Structure and Magnetic Property of an Octadecanuclear Cu(II) Complex

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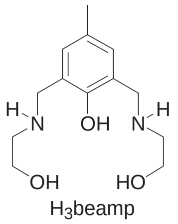
A reaction of copper acetate with a phosphate salt of pentadentate ligand yielded octadecanuclear complex, $[Cu_{18}(Hbeamp)_6(PO_4)_8]\cdot C_3H_7OH\cdot 24H_2O$ (H_3beamp = 2,6-bis[*N*-(2-hydroxyethyl)aminomethyl]-4-methylphenol), in which Cu(II) ions were bridged by alkoxo, phenoxo, and phosphate groups. Magnetic susceptibility measurements revealed the presence of antiferromagnetic interaction through bridges.

One of the main challenges in the field of molecular magnetism is to prepare discrete polynuclear molecules with high-spin ground states and tunable magnetic properties.[1–5] To explore synthetic routes for preparing metal complexes with higher nuclearity, the choice of bridging ligands is important. Alkoxo and phosphate groups bridge metal ions to form polynuclear complexes[6,7] and Schiff bases have been often used to prepare multinuclear high-spin molecules.[4,5] It is, therefore, expected that combination of alkoxo and phosphate bridges might give larger multinuclear complexes. We report here structure and magnetic property of an alkoxo and phosphate bridged octadecanuclear Cu(II) complex of $[Cu_{18}(Hbeamp)_6(PO_4)_8]\cdot C_3H_7OH\cdot 24H_2O$ ($\mathbf{1}\cdot C_3H_7OH\cdot 24H_2O$).

A pentadentate ligand (H_3beamp) (Scheme 1) was obtained by the reduction of 2,6-bis[*N*-(2-hydroxyethyl)iminomethyl]-4-methylphenol with $NaBH_4$,[8,9] and a crude product was treated with H_3PO_4 and purified as phosphate salt. A reaction of $Cu(OAc)_2\cdot H_2O$ with $H_3beamp\cdot H_3PO_4$ and Et_3N in methanol yielded octadecanuclear Cu(II) complex of **1**.[10]



Scheme 1.

Complex $\mathbf{1}\cdot C_3H_7OH\cdot 24H_2O$ crystallizes in orthorhombic space group *Pnma*.[11] A molecular structure of **1** is shown in Figure 1, and its illustrative view of the core structure is depicted in Figures 2 and 3. **1** has a mirror plane and pseudotrigonal axis along O10–P1–P1*–O10* vector. **1** is composed of eighteen Cu(II) ions, six $Hbeamp^{2-}$, and eight phosphate ions. Cu(II) ions are bridged by 39 oxygen atoms from $Hbeamp^{2-}$ and $PO_4{}^{3-}$ ions. Phosphate ions bridge Cu(II) ions with μ_6-(P1 and P1*), μ_4-(P2, P4, and P6) and μ_8-(P3, P5, and P7) modes. $Hbeamp^{2-}$, acting as a pentadentate ligand with one alcohol and one alkoxo groups, forms a dinuclear Cu(II) unit of (Cu1,Cu2), (Cu3,Cu4), and (Cu5,Cu6) pairs and their reflections. Six dinuclear units are related by pseudotrigonal axis. Cu1–Cu6 ions have square pyramidal coordination geometry with CuN_1O_4 chromophores, while Cu7–Cu9 ions have trigonal bipyramidal CuO_5 environments.

μ_6-$PO_4{}^{3-}$ ions (P1 and P1*) bridge six Cu(II) ions (Cu2, Cu4, Cu6, Cu7, Cu8, Cu9, and their reflections, respectively), and these Cu(II) ions are linked to Cu1–Cu6 and Cu1*–Cu6* ions through alkoxo or phenoxo groups in $Hbeamp^{2-}$. μ_4-$PO_4{}^{3-}$ ions (P2, P4, and P6) bridge four Cu(II) ions ((Cu1, Cu1*, Cu9, Cu9*), (Cu7, Cu7*, Cu3, Cu3*), and (Cu8, Cu8*, Cu5, Cu5*), respectively), and μ_8-$PO_4{}^{3-}$ ions (P3, P5, and P7) bridge eight

