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Intervalence Charge-Transfer System by 1D Assembly of New Mixed-Valence Octanuclear $Cu^I/Cu^{II}/Cu^{III}$ Cluster Units

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S Supporting Information

ABSTRACT: The reaction of Cu(Hm-dtc)$_2$, Br_2, and $CuBr_2$ yielded a new mixed-valence octanuclear $Cu^I/Cu^{II}/Cu^{III}$ cluster, encapsulating a Br anion in the center of the cluster cage. The octanuclear cluster units form a 1D assemblage, which induces intervalence charge-transfer transitions from Cu^{II} ions to Cu^{III} ions between the clusters.

Polynuclear metal complexes represent one of the most attractive areas in the field of materials science because their characteristic assembled structures and electronic states, which have features of organic−inorganic hybrid materials, have new chemical and/or physical properties such as catalytic activity,[1] gas adsorption,[2] and conductive,[3] magnetic,[4] and nonlinear optical properties.[5] There is much interest in their design and synthesis; in particular, the establishment of a rational synthetic method for mixed-valence polynuclear metal complexes such as mixed-valence coordination polymers and mixed-valence metal clusters is important in the development of the chemistry of functional materials because these complexes have potential applications as new optoelectronic materials based on carrier-transport properties, valence fluctuations, and intervalence charge-transfer (IVCT) transitions.[6]

Dithiocarbamate (dtc) derivatives are good candidates for ligands in mixed-valence polynuclear metal complexes. This is because ligands that contain dithiocarboxyl groups have the ability not only to bridge metal ions by S atoms, which have large atomic orbitals, in the ligands but also to stabilize copper complexes in a wide range of oxidation states such as Cu^I, Cu^{II}, and Cu^{III}.[7−10] To date, several mixed-valence metal clusters and coordination polymers have been synthesized from dtc derivatives.[8] We demonstrated that 1D mixed-valence Cu^I/Cu^{II} coordination polymers containing a dtc ligand and Br or I anions, $[Cu^I_2Cu^{II}X_2(\text{Hm-dtc})_2(CH_3CN)_2]_n$ (Hm-dtc$^-$ = hexamethylenedithiocarbamate; X = Br^- or I^-), exhibited semiconducting properties at relatively small activation energies (E_a = 0.56 eV, X = Br^-; E_a = 0.48 eV, X = I^-)[8a] and that they could be employed as sensitizing materials for dye-sensitized solar cells.[8b] In this paper, we present a new mixed-valence system consisting of a cluster unit in which Cu^I, Cu^{II}, and Cu^{III} ions coexist; the formula of these systems is $[Cu^I_6Cu^{II}Cu^{III}Br_7(\text{Hm-dtc})_4]\cdot 3CHCl_3$ (**1**). This complex shows a unique IVCT band in the UV−vis−near-IR region in the solid state, which is induced by the assembly of mixed-valence octanuclear $Cu^I/Cu^{II}/Cu^{III}$ units.

Complex **1** was synthesized by the reaction of a $CHCl_3$ solution of Cu(Hm-dtc)$_2$ with a $CHCl_3$ solution of Br_2 and $CuBr_2$ (Scheme 1). The reaction mixture was filtered for $^1/_2$ h, and black single crystals with needle shape suitable for X-ray diffraction were obtained from the filtrate in a couple of days by the slow diffusion of hexane (yield: 8.6%). The yields of the complex **1** increased by the further diffusion of hexane in the reaction (5 days, 34.7%; 14 days, 37.9%). From the reaction mixture without Br_2, we obtained small flakelike microcrystals, but unfortunately the crystal structure was unclear. In addition, when we used an acetone solution of $CuBr\cdot S(CH_3)_2$ instead of the $CHCl_3$ suspension of Br_2 and $CuBr_2$, a mixed-valence 1D coordination polymer was synthesized.[8a]

