

A New Class of Hydroxo-Bridged Heptacopper(II) Clusters with an Acentrosymmetric Corner-Sharing Double-Cubane Framework Supported by D-Penicillaminedisulfides

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Transition-metal clusters with a cubane-like framework have received increasing attention because of their attractive physicochemical properties and biological relevance to metalloenzymes.^[1,2] In particular, considerable research efforts have been devoted to the design and creation of polycopper(II) clusters with a Cu_4X_4 cubane framework, which show ferromagnetic or antiferromagnetic behavior depending on $\text{Cu}^{\text{II}}\cdots\text{Cu}^{\text{II}}$ distances and relative orientations of the Jahn–Teller axes of Cu^{II} ions.^[3–5] To date, a number of tetra-copper(II) single-cubane clusters have been prepared and their magnetostructural correlation has been extensively investigated by means of both experimental and theoretical methods.^[3] On the other hand, examples of heptacopper(II) clusters featuring a corner-sharing double-cubane structure are limited in number, and only three structural types of compounds with an oxygen-bridged heptacopper(II) double-cubane framework have been reported so far.^[4] In these compounds, an inner Cu^{II} atom that connects two cubanes is commonly situated in an axially elongated octahedral environment and lies on an intramolecular inversion center (*i*). For corner-sharing double-cubane clusters, another type of structure that does not possess an inversion center is also possible (Figure 1). However, this type of cluster without *i* has not been prepared for any oxygen-bridged metal com-

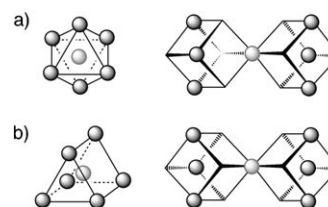


Figure 1. Two types of corner-sharing double-cubane framework a) with an inversion center and b) without an inversion center.

pounds, presumably owing to an unfavorable trigonal-prismatic coordination geometry required for a central metal in this structure.^[6] Thus, it is a great challenge to create heptacopper(II) double-cubane clusters without *i*, which are expected to exhibit intriguing physicochemical properties different from that found in related double-cubane clusters with *i*.

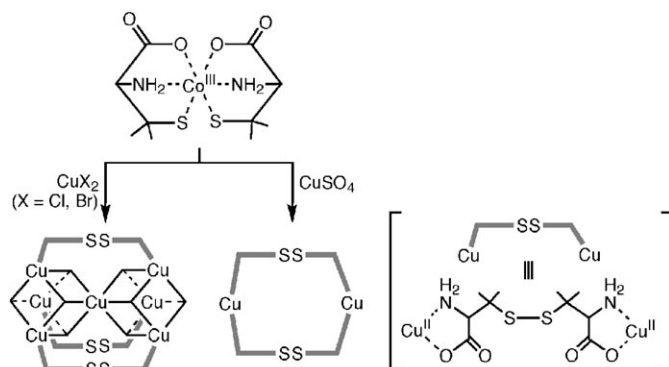
In the course of studying the reactivity of thiolate ligands bound to a cobalt(III) center toward various transition metal ions,^[7] we noticed that the reactions of $[\text{Co}(\text{D-pen-}N,O,S)_2]^-$ ($\text{D-H}_2\text{pen} = \text{D-penicillamine}$) with copper(II) salts afford blue copper(II) compounds that do not contain Co^{III} ions, contrary to our expectation for the formation of some sulfur-bridged $\text{Co}^{\text{III}}\text{Cu}^{\text{II}}$ species. Here we report that the copper(II) compounds obtained from the reactions of $[\text{Co}(\text{D-pen-}N,O,S)_2]^-$ with CuX_2 ($\text{X} = \text{Cl}, \text{Br}$) have a novel corner-sharing double-cubane heptacopper(II) structure without *i*, whereas the reaction with CuSO_4 constructs a dicopper(II) structure (Scheme 1). Remarkably, these structures were found to contain D-penicillaminedisulfide ($\text{D-H}_2\text{pens}$) as an auxiliary ligand that connects two Cu^{II} ions, indicative of the occurrence of a thiolate-to-disulfide oxidation. As far as we know, such an oxidation of thiolate ligands bound to a cobalt(III) center, followed by the transfer of resulting disulfides to copper(II) centers, has not been reported. The magnetic behavior of the obtained double-cubane heptacop-

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Scheme 1. The reactions of $[\text{Co}(\text{d-pen-N,O,S})]^-$ with CuX_2 (X = Cl, Br) or CuSO_4 , which form heptacopper(II) and dicopper(II) structures.

per(II) clusters without *i*, which is different from that of related heptacopper(II) clusters with *i*, is also presented.

