate ion [Cu1′–O15, 2.783(3) Å]. For the second lateral $[Cu_5(ahpha)_4]^{2+}$ cation, the central Cu^{2+} ion (Cu1′′) has only a long contact [3.023(7) Å for Cu1′′–O30] with an O atom from the middle pentanuclear block, and the Cu1′′–O(oxalate) is the same. Among the peripheral Cu^{2+} ions, only Cu4 exhibits distorted square-planar coordination, with a CuN_2O_2 chromophore, while the other Cu^{2+} ions have distorted square pyramidal donor sets with oxygen atoms in axial positions. The coordination spheres of Cu2 and Cu3 are completed with axially bonded water molecules [Cu2–O25w, 2.386(4) Å and Cu3–O26w, 2.376(3) Å] yielding CuN_2O_3 chromophores. The coordination sphere of Cu5 is completed by an oxalate oxygen atom [Cu5–O13, 2.466(4) Å] corresponding to an N_2O_3 donor set.

The generally longer axial Cu–O bonds vs. the in-plane Cu–O or Cu–N bonds are clear evidence for Jahn–Teller distortion.

As part of these Cu–O interactions, two $Cr(C_2O_4)_3{}^{3-}$ anions are each bound to two coppers of lateral $[Cu_5(ahpha)_4]^{2+}$ cations by two oxygens from the same oxalate, so that $C_2O_4{}^{2-}$ groups act as tetradentate bridging ligands between Cr^{III} and Cu^{II} [the Cu1···Cr1 and Cu5···Cr1 separations are 5.552(3) Å and 5.602(2) Å, respectively]. Each Cr^{3+} cation has a distorted octahedral donor set, with Cr–O bonds are in the range 1.951(3)–1.966(3) Å. In each $Cu_{15}Cr_2$ unit, the two chromate ions are inversion-related, so as to be enantiomeric. This inversion pseudosymmetry includes the lateral (A/A′) pentacopper moieties, which are oriented mutually parallel, with the axial Cu–O bonds signalling their inversion relationship. However, the inversion symmetry of each $Cu_{15}Cr_2$ unit is broken and the chirality maintained because the disordered middle $[Cu_5(ahpha)_4]^{2+}$ unit is noncentrosymmetric and "flipped" with respect to the lateral ones. Random distribution of these nonsymmetric $[Cu_5(ahpha)_4]_3[Cr(C_2O_4)_3]_2$ units throughout the lattice effects its racemicity, and the crystals can be regarded as a solid solution of the enantiomers.

There are several Cu–O contacts of about 2.9–3.0 Å, which additionally link lateral and middle $[Cu_5(ahpha)_4]^{2+}$ units [such as Cu8–O7′ 2.982(4) Å, Cu7–O4″ 2.917(4) Å, Cu1″–O30 3.023(7) Å]. Selected bond lengths and angles are in Table S1 (see Supporting Information).

In the crystal, separate molecules of **1** and solvating water molecules are linked by an extensive system of hydrogen bonds. Due to the features of crystal packing of **1**·$14H_2O$, the compound contains channels in the direction of the *c* axis with a cross-section of about 9 × 12 Å (taking van der Waals radii into account, Figure 3). A Platon-based[13] estimation of solvent-accessible pore volume gives a value of 26.6% for a probe molecule with r = 1.4 Å for the cell where all non-coordinated solvate molecules are removed.

