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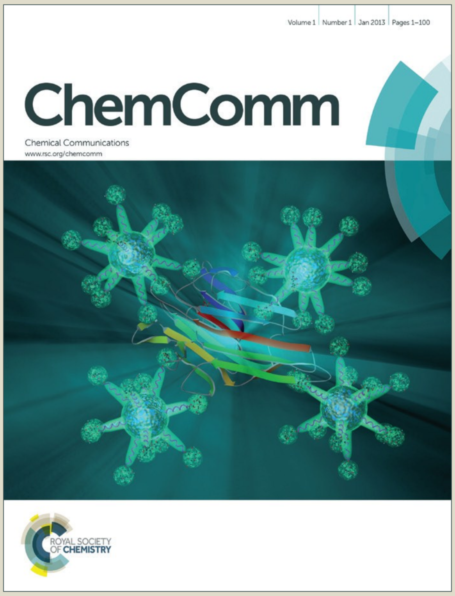

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ARTICLE TYPE

A Magnetically highly frustrated Cu^{II}_{27} Coordination Cluster Containing a Cu_{18} Folded-Sheet Motif

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$[Cu^{II}_{27}(\mu_4\text{-}O)_2(OH)_{13}(OMe)_7(vanox)_{10}(NO_3)_8(OH_2)_2(MeOH)_7](NO_3)_2\cdot 2H_2O\cdot 11MeOH$ (1) was synthesised from $Cu(NO_3)_2\cdot 3H_2O$ and *o*-vanillin-oxime. Structural analysis shows a molecule composed of a Cu_{18} "folded-sheet" motif linked to a Cu_9 bridging unit. The cluster is highly frustrated and has an S = ½ spin ground state.

Polynuclear transition-metal clusters continue to attract much attention in the field of coordination chemistry, not only because of their fascinating chemical and physical properties but also due to the architectural beauty of their structures. In the last two decades several high nuclearity species such as Mn_{44}[1], Co_{36}[2], Ni_{38}[3], and including up to 84 metal centres for a Mn_{84} giant wheel,[4] have been reported. In Cu^{II} chemistry, our group and others have focused on the synthesis of compounds with high nuclearity. We have previously reported the highest nuclearity Cu_{44} cluster[5] and a compound with one of the two different Cu_{36} structural motifs so far reported.[6,7] Such systems based on spin ½ metal ions provide a playground for physicists interested in highly frustrated systems. Clearly odd-numbered examples of such high nuclearity clusters provide systems forced to have non-zero spin ground states. However, such systems are rare in Cu^{II} chemistry. The *o*-vanillin-oxime ligand has been employed in the synthesis of several higher nuclearity compounds such as a Co_{13} cluster.[8] In addition, its deprotonated oxime group is well-known for mediating ferromagnetic interactions in 3d complexes.[9] More recently it has been employed in the synthesis of Cu-4f clusters such as Cu_8Dy_3[10] and Cu_4Dy_4[11]. In this work we report the use of this ligand in the synthesis of a high-nuclearity homometallic Cu^{II} coordination cluster.

Reaction of $Cu(NO_3)_2\cdot 3H_2O$ with H_2vanox (3-methoxy-2-hydroxy-benzaldoxime) in the presence of NaOH resulted in the isolation of $[Cu^{II}_{27}(\mu_4\text{-}O)_2(OH)_{13}(OMe)_7(vanox)_{10}(NO_3)_8(OH_2)_2(MeOH)_7](NO_3)_2\cdot 2H_2O\cdot 11MeOH$ (**1**) as very dark green crystals in 20 % yield for the sample used for the X-ray structure determination. (For further information see ESI).

Although the crystals are remarkably stable and form easily as relatively large blocks, the crystals only diffract weakly and were therefore measured at the ANKA synchrotron source, Karlsruhe. The structure of **1** reveals that the complex crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$. The molecular structure of the complex is shown in Figure 1. For clarity (in this and Figures 2-4), Cu-O bonds involved in (μ_2-OR) or (μ_3-OR) bridges are shown in orange to emphasize the cluster core topology, while Cu-O bonds to the two (μ_4-O) ligands, which will be seen to play a crucial role in the overall structure of the cluster, are shown as purple. The Cu_{27} cluster core exhibits a pseudo twofold rotational symmetry with the twofold axis passing through both Cu(27) and the midpoint between Cu(2) and Cu(3) (see ESI Fig. S1).