Treatment of a dark brown aqueous solution of $\text{K}[\text{Co}(\text{d-pen-N,O,S})_2]$ with 2 molar equivalents of CuCl_2 , followed by allowing to stand at room temperature, led to the formation of blue crystals with a trigonal-pyramidal-like shape (**1**). X-ray fluorescence spectrometry indicated that **1** does not contain Co but only Cu as a metal component. The presence of d-penicillamine-residues bound to a copper(II) center in **1** was confirmed by studies of its solid sample by using infrared spectroscopy ($\bar{\nu}_{\text{CO}} = 1636 \text{ cm}^{-1}$), UV/vis spectroscopy (a broad band, $\lambda = 697 \text{ nm}$), and circular dichroism (a negative band at $\lambda = 557 \text{ nm}$), together with the elemental analysis.^[8,9] The structure of **1** was determined by single-crystal X-ray crystallography (Figure 2).^[8] Complex **1** is a neutral compound consisting of seven Cu^{II} , six OH^- , and two Cl^- , together with three d-pends with the averaged S–S distance of $2.031(3) \text{ \AA}$. The inner Cu^{II} (Cu1) atom is linked with six outer Cu^{II} atoms (Cu2–Cu7) through $\mu_3\text{-OH}^-$ ions to construct an oxygen-bridged heptacopper(II) structure. The two outer Cu^{II} trigonal faces are each capped with a terminal Cl^- ion, completing a corner-sharing double-cubane framework of $[\text{Cu}_7(\mu_3\text{-OH})_6(\mu_3\text{-Cl})_2]^{6+}$. Each of three d-pends ligands links two outer Cu^{II} atoms in a bis(bidentate-*N,O*) coordination mode so as to wrap the double-cubane core. This linkage forces the six outer Cu^{II} atoms to sit at the vertexes of a trigonal prism such that the double-cubane core does not possess an intramolecular inversion center. It is noted that the two cubanes shared by the inner Cu^{II} atom are not symmetric, as shown by the different Cu...Cu distances (Cu1–Cu2 = $2.811(1) \text{ \AA}$, Cu1–Cu3 = $3.365(1) \text{ \AA}$, Cu1–Cu4 = $3.271(1) \text{ \AA}$, Cu1–Cu5 = $2.862(1) \text{ \AA}$, Cu1–Cu6 = $3.103(1) \text{ \AA}$, Cu1–Cu7 = $3.093(1) \text{ \AA}$). The inner Cu^{II} atom is situated in a distorted trigonal-prismatic coordination environment with four normal (Cu1–O1 = $1.939(4) \text{ \AA}$, Cu1–O2 = $1.979(4) \text{ \AA}$, Cu1–O4 = $1.969(4) \text{ \AA}$, Cu1–O5 = $1.963(4) \text{ \AA}$) and two cis elongated (Cu1–O3 = $2.758(5) \text{ \AA}$, Cu1–O6 = $2.354(5) \text{ \AA}$) Cu–O bonds.^[10] This distortion seems to be a result of the Jahn–Teller effect for the trigonal-prismatic geometry. On the other hand, each of the outer Cu^{II} atoms adopts a square-pyramidal geometry, coordinated by N and O atoms

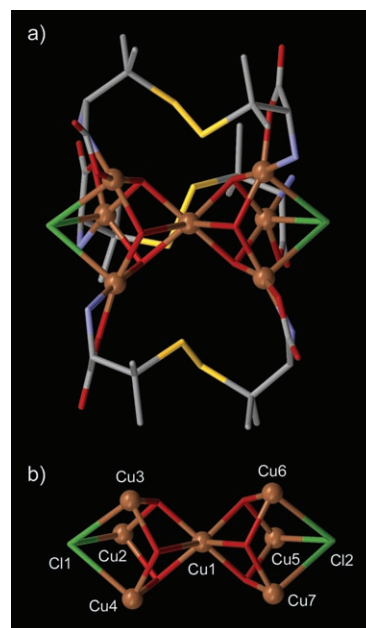


Figure 2. a) A molecular structure of **1** and b) its core structure. Hydrogen atoms and a disordered copper atom (Cu1B) are omitted for clarity. Cl green, Cu brown, C gray, N blue, O red, S yellow.