Single-crystal X-ray analysis reveals the formation of a mixed-valence $Cu^I/Cu^{II}/Cu^{III}$ cluster of formula $[Cu^I_6Cu^{II}Cu^{III}Br_7(\text{Hm-dtc})_4]\cdot 3CHCl_3$ (**1**). The structure of the octanuclear cluster is shown in Figure 1, where H atoms and disordered C atoms [C(5A1), C(6A1), C(24A1), and C(27A1)] in the Hm-dtc$^-$ ligands and the $CHCl_3$ crystal solvents are omitted for clarity. Two mononuclear Cu(Hm-dtc)$_2$ units are connected by six Cu ions and six Br anions, constructing a cage structure, and Br1 is incorporated in the center of the cage through bonding to the Cu6 ion. The Cu ions of the mononuclear units, Cu1 and Cu2, have distorted square-planar coordination geometries in which the Hm-dtc$^-$ ligands coordinate with the Cu ions in four-membered chelate rings. The Cu6 ion forms a tetrahedral S_1Br_3 coordination geometry. The other Cu ions connecting the mononuclear units, Cu4, Cu5, Cu6, Cu7, and Cu8, have trigonal-pyramidal S_1Br_2 coordination geometries, where the Br1 ion is located close to the Cu ions, thereby forming a pseudotetrahedral geometry for the Cu ions; the Cu3···Br1, Cu4···Br1, Cu5···Br1, Cu7···Br1, and Cu8···Br1 separations are 3.2109(7), 2.8239(7), 2.7944(9), 2.8707(8), and 2.9196(7) Å, respectively. The separations between the Cu ions of the mononuclear Cu(Hm-dtc)$_2$ unit and Br1 are 3.3847(5) Å (Cu1···Br1) and 3.0756(5) Å (Cu2···Br1); i.e., the Cu1···Br1 separation is larger than the Cu2···Br1 separation.

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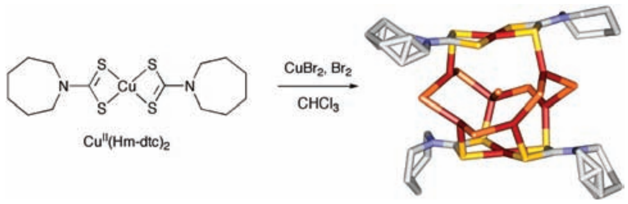
Scheme 1. Synthesis of Octanuclear Cluster 1



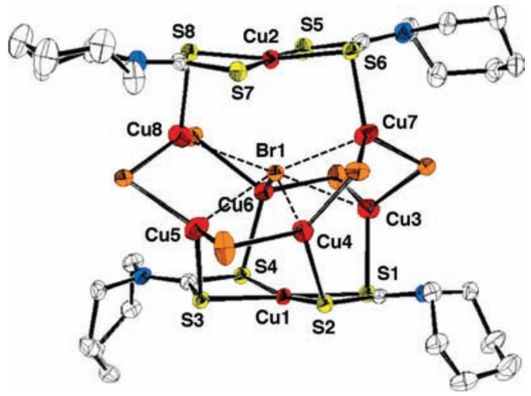


Figure 1. ORTEP view of octanuclear Cu^{I}/Cu^{II}/Cu^{III} cluster **1** with 50% probability level ellipsoids. Color code: Cu, red-brown; Br, orange; S, yellow; C, white; N, blue. H atoms, disordered C atoms, and crystal solvents are omitted for clarity.

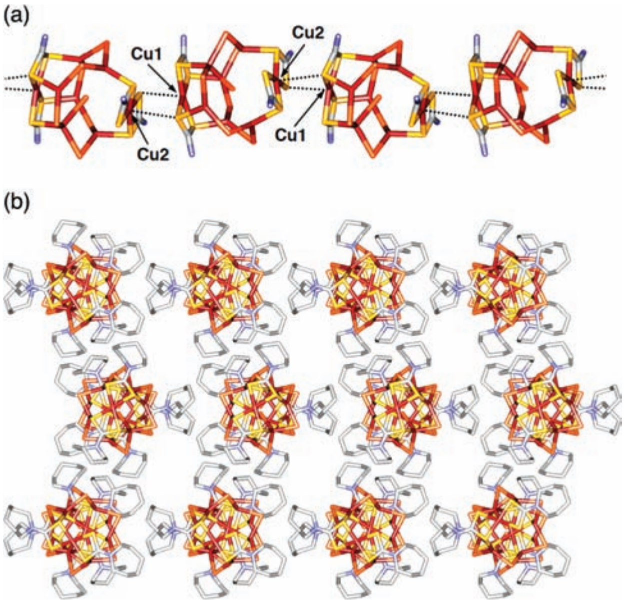


Figure 2. (a) Infinite chain structures formed by the assembly of octanuclear cluster units of **1**. Hexamethylene groups of Hm-dtc ligands are omitted for clarity. (b) Packing diagram of **1** viewed along the diagonal of the *a* and *c* axes. H atoms, disordered C atoms, and crystal solvents are omitted for clarity.

