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Interpretation of the Magnetic Properties of a Compound Consisting of Cocrystallized Cu^{II}_3 and Cu^{II}_4 Clusters through the Targeted Synthesis and Study of Its Discrete Cu^{II}_4 Component

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The use of the binary "blend" of $MeCO_2^-$/$pdmH_2$ ligands ($pdmH_2$ = pyridine-2,6-dimethanol) in copper(II) chemistry has provided access to a compound consisting of discrete linear Cu^{II}_3 and cubane Cu^{II}_4 clusters. The complicated magnetic behavior of the Cu^{II}_3 + Cu^{II}_4 complex was clarified and interpreted through the designed synthesis of the individual Cu^{II}_4 component; a unique 1D $(Cu^{II}_5)_n$ compound containing a Cu^{II}_3 subunit, which is structurally similar to the trinuclear cluster in the Cu^{II}_3 + Cu^{II}_4 compound, was also isolated and structurally characterized.

Molecular 3d metal cluster chemistry has been attracting intense interest during the last 2 decades.[1] Among the diverse reasons for this are the aesthetically pleasing structures that many such molecular clusters possess[2] and the search for models of metal-containing sites in biology[3] and compounds with interesting magnetic properties.[4] A synthetic challenge involves discovering simple and efficient approaches to the incorporation of many metal ions in a small, single molecular entity, simultaneously building into the resulting system useful magnetic properties. If the metal ions are *not* incorporated in a single molecular entity, but in two or more instead, the interpretation of magnetic properties is difficult or impossible. Ligands used in the synthesis of molecular clusters can be classified into two main classes: (i) relatively simple ligands or a combination of ligands with appended potentially bridging groups, e.g., carboxylates, alkoxides, oximates, etc., that can aggregate metal ions in a polynuclear system through a network of bridges[1,5] and (ii) large ligands with arrays of coordination pockets suitably organized to create specific geometric arrangements of metal centers through bridging connections, e.g., RO^-, $R-N=N-R'$, etc., built into the ligand backbone.[6] The ligands of the former class are, however, comparatively restricted,[1,6] and thus the use of new or less developed ligands, or a combination of ligands, remains important in the field.

The focus of this Communication is on two of the above-mentioned aspects. First, we shall report the initial use of pyridine-2,6-dimethanol ($pdmH_2$) in copper(II) cluster chemistry by describing the products of its reactions with $[Cu_2(O_2CMe)_4(H_2O)_2]$. On deprotonation, this ligand will provide alkoxide group(s), which are excellent bridging units that can foster the formation of high-nuclearity clusters. The presence of a tridentate *chelate O,N,O′* unit within $pdmH^-$/pdm^{2-} was expected to give high thermodynamic stability in the products, and $pdmH_2$ can thus be considered as a "borderline" ligand in the above-mentioned classification. Acetates are also excellent bridging groups in copper(II) chemistry. Despite its rather extensive employment in *trivalent* 3d metal cluster chemistry,[7] there has been only very limited use of $pdmH_2$ in copper(II) chemistry (and generally in the *divalent* 3d metal chemistry), and only one dinuclear[8] and a few mononuclear[8] complexes have been reported. Because the initially isolated compound from the $[Cu_2(O_2CMe)_4(H_2O)_2]$/$pdmH_2$ reaction system consists of two cocrystallized clusters (vide infra), the question arose as to how to interpret its magnetic properties. In order to contribute to the solution of this problem, we turned back to the synthetic bench and tried to prepare each cluster separately; this effort is the second important topic of the present work.

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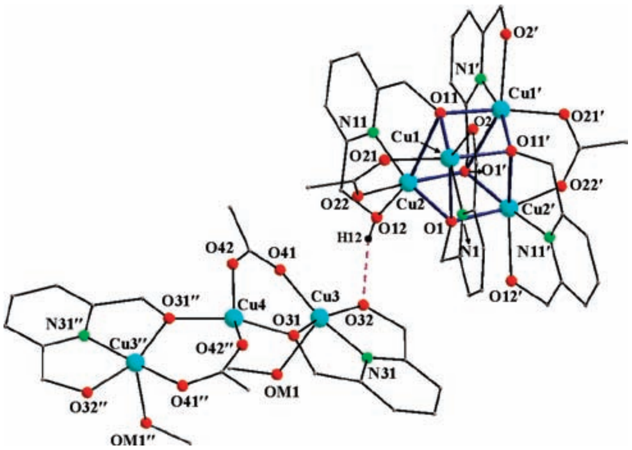
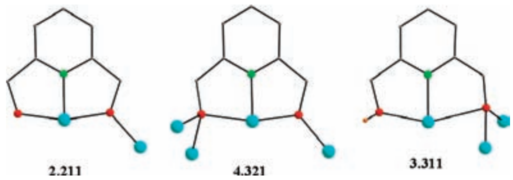


Figure 1. Molecular structures of the discrete Cu_3 and Cu_4 cluster components of **1**. The cubane core of the Cu_4 cation is outlined in dark-purple bold. The dashed line represents the crystallographically unique Cu_3-to-Cu_4 hydrogen bond. Single and double primes are used for symmetry-related atoms.