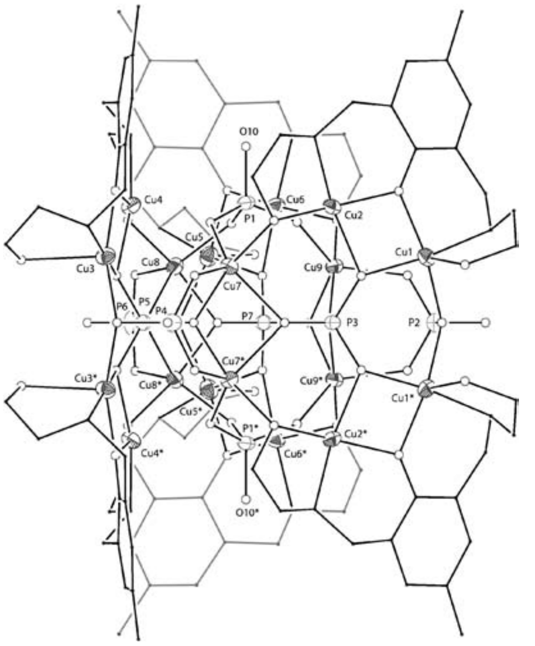


Figure 1. A molecular structure of **1**.

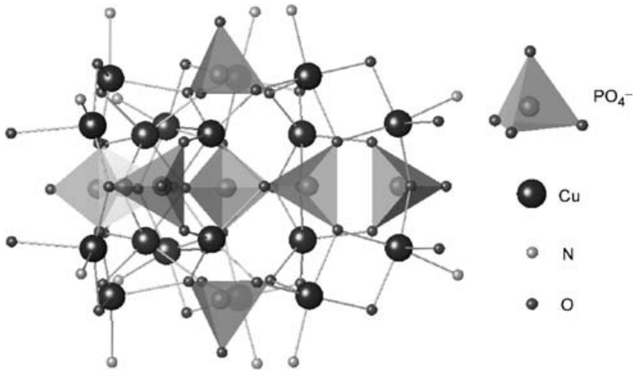


Figure 2. Ball and stick representation of **1**. The polyhedra represent phosphate ions. This figure was drawn with VENUS developed by Dilanian and Izumi.

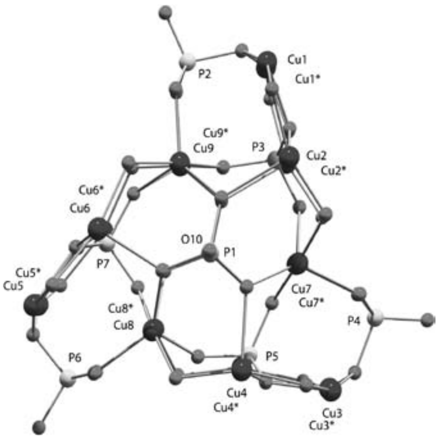


Figure 3. An illustrative drawing of the core structure for **1** viewed down from a pseudotrigonal axis along O10–P1–P1*–O10* vector.

Cu(II) ions ((Cu1, Cu1*, Cu2, Cu2*, Cu7, Cu7*, Cu9, Cu9*), (Cu3, Cu3*, Cu4, Cu4*, Cu8, Cu8*, Cu7, Cu7*), and (Cu5, Cu5*, Cu6, Cu6*, Cu9, Cu9*, Cu8, Cu8*), respectively). It should be noted that μ_6- and μ_8-phosphate bridges have not been known in discrete molecules except for polyoxometallates. In the dinuclear unit, the separations between Cu(II) ions are 3.014–3.021 Å, and Cu–O(phenoxo)–Cu angles lie between 101.55 and 101.81°. μ_8-, μ_6-, and μ_4-Phosphate bridges separate Cu(II) ions by 3.041–3.048, 3.558–3.579, and 3.542–3.590 Å, respectively.

Magnetic susceptibility measurements for $\mathbf{1}\cdot C_3H_7OH\cdot 4H_2O$ were performed in the temperature range of 1.8–300 K (Figure 4). The $\chi_m T$ value at 300 K is 4.42 emu mol^{-1} K, which is smaller than the value expected for uncorrelated eighteen Cu(II) ions (6.75 emu mol^{-1} K with $g = 2$). The $\chi_m T$ value gradually decreased as the temperature was lowered, and reached a value of 0.92 emu mol^{-1} K at 1.8 K. Curie–Weiss plots were shown in the inset of Figure 2 ($C = 5.67$ emu mol^{-1} K and $\theta = -87.6$ K). Phenoxo bridges mediate strong antiferromagnetic interactions ($J \approx -200\,\mathrm{cm}^{-1}$) between Cu(II) ions,[12] and magnetic interactions through a single oxygen atom of phosphate are strong, which is in contrast to weak magnetic interactions through O–P–O pathways ($J \approx -10\,\mathrm{cm}^{-1}$).[13,14] Magnetic susceptibility data for **1** suggests that substantial antiferromagnetic interactions are operative through bridges.

