A Heterometallic (Ni^II−Cu^II) Decanuclear Cluster Containing Two Distorted Cubane-like Pentanuclear Cores: Synthesis, Structure, and Magnetic Properties

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Ⓢ *Supporting Information*

ABSTRACT: A new heterometallic Ni^II−Cu^II decanuclear cluster, $\{[Ni_4Cu_6(\mu\text{-}OH_2)_2(dpkO_2)_8(OAc)_4(H_2O)_4]\cdot 2CH_3OH\cdot 17H_2O\}$ (**1**), has been synthesized by self-assembly of the constituent metal ions and the precursor di-2-pyridylketone (dpk) of multinucleating ligand $dpkO_2^{2-}$ and is structurally characterized. The cluster **1** is formed by the union of two symmetry-related distorted cubane-like pentanuclear cores. A magnetic study of **1** reveals strong antiferromagnetic interactions operating through the Ni−O−Ni pathway, which is independent of the assumption $D = 0$ or $D \neq 0$. The pentanuclear cores are ferromagnetically coupled, as supported by density functional theory calculations.

T he chemistry of high-spin clusters or coordination polymers is an area of extensive research because of the large diversity in intriguing structures and potential applications in the field of molecular magnetism.[1] Recently, enormous interest has been directed toward the study of polynuclear clusters to explore their importance in bioinorganic chemistry[2] and also as new molecule-based materials.[3] In the context of molecular magnetism, polynuclear heterometallic clusters are promising candidates as single-molecule magnets (SMMs),[4] which have potential applications in high-density information storage, quantum computation, and spintronics.[5] Although there are some reports on small SMMs, consisting of heterometallic 3d−4f polynuclear clusters,[6] a larger database is required to get insight into their magneto-structural correlations. However, the design and synthesis of higher-nuclearity clusters based on two transition-metal ions with different coordination geometries remain a challenge because precise control over the nuclearity of the clusters is very difficult.[7] To achieve the desired structure by self-assembly, it is necessary to conceive a rational approach based on the ligational motifs of organic spacers and a malleable coordination environment of metal ions. Polytopic ligands like di-2-pyridylketone (dpk) with well-defined and appropriately separated coordination compartments, in principle, have better control over the outcome of a self-assembly process to afford

clusters with predefined nuclearities.[7b] Moreover, dpk can be in situ translated into a new ligand in an aqueous or alcoholic medium through nucleophilic attack on the keto group in the presence of metal ions.[7c] This in situ generation of a new ligand renders further flexibility toward binding a larger number of metal centers. Here we envisioned that the spontaneous self-assembly of dpk with two different 3d ions, Ni^II and Cu^II, would produce a heterometallic cluster through the subtle balance between a coordination algorithm of metal ions and flexible coordination motifs of the ligand. In this Communication, we report the synthesis, structure, and magnetic properties of a heterometallic decanuclear cluster, $\{[Ni_4Cu_6(\mu\text{-}OH_2)_2(dpkO_2)_8(OAc)_4(H_2O)_4]\cdot 2CH_3OH\cdot 17H_2O\}$ [**1**; $dpkO_2^{2-} = (C_5NH_4)_2CO_2$; Scheme S1 in the Supporting Information (SI)], formed by the self-assembly of Ni^II, Cu^II, and the ligand dpk. The two pentanuclear cores $[Ni_2Cu_3(\mu\text{-}OH_2)(dpkO_2)_4(OAc)_2(H_2O)]$ are connected by a water bridge to form the decanuclear cluster, and to the best of our knowledge, this is the first example of such a heterometallic decanuclear cluster of Ni^II and Cu^II.