Usually, the oxidation states of copper complexes with dtc ligands can be determined by the Cu−S distances. In the mononuclear Cu1(Hm-dtc)$_2$ and Cu2(Hm-dtc)$_2$ units, the average Cu−S distances are 2.3106 and 2.2186 Å, respectively; the Cu−S distance in the Cu1(Hm-dtc)$_2$ unit is larger than that in the Cu2(Hm-dtc)$_2$ unit. The Cu−S distance in the Cu1(Hm-dtc)$_2$ unit is similar to the typical Cu^{II}−S distances for copper(II) dithiocarbamate complexes such as Cu^{II}(Et$_2$dtc)$_2$ (2.312 Å av), Cu^{II}(EtPr-dtc)$_2$ (2.284 Å av), Cu^{II}(*n*-Bu$_2$dtc)$_2$ (2.308 Å av), and Cu^{II}(Bz$_2$dtc)$_2$ (2.293 Å av).[9] The Cu−S distances in the Cu2(Hm-dtc)$_2$ unit are similar to the typical Cu^{III}−S distances for copper(III) dithiocarbamate complexes such as [Cu(Me$_2$dtc)$_2$](ClO$_4$) (2.234 Å av) and [Cu(Et$_2$dtc)$_2$](FeCl$_4$) (2.208 Å av).[10] On the basis of its charge neutrality, it is concluded that this complex is in the mixed-valence state with formula [Cu$^{I}_6$Cu^{II}Cu^{III}Br$_7$(Hm-dtc)$_4$]·3CHCl$_3$, in which the square-planar Cu1 with the longest Cu−S distance is divalent, the square-planar Cu2 with the shortest Cu−S distance is trivalent, and the other Cu ions of Cu3, Cu4, Cu5, Cu6, Cu7, and Cu8 with distorted tetrahedral or trigonal-pyramidal coordination geometries are monovalent, consistent with the results of magnetic measurements reported below.

The octanuclear clusters align with a head-to-tail linkage on the basis of the formation of weak coordination bonds between these clusters, constructing an infinite 1D assemblage in the crystal, as shown in Figure 2a. In this 1D assemblage, two Cu(Hm-dtc)$_2$ units are joined to each other and form a dimer unit with weak Cu−S bonds; the Cu1−S7* and Cu2*−S1 separations are 2.9662(10) and 3.3300(10) Å, respectively, which are longer than the intramolecular Cu1−S and Cu2−S distances in the mononuclear units. Note that the Cu(Hm-dtc)$_2$ units Cu^{II}(Hm-dtc)$_2$ and Cu^{III}(Hm-dtc)$_2$ in the dimer have different oxidation states and a small Cu^{II}···Cu^{III} separation [3.8543(6) Å]; this separation is smaller than the intracluster Cu^{II}···Cu^{III} separation [6.4509(6) Å]. Figure 2b is a packing diagram viewed along the 1D assemblages, which are fully isolated from each other because of the hexamethylene groups of the dtc ligands and the CHCl$_3$ crystal solvents. The nearest-neighbor Cu^{II}···Cu^{II}, Cu^{III}···Cu^{III}, and Cu^{II}···Cu^{III} separations between the 1D assemblages are 11.6414(6), 12.6294(7), and 12.7104(6) Å, respectively.

The magnetic susceptibility of a polycrystalline sample of **1** was measured using a SQUID magnetometer at 10 kOe in the temperature range of 5−300 K (Figure S1 in the Supporting Information). The effective magnetic moment at 300 K is 1.49 μ_B, which indicates that this octanonuclear cluster **1** includes one unpaired electron of the Cu^{II} ion ($S = {}^1/_2$), as characterized by the X-ray study. The direct-current electrical resistivity of powder-pressed pellet samples sandwiched by brass electrodes (diameter, 13 mm) of the octanuclear cluster **1** was measured in the temperature range of 250−300 K, which indicates that this complex is a semiconducting material (E_a = 0.31 eV) with low conductivity ($\sigma_{300\ K} = 2.9 \times 10^{-11}$ S cm^{-1}; Figure S3 in the Supporting Information).