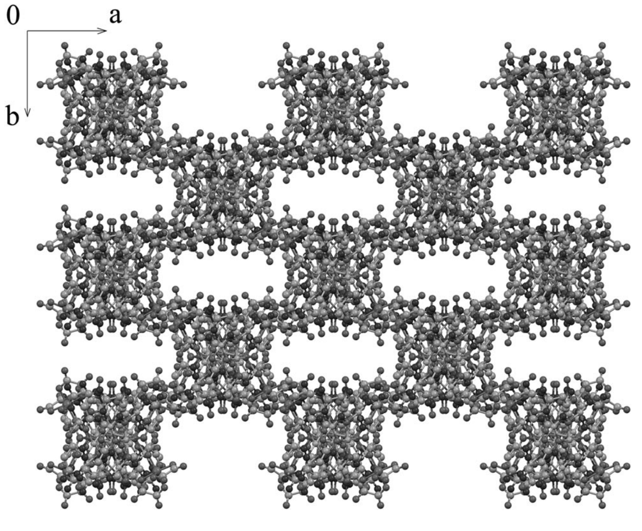


Figure 3. A fragment of the **1**·$14H_2O$ lattice, viewed along the *c* axis, illustrating the structural voids. Solvent molecules are omitted for clarity of presentation.

To the best of our knowledge, only a few compounds, possessing a porous structure based on metallacrowns as "building blocks", have previously been reported.[15]

Thermal Analysis and Powder X-ray Diffraction

In order to obtain information about the thermal stability of complex **1**, differential thermogravimetric analysis was performed for several samples, which were dried under different conditions. The compound taken from mother liquor begins to lose weight at 40 °C, and at 70 °C significant weight loss starts, which may be associated with the elimination of solvent from voids. Though the curves for the "wet" samples seem not to be informative in terms of exact formula determination, the results indicate that the quantity of solvent in the voids of **1** may vary over a wide range depending on the precise crystallization/drying conditions, and leads to the requirement for a weighting factor during fitting of the magnetic data (vide infra). Even for the sample dried in vacuo at 120 °C, some insignificant weight loss was found already at 70 °C (Figure 4), likely due to water captured from the air after the sample's drying. Abrupt weight loss at ca. 230–270 °C is clearly associated with decomposition of compound **1**. The second decomposition step starts at 460 °C and the sample weight stabilises at 640–650 °C. The total weight loss is consistent, within experimental error, with decomposition to CuO and Cr_2O_3, assuming initial compositions such as $\{[Cu_5(ahpha)_4]_3[Cr(C_2O_4)_3]_2\}$ (**1**–$8H_2O$) (expected total weight loss 57%; found 55%).

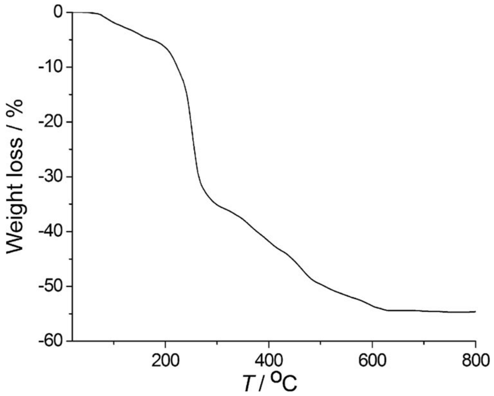


Figure 4. TGA curve for complex **1**·(solvents), dried in vacuo at 120 °C before the measurement.

Estimation of the accessible void volume in **1**, performed as above (see X-ray structure description; coordinated water is retained for calculation), gives a value of 840 $Å^3$ per $Cu_{15}Cr_2$ formula unit. From simple geometry considerations, this volume may fit 28 H_2O or 6.5 DMF molecules. The solvent content, estimated from TG curves for samples taken from the mother liquor, fits these values quite well.

The powder X-ray diffraction pattern of the sample of **1**·(solvents), taken from the reaction mixture is consistent with that calculated from the single-crystal X-ray structure determination (Figure 5). Drying of the compound in

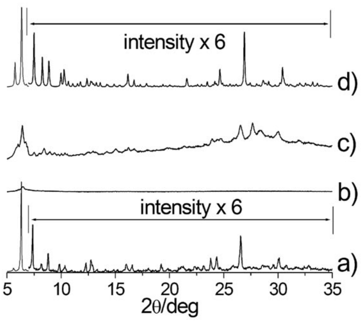


Figure 5. Powder X-ray diffraction patterns for **1**·(solvents), (a) taken from the mother liquor, (b) the same sample after drying at 120 °C in vacuo, (c) sample "b" after resolvation in DMF/water during 2 d, and (d) calculated from the single-crystal X-ray structure.