The reaction of $Cu(OAc)_2\cdot H_2O$ and $Ni(OAc)_2\cdot 4H_2O$ with dpk in a 1:1:1 molar ratio in a $H_2O/MeOH$ medium results in a green solution, the slow evaporation of which affords green single crystals of **1** [an IR spectrum and a powder X-ray diffraction (PXRD) pattern are given in Figures S1 and S2 in the SI]. The formulation and composition of Cu^II and Ni^II in **1** are confirmed from the inductively coupled plasma mass spectrometry (ICP) and energy-dispersive X-ray spectroscopy (EDX) results (Figure S3 in the SI). A single-crystal XRD study reveals that **1** crystallizes in the monoclinic $P2_1/c$ space group and contains a decanuclear cluster with two symmetry-related pentanuclear cores (Figure 1). The pentanuclear core (Figure S4 in the SI) contains two crystallographically independent Ni^II centers and three crystallographically independent Cu^II centers with different coordination environments. The metal centers are bridged by three $dpkO_2$, doubly deprotonated anions of the *gem*-diol form $(C_5NH_4)_2C(OH)_2$, formed by in situ reaction in
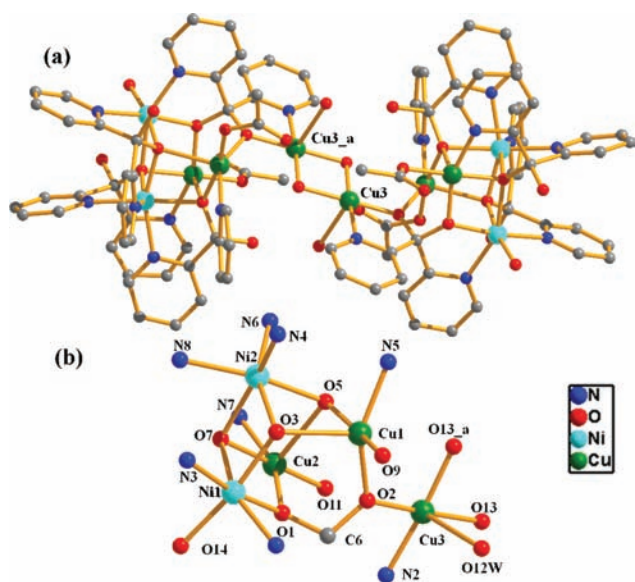
Figure 1. (a) View of the heterometallic Ni^{II}−Cu^{II} decanuclear core of **1**. (b) Pentanuclear core showing metal−ligand bridging. Nonbonding atoms are omitted for clarity.

Figure 2. (a) Experimental (black points) $\chi_M T$ versus T plot for **1**. The red line indicates the best fit obtained considering D (for J and D values, see Table 1). (b) M versus H curve for **1** at 3 K.

the presence of metal ions. The positions of the metal atoms were assigned on the basis of the coordination geometry and structure refinement parameters. Ni1 adopts a distorted octahedral geometry and is chelated to two different dpkO$_2$ ligands (O1, N1 and O3, N3 atoms); the other two coordination sites are furnished by the O7 atom of another dpkO$_2$ ligand and the O14 atom of a coordinated water molecule. Ni2 also locates itself in a distorted octahedral geometry. Three different dpkO$_2$ ligands (O3, N4; O5, N6; and O7, N8 atoms) chelate the Ni2 center. Ni−O and Ni−N bond lengths are in the range of 2.001(8)−2.199(7) Å and 2.052(10)−2.114(10) Å, respectively. All of the Cu centers adopt a distorted square-pyramidal (4 + 1) geometry.