Figure 3a shows the absorption spectra of the mononuclear complex Cu(Hm-dtc)$_2$ and of metal cluster **1** in a CHCl$_3$ solution. The mononuclear complex Cu(Hm-dtc)$_2$ exhibits broad absorption in the visible range, with a maximum at 437 nm (ε = 12 100 M^{-1} cm^{-1}) and a shoulder at 620 nm (ε = 1100 M^{-1} cm^{-1}). The intense absorption band at 437 nm is attributed to ligand-to-metal charge transfer.[11] The broad shoulder at 620 nm may be attributed to the d−d transition of the Cu^{II} ion; this absorption is enhanced by mixing of the d orbitals of the Cu^{II} ion and highest occupied molecular orbitals of the dtc ligands. The octanuclear cluster also shows large absorption bands with a maximum at 424 nm (ε = 23 200 M^{-1} cm^{-1}), a shoulder at

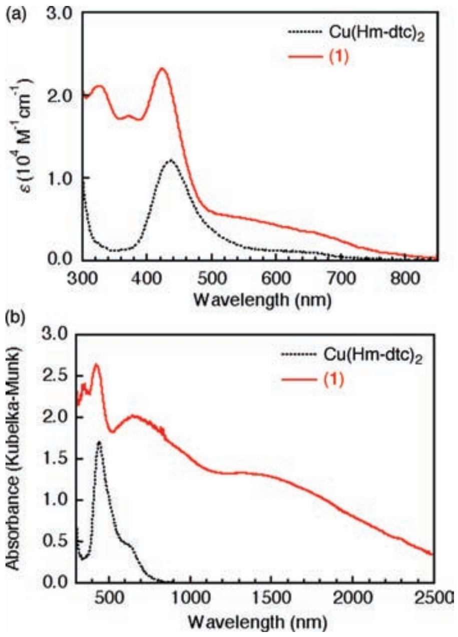


Figure 3. (a) Absorption spectra of mononuclear complex Cu(Hm-dtc)$_2$ and octanuclear cluster **1** in a $CHCl_3$ solution and (b) diffuse-reflectance UV−vis−near-IR absorption spectra of solid samples of Cu(Hm-dtc)$_2$ and **1** (0.01 mmol) doped in MgO (80 mg) obtained via Kubelka−Munk analysis of the reflectance spectra.

580 nm (ε = 4700 M^{-1} cm^{-1}), and an additional new absorption band at 372 nm (ε = 17 500 M^{-1} cm^{-1}), in which the solution shows a brown color. Figure 3b shows the absorption spectra, obtained by diffuse-reflectance spectroscopy, of the solid samples of mononuclear complex Cu(Hm-dtc)$_2$ (0.01 mmol; black) and octanuclear cluster **1** (0.01 mmol; red) doped in MgO (80 mg); the absorbance is plotted as the Kubelka−Munk function[12] $f(R) = (1 - R^2)/2R$, where R is the absolute reflectance of the samples. The spectrum of a solid sample of mononuclear complex Cu(Hm-dtc)$_2$ exhibits absorptions similar to those of its spectrum in a $CHCl_3$ solution, with a maximum at 439 nm and a shoulder at 620 nm. In contrast, the octanuclear cluster **1** assemblage has an additional broad absorption band (λ_{max} = 1400 nm) extended to near-IR regions in the solid state. This unusual absorption band is never observed in mononuclear and polynuclear copper complexes containing dtc ligands. We attribute this broad absorption to IVCT transitions from the Cu^{II}(Hm-dtc)$_2$ unit to the Cu^{III}(Hm-dtc)$_2$ unit between the clusters through the weak Cu−S bonds. In other words, the IVCT transitions were induced by the assembly of mixed-valence $Cu^I/Cu^{II}/Cu^{III}$ clusters.

In summary, we synthesized a new mixed-valence octanuclear $Cu^I/Cu^{II}/Cu^{III}$ cluster with an infinite 1D assemblage. In this complex, the IVCT transitions between the clusters are induced by the assembly of mixed-valence clusters. Such mixed-valence clusters may open up new opportunities for the development of nanofunctional materials.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis, magnetic and conductive results, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Zou, R.; Sakurai, H.; Xu, Q. *Angew. Chem., Int. Ed.* **2006**, *45*, 2542–2546. (b) Cho, S.-H.; Ma, B.; Nauyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun.* **2006**, 2563–2565. (c) Uemura, T.; Kiraura, R.; Ohta, Y.; Nagaoka, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 4112.

(2) (a) Yagi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaouji, M.; Kim, J. *Nature* **2003**, *423*, 705–714. (b) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (c) Noro, S. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2519.