vacuo at 120 °C results in substantial diminution of reflections in the powder pattern, but the most intense reflection at $2\theta = 6.5°$, for one of the largest interplanar spacings, is still present. This reflection represents the (100) plane, which is parallel to the *c* axis and also passes through the diagonal of the crystallographic *ab* plane. This reflection is shifted slightly to higher angle compared to that for the sample taken from mother liquor ($2\theta = 6.3°$). These changes evidence growing disorder within the crystal structure, but not its complete collapse, and the main framework of **1** seems to stay intact even after loss of most of the solvent molecules. Notably, neither the color nor the external morphology of the crystals are changed by desiccation at 120 °C.

Resolvation of dry sample in DMF/water for two days resulted in partial recovery of the crystal structure, as evidenced by the growth in intensity of the reflection at $2\theta = 6.5°$ (Figure 5). However, several new reflections appeared at $2\theta > 25°$, and the intensity of the reflections at $2\theta > 25°$ was relatively diminished compared to the low-angle reflections. We conclude that the pseudomorph formed by desolvation has access to resolvation pathways other than the one leading to the original compound, so that crystal structure recovery is not reversible.

Sorption Properties

Compound **1**, dried at 130 °C in vacuo, showed only surface adsorption of N_2 and H_2 at 77 K, evidencing that the voids in its crystal structure are not accessible for these gases, or collapse on desolvation. However, it absorbed a comparatively large amount of ethanol from the gaseous phase at 293 K (Figure 6). The quantity of absorbed ethanol grew with increasing partial pressure (*p*), reaching *ca.* 0.05 $cm^3 g^{-1}$ (0.85 $mmol\,g^{-1}$ or 2.8 molecules per $Cu_{15}Cr_2$ formula unit) at $p{\cdot}p_S^{-1} = 0.93$, where p_S is the saturation vapour pressure of ethanol at 293 K. Further pressure increase led to a sharp growth in ethanol uptake, up to 0.086 $cm^3 g^{-1}$ (1.47 $mmol\,g^{-1}$ or 4.8 molecules per $Cu_{15}Cr_2$ formula unit) at $p = p_S$, which may be associated with "pore opening" due to H-bonding interactions of the ethanol molecules with structural elements of the lattice.[20] The ethanol desorption curve displayed hysteresis with respect to the absorption curve, and some quantity of this absorbate could not be desorbed at room temperature and 10^{-2} Torr, acting as additional evidence for strong interactions of C_2H_5OH molecules in the voids of **1**. Coordination of absorbed C_2H_5OH to Cu^{II} ions also cannot be excluded as a basis for the implied interaction. In any case, from the shape of the absorption isotherms, it may be concluded that interaction of complex **1** with ethanol results in structural rearrangement, probably associated with separation of $Cu_{15}Cr_2$ units. In such case maximal absorption capacity is governed by the interplay between the energy of interaction of substrate with structural units of the coordination compound and the energy of the crystal lattice.[21] Nonetheless, the quantity of absorbed alcohol is comparable with the sorption capacity of porous MOFs vs. similar substrates.[22]

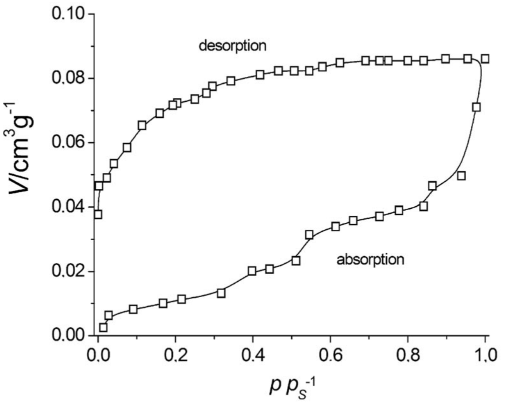


Figure 6. Ethanol sorption and desorption isotherms for activated complex **1** (293 K). The quantity of ethanol is recalculated to its volume at 293 K (which may correspond to the volume of voids in **1**).