Cu1 is coordinated to three different dpkO$_2$ ligands (ligated through N5, O5; O2; and O3) and one acetate ligand (O9 atom). Similarly for Cu2, three different dpkO$_2$ ligands and one acetate ligand furnish the coordinations sites (O7, N7; O1; and O5 and O11). Cu3 is ligated to one dpkO$_2$ ligand (O2 and N2), two bridging μ-OH$_2$ (O13 and O13_a), and one coordinated water molecule (O12w). The Cu−O/N equatorial bond lengths are in the range of 1.905(7)−2.035(10) Å, and the Cu−O apical bond lengths vary from 2.312(7) to 2.73(2) Å. Ni1, Ni2, Cu1, and Cu2 form a distorted cubane-like structure with one missing edge (Figure 1b). In the cubane core, μ_3-O5, μ_3-O3, and μ_3-O7 atoms coming from three different dpkO$_2$ ligands bridge Cu1, Cu2, Ni2; Cu1, Ni1, Ni2; and Ni1, Ni2, Cu2, respectively, while Cu2 and Ni1 atoms are doubly bridged by the μ_2-O1 atom. The μ_2-O2 atom bridges Cu1 and Cu3, which results in the extension of this cubane to the pentanuclear core (Figure S4 in the SI). Two pentanuclear cores are further bridged by two water molecules (μ_2-O13 and μ_2-O13_a) to form the novel decanuclear cluster (Figure 1a). The clusters are connected through hydrogen bonding via the O atoms of dpkO$_2$(O4), coordinated water (O14), and guest water molecules (Figure S5 in the SI).

The temperature-dependent magnetic studies have been performed for the polycrystalline powder sample of **1** in the temperature range 300−3 K (Figure 2). At room temperature, the $\chi_M T$ value is 7.3 cm^3 mol^{-1} K, which is consistent with four
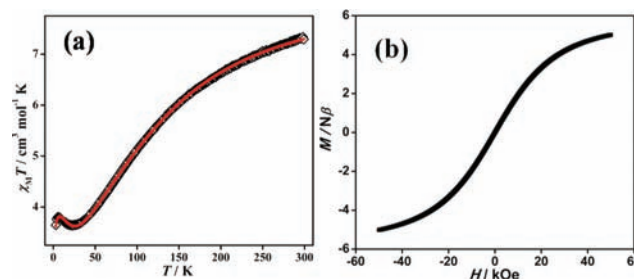
quasi-isolated Ni^{II} ions and six quasi-isolated Cu^{II} ions; the corresponding theoretical value would be 6.25 cm^3 mol^{-1} K, assuming the lower theoretical limit of g = 2.00. The $\chi_M T$ value decreases monotonically up to 30 K; after that, there is a small increase of the $\chi_M T$ value, which finally shows a small decrease beyond 5 K with a value of 3.6 cm^3 mol^{-1} K, presumably because of the D parameter (zero-field splitting of the Ni^{II} ions) and interdecanuclear interactions through hydrogen bonding. The decanuclear structure is formed by the union of two symmetry-related pentanuclear cores via diaqua bridging ligands. Density functional theory (DFT) calculations (see below) have demonstrated that this coupling interaction is ferromagnetic. Indeed, from a qualitative point of view this interaction cannot be antiferromagnetic (with $H = -J\sum S_i S_j$), as in that case, the $\chi_M T$ of both pentanuclear moieties would be cancelled due to the presence of inversion center and the final $\chi_M T$ would be zero, which is not the case here.

At 3 K, the reduced magnetization of **1** (Figure 2b) tends to $6M/N\beta$, corresponding to six unpaired electrons. This feature is consistent with the following assumption: the presence of antiferromagnetism in the $\chi_M T$ versus T plot is due to the antiferromagnetic character of the Ni−O−Ni pathway, which is well documented in the literature with such kinds of geometries.[8] Thus, once the spins of the Ni^{II} ions are canceled, it seems that there are six unpaired electrons arising from the six Cu^{II} ions, which may be in isolated form or ferromagnetically coupled.