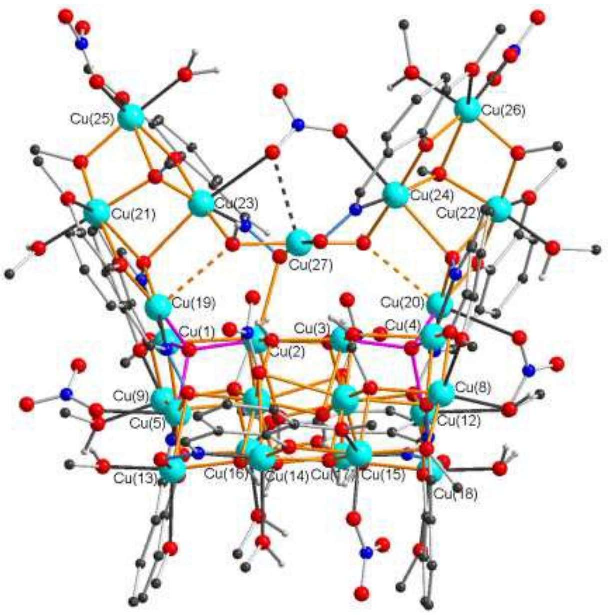

Fig. 1: The molecular structure of the Cu_{27} cluster in **1**. (Cu cyan, O red, N dark blue, C dark grey, H pale grey; organic H-atoms omitted for clarity. Cu-O bonds to μ_2 or μ_3-bridges orange, to (μ_4-O) purple; bonds with 2.8 > Cu-O > 2.6 Å shown dashed

The ten oxime ligands in the molecule all coordinate in a similar fashion and are doubly-deprotonated. In each case the imine nitrogen and the phenoxo oxygen chelate to one Cu^{II}, and the phenoxo and methoxy oxygens to a second Cu^{II} with the phenoxo oxygen forming a bridge between the two. However, the coordination modes of the oxime ligands differ in terms of the number of further copper centres to which the oximato oxygens coordinate (see also ESI Fig. S2). We designate the ligands according to the number of their respective nitrogen atoms. Thus, the oximato oxygens of three ligands, 3, 4 and 10, only coordinate to one copper, giving overall $(\mu_3\text{-vanox})^{2-}$ ligands. The oximato oxygen of ligand 9 bridges two copper centres, while those of ligands 1, 2, 5, 6, 7 and 8 link three coppers, resulting in a $(\mu_4\text{-vanox})^{2-}$ and six $(\mu_5\text{-vanox})^{2-}$ ligands.

In order to simplify the description of the Cu_{27} complex, the structure can be conveniently divided into two parts: a Cu_{18} folded sheet moiety and a Cu_9 bridging unit. An alternative view of the structure is as a "chicken in the basket" motif (see Figure S3). These structural motifs are shown in Figures 2 and 3. The two $(\mu_4\text{-O})^{2-}$ ligands, O(1) and O(2), form the two junctions of the subunits. Cu(1) to Cu(18) form a sheet topology, familiar from solid-state chemistry for double-layered metal hydroxide structures, as exemplified in $Fe(OH)_2$ and brucite. This structural type is also seen in many cores of transition-metal coordination clusters, where a planar sheet of metal centres is bridged usually by μ_3-oxygen-based ligands such as $(\mu_3\text{-OH})^-$, with these bridges alternately above and below the plane of metal ions. The largest such triangulated sheet of metal cations in a coordination cluster to date is found in a Mn^{II}_{19} system[12,13], although in this case the μ_3-bridges are mostly provided by OR-groups, constituting the oximato groups of the same $(\text{vanox})^{2-}$ ligands as found in **1**.[8]

The Cu_{18} moiety in **1** is second in size only to the largest such unit so far reported, but more importantly, it is not all in one plane, but rather folded with the crease defined by the four centres Cu(1) to Cu(4). The dihedral angle between the mean planes of each of the two halves of the sheet is 101.7° (Figure 2 and Figure S4).