Magnetic Properties of the Complex $1{\cdot}8H_2O{\cdot}1/3(DMF)$

Magnetic susceptibility measurements in the temperature range 2–300 K were performed for a polycrystalline sample of **1**·(solvents), for which the formula $\mathbf{1}{\cdot}8H_2O{\cdot}1/3(DMF)$ could be assigned on the grounds of the C,H,N analysis. The ambient-temperature value of $\chi_M T$ for complex $\mathbf{1}{\cdot}8H_2O{\cdot}1/3(DMF)$ is 6.38 $cm^3 mol^{-1} K$, which is significantly lower than the expected spin-only value (9.375 $cm^3 mol^{-1} K$) for fifteen Cu^{2+} ($S = 1/2$) and two Cr^{3+} ($S = 3/2$) ions with $g_{Cu} = g_{Cr} = 2.000$. At lower temperature, $\chi_M T$ falls, to 4.06 $cm^3 mol^{-1} K$ at 2 K, indicating that antiferromagnetic interactions dominate in the compound (Figure 7).

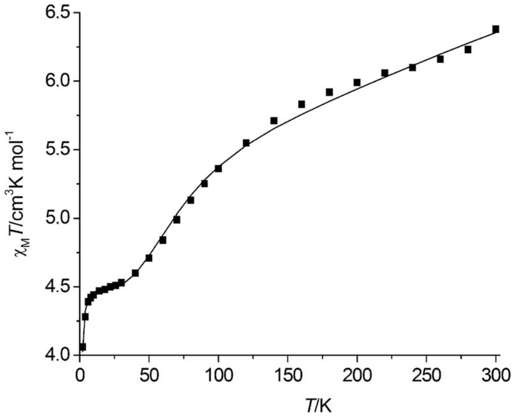


Figure 7. $\chi_M T$ vs. T plot for complex $1{\cdot}8H_2O{\cdot}1/3(DMF)$: ■ experimental data, − best fit for $D_{Cr} = 0$. The curves for $D_{Cr} = 0$ and non-zero D_{Cr}, as well as the curve for fit with non-zero α (see text) are visually the same.

Since estimation of all the possible couplings within the system of seventeen ions from one $\chi_M T$ vs. T curve is not possible because of unavoidable overparametrization, a simplified model was adopted, in which it was assumed that exchange interactions within $[Cu_5(ahpha)_4]^{2+}$ cations dominate, and the magnetic properties of **1**·8H$_2$O·1/3(DMF) were fit using simplified model, based on the following approach [Equation (1)].

$$\chi_M T(total) = 3\chi T\{Cu_5(ahpha)_4^{2+}\} + 2\chi T\{Cr(C_2O_4)^{3-}\} \tag{1}$$

Potential intermolecular interactions were taken into account by a molecular field model [Equation (2)].[16]

$$\chi_{MF} T = \frac{\chi_M T}{1 - \dfrac{zJ'\chi_M}{N_A g^2 \beta^2}} \tag{2}$$

For the [Cu$_5$(ahpha)$_4$]$^{2+}$ cation, the theoretical expression for the $\chi_M T$ vs. T curve was derived from the Hamiltonian[10] $\hat{H}(Cu_5) = -2J_1(S_1{\cdot}S_5 + S_2{\cdot}S_5 + S_3{\cdot}S_5 + S_4{\cdot}S_5) - 2J_2(S_1{\cdot}S_2 + S_2{\cdot}S_3 + S_3{\cdot}S_4 + S_4{\cdot}S_1)$, where J_1 is the exchange integral between the central Cu^{2+} ion [Cu(5)] and each of the four peripheral Cu^{2+} ions [Cu(1), Cu(2), Cu(3) and Cu(4)], and J_2 is the exchange integral between each pair of adjacent peripheral Cu^{2+} ions. As one more approximation, $\chi_M T$ for Cr(C$_2$O$_4$)$_3^{3-}$ was assumed to be temperature-independent (zero-field splitting $D_{Cr} = 0$).

