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Polynuclear $Cu^{II}_{12}M^{III}_6$ (M = Y, Nd, or Gd) Complexes Encapsulating a ClO_4^- Anion: $[Cu_{12}M_6(OH)_{24}(H_2O)_{18}(pyb)_{12}(ClO_4)](ClO_4)_{17}\cdot nH_2O$ (Pyb = Pyridine Betaine)

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The synthesis of polynuclear mixed copper−lanthanoid complexes has attracted attention for several reasons.[5−8] The nature of magnetic exchange interactions between rare-earth and transition-metal ions is not only of theoretical interest[6,7] but also relevant to the possible use of rare-earth orthoferrites and related materials as magnetic bubble devices.[9] Yttrium and rare-earth copper oxide compounds exhibit superconductivity with relatively high T_c values.[10] It also is of current interest to prepare high-nuclearity metal complexes in an effort to make nanoscale magnetic materials.[11] In this paper we report the synthesis, X-ray structure, and magnetochemical properties of three $Cu^{II}_{12}M^{III}_6$ (M = Y, Nd, or Gd) ionic complexes of the composition $[Cu_{12}M_6(OH)_{24}(H_2O)_{18}(pyb)_{12}(ClO_4)](ClO_4)_{17}\cdot nH_2O$. The 17+ cations are of particular interest not only because they are polynuclear Cu^{II}−lanthanoid complexes but also because they include an encapsulated μ_{12}-ClO_4^- anion. Molecules that imbibe anions are of considerable interest.[12]

To an aqueous solution (5 mL, 60 °C) of pyridine betaine (pyb; IUPAC, pyridinioacetate) (0.822 g, 6.0 mmol) was added $Cu(NO_3)_2\cdot 2.5H_2O$ (0.232 g, 1.0 mmol), and the solution was stirred for 5 min. An aqueous solution (2.5 mL) containing 4 mmol of $M(NO_3)_3\cdot nH_2O$ (M = Y, Nd, or Gd) was then added, followed by an aqueous solution (3 mL) of $NaClO_4\cdot H_2O$ (1.40 g, 10 mmol). The pH of the resulting solution was adjusted to ~3.5 by slow addition of 0.1 N NaOH, and then the solution was put into a desiccator charged with silica gel. After several days, gray-blue polyhedral crystals of complexes **1** (Gd), **2** (Y), or **3** (Nd) began to appear. The X-ray structure of $[Cu_{12}Gd_6(OH)_{24}(H_2O)_{18}(pyb)_{12}(ClO_4)](ClO_4)_{17}\cdot 10H_2O$ (**1**)[13] revealed the presence of the discrete molecular cation $[Cu_{12}Gd_6(\mu_3\text{-}OH)_{24}(\mu_{12}\text{-}ClO_4)(H_2O)_{18}(pyb)_{12}]^{17+}$ (**1a**) shown in Figure 1.

The cation (**1a**) of **1** may be conceptually described in terms of a $[Cu_{12}Gd_6(\mu_3\text{-}OH)_{24}]^+$ core of pseudocubic O_h symmetry, with the six Gd^{3+} ions positioned at the vertices of a regular nonbonding octahedron and the 12 Cu^{2+} ions located at the midpoints of the 12 octahedral edges. The polyhedron of 12 Cu^{2+} ions may be visualized as a cuboctahedron which is capped on the six square faces by the 6 Gd^{3+} ions. This Cu^{2+}−Gd^{3+} metal framework is interconnected by 24 symmetry-equivalent μ_3-OH ligands (under assumed O_h symmetry) that are each linked to one Gd^{3+} ion and two Cu^{2+} ions such that each $Gd(\mu_3\text{-}OH)_4$ fragment is square-pyramidal and each $Cu(\mu_3\text{-}OH)_4$ fragment is square-planar (Figure 1). Inclusion of the encapsulated tetrahedral μ_{12}-ClO_4 anion, in which each of the four oxygen atoms is connected to three Cu^{2+} ions, lowers the resulting pseudosymmetry from O_h to T_d. The crystallographically required site symmetry necessitates that the ClO_4^- anion be equally distributed over two centrosymmetrically-related orientations (corresponding to eight half-weighted oxygen atoms at the vertices of a cube); the resulting crystal-disordered average geometry of the central $[Cu_{12}Gd_6(\mu_3\text{-}OH)_{24}(\mu_{12}\text{-}ClO_4)]^{17+}$ kernel thereby conforms ideally to the O_h symmetry, whereas each kernel has T_d symmetry. The entire cation (**1a**) is then generated by addition of the 18 H_2O and 24 carboxylate oxygen atoms of the 12 pyridinoacetate (pyb) ligands. The external linkage of one acetate oxygen atom to each Cu^{2+} ion results in a six-coordinate oxygen environment with Cu−O bond lengths characteristic[14] of an elongated octahedron. Each nine-coordinated Gd^{3+} ion is connected to four μ_3-OH ligands, three H_2O oxygen atoms, and two carboxylate oxygen atoms from two different pyb ligands. All of the Gd−O bond lengths are reasonable.