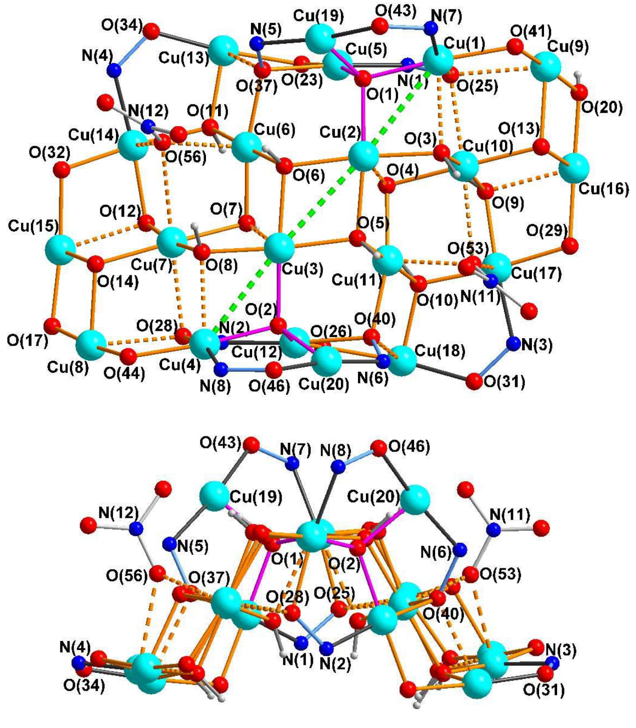

Fig. 2: Structure of the Cu_{18} folded sheet sub-unit in **1** shown in two different views with the elongated Jahn-Teller bonds shown as dashed lines. In the upper graphic, the "crease" of the fold is shown as a green dashed line. Cu(19) and Cu(20) are the first copper ions of the "bridge" moiety.

From Figure 2 it can be clearly seen that the $(\text{vanox})^{2-}$ ligands 1 and 2 are primarily responsible for this folding. Each chelates and bridges two coppers from one half of the sheet with its oximato oxygen forming a $(\mu_3,\eta^1\text{-O-NR})$ bridge between three copper centres on the other side of the fold. Of the twenty triply-bridging ligands, ten hydroxo and two methoxo are typical for such a triangulated sheet topology. Less usual are the two oxo ligands O(1) and O(2), which, as well as each bridging three copper centres in the sheet, also coordinate to a copper, Cu(19) or Cu(20) respectively, from the bridge moiety. The resulting $(\mu_4\text{-O})^{2-}$ ligands form the principal linkage between the two cluster sub-units. Also very unusual are the two $(\mu_3,\eta^1\text{-ONO}_2)^-$ nitrato ligands. From each of these nitrates just one oxygen, O(53) or O(56), bridges a triangle of coppers. These oxygens all occupy a Jahn-Teller axial site on each of the Cu^{II} ions. The four remaining triple-bridges are formed by the oximato-oxygens O(25), O(28), O(37) and O(40) (of ligands 1, 2, 5 and 6, respectively). Two of the Cu_3 triangles in the folded sheet, Cu(1/5/10) and Cu(2/6/9) have no triply-bridging ligand and this is a consequence of the requirement for such bridges to be alternately above and below the sheet of metal ions. Here, the folded nature of the sheet means that bridges over these two triangles would be sterically impossible. The coppers around the outer edges of the sheets are bridged by $(\mu_2\text{-OH})$ (O(20)) and $(\mu_2\text{-OMe})$ (O(17)) ligands provided by either phenoxo oxygens or N-O groups from $(\text{vanox})^{2-}$ ligands or by terminal aqua or methanol ligands.

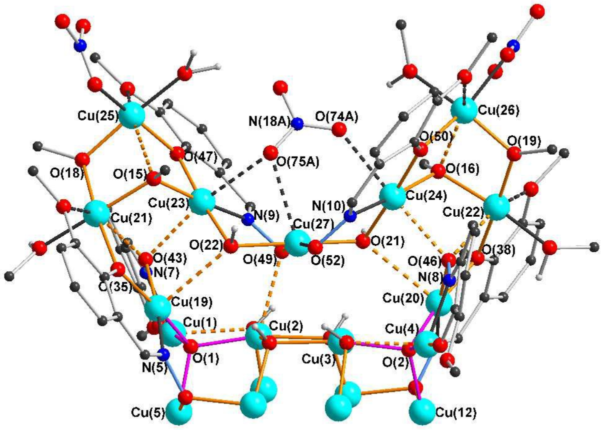

Fig. 3: Structure of the Cu_9 bridge with its connection to the Cu_{18} moiety with the elongated Jahn-Teller bonds shown as dashed lines.