The fitting of the magnetic data for the decanuclear core has been performed using the *MAGPACK* program[9] with or without the D parameter. The spin part of the Hamiltonian in this program is $H = -2J\sum S_i S_j$. The magnetic pathways are shown in Figure 1b and Scheme S2 in the SI, and the calculated J values with or without D are presented in Table 1. It is worth mentioning that there are only small differences in the calculations of the J parameters whether D is considered or not. In both cases, the interaction between Cu1 and Cu3 remains antiferromagnetic with a very small J value (<-1 cm^{-1}). Although a strong interaction is expected because of the Cu−O−Cu angle of magnitude 119.7(4)°,[10] the trigonal-bipyramidal distortion of Cu1 coordination would reduce the magnitude of the interaction. The best fit obtained with D or without D are presented in Figure 2a and Figure S6 in SI, respectively. However, with invoking D the result is slightly better. It is also logical to assume that the D parameter is not zero for Ni^{II} ions (see Table 1) with S = 1. The D parameter obtained with the fit is too high for standard Ni^{II} ions,[11] which may be a simple mathematical artifact arising from other antiferromagnetic pathways. The intricate structure may result in some spin frustrations among Cu^{II} and Ni^{II} ions (see Table

Table 1. J and D Values for the Decanuclear Entity Following the Labels of Figure 1b

magnetic pathway	J (cm^{-1})		$D = 0$	D variable (cm^{-1})^c
Ni1−Ni2	J_1		−49.2	−49.7
Ni1−Cu2	J_2		29.5	28.9
Ni1−Cu1	J_3		62.1	62.8
Ni2−Cu2	J_4		26.1	26.7
Ni2−Cu1	J_5		−13.3	−11.7
Cu1−Cu3	J_6		−0.45	−0.28
Cu3−Cu3_a	J_7		13.6^a	13.6^a
	g		2.29	2.29
	D		0	29.6
	R^b		7.4 × 10^{-6}	6.9 × 10^{-6}
Cu1−Cu2			negligible d(Cu2−O) = 2.5 Å	
Ni1−Cu3			negligible (syn−anti quasi-perpendicular)	
Cu2−Cu3			negligible (syn−anti quasi-perpendicular)	

^{a}Fixed from the value of the DFT calculations. ^{b}The R factor is the agreement factor defined as $\sum_i [(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2 / \sum_i [(\chi_m T)_{obs}]^2$. ^{c}The parameter D contains zJ' (intermolecular interactions).

1). These findings indicate that the system has several analytical solutions, and the most reliable value should be assumed to be the one calculated with an average of those with appreciable D or with $D = 0$. Some of the coupling constants have been assumed to be negligible (see Table 1) to minimize the number of variables in the fitting process. The assumption of six unpaired electrons in the ground state, accounting for saturation of the magnetization curve at 3 K, which corresponds to six quasi-isolated Cu^{II} ions, is corroborated by calculations with $J_{Cu1−Cu2}$ and $J_{Cu2−Cu3}$ to be negligible (Table 1) and with $J_{Cu1−Cu3}$ to be almost zero.

The central magnetic pathway Cu$_2$O$_2$ should be ferromagnetic, as anticipated from the Cu3−O−Cu3_a angle of 95.4(3) °.[10] To understand the interaction between the pentanuclear cores, a computational study based on DFT was performed (see the SI). The water-bridged cluster comprised of two Cu^{II} centers has been considered to calculate the ground-state energy of the singlet and triplet states. The results show that the triplet state is more stable than the singlet state by 0.003371 eV (27.2 cm^{-1}), suggesting the dominant ferromagnetic exchange interaction between the two pentanuclear cores. The spin-density plot is given in Figure S7 in the SI.

In summary, a facile synthetic route for a new heterometallic decanuclear cluster has been perceived through the self-assembly of two different 3d ions, Ni^{II} and Cu^{II}, and the ligand dpk. Compound **1** represents the first example of a heterometallic decanuclear cluster based on Ni^{II} and Cu^{II}. The pentanuclear core shows dominant antiferromagnetic interactions between the metal centers, while ferromagnetic interaction operates between the two pentanuclear cores. Thus, the judicious choice of the blocking ligand with suitable coordination compartments and their self-assembly with metal ions with compatible geometry can lead to formation of the desired heterometallic cluster.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedure and crystallographic refinement details, IR, EDX, and DFT results for **1**, as well as the scheme of the magnetic pathway of the pentanuclear moiety. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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