Chart 1. Crystallographically Established Coordination Modes of $pdmH^-$ and pdm^{2-} in **1**−**3**[a]



[a] The 2.211 and 4.321 modes are novel; i.e., they have not been observed previously in complexes of any metals.

The reaction of $[Cu_2(O_2CMe)_4(H_2O)_2]$, $pdmH_2$ and $LiClO_4$ in an 1.2:2:2 molar ratio in MeOH led to a blue solution that upon slow evaporation at room temperature gave blue crystals of $\{[Cu_3(O_2CMe)_2(pdm)_2(MeOH)_2][Cu_4(O_2CMe)_2(pdmH)_4]\}(ClO_4)_2 \cdot 4MeOH$ (**1**·4MeOH) in 55% yield.[9] The $[Cu_4(O_2CMe)_2(pdmH)_4]^{2+}$ cation of **1** (Figure 1) lies on a crystallographic C_2 axis and has a cubane $\{Cu_4(\mu_3\text{-}OR)_4\}^{4+}$ core with the four distorted octahedral Cu^{II} atoms and the deprotonated μ_3-O atoms from the four 3.311 (Harris notation;[10] Chart 1) $pdmH^-$ ligands occupying alternate vertices. The two *syn,syn*-2.11 $MeCO_2^-$ groups bridge Cu_2 pairs that belong to two opposite faces of the cube. The central atom Cu4 of the $[Cu_3(O_2CMe)_2(pdm)_2(MeOH)_2]$ molecule of **1** (Figure 1) lies on a crystallographic C_2 axis and is coordinated by two O atoms that belong to different *syn,syn*-2.11 $MeCO_2^-$ groups and two μ-O atoms from the two 2.211 (Chart 1) pdm^{2-} ligands in a distorted square-planar fashion. Square-pyramidal atoms Cu3 and Cu3″ are each coordinated by one N and two O atoms belonging to the “chelate” part of one pdm^{2-} ligand, one $MeCO_2^-$ O atom, and one MeOH group. The Cu^{II}_3 and Cu^{II}_4 clusters of **1** are linked through strong hydrogen bonds involving O12 ($pdmH^-$) as the donor and O32 (pdm^{2-}) as the acceptor (O12···O32, 2.632 Å; O12−HO12···O32, 156.6°).

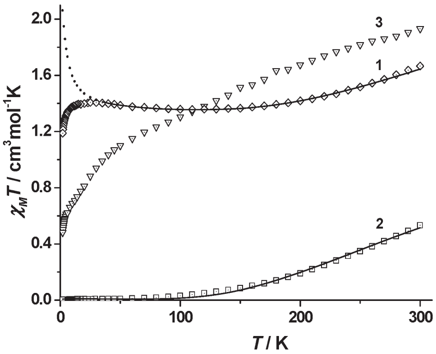


Figure 2. $\chi_M T$ vs T plots for complexes **1**−**3** in a 1 kG field. The solid lines for **1** and **2** are the fits of the data; see the text for the fit parameters. The dotted line for **1** is the low-T (<25 K) simulation of its magnetic response.

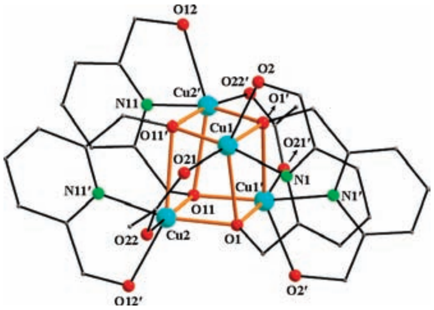


Figure 3. Molecular structure of the cation of **2**. Primes are used for symmetry-related atoms.

The room-temperature $\chi_M T$ value for **1** (1.67 cm^3 K mol^{-1}) is lower than the value expected for seven $S = {}^1/_2$ uncoupled spins (2.625 cm^3 K mol^{-1} with $g = 2.0$). The shape of the $\chi_M T$ vs T plot (Figure 2) suggests a combination of strongly antiferromagnetic and moderately ferromagnetic responses for the two clusters that are present in this compound (Figure S1 in the Supporting Information). Further analysis of the magnetic data is not reliable.