Figure 3 shows the Cu_9 "bridging" sub-unit, and its connection to the folded sheet. The two buttresses of the bridge are made up of similar Cu_4 defect-dicubane moieties, in which the two triple-bridges are provided by a $(\mu_3\text{-OMe})$ and an oximato oxygen in both cases. Of the four double bridges around the edges of each Cu_4 quadrilateral, one is provided by a $(\mu_2\text{-OMe})$ and two by bridging phenoxo oxygens from $(\text{vanox})^{2-}$ ligands. The fourth is provided by a very unsymmetrical hydroxo bridge, which also coordinates to the final copper in the cluster, Cu(27). In this way Cu(27) is suspended between the two buttresses over the top of the Cu_{18} sub-unit. The Cu(19)-O(22) and Cu(20)-O(21) distances are both long at *ca.* 2.80 Å, but the geometries at O(21) and O(22) both indicate that there is at least a weak interaction to Cu(20) or Cu(19) and these ligands should therefore be formulated as $(\mu_{2\frac{1}{2}}\text{-OH})$ bridges. Cu(27) is also supported by the oximato oxygens O(49) and O(52) from ligands 9 and 10. Above Cu(27), a nitrate anion is very weakly and unsymmetrically coordinated to three copper centres. Although the Cu-O distances all exceed 2.60 Å it is better to consider this as a weakly-bound ligand rather than an uncoordinated counteranion.

Adopting a recent topological approach to describe polynuclear compounds, the core of compound **1** can be enumerated using the TOPOS software[14] as **2,2,3,3,3,3,4,4,5,5,5,6,6,7M27-1**. This topological structure is shown in Fig. 4, in which the Cu··Cu linkages within the folded sheet, within the bridge or linking between these moieties are highlighted in different colours for clarity.

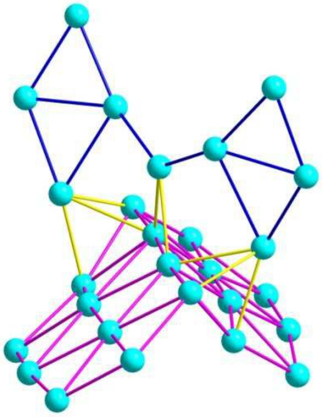

Fig. 4: Topological scheme of the Cu_{27} core of **1**. Cu-Cu linkages within the folded sheet are drawn as purple, those within the "bridge" as blue, and those between the folded sheet and bridge as yellow.

Magnetic susceptibility measurements were carried out on a polycrystalline sample of **1** from 300 to 1.8 K under an external dc field of 0.1 T (Figure 5). At room temperature, the χT product is 5.52 cm^3K/mol, significantly less than the theoretical value of 10.125 cm^3K/mol for 27 non-interacting Cu^{II} metal centres ($S = ½$, $g = 2$: $C = 0.375$ cm^3K/mol) indicating the presence of strong antiferromagnetic coupling. Consistent with this, χT immediately starts to decline on cooling, reaching 0.61 cm^3K/mol at 1.8 K, at which temperature it is still decreasing rapidly, suggesting that the ground state probably corresponds to $S = ½$, but with a number of nearby and accessible low-lying excited states with higher spins.

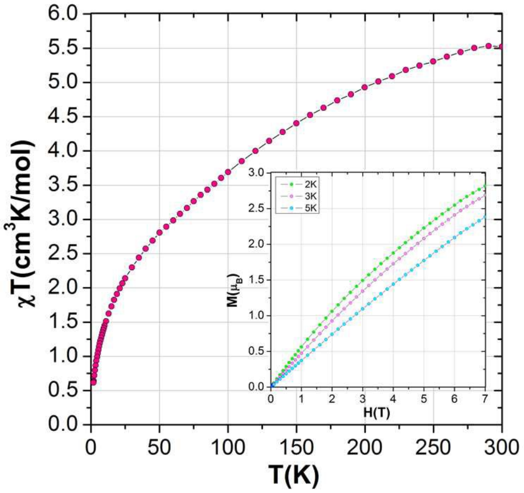

Fig. 5: Temperature dependence of χT for **1**, with the field dependence of the magnetization for **1** (inset).