from a d-pends ligand (av. Cu–O = $1.945(5) \text{ \AA}$, Cu–N = $1.977(5) \text{ \AA}$) and two OH^- ions (av. Cu–O = $1.978(4) \text{ \AA}$) in an equatorial plane and a Cl^- ion in an apical position (av. Cu–Cl = $2.696(2) \text{ \AA}$). The vacant sixth coordination site of each outer Cu^{II} atom is covered by a disulfide fragment with the averaged Cu...S separation of $3.314(2) \text{ \AA}$.^[11]

Similar treatment of $\text{K}[\text{Co}(\text{d-pen-N,O,S})_2]$ with CuBr_2 also gave blue trigonal-pyramidal crystals (**2**), the spectroscopic features of which agree with those of **1**.^[8] X-ray analysis demonstrated that **2** has a corner-sharing double-cubane structure in $[\text{Cu}_7(\mu_3\text{-OH})_6(\mu_3\text{-Br})_2(\text{d-pends})_3]$ having an acentrosymmetric $[\text{Cu}_7(\mu_3\text{-OH})_6(\mu_3\text{-Br})_2]^{6+}$ framework.^[8] The overall structure of **2** is very similar to that of **1**, except the presence of two Br^- ions at the terminal in place of Cl^- ions. If $\text{K}[\text{Co}(\text{d-pen-N,O,S})_2]$ was reacted with CuSO_4 , instead of CuCl_2 or CuBr_2 , however, deep blue block crystals (**3**) were produced. This compound was also obtained by the reactions with $\text{Cu}(\text{BF}_4)_2$, $\text{Cu}(\text{ClO}_4)_2$, or $\text{Cu}(\text{NO}_3)_2$. Whereas **3** shows a $\bar{\nu}_{\text{CO}}$ band assigned to COO^- groups ($\bar{\nu} = 1615 \text{ cm}^{-1}$), as do **1** and **2**, its solid state UV/vis (a broad band $\lambda = 631 \text{ nm}$) and CD (a positive band $\lambda = 614 \text{ nm}$) spectra are significantly different.^[8] X-ray analysis revealed that **3** has a dicopper(II) structure in $[\text{Cu}_2(\text{d-pends})_2(\text{H}_2\text{O})_2]$, in which two Cu^{II} ions are spanned by two d-pends ligands.^[12] These results point out that the construction of the heptacopper(II)/dicopper(II) structures is highly dependent on the presence/absence of halide ions that can cap the terminal Cu^{II} faces to complete the double-cubane framework.

Magnetic susceptibility data for **1** and **2** having a double-cubane framework were recorded in the temperature range of 2–300 K; the $\chi_{\text{M}}T$ vs. T plots for **1** are shown in Figure 3.^[8] At 300 K, the $\chi_{\text{M}}T$ values for **1** ($2.46 \text{ cm}^3 \text{ K mol}^{-1}$)

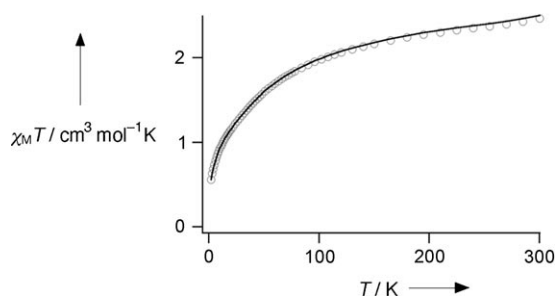


Figure 3. A plot of $\chi_M T$ versus T of **1**. The solid line is a theoretical curve considering four magnetic interactions.