(3) (a) Otsubo, K.; Kobayashi, A.; Kitagawa, H.; Hedo, M.; Uwatoko, Y.; Sagayama, H.; Wakabayashi, Y.; Wawa, H. *J. Am. Chem. Soc.* **2006**, *128*, 8140–8141. (b) Mitsumi, M.; Murase, T.; Kishida, H.; Yoshinari, T.; Ozawa, Y.; Toriumi, K.; Sonoyama, T.; Kitagawa, H.; Mitani, T. *J. Am. Chem. Soc.* **2001**, *123*, 11179–11192.

(4) (a) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993. (b) Ferlay, S.; Mallah, T.; Ouahes, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701–703.

(5) (a) Zhang, Q.-F.; Ding, J.; Yu, Z.; Song, Y.; Rothenberger, A.; Fenske, D.; Leung, W.-H. *Inorg, Chem.* **2006**, *45*, 8638–8647. (b) Huang, K.; Song, Y.; Pan, Z.; Li, Y.; Zhuo, X.; Zheng, H. *Inorg. Chem.* **2007**, *46*, 6233–6235.

(6) (a) D’Alessandro, D. M.; Davies, M. S.; Keene, F. R. *Inorg. Chem.* **2006**, *45*, 1656–1666. (b) D’Alessandro, D. M.; Dinolfo, P. H.; Davis, M. S.; Hupp, J. T.; Keene, F. R. *Inorg. Chem.* **2006**, *45*, 3261–3274.

(7) (a) Kumar, A.; Mayer-Figge, H.; Sheldrick, W. S.; Singh, N. *Eur. J. Inorg. Chem.* **2009**, 2720–2725. (b) Padilla-Tosta, M.; Fox, O. D.; Drew, M. G. B.; Beer, P. D. *Angew. Chem., Int. Ed.* **2001**, *40*, 4235–4239. (c) Fox, O. D.; Drew, G. B.; Beer, P. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 136–140. (d) Konarev, D. V.; Kovalevsky, A. Y.; Khasanov, S. S.; Saito, G.; Lopatin, D. V.; Umrikhin, A. V.; Otsuka, A.; Lyubovskaya, N. *Eur. J. Inorg. Chem.* **2006**, 1881–1895.

(8) (a) Okubo, T.; Tanaka, N.; Kim, K. H.; Yone, H.; Maekawa, M.; Kuroda-Sowa, T. *Inorg. Chem.* **2010**, *49*, 3700–3702. (b) Kim, K. H.; Okubo, T.; Tanaka, N.; Mimura, N.; Maekawa, M.; Kuroda-Sowa, T. *Chem. Lett.* **2010**, *39*, 792–793. (c) Okubo, T.; Kawajiri, R.; Mitani, T.; Shimoda, T. *J. Am. Chem. Soc.* **2005**, *127*, 17598–17599. (d) Kawajiri, R.; Okubo, T.; Mitani, T. *Polyhedron* **2006**, *25*, 2650–2654. (e) Golding, R. M.; Rae, A. D.; Ralph, B. J.; Sulligoi, L. *Inorg. Chem.* **1974**, *13*, 2499. (f) Hendrickson, A. R.; Martin, R. L.; Taylor, D. *Chem. Commun.* **1975**, 843.

(9) (a) Jian, F.; Wang, Z.; Bai, Z.; You, X.; Fun, H.-K.; Chinnakali, K.; Razak, I. A. *Polyhedron* **1990**, *18*, 3401. (b) Ngo, S. C.; Banger, K. K.; Dela Rosa, M. J.; Toscano, P. J.; Welch, J. T. *Polyhedron* **2003**, *22*, 1575.

(10) Hogarth, G.; Pateman, A.; Redmond, S. P. *Inorg. Chim. Acta* **2000**, *306*, 232–236.

(11) (a) Sarova, G. H.; Jeliazkova, B. G. *Transition Met. Chem.* **2001**, *26*, 388. (b) Cookson, J.; Evans, E. A. L.; Maher, J. P.; Serpell, C. J.; Paul, R. L.; Cowley, A. R.; Drew, M. G. B.; Beer, P. D. *Inorg. Chem. Acta* **2010**, *363*, 1195–1203.

(12) (a) Kubelka, P.; Munk, F. *Zh. Tekh. Fiz.* **1931**, *12*, 593–601. (b) Groothaert, M. H.; Smeets, P. J.; Sels, B. F.; Jacobs, P. A.; Schoonheydt, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 1394–1395.