A particularly novel feature of the structure of complex **1** is the one ClO_4^- anion which is encapsulated in the center of cation **1a**. As can be seen in Figure 1, this encapsulated ClO_4^- ion exhibits the very rare 12-coordination mode of XO_4^{n-} anions. Each oxygen atom of the ClO_4^- ion interacts (Cu−O = 2.32−2.47Å) with three Cu^{2+} ions. Thus, the ClO_4^- ion is 12-coordinate. There is only one other known[15] example of a 12-coordinate XO_4-type anion. In $[Hg_2(O_4Ge)]$, the $[GeO_4]^{4-}$ anion is 12-coordinate, where each O atom of the tetrahedral anion has three nonequivalent bond distances to Hg^{2+} ions.[16]

The Y^{III} complex **2** and the Nd^{III} complex **3** are isostructural to the Gd^{III} complex **1**. In the case of $[Cu_{12}Nd_6(OH)_{24}(H_2O)_{18}(pyb)_{12}(ClO_4)](ClO_4)_{17}\cdot 14H_2O$ (**3**), the X-ray structure[17] shows that the 17+ complex cations in complexes **1** and **3** are structurally very similar.

One goal of supramolecular chemistry is to prepare molecular receptors that selectively bind certain substrates.[12,18] Cryptates

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(13) Crystal data (21 °C) for $C_{84}H_{164}Cl_{18}Cu_{12}Gd_6N_{12}O_{148}$ (**1**): triclinic space group, a = 17.427(3) Å, b = 17.602(4) Å, c = 19.318(4) Å, α = 113.32(3)°, β = 102.15(3)°, γ = 107.47(3)°, V = 4810(2) Å^3, Z = 1, D_{calcd} = 2.09 g cm^{-3}. Structure solution and refinement based on 15 956 observed [$F > 4.0\sigma(F)$] reflections converged at R = 0.0875.

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(17) Crystal data (−100 °C) for $C_{84}H_{172}Cl_{18}Cu_{12}Nd_6N_{12}O_{152}$ (**3**): triclinic space group, a = 17.289(7) Å, b = 17.482(6) Å, c = 19.129(6) Å, α = 113.84(2)°, β = 101.95(3)°, γ = 107.78(3)°, V = 4659(3) Å^3, Z = 1, D_{calcd} = 2.156 g cm^{-3}. Structure solution and refinement based on 13 839 observed [$F > 4.0\sigma(F)$] reflections converged at R = 0.0591.

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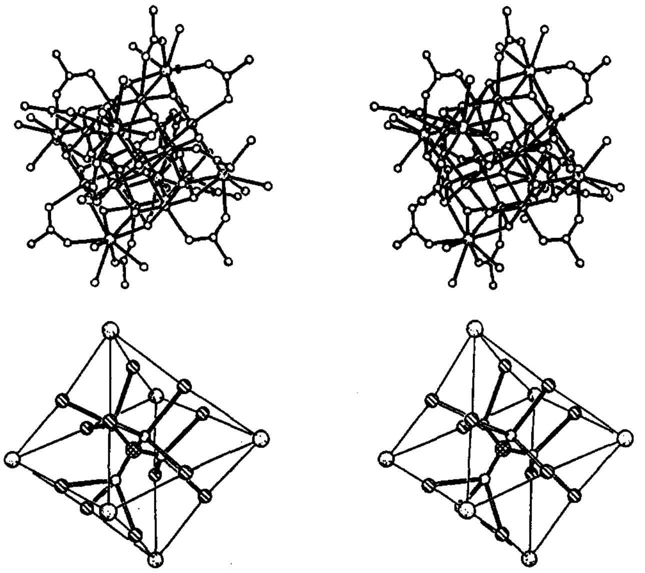

Figure 1. Stereoviews of the structure of [Cu$_{12}$Gd$_6$(OH)$_{24}$(H$_2$O)$_{18}$(pyb)$_{12}$(ClO$_4$)](ClO$_4$)$_{17}$·10H$_2$O (**1**). (Top) Stereoview of the 17+ cation complex **1a**. Only the C−CO$_2$ units of the pyridine betaines are shown (solid lines). (Bottom) Stereoview of the Gd$_6$Cu$_{12}$ClO$_4$ core inscribed inside an octahedron, where the Cl atom at the center is cross-hatched, the Cu atoms are marked with lines, and the Gd atoms are speckled.

have been designed that bind not only spherical cations and anions but also tetrahedral substrates such as the NH$_4^+$ ion.[12] Recently, interest has turned to designing molecular receptors for anions such as N$_3^-$,[19] carboxylates and phosphates,[12] and transition-metal hexacyanide anions.[20] Very recently, large polynuclear transition-metal complexes have been reported that serve as hosts for small molecules: polyoxovanadate clusters that incorporate CH$_3$CN,[21] F$^-$,[22] Cl$^-$,[22,23] Br$^-$,[23] and I$^-$,[23]; a polyoxoalkoxomolybdate cluster encapsulating a [Na(H$_2$O)$_3$]$^+$ moiety;[24] and tetranuclear iron complexes with an incorporated NH$_4^+$ cation.[25] It will prove interesting to see how critical the encapsulated ClO$_4^-$ anion is to the structure of cation **1a**. Does it serve as a nucleation site for the formation of the Cu$_{12}$M$_6$ cation? Can other anions replace the ClO$_4^-$ anion?