Our next synthetic goal was to prepare a discrete cluster containing only the cubane cation $[Cu_4(O_2CMe)_2(pdmH)_4]^{2+}$. Because the $Cu^{II}/pdmH^-$ ratio in such a cubane is 1:1, we decreased the ratio from 1.2 (this value led to pure **1**) to 1.0. Thus, the 1:2 reaction between $[Cu_2(O_2CMe)_4(H_2O)_2]$ and $pdmH_2$ ($Cu^{II}/pdmH_2 = 1.0$) in MeOH led to a precipitate. A MeCN solution of the solid was layered with Et_2O to give greenish-blue crystals of $[Cu_4(O_2CMe)_2(pdmH)_4](O_2CMe)_2 \cdot 5H_2O \cdot 2MeCN$ (**2**·$5H_2O$·2MeCN) in 80% yield.[9] The molecular structure of the cubane cation of **2** (Figure 3) is almost identical with that present in **1**. The two cations are in between the 2 + 4 and 4 + 2 families of Cu^{II} cubane complexes according to the classification scheme of Ruiz and co-workers;[11] although they have four short and two long Cu···Cu distances (formally 4 + 2), the cubanes can be considered as formed by two stacked dinuclear units (those containing Cu1/Cu2′ and Cu1′/Cu2 in **2** and Cu1/Cu1′ and Cu2/Cu2′ in **1**)

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(9) Crystal structure data for **1**·4MeOH: $C_{56}H_{82}Cu_7N_6O_{34}Cl_2$, M_w = 1898.96, orthorhombic, space group *Pnaa* with a = 20.42 (1) Å, b = 14.89 (1) Å, c = 24.38(2) Å, V = 7413(9) Å^3, T = 298 K, Z = 4, R1 [$I > 2\sigma(I)$] = 0.0590, wR2 = 0.1721 (F^2, all data). Crystal structure data for **2**·$5H_2O$·2 MeCN: $C_{40}H_{60}Cu_4N_6O_{21}$, M_w = 1215.10, orthorhombic, space group *C*2221 with a = 17.560(10) Å, b = 14.205(8) Å, c = 20.820(10) Å, V = 5193(5) Å^3, T = 298 K, Z = 4, R1 [$I > 2\sigma(I)$] = 0.0250, wR2 = 0.0648 (F^2, all data). Crystal structure data for **3**: $C_{26}H_{32}Cu_5N_2O_{16}$, M_w = 946.24, triclinic, space group $P\bar{1}$ with a = 9.577(6) Å, b = 11.739(8) Å, c = 7.765(5) Å, α = 72.00(3)°, β = 75.60(3)°, γ = 70.83(3)°, V = 773.6(9) Å^3, T = 298 K, Z = 1, R1 [$I > 2\sigma(I)$] = 0.0445, wR2 = 0.1248 (F^2, all data).

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with four long Cu−O distances (~2.5 Å) between the two units, the latter being a typical feature of the 2 + 4 family.[11]

The room-temperature $\chi_M T$ value for **2** is 0.53 cm^3 K mol^{-1}, much lower than the value expected for four $S = {}^1/_2$ uncoupled spins (1.50 cm^3 K mol^{-1} with $g = 2.0$), tending quickly to zero upon cooling (Figure 2), indicating a very strong antiferromagnetic coupling. The χ_M vs T plot shows a broad maximum around room temperature. A fit of the experimental data of **2** to the expression derived from the spin Hamiltonian (using the atomic numbering in Figure 3) gives the parameters $J_1 = -480$ cm^{-1}, $J_2 = -12$ cm^{-1}, and $g = 2.095$. Neglecting J_2, i.e., considering the complex as a pair of two isolated dimers, best-fit parameters are $J_1 = -480$ cm^{-1} and $g = 2.096$. The large intradinuclear Cu−O−Cu angles (101.0 and 101.4°) are considered to be responsible for the very strong antiferromagnetic J_1 coupling.[11,12]

$$H = -J_1(S_1S_{2'} + S_{1'}S_2) - J_2(S_1S_2 + S_{1'}S_{2'}) \qquad (1)$$

With the knowledge obtained from the magnetic treatment of **2**, we can explain the magnetic properties of **1**, whose cubane cation is structurally identical with that in **2**. A very strong antiferromagnetic coupling would be expected for the cation of **1**, and the increase of the $\chi_M T$ value from ~110 K down to 25 K is attributed to ferromagnetic interactions within the trinuclear molecule of the complex. Applying the spin Hamiltonian (see also Figure 1)

$$H = -J_1(S_1S_{1'} + S_2S_{2'}) - J_2(S_1S_2 + S_{1'}S_{2'}) - J_3(S_3S_4 + S_4S_{3''}) \qquad (2)$$

best-fit parameters, in the 300−25 K range, are $J_1 = -624$ cm^{-1}, $J_2 = -11$ cm^{-1}, $J_3 = +4.8$ cm^{-1}, and $g = 2.170$. The fit was performed between 300 and 25 K to avoid intercluster antiferromagnetic interactions responsible for the low-T decay of $\chi_M T$. Again the J_2 parameter is not relevant to the fit. The magnetization at 2 K tends to a value close to the equivalent of three electrons under a field of 5 T, in good agreement with the susceptibility study.[12]

