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Redox-Mediated Self-Organization of Metallosupramolecular Architectures Composed of D-Penicillaminato $Cu^{I}_{8}Cu^{II}_{6}$ Clusters: Drastic Structural Change by Subtle pH Changes

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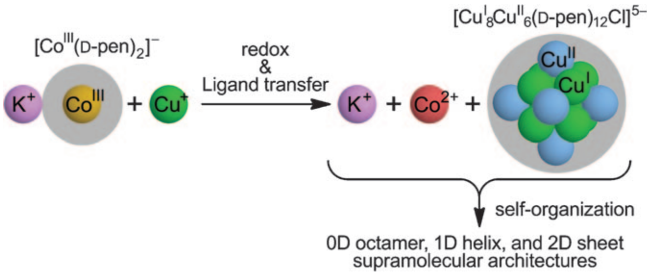
It is known that a thiolate sulfur atom possesses a relatively high nucleophilicity even after coordination to a metal center,[1] which allows it to coordinate to second metal ion(s) to form μ_2- or μ_3-thiolato structures. By utilizing this property, a large number of thiolato-bridged polynuclear and supramolecular coordination compounds that show unique structures and properties have been synthesized from the reactions of thiolato metal complexes with thiophilic metal ions.[2] In many cases, the coordination environment of thiolato metal complexes is retained in the course of reactions with metal ions, thus forming thiolato-bridged structures that are predictable from the coordination geometry of reacting metal ions, as well as from the geometry of thiolato complexes. However, this is not common for reactions with redox-active metal ions, which often result in the transformation of thiolato complexes into unexpected products.[3] Recently, we have found an intriguing example of this class of reactions, in which a novel heptacopper(II) cluster with D-penicillaminedisulfide (D-H_2pends), $[Cu_7(\mu_3\text{-}OH)_6(\mu_3\text{-}X)_2(\text{D-pends})_2]$, is created from $K[Co(\text{D-pen})_2]$ (D-H_2pen = D-penicillamine) and $Cu^{II}X_2$ (X = Cl, Br), owing to the three-center redox reaction of cobalt(III), thiolate, and copper(II) to afford cobalt(II), disulfide, and copper(I), followed by auto-oxidation from copper(I) to copper(II).[3c] This result prompted us to investigate the reaction system of thiolato cobalt(III) complexes and $Cu^{I}X$, which is expected to show different three-center redox behavior. Herein, we report that the reaction of $K[Co(\text{D-pen})_2]$ with CuCl does not give a simple thiolato-bridged $Co^{III}Cu^{I}$ compound, but produces a fascinating metallosupramolecular compound consisting of thiolato-bridged $Cu^{I}_{8}Cu^{II}_{6}$ clusters, $[Cu^{I}_{8}Cu^{II}_{6}(\text{D-pen})_{12}Cl]^{5-}$, that are linked by Co^{II} and/or K^{I} ions. Remarkably, three types of metallosupramolecular compounds with different dimensional structures were constructed only by a slight change in the buffer solutions used for the reactions (Scheme 1).



Scheme 1. Redox-mediated self-organization of metallosupramolecular architectures.

Treatment of *trans*(*N*)-$K[Co(\text{D-pen-}N,O,S)_2]$[4] with CuCl in a 1:2 ratio in a potassium acetate buffer solution at pH 5.0 (HOAc/KOAc = 1:2) at room temperature caused a solution color change from brown to dark purple. From the reaction solution, purple–black crystals (**1**) with a rod shape, which are slightly soluble in water, were isolated on allowing the solution to stand at room temperature.[5] The absorption spectrum of **1** in water is characterized by an intense absorption band at 520 nm. Compound **1** is optically active, as evidenced by the CD spectrum, which has negative, positive, and negative CD bands at 567, 482, and 410 nm, respectively. X-ray fluorescence spectrometry indicated that **1** contains Cu and Co as the metal components. In the IR spectrum, compound **1** exhibits an intense ν(C=O) band at 1609 cm^{-1}, indicative of the presence of carboxyl groups that exist as a deprotonated form.[6]