The best fit[17] to the above model corresponded to $J_1 = -146(4)$ cm^{-1}, $J_2 = -69(1)$ cm^{-1}, $zJ' = -0.056(4)$ cm^{-1} and $g_{Cr} = 1.913(4)$ for fixed $g_{Cu} = 2.0$, and $R^2 = 2.91 \times 10^{-5}$.

In order to examine the response of the fit to additional parameters D_{Cr} was introduced, obtained from the Hamiltonian[16,18] $\hat{H}(Cr) = g\beta SH + D\hat{S}_z^2$. However, no improvement even in the value of R^2 was obtained. The reported[19] small value (-0.143 cm^{-1}) for D_{Cr} in K$_3$Cr(C$_2$O$_4$)$_3$ is consistent with our finding that introduction of non-zero D_{Cr} did not improve the fit.

The rather small g factors for Cu^{2+} and Cr^{3+} obtained above likely result from underestimation of this particular sample's solvent content, and we suggest application of a weighting factor a [Equation (3)].

$$\chi_M T_{weighted} = a{\cdot}\chi_M T_{Cu15Cr2} \tag{3}$$

where $\chi_M T_{Cu15Cr2}$ is calculated according to the above Equation (2).

For this fit with variable a, g_{Cu} was fixed at 2.066 (the value found for [Cu$_5$(ahpha)$_4$](NO$_3$)$_2$·4H$_2$O[10]) and g_{Cr} at 1.959 [the value for K$_3$Cr(Ox)$_3$[19]]. This approach yielded $J_1 = -153(5)$ cm^{-1}, $J_2 = -71(2)$ cm^{-1}, $zJ' = -0.058(4)$ cm^{-1}, $a = 0.951(2)$ and $R^2 = 2.4 \times 10^{-5}$. The values of J match closely those for the formulation **1**·8H$_2$O·1/3(DMF), indicating that the J's are determined by the *shape* of the $\chi_M T$ vs. T curve (within certain limits), rather than by the absolute values of $\chi_M T$. The value of a corresponds to a formula weight of about 3575 g mol^{-1}, which is higher than the formula weight of **1**·8H$_2$O·1/3(DMF) by 175 g mol^{-1}.

The values of J_1 and J_2 for **1**·8H$_2$O·1/3(DMF) are consistent with exchange coupling parameters for similar pentanuclear metallacrowns (Table 1).

Table 1. Magnetic properties of pentanuclear Cu^{II} metallacrowns.

Compound	g_{Cu}	J_1 [cm^{-1}]	J_2 [cm^{-1}]	zJ' [cm^{-1}]	Ref.
1·8H$_2$O·1/3(DMF)	2.066[a]	–153(5)	–71(2)	–0.058(4)	this work
Complex **2**[b]	2.066(3)	–119.9(7)	–79.0(4)	–0.69(7)	[17]
Complex **3**[c]	2.089(3)	–163(2)	–85.1(6)	–0.61(7)	[17]

[a] Fixed value. [b] Complex **2**: [Cu$_5$(ahpha)$_4$](NO$_3$)$_2$·4H$_2$O. [c] Complex **3**: [Cu$_5$(hbha)$_4$](NO$_3$)$_2$·8H$_2$O, where H$_2$hbha is 3-(hydroximino)butanehydroxamic acid.