The field-dependence of the magnetization (Figure 5, inset) shows an almost linear increase up to 7 T, consistent with the field-induced population of states with higher spins. The simplest rationalization of a ground state with $S = ½$ takes the approximate two-fold symmetry of the molecule into account. If the spins on Cu(2) and Cu(3) are antiparallel, the individual spins on each half of the molecule would each be antiparallel to the corresponding spin on the other half, resulting in compensation of the spins on Cu(1) to Cu(26). Only the spin on Cu(27), which lies on the quasi twofold molecular axis, and thus has no partner, remains uncompensated, giving the observed $S = ½$**.** However, the linear shape of the magnetization curves measured at various low temperatures (Fig. 5) suggests that this system must be highly frustrated since saturation corresponding to an $S = ½$ spin ground state is never achieved even at 7 T. This situation is similar to the observed behavior of the Mn_{19} sheet[12,13,15] which has a frustrated spin structure and a ground spin state of $S = 5/2$. The magnetization curves for this system show a similar linear increase which is attributed to the population of the excited states of the frustrated system. In our case, the situation is made more complex as a result of the bent sheet topology.

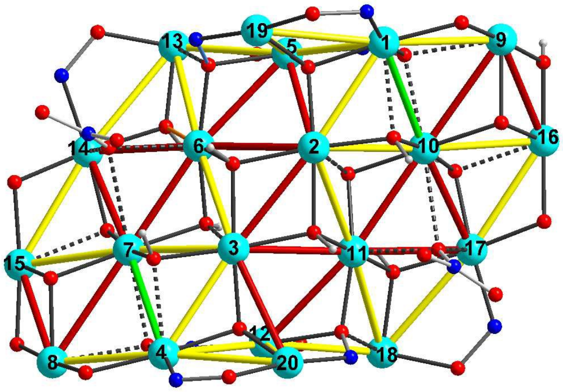

Fig. 6: Coupling between the 18 Cu^{II} centres of the folded sheet of **1** (red: strong antiferromagnetic, yellow: moderate antiferromagnetic, green: weak ferromagnetic, see text)**.**

It is known for dinuclear complexes with μ_2-oxygen bridges that the coupling between the Cu^{II} ions depends on whether the bridging atoms coordinate in axial or equatorial positions.[16] An oxygen atom in an axial position on one copper and in an equatorial position on the second usually mediates weak ferromagnetic interactions, whereas oxygen atoms in equatorial positions on both coppers will mediate strong antiferromagnetic interactions. In the present case, within the folded sheet moiety there are 18 Cu^{II} ions mostly linked by triply-bridging oxygens. In Figure 6, Cu-Cu linkages involving two *eq-eq* bridges are shown in red. These probably lead to strongly antiferromagnetic interactions. Linkages involving competing *eq-eq* and *eq-ax* bridges are shown in yellow with the antiferromagnetic component probably dominating. Just two linkages involve a pair of *eq-ax* bridges expected to ferromagnetic (shown in green). It is clear from Figure 6 that antiferromagnetic interactions of different magnitudes will dominate within this triangulated sheet and thus result in a highly frustrated spin structure.

Conclusions

In conclusion, we have described a remarkably stable, odd-numbered Cu_{27} coordination cluster compound. The system not only represents the largest odd-numbered Cu^{II} coordination so far characterised, but also has a core structure with an unusual and new topology equating to a bent triangulated sheet. Whilst flat triangulated sheet structures are known to display frustration effects when based on half-integer spin metal ions, our case adds the further complication arising from the folding of the sheet. This system should thus provide a fascinating challenge for physicists interested in exploring systems with half-integer spins.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Crystal Data for **1**: $C_{105}H_{184}Cu_{27}N_{20}O_{74}$, 4626.30 g mol^{-1}, monoclinic, $P2_1/c$, a = 31.939(3), b = 18.8704(16), c = 32.730(3) Å, β = 117.116(2)°, V = 17558(3) Å^3, Z = 4, T = 150(2) K, ρ_{calc} = 1.932 g cm^{-3}, F(000) = 10276, λ = 0.8000 Å, μ = 4.581 mm^{-1}; 194764 data, 39592 unique (R_{int} = 0.0595), 2235 parameters, final wR_2 = 0.1490, S = 1.046 (all data), R_1 (32186 data with $I > 2\sigma(I)$) = 0.0507. CCDC 1036132.

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