Single-crystal X-ray analysis revealed that **1** does not contain the parental $[Co(\text{D-pen-}N,O,S)_2]^-$ anions, but mixed-valent $Cu^{I}_{8}Cu^{II}_{6}$ cluster anions, $[Cu^{I}_{8}Cu^{II}_{6}(\text{D-pen})_{12}Cl]^{5-}$, as a building unit. As shown in Figure 1a, the cluster anion con-

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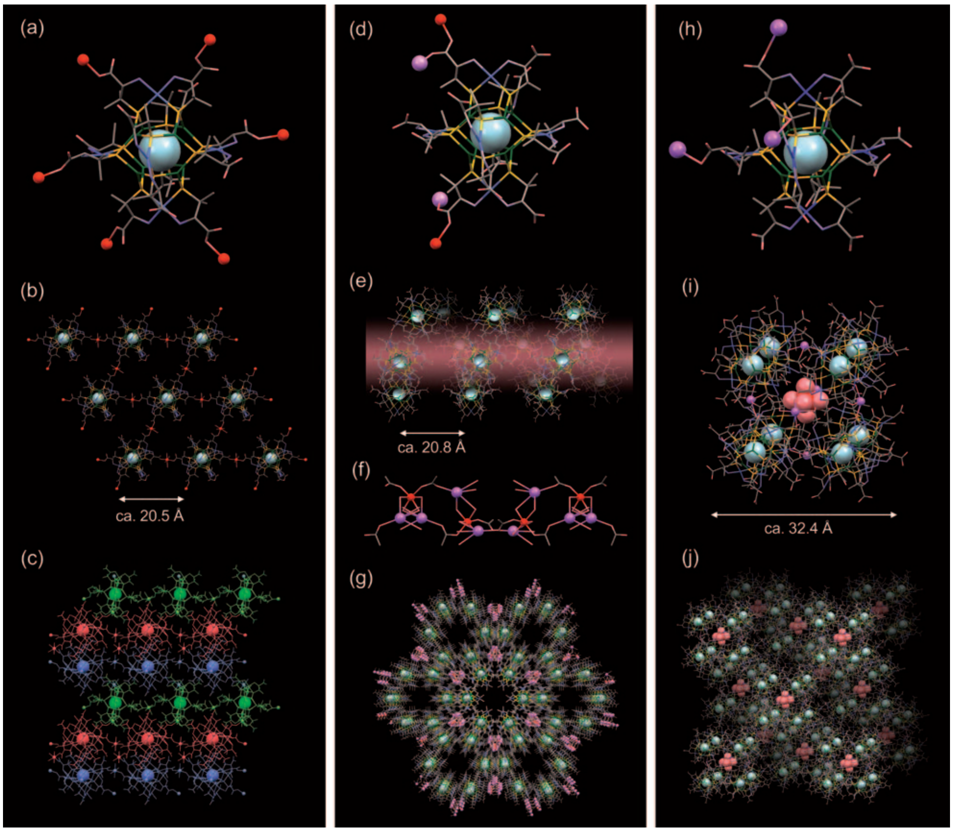
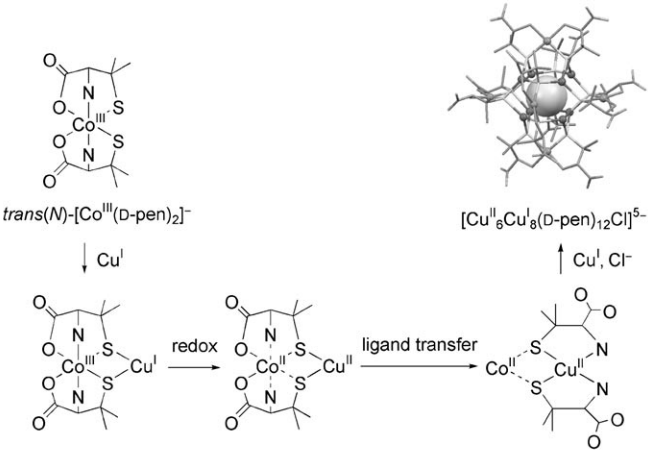