Thus, the magnetic properties of **1**·8H$_2$O·1/3(DMF), containing three pentanuclear [Cu$_5$(ahpha)$_4$]$^{2+}$ cations and two Cr(C$_2$O$_4$)$_3^{3-}$ anions, can be well-described by superposition of the properties of its separate structural elements, exchange interactions between these elements being minor. This is consonant with the lack of unpaired electron density in the axial d-orbitals of the coppers, which are interacting with the oxalates bound to the $S = 3/2$ chromium(III) center. Similar systems have been reported, for which the magnetic properties are governed by the independent properties of their structural elements.[23]

Conclusions

It has been shown that reaction of [Cu$_5$(ahpha)$_4$]$^{2+}$ with Cr(C$_2$O$_4$)$_3^{3-}$ results in formation of an unprecedented heptadecanuclear Cu$^{II}_{15}$Cr$^{III}_2$ complex, containing a "trimer" of pentanuclear metallacrown building blocks. Due to the specific features of crystal packing, the compound absorbs a significant quantity of ethanol, but is not porous for N$_2$ or H$_2$. The magnetic properties of this compound may be fit as a superposition of the magnetism of its separate structural elements ([Cu$_5$(ahpha)$_4$]$^{2+}$ and Cr(C$_2$O$_4$)$_3^{3-}$) with a small molecular field parameter, indicating that intramolecular exchange interactions in the Cu$_5$ unit dominate and intermolecular coupling is negligible. The approach developed in this study may be used for assembling heteropolynuclear complexes and coordination polymers, the magnetic properties of which will be governed by the properties of the individual structural elements.

Experimental Section

General

Commercially available reagents and solvents (Merck and Aldrich) were used without further purification. The complex K$_3$Cr(C$_2$O$_4$)$_3$·3H$_2$O was prepared according to a reported procedure.[19] 3-Amino-3-hydroximinopropane (H$_2$ahpha) was synthesized as described previously.[10] [Cu$_5$(ahpha)$_4$](ClO$_4$)$_2$ was prepared using a modification of the procedure for [Cu$_5$(ahpha)$_4$](NO$_3$)$_2$·4H$_2$O, namely, Cu(ClO$_4$)$_2$·6H$_2$O was used instead of copper(II) nitrate.[10]

Caution: Perchlorate salts are potentially explosive and should be handled with care and in small quantities only.

C,H,N analyses were carried out on a Carlo Erba 1106 instrument. IR spectra (in KBr pellets, 400–4000 cm^{-1}) were obtained with a Perkin–Elmer Spectrum BX FT-IR and UV/Vis spectra were recorded in DMF/water solution on a Cary 50 spectrophotometer.

Single-crystal X-ray diffraction was performed at 100 K on an Apex diffractometer with Apex2 software using graphite-monochromated Mo-K_α radiation of wavelength 0.71073 Å, while powder data were measured on a Bruker X9 diffractometer (radiation of wavelength 1.54056 Å). A crystal suitable for X-ray data collection was taken from the reaction mixture. Thermogravimetric analysis (TGA) was performed in air on Q1500 instrument. Sorption of N_2 and H_2 was measured using a Sorptomatic-1990 instrument (77 K), while absorption of ethanol was measured gravimetrically, using a quartz microbalance (293 K). Each point on the absorption and desorption isotherms corresponds to equilibrium conditions (no change of sample weight at certain $p \cdot p_S^{-1}$). All sorption measurements were performed for samples of the complex **1** activated at 130 °C in vacuo at 10^{-2} Torr. Variable-temperature magnetic data (3–300 K) were obtained by means of a Quantum Design MPMS5S SQUID magnetometer with field strengths in the range 0.1–1.0 T. Samples were prepared in gelatin capsules, mounted inside straws, and then fixed to the end of the sample transport rod. Background corrections for the sample holder assembly were applied. Susceptibility data were corrected for diamagnetism using Pascal's constants,[16] Co[Hg(SCN)$_4$] being used as a calibration standard.

{[Cu$_5$(ahpha)$_4$]$_3$[Cr(C$_2$O$_4$)$_3$]$_2$·4H$_2$O}·8H$_2$O·1/3(DMF) [1·8H$_2$O·1/3(DMF)]: A solution of $K_3Cr(C_2O_4)_3$ (6.2 mg, 0.013 mmol) in water (3 mL) was added to a stirred solution of [Cu$_5$(ahpha)$_4$]-(ClO$_4$)$_2$·4H$_2$O (20 mg, 0.019 mmol) in DMF (1.5 mL). After one day, needle-shaped green crystals had formed; these were collected by filtration, washed with water and air-dried (yield 17.6 mg, 78 %). $Cu_{15}Cr_2C_{48.999}H_{86.331}N_{36.333}O_{72.333}$, calcd. C 17.31, H 2.56, N 14.97; found C 17.45, H 2.16, N 14.57 %. Crystal data, data collection parameters and structure refinement details for complex **1** are given in Table 2.