In summary, we developed a new synthetic route for obtaining large polynuclear molecules by using mixed bridging ligands of alkoxo and phosphate groups. Further synthetic approaches by using hydrothermal technique are currently applied to prepare larger discrete molecules.

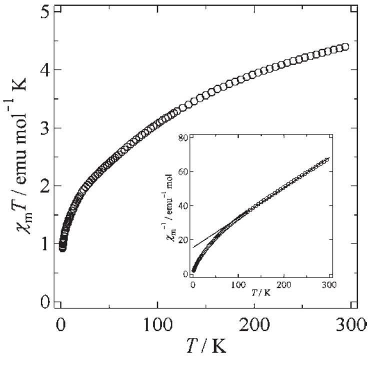


Figure 4. $\chi_m T$ vs T plot for $\mathbf{1}\cdot C_3H_7OH\cdot 4H_2O$. The inset shows Curie–Weiss plots.

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8 Schiff-base ligand, 2,6-bis[*N*-(2-hydroxyethyl)iminomethyl]-4-methylphenol, was prepared by a condensation reaction of 2-aminoethanol with 2,6-diformyl-4-methylphenol.

9 Synthesis of $H_3beamp\cdot H_3PO_4$: $NaBH_4$ (87 mg, 2.3 mmol) was gradually added to an ethanol solution of 2,6-bis[*N*-(2-hydroxyethyl)iminomethyl]-4-methylphenol (573 mg, 2.3 mmol), and then the solvent was removed. A yellow residue was neutralized by 10% phosphoric acid. The mixture was concentrated in vacuo and stood at room temperature to form colorless crystals of $H_3beamp\cdot H_3PO_4$. Anal. Calcd for $C_{13}H_{31}N_2O_{10}P_1$: C, 38.42; H, 7.69; N, 6.89%. Found: C, 38.36; H, 7.26; N, 6.78%. ^{1}H NMR (270 MHz, in D_2O): δ 7.08 (2H, s, ArH), 4.14 (4H, s, CH_2), 3.76 (4H, t, CH_2), 3.08 (4H, t, CH_2), 2.15 (3H, s, CH_3) ppm.

10 Synthesis of $\mathbf{1}\cdot C_3H_7OH\cdot 24H_2O$: A methanol solution (10 mL) of $Cu(OAc)_2\cdot H_2O$ (100 mg, 2.0 mmol) was added to a mixture of $H_3beamp\cdot H_3PO_4$ (303 mg, 1.0 mmol) and Et_3N (304 mg, 3.0 mmol), resulting in a green solution. The reaction solution was diffused with diethyl ether to give green powder. The green powder was collected by filtration and recrystallized from 2-propanol to give green columnar crystals of $[Cu_{18}(Hbeamp)_6(PO_4)_8]$ ($\mathbf{1}\cdot C_3H_7OH\cdot 24H_2O$). Elemental analysis and magnetic susceptibility measurements were performed on dried sample. Anal. Calcd for $\mathbf{1}\cdot C_3H_7OH\cdot 4H_2O$: C, 26.45; H, 3.73; N, 4.57%. Found: C, 26.68; H, 3.98; N, 4.27%.

11 Crystal data for $\mathbf{1}\cdot C_3H_7OH\cdot 24H_2O$: $C_{84}H_{124}Cu_{18}N_{12}O_{76}P_8$, $M_r = 3909.43$, orthorhombic, space group *Pnma*, $a = 28.958(5)$, $b = 30.017(5)$, $c = 17.204(3)$ Å, $V = 14954(5)$ Å^3, $T = 200$ K, $Z = 4$, $D_{calcd} = 1.736\,\mathrm{Mg\,m^{-3}}$, $F(000) = 7848$, $\mu(\mathrm{Mo}\,K\alpha) = 2.682\,\mathrm{mm}^{-1}$, 71297 reflections measured, 11037 unique ($R_{int} = 0.0756$), $R1 = 0.0913$, $wR2 = 0.1954$ (all data).

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