Figure 1. Perspective views of the $[Cu_{14}(\text{D-pen})_{12}Cl]^{5-}$ cluster bound to Co^{2+} ions (a), the (4,4) net framework of the Cu_{14} clusters (b), the $(ABC)_n$ stacked structure (c) in **1**; the $[Cu_{14}(\text{D-pen})_{12}Cl]^{5-}$ cluster bound to K^+ and Co^{2+} ions (d), the left-handed 1D helix structure of the Cu_{14} clusters (e), the 1D helical structure of $\{[CoK_2(\mu\text{-}H_2O)_4(H_2O)_4]^{4+}\}_n$ with a threefold left-handedness (f), the arrangement of the Cu_{14} clusters and $\{[CoK_2(\mu\text{-}H_2O)_4(H_2O)_4]^{4+}\}_n$ (g) in **2**; the $[Cu_{14}(\text{D-pen})_{12}Cl]^{5-}$ cluster bound to K^+ ions (h), the cubic structure of $[\{Co(H_2O)_6\}@K_6\{Cu^{I}_8Cu^{II}_6(\text{D-pen})_{12}Cl\}_8]^{32-}$ (i), the face-centered cubic lattice of the cubic structure (j) in **3**. Cu^{II}: blue, Cu^{I}: green, Co: orange, Cl: pale blue, C: gray, K: red purple, N: purple, O: red, S: yellow.

sists of 6 square-planar $cis(S)$-$[Cu^{II}(\text{D-pen-}N,S)_2]^{2-}$ units that bind to a cubic $[Cu^{I}_8Cl]^{7+}$ core (av. Cu^{I}–Cl = 2.85 Å, $Cu^{I}\cdots Cu^{I}$ = 3.29 Å) through thiolato groups, forming a 14-nuclear cage-type structure in $[Cu^{I}_8Cu^{II}_6(\text{D-pen})_{12}Cl]^{5-}$ (av. Cu^{II}–S = 2.26 Å, Cu^{II}–N = 2.02 Å, Cu^{I}–S = 2.28 Å). The overall structure of this cluster anion in **1** is very similar to that in $Tl_5[Cu^{I}_8Cu^{II}_6(\text{D-pen})_{12}Cl]$, which has been prepared by the direct reaction of $CuCl_2$ with D-H_2pen in the presence of $TlNO_3$.[7] In **1**, each $Cu^{I}_8Cu^{II}_6$ cluster anion binds to 4 *trans*-$[Co(H_2O)_4]^{2+}$ and 2 *cis*-$[Co(H_2O)_4]^{2+}$ cationic moieties using 6 of 12 carboxylate groups. Each *trans*-$[Co(H_2O)_4]^{2+}$ moiety is coordinated by 2 carboxylate groups from 2 different $Cu^{I}_8Cu^{II}_6$ cluster anions (av. Co–O = 2.10 Å) to construct a 2D sheetlike supramolecular structure, in which $Cu^{I}_8Cu^{II}_6$ cluster anions form a (4, 4) net framework with a separation of about 20.5 Å (Figure 1b). In addition, the supramolecular sheets are linked by *cis*-$[Co(H_2O)_4]^{2+}$ cationic moieties through Co–OOC bonds (av. Co–O = 2.14 Å) in an $(ABC)_n$ stacking mode, completing a 3D metallosupramolecular structure (Figure 1c).[8]