and **2** ($2.55 \text{ cm}^3 \text{ K mol}^{-1}$) are slightly smaller than the spin-only value of $2.63 \text{ cm}^3 \text{ K mol}^{-1}$ for the magnetically dilute seven Cu^{II} centers with the g value of 2.0. On lowering the temperature, the $\chi_M T$ values for each of **1** and **2** continuously decrease, indicative of an overall antiferromagnetic character of interaction between Cu^{II} centers. Notably, no plateau is observed up to 2 K, and the $\chi_M T$ values at 2 K ($0.56 \text{ cm}^3 \text{ K mol}^{-1}$ for **1** and $0.53 \text{ cm}^3 \text{ K mol}^{-1}$ for **2**) are appreciably greater than the value expected for an $S = 1/2$ ground state ($\chi_M T = 0.38 \text{ cm}^3 \text{ K mol}^{-1}$). In addition, the field dependent magnetization studies for **1** and **2** at 2 K commonly gave magnetization values greater than the theoretical values for $S = 1/2$.^[13] These results obviously imply that for **1** and **2** the thermal excitation from an $S = 1/2$ ground state to a higher spin state takes place even at 2 K. An overall antiferromagnetic interaction has also been recognized for related heptacopper(II) double-cubane clusters, $[\text{Cu}_7(\text{Hpz}^{\text{tBu}})_{12}(\mu_3\text{-X})_2(\mu_3\text{-OH})_6]^{6+}$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$) ($\text{Hpz}^{\text{tBu}} = 5\text{-tert-butylpyrazole}$), which possess an inversion center at the inner Cu^{II} atom.^[14a,b] However, the $\chi_M T$ values for these heptacopper(II) compounds with i reach a plateau of $0.45 \text{ cm}^3 \text{ K mol}^{-1}$ at 15 K, which is close to the value for an $S = 1/2$ ground state ($\chi_M T = 0.41 \text{ cm}^3 \text{ K mol}^{-1}$ for $g = 2.1$). Thus, the magnetic structures of **1** and **2** are different from that of $[\text{Cu}_7(\text{Hpz}^{\text{tBu}})_{12}(\mu_3\text{-X})_2(\mu_3\text{-OH})_6]^{6+}$, which is ascribed to the acentrosymmetric arrangement of Cu^{II} atoms in the chiral $[\text{Cu}_7(\mu_3\text{-OH})_6(\mu_3\text{-X})_2]^{6+}$ double-cubane framework.^[14]

In summary, we have shown that the facile reactions of the D -penicillaminato cobalt(III) complex, $[\text{Co}(\text{D-pen-N,O,S})_2]^-$, with CuX_2 ($\text{X} = \text{Cl}, \text{Br}$) afford optically active heptacopper(II) clusters bearing D -penicillaminedisulfide, $[\text{Cu}_7(\mu_3\text{-OH})_6(\mu_3\text{-X})_2(\text{D-pends})_3]$. It has been reported that the direct reaction of CuX_2 and $\text{D-H}_2\text{pends}$ gives the dicopper(II) complex with D-pends (**3**),^[12] whereas the reaction of CuCl_2 and $\text{D-H}_2\text{pen}$ in the presence of base produces the mixed-valence $\text{Cu}^{\text{I}}_8\text{Cu}^{\text{II}}_6$ complex with D-pen ($[\text{Cu}^{\text{I}}_8\text{Cu}^{\text{II}}_6(\text{D-pen})_{12}\text{Cl}]^{5-}$).^[15] Thus, an intramolecular redox reaction between Co^{III} and coordinated thiolate, which is induced by Cu^{II} , led to the formation of a heptacopper(II) species with disulfide.^[16] Note that the resulting D-pends ligand links outer Cu^{II} centers of the heptacopper(II) double-cubane core, which is a key to the construction of the first example of an oxygen-bridged corner-sharing double cubane framework without i . Finally, the present results should provide

an insight into the metal-mediated thiolate-disulfide conversion that is an important redox reaction in biological systems,^[17] and also open the way to the creation of novel transition-metal clusters that exhibit unique structural and magnetic properties.

Experimental Section

Experimental details, together with spectroscopic data, are given in the Supporting Information.

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Keywords: amino acids • copper clusters • double-cubane framework • magnetic properties • redox chemistry