In order to further confirm the ferromagnetic intratrinuclear coupling of **1**, we tried to prepare its neutral, trinuclear $[Cu_3(O_2CMe)_2(pdm)_2]$ component as a discrete cluster. Because the Cu/pdm^{2-} ratio in such a molecule is 1.5:1, we increased the ratio from 1.2 (this value led to pure **1**) to 2.0 and omitted the ClO_4^- ions (which stabilize the cubane cation of **1**) from the reaction system. Thus, the 1:1 reaction between $[Cu_2(O_2CMe)_4(H_2O)_2]$ and pdmH$_2$ (Cu^{II}/pdmH$_2$ = 2.0) in MeOH led to a green solution, which upon layering with Et$_2$O/*n*-hexane (1:1, v/v) gave bluish-green crystals of $[Cu_5(O_2CMe)_6(pdm)_2]_n$ (**3**) in 70% yield; this is the first complex of any divalent metal containing exclusively the doubly deprotonated form of the ligand. X-ray crystallography[9] revealed that the complex was not the desired cluster but instead an interesting 1D coordination polymer (Figure 4). Each repeat pentanuclear unit consists of centrosymmetric $\{Cu_3(O_2CMe)_2(pdm)_2\}$ and $\{Cu_2(O_2CMe)_4\}$ subunits. The trinuclear subunit of **3** (Cu3/Cu1/Cu3′) is structurally very similar to the trinuclear cluster of **1**; however, the MeCO$_2^-$ and pdm^{2-} groups adopt the 2.21 and novel 4.321 (Chart 1) coordination modes, respectively, in the former to provide its linkage with the two neighboring dinuclear subunits. The dinuclear subunit of **3** (Cu2/Cu2^a) contains the $\{Cu_2(\mu_2\text{-}OR)_2\}^{2+}$ core and links up two trinuclear subunits through two 2.11 and two 2.21 MeCO$_2^-$ ions; as a result, the two terminal metal ions (Cu3 and Cu3′) of the trinuclear subunit are six-coordinate (and not five-coordinate as in the Cu$^{II}_3$ component of **1**)

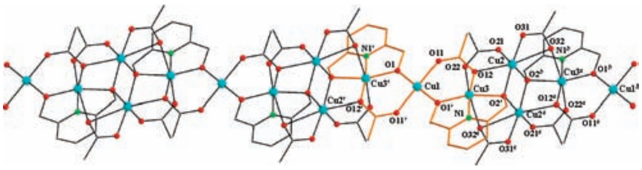

Figure 4. Portion of the polymeric structure of **3**. Symmetry code: ′, 1 − *x*, 5 − *y*, 1 − *z*; *a*, 1 − *x*, 6 − *y*, 1 − *z*; *b*, *x*, 5 + *y*, *z*. The Cu$^{II}_3$ subunit that is also present in **1** is outlined in thick orange.

The room-temperature $\chi_M T$ value for **3** (1.93 cm^3 K mol^{-1}) is slightly higher than that expected for five $S = {}^1/_2$ uncoupled spins (1.875 cm^3 K mol^{-1} with $g = 2.0$). Upon cooling, the $\chi_M T$ product decreases continuously down to a value of 0.48 cm^3 K mol^{-1} at 2.0 K, indicating an overall, moderate antiferromagnetic behavior. The compound exhibits a complicated pattern of interactions along the chain, and a fit of the data by means of analytical equations is not possible. Magnetization experiments indicate that there is one unpaired electron per Cu$^{II}_5$ unit at 2 K; there are several pathways to reach an $S = {}^1/_2$ ground state, and any proposals about the coupling pattern are speculative.

The chemical message of this work is that interesting clusters and polymers have resulted from the initial use of pdmH$_2$ in copper(II) acetate chemistry. Equally important is the magnetochemical lesson of the research story presented here: Complicated magnetic behavior in molecular materials consisting of discrete, cocrystallized clusters can be clarified and analyzed through the designed synthesis (and study) of their individual cluster components. Work in progress shows that the reactions of pdmH$_2$ with a host of other divalent 3d metals deliver many exciting clusters.

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Supporting Information Available: Crystallographic data for **1**·4MeOH, **2**·5H$_2$O·2MeCN, and **3** in CIF format and magnetism data for **1**·4MeOH. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] A full magnetic discussion will be provided in the full paper.