The most probable mechanism of the production of **1** from K[Co(D-pen-*N,O,S*)$_2$] and CuCl is as follows: In the first stage, thiolato groups in $[Co(\text{D-pen-}N,O,S)_2]^-$ coordinate to Cu^+ to give a thiolato-bridged $[\{Co^{III}(\text{D-pen-}N,O,S)_2\}Cu^{I}]$ species. Then, this species undergoes an intramolecular redox reaction to be converted into a $[\{Cu^{II}(\text{D-pen-}N,S)_2\}Co^{II}]$ species, by way of $[\{Co^{II}(\text{D-pen-}N,O,S)_2\}Cu^{II}]$, followed by the dissociation of Co^{2+} and the concomitant coordination of Cu^+ to form $[Cu^{I}_8Cu^{II}_6(\text{D-pen-}N,S)_{12}Cl]^{5-}$ templated by Cl^- (Scheme 2). Finally, the $Cu^{I}_8Cu^{II}_6$ cluster anions formed are self-organized into the metallosupramolecular structure in **1** linked by aqua Co^{2+} ions.

Whereas a similar reaction of *trans*(*N*)-K[Co(D-pen-*N,O,S*)$_2$] with CuCl in a potassium acetate buffer solution at pH 5.5 (HOAc/KOAc = 1:6) also gave only rod crystals of **1**, block crystals (**2**) that are highly soluble in water were produced when the pH of a buffer solution was increased to 6.0 (HOAc/KOAc = 1:20).[5] The absorption and CD spectra of **2** in water are essentially the same as those of **1**, and the IR spectrum that gives an intense ν(C=O) band at 1599 cm^{-1} is also similar to that of **1**. However, X-ray fluorescence spectrometry indicated the presence of K atoms in **2**, besides Cu and Co atoms. Single-crys-



Scheme 2. Proposed mechanism of the formation of $[Cu_{14}(\text{D-pen})_{12}Cl]^{5-}$ from K[Co(D-pen-*N,O,S*)$_2$] and CuCl.

tal X-ray analysis demonstrated that **2** consists of $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$ anions and $\mathrm{Co^{2+}}$ and $\mathrm{K^+}$ cations in a 1:1:3 ratio. While the overall structure of $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$ in **2** (av. $\mathrm{Cu^{II}{-}S} = 2.26$ Å, $\mathrm{Cu^{II}{-}N} = 2.01$ Å, $\mathrm{Cu^{I}{-}S} = 2.31$ Å) is essentially the same as that of **1**, each of two carboxylate groups of $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$ in **2** binds to $\mathrm{Co^{2+}}$ and $\mathrm{K^+}$ cations (av. $\mathrm{Co{-}O} = 2.12$ Å, $\mathrm{K{-}O} = 2.72$ Å) (Figure 1 d). A remarkable structural feature of **2** is that the $\mathrm{Cu^I_8Cu^{II}_6}$ cluster anions are connected to each other through double N–H···O hydrogen bonds (av. N···O = 2.98 Å) to form a 1D tubular helix with a sixfold left-handedness (Figure 1 e). In addition, $\mathrm{Co^{2+}}$ and $\mathrm{K^+}$ cations are aggregated into a 1D helical structure in $\{[\mathrm{CoK_2}(\mu\text{-}\mathrm{H_2O})_4(\mathrm{H_2O})_4]^{4+}\}_n$ (av. $\mathrm{Co{-}O} = 2.16$ Å, $\mathrm{K{-}O} = 2.96$ Å) with a threefold left-handedness (Figure 1 f). This 1D helix connects three tubular helixes through COO–Co/K coordination bonds, completing a hexagonal columnar metallosupramolecular structure in **2** (Figure 1 g).