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- [8] See the Supporting Information.
- [9] The reaction of $\text{K}[\text{Co}(\text{L-pen})_2]$ with 2 molar equiv of CuCl_2 also produced X-ray-quality crystals of $[\text{Cu}_7(\mu_3\text{-OH})_6(\mu_3\text{-Cl})_2(\text{L-pens})_3]$ (**1**),^[8] whereas the reaction using a mixture of $\text{K}[\text{Co}(\text{D-pen})_2]$ and $\text{K}[\text{Co}(\text{L-pen})_2]$ gave only an unidentified blue precipitate.
- [10] The inner Cu^{II} ion is disordered in two positions with site occupancy factors of 0.9 (Cu1) and 0.1 (Cu1B), which are situated in a coordination environment very similar to each other.^[8]
- [11] In **1** and **2**, each heptacopper(II) molecule is surrounded by six neighboring molecules in a twisted triangular prismatic arrangement through $\text{COO}\cdots\text{H}\cdots\text{N}$ hydrogen bonds with $\text{N}\cdots\text{O}$ distances of 2.852(7)–2.934(7) Å.^[8]
- [12] In **3**, each Cu^{II} atom has a square-pyramidal geometry, coordinated by two N and two O atoms from two D-pends ligands (av. $\text{Cu}\text{--}\text{O}$ = 1.964(3), $\text{Cu}\text{--}\text{N}$ = 1.984(3) Å) in an equatorial plane and a H_2O molecule in an apical position (av. $\text{Cu}\text{--}\text{O}$ = 2.382(4) Å).^[8] This dicopper(II) complex has been prepared by the direct reaction of CuCl_2 with D- H_2pend s. J. A. Thich, D. Mastropaolo, J. Potenza, H. J. Schugar, *J. Am. Chem. Soc.* **1974**, 96, 726–731.
- [13] The experimental magnetic data were analyzed using the spin Hamiltonian $H = -2J_1(\mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_1\mathbf{S}_5) - 2J_2(\mathbf{S}_1\mathbf{S}_3 + \mathbf{S}_1\mathbf{S}_4 + \mathbf{S}_1\mathbf{S}_6 + \mathbf{S}_5\mathbf{S}_7) - 2J_3(\mathbf{S}_2\mathbf{S}_3 + \mathbf{S}_2\mathbf{S}_4 + \mathbf{S}_5\mathbf{S}_6 + \mathbf{S}_5\mathbf{S}_7) - 2J_4(\mathbf{S}_3\mathbf{S}_4 + \mathbf{S}_6\mathbf{S}_7)$,^[18] based on four magnetic interactions (J_1 , J_2 , J_3 , and J_4) between Cu^{II} centers; the two cubanes shared by the inner Cu^{II} atom were regarded to be equivalent.^[8] The most reliable parameter sets obtained from this analysis; **1**: $g = 2.03$, $J_1 = -0.9$, $J_2 = -20.9$, $J_3 = -4.1$, $J_4 = -24.0 \text{ cm}^{-1}$; **2**: $g = 2.06$, $J_1 = -1.1$, $J_2 = -20.9$, $J_3 = -4.7$, $J_4 = -24.4 \text{ cm}^{-1}$. The spin-state energy levels for **1** and **2** were calculated from these J values, and it was shown that the ground state and the excited state are $S = 1/2$ and $S = 3/2$, respectively, which are separated only by 2.6 cm^{-1} for **1** and 3.2 cm^{-1} for **2**.^[8]
- [14] The magnetic structure of $[\text{Cu}_7(\text{Hpz}^{\text{tBu}})_{12}(\mu_3\text{-X})_2(\mu_3\text{-OH})_6]^{6+}$ is composed of three discrete spin systems, two dimers and a trimer,^[4a,b] and the spin density is symmetrically located on the trimer unit. On the other hand, in **1** the spin density is dominantly located on one of outer Cu atom, representing a unique, quite unsymmetrical magnetic structure. This result, obtained by the DFT calculations, will be reported elsewhere.
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- [16] The detailed mechanism of this reaction is not clear at present, but it is considered that a thiolato-bridged $\text{Co}^{\text{III}}(\text{D-pen})_2\text{Cu}^{\text{I}}$ species created at the first stage undergoes an intramolecular redox reaction to be converted into a $\text{Co}^{\text{II}}(\text{D-pends})\text{Cu}^{\text{I}}$ species, followed by the dissociation of Co^{II} and the auto-oxidation of Cu^{I} to give polycopper(II) compounds with *N,O*-chelating D-pends ligands. The formation of a thiolato-bridged $\text{Co}^{\text{III}}(\text{D-pen})_2\text{Cu}^{\text{II}}$ species was indicated by stopped-flow absorption spectroscopy, and the presence of dissociated Co^{II} ions in the reaction solution was confirmed by cation-exchange (SP-Sephadex C-25) column chromatography.
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