Table 2. Single crystal data and structure refinement details for complex **1**·14H$_2$O.

Formula	$C_{48}H_{92}Cr_2Cu_{15}N_{36}O_{82}$
M [g mol^{-1}]	3542.63
Crystal system	monoclinic
Space group	$C2/c$
Crystal size [mm]	0.55 × 0.45 × 0.31
Unit cell parameters	a = 23.743(2) Å
	b = 17.2228(16) Å
	c = 30.952(3) Å
	β = 96.7801(15)°
Volume [Å^3]	12569(2)
Z	4
T [K]	100(2)
Diffraction reflections, range [°]	0.986–28.28
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.872
Absorption coefficient [mm^{-1}]	2.764
μ (Mo-K_α) [mm^{-1}]	0.71073
F(000)	7084
Collected reflections	36835
Unique reflections	15388
R_{int}	0.0306
Goodness-of-fit on F^2	1.049
R_1([$I > 2\sigma(I)$][a]	0.0550
wR_2[$I > 2\sigma(I)$][b]	0.1557

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Description of Disorder in 1·14H$_2$O: Major disorder is observed for this compound. The structure exhibits triple-decker like moieties of $C_{12}H_{16}Cu_5N_{12}O_{12}$ units. The central of these three units is located slightly offset on a crystallographic inversion center and is disordered in a 1:1 ratio over two positions created from each other by this inversion center. Equivalent bond lengths within this unit were restrained to be the same and each C-H-N-O unit was restrained to resemble that of one such unit from the non-disordered molecule. ADPs of equivalent atoms were constrained to be the same. Disordered atoms of the central unit were restrained to be isotropic within a standard deviation of 0.01 Å^2 (the unit seems to be at least somewhat dynamically disordered with large asymmetric ADPs with a lower esd, thus the strong restraint). Bonded to the non-disordered $C_{12}H_{16}Cu_5N_{12}O_{12}$ are several water molecules and a tris(oxalato)chromate anion. One of the oxalate anions is disordered, over two close-by positions. The occupancy ratio refined to 0.454(8) to 0.542(8) (it thus could be exactly 1:1 disordered). The two oxalate moieties were restrained to have the same geometry and to be flat. ADPs of equivalent disordered atoms were constrained to be identical. Water molecules tightly hydrogen-bonded to the flat side of the outer $C_{12}H_{16}Cu_5N_{12}O_{12}$ units are well defined. Water molecules further out become less well defined and solvent molecules in several areas could not be unambiguously defined. The difference map also suggested the presence of a DMF molecule, disordered with solvating water molecules. It was however not well enough resolved for an unambiguous refinement. Eventually these ill-defined solvent molecules were thus omitted from the refinement and their electron density was instead compensated for, using the SQUEEZE procedure implemented in Platon.[13] Four voids of volume 494 Å^3, each with 167 electrons per void were compensated for per unit cell (see Squeeze report attached to the cif file). Carbon-bound H atoms were assigned in calculated positions. All other H atoms were assigned based on hydrogen bonding and distance considerations and initially refined using distance restraints. In the final cycles of the refinement they were set to ride on the atoms they are bonded to.

CCDC-769756 contains the supplementary crystallographic data for **1·14H$_2$O**. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected bond lengths and angles for complex **1** (Table S1), stereoviews of the complex cation {Cu$_5$(ahpha)$_4$}$_3^{6+}$ (Figures S1–S3), UV/Vis (Figure S4), IR (Figure S5) spectra for complex **1**·8H$_2$O·1/3(DMF) and colour versions of Figures 1–3 (Figures S6–S8).

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