To further investigate the influence of a buffer reaction solution on the resulting structures, the same reaction of *trans*(*N*)-K[Co(D-pen-*N*,*O*,*S*)$_2$] with CuCl was carried out by using an acetate buffer solution at pH 4.5 (HOAc/KOAc = 3:2). Interestingly, cubic crystals that are insoluble in water were produced in this reaction.[5] The absorption, CD, and IR spectra of **3** in the solid state are very similar to those of **1** and **2**, indicating that **3** also contains $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$ as a building unit. The presence of Co and K atoms in **3**, besides Cu atoms, was indicated by X-ray fluorescence spectrometry. Consistent with these spectroscopic data, single-crystal X-ray analysis revealed the presence of $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$ cluster anions (av. $\mathrm{Cu^{II}{-}S} = 2.25$ Å, $\mathrm{Cu^{II}{-}N} = 2.01$ Å, $\mathrm{Cu^{I}{-}S} = 2.27$ Å) and $\mathrm{Co^{2+}}$ and $\mathrm{K^+}$ cations. However, $\mathrm{Co^{2+}}$ cations in **3** exist as a hexaaqua ion, $[\mathrm{Co(H_2O)_6}]^{2+}$ ($\mathrm{Co{-}O} = 2.19$ Å), and do not involved in the direct binding with $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$. In **3**, each cluster anion binds to three $\mathrm{K^+}$ cations by using three carboxylate groups ($\mathrm{K{-}O} = 2.92$ Å) (Figure 1 h), while each $\mathrm{K^+}$ cation is bound by four carboxylate groups from four different cluster anions. As a result, a giant metallosupramolecular structure in $[\mathrm{K_6}\{\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}\}_8]^{34-}$, in which eight cluster anions are bridged by six $\mathrm{K^+}$ ions in a discrete cubic arrangement, is constructed (Figure 1 i). Note that the supramolecular cube encapsulates a $[\mathrm{Co(H_2O)_6}]^{2+}$ cation at the center of the cube. Thus, this compound is formulated as $[\{\mathrm{Co(H_2O)_6}\}@\mathrm{K_6}\{\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}\}_8]^{32-}$, and its total charge is balanced by 16 $[\mathrm{Co(H_2O)_6}]^{2+}$ cations that are located outside the cube.[9] In crystals, the highly negatively charged supramolecular cubes are closely packed in a face-centered cubic lattice by forming $\mathrm{NH_2}$···OOC hydrogen bonds (av. N···O = 2.91 Å) between the cubes (Figure 1 j). In addition, $[\mathrm{Co(H_2O)_6}]^{2+}$ cations connect the anionic cubes through $\mathrm{OH_2}$···OOC hydrogen bonds (av. O···O = 2.82 Å), which might be responsible for the insolubility of **3** in solution.

The most important factor that caused the drastic structural change of the constructed metallosupramolecular structures (**1**, **2**, **3**) is the difference in metal ions ($\mathrm{Co^{2+}}$, $\mathrm{K^+}$) bound to carboxylate groups of $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$. In **1**, only $\mathrm{Co^{2+}}$ ions are bound to the carboxylate groups of $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$. This is not surprising because the bonding interaction between $\mathrm{Co^{2+}}$ and carboxylate is stronger than that between $\mathrm{K^+}$ and carboxylate due to the ligand-field stabilization energy. The binding of both $\mathrm{Co^{2+}}$ and $\mathrm{K^+}$ ions in **2** is understood by the existence of a large amount of $\mathrm{K^+}$ ions in the employed buffer solution with pH 6.0. The question is why only $\mathrm{K^+}$ ions are bound to carboxylate groups in **3**, despite the presence of a smaller amount of $\mathrm{K^+}$ ions in the employed buffer solution of pH 4.5 than the buffer solution with pH 5.0. From the potentiometric titration of $\mathrm{K_5}[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]$ with aqueous HCl, followed by the analysis of the obtained titration curve,[10] it was found that the fully deprotonated form of $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$ is dominant in an aqueous solution when the solution pH is higher than 5.0, while the protonated forms of $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-Hpen})_n(\text{D-pen})_{12-n}\mathrm{Cl}]^{(5-n)-}$ coexist in an aqueous solution at pH 4.5. Thus, we speculate that the presence of the protonated forms restricts the binding of carboxylate groups of $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$ anions toward aqua $\mathrm{Co^{2+}}$ ions, resulting in the binding with $\mathrm{K^+}$ ions to form **3**, which is insoluble in solution, assisted by hydrogen-bonding interactions with $[\mathrm{Co(H_2O)_6}]^{2+}$.