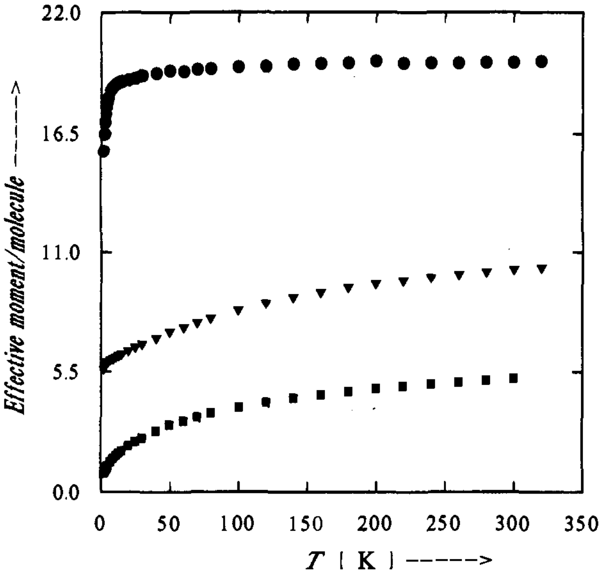

Figure 2. Plots of the effective magnetic moment, μ_{eff}, per molecule versus temperature for complexes **1** (●, Gd), **2** (■, Y), and **3** (▼, Nd).

Complexes **1−3** also have interesting magnetochemical characteristics. In the series of Cu$^{\text{II}}_{12}$M$^{\text{III}}_6$ complexes, Y$^{\text{III}}$ has no unpaired electrons, Nd$^{\text{III}}$ is f^3 ($^4I_{9/2}$), and Gd$^{\text{III}}$ is f^7 ($^8S_{7/2}$). In Figure 2 are given plots of the effective magnetic moment, μ_{eff}, versus temperature determined for parafilm-restrained, polycrystalline samples of complexes **1−3** in a 10.0 kG field. In the Y$^{\text{III}}$ complex **2**, there is an antiferromagnetic exchange interaction between pairs of Cu$^{\text{II}}$ ions. Since $\chi_M T$ approaches zero as the temperature is decreased to zero, the ground state of the Y$^{\text{III}}$ complex **2** has $S = 0$. At 300 K, complex **2** has $\mu_{\text{eff}} = 5.20\ \mu_B$ per Cu$_{12}$Y$_6$ complex. For the Nd$^{\text{III}}$ complex **3**, $\mu_{\text{eff}} = 10.3\ \mu_B$ per molecule at 320 K, which decreases gradually to 5.60 μ_B at 2.0 K. At room temperature, μ_{eff} per Nd^{3+} ion is expected[26] to be ~3.5 μ_B; for a Cu^{2+} ion, μ_{eff} is ~2.1 μ_B. For a Cu$^{\text{II}}_{12}$Nd$^{\text{III}}_6$ complex with noninteracting metal ions, μ_{eff} is expected to be ~11.2 μ_B. In the Nd$^{\text{III}}$ complex **3**, there seems to be both Cu^{2+}···Cu^{2+} exchange interactions and Cu^{2+}···Nd^{3+} interactions. It will require detailed additional experiments and data analysis to characterize the magnetic exchange interactions present not only in Nd$^{\text{III}}$ complex **3** but also in the Gd$^{\text{III}}$ complex **1**. In the latter complex, μ_{eff} per molecule decreases gradually from 20.3 μ_B at 320 K to 18.8 μ_B at 9.0 K, whereupon there is a more dramatic decrease to 15.8 μ_B at 2.0 K. At room temperature μ_{eff} for a Gd^{3+} ion is expected[26] to be ~7.9 μ_B; for a noninteracting Cu$^{\text{II}}_{12}$Gd$^{\text{III}}_6$ complex, $\mu_{\text{eff}} = 20.2\ \mu_B$ is expected. Since the experimental value of μ_{eff} is quite close to this noninteraction value, the question arises as to what became of the Cu^{2+}···Cu^{2+} exchange interactions in complex **1**. Preliminary X-ray structural results for the Y$^{\text{III}}$ complex **2** show that not only are the cluster structures the same in complexes **1** and **2**, but also there only small metric changes. Ferromagnetic Cu^{2+}···Gd^{3+} exchange interactions have been noted[6,7] for a few polynuclear Cu$_x$Gd$_x$ complexes.

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Supporting Information Available: Tables of crystal data and experimental conditions for **1−3**; atomic positional parameters, bond lengths, bond angles, and anisotropic temperature factors for the X-ray study of **1** and **3** (33 pages); tables of calculated and observed structure factors for **1** and **3** (73 pages). This material is contained in many libraries on microfiche, immediately follows this article in the micofilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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