In conclusion, we have shown a unique redox reaction between $\mathrm{K}[\mathrm{Co^{III}}(\text{D-pen-}N,O,S)_2]$ and $\mathrm{Cu^ICl}$, which leads to $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$ anionic clusters that are linked by $\mathrm{Co^{2+}}$ and/or $\mathrm{K^+}$ ions through D-pen carboxylate groups. Remarkably, three kinds of metallosupramolecular compounds showing quite different structures (2D sheet with $(\mathrm{ABC})_n$ stacking for **1**, 1D helix for **2**, and discrete octamer for **3**) were created by only slight pH changes in a potassium acetate buffer solution (pH 4.5 for **3**, pH 5.0 for **1**, pH 6.0 for **3**).[11] This is thanks to the presence of 12 free carboxyl groups in $[\mathrm{Cu^I_8Cu^{II}_6}(\text{D-pen})_{12}\mathrm{Cl}]^{5-}$, the binding modes of which can be controlled by the pH of the solution, as well as by metal ions coexisting in solution. While the construction of metallosupramolecular architectures by self-organization of molecular building units assisted by metal ions is an active area of research in recent years,[12] this kind of self-organization induced by a redox reaction between two metal compounds, accompanied by a ligand-transfer reaction, is unprecedented. Thus, this synthetic methodology would open a way to create new metallosupramolecular species that are not obtained by classical self-organization processes.

Experimental Section

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

Keywords: cluster compounds · cobalt · copper · redox chemistry · S ligands · supramolecular chemistry

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[8] Magnetic susceptibility data for **1** were recorded in the temperature range of 2–300 K.[5] The $\chi_M T$ value at 300 K (10.46 $cm^3 K mol^{-1}$) is much larger than the spin-only value of 7.88 $cm^3 K mol^{-1}$ for the magnetically diluted 6 Cu^{II} and 3 high-spin Co^{II} centers with the g value of 2.0. On lowering the temperature, the $\chi_M T$ values continuously decrease due to the presence of large magnetic anisotropy of Co^{II} centers, which prevented the further analysis of the magnetic behavior of **1**.

[9] A similar octameric cubic structure was found in $Tl_5[Cu^I_8Cu^{II}_6(\text{D-pen})_{12}]$, but the encapsulation of cationic species inside the cube was not observed for this compound.

[10] The pK_{a_i} ($i=1$–12) values for $[Cu^I_8Cu^{II}_6(\text{D-pen})_{12}Cl]^{5-}$ were calculated from the analysis of the titration curve of **1** with aqueous HCl, assuming that the difference between pK_{a_i} and $pK_{a_{i+1}}$ is constant (C). The most reliable values obtained from this analysis is $pK_{a_1}=4.35$ and $C=0.54$ with the final agreement factor $R=2.1\times10^{-4}$. In addition, the molar fractions of $[Cu_{14}(\text{D-Hpen})_n(\text{D-pen})_{12-n}Cl]^{(5-n)-}$ ($n=$ 0–12) at each pH were evaluated based on the calculated pK_{a_i} values. The distribution diagram of the deprotonated and protonated species in the pH range of 4.0–7.0 indicates that the fully deprotonated form is dominant when the solution pH is larger than 5.0, while the deprotonated and protonated species coexist comparably at pH 4.5.[5]

[11] The use of a more acidic buffer solution ($pH<4.0$) gave an insoluble brown powder that contains unreacted CuCl, whereas the use of a more basic buffer solution ($pH>6.5$) gave a colorless powder that contains organic species.

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