Synthesis, Structure, and Electrochemistry of a Dodecanuclear Chromium Cluster Complex $[Cr_{12}S_{16}(PEt_3)_{10}]$

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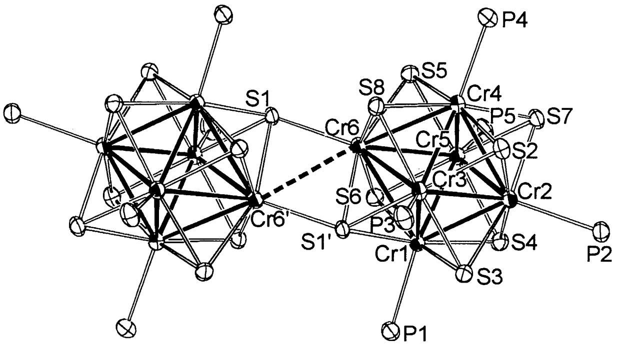
A dodecanuclear chromium sulfide cluster complex $[Cr_{12}S_{16}(PEt_3)_{10}]$ has been synthesized by the reaction of a hexanuclear cluster complex $[Cr_6S_8(PEt_3)_6]$ with sulfur. This complex has two octahedral Cr_6S_8 cores that are linked by two Cr-S bonds. The intercluster bonding mode is similar to that in the Chevrel phases. Cyclic voltammetry shows the existence of the intercluster electronic interaction between the two Cr_6S_8 cluster units.

The chemistry of the superconducting Chevrel phases $M_xMo_6E_8$ (M = Pb, Sn, Cu, etc.; E = S, Se, Te) has been well-developed.[1] They have the Mo_6E_8 cluster unit consisting of a Mo_6 octahedron and eight face-capping chalcogen atoms. The chalcogen atoms additionally bond to the molybdenum atoms of adjacent octahedral clusters forming a three-dimensional cluster network. The interactions between the cluster units through the intercluster bondings have been considered to be responsible for the characteristic band structure and superconductivity.[2] In contrast to the extensive studies on these molybdenum compounds, no chromium analogue is known. A molecular cluster complex $[Cr_6Te_8(PEt_3)_6]$ has been reported by Steigerwald et al., but attempts to prepare a chromium Chevrel compound has been unsuccessful.[3] Recently, we have prepared a molecular cluster complex $[Cr_6S_8(PEt_3)_6]$ (**1**) with a Cr_6S_8 cluster unit.[4] As the first step for the preparation of still unknown solid-state "chromium Chevrels," we have tried to prepare the dimer of octahedral clusters of **1**. We have found that removal of a triethylphosphine from **1** by elemental sulfur leads to the cluster condensation and, as a result, the formation of a dodecanuclear cluster complex $[Cr_{12}S_{16}(PEt_3)_{10}]$ (**2**), a dimer of octahedral clusters. The synthesis, structure, and electrochemical study of **2** are described in this paper.

All manipulations were carried out under an inert atmosphere. Elemental sulfur (0.0817% w/w in toluene, 12 cm^3, 0.28 mmol) was added to a solution of $1{\cdot}2C_6H_6$ (0.40 g, 0.28 mmol) in 80 cm^3 of toluene, and the mixture was refluxed for 24 h. Toluene was removed under reduced pressure, the residue was extracted with hexane, and hexane was removed under reduced pressure. The residue was washed with acetonitrile for the removal of triethylphosphine sulfide, and extracted with dichloromethane. The resulting dark brown solution was kept at 5 ℃ to afford black crystals of $2{\cdot}2CH_2Cl_2$ in 39% yield.

The structure of **2** was determined by the single-crystal X-ray analysis.[5] X-ray data were collected at a low temperature (207 K) because solvent molecules escaped quickly from the crystal at room temperature. The ORTEP drawing and the selected bond distances are shown in Figure 1. There is a crystallographic inversion center at the middle point of Cr6 and Cr6′ and the molecule has $\bar{1}$ (C_i) point group symmetry. This complex has two Cr_6S_8 cores in one molecule. Each core consists of a Cr_6 octahedron and eight face-capping sulfur atoms. Each chromium atom except Cr6 is additionally coordinated to one triethylphosphine ligand. The Cr6 atom is bound to one of the sulfur atoms in the adjacent Cr_6S_8 unit. Thus, the two Cr_6S_8 units are linked by two Cr–S bonds. This intercluster bonding mode is similar to those in the Chevrel phases. Therefore, the $Cr_{12}S_{16}$ cluster framework in **2** may represent two neighboring cluster units in the "chromium Chevrel phases."



Cr1-Cr2	2.666(2)	Cr1-Cr3	2.662(3)
Cr1-Cr5	2.597(3)	Cr1-Cr6	2.779(2)
Cr2-Cr3	2.639(3)	Cr2-Cr4	2.657(3)
Cr2-Cr5	2.658(2)	Cr3-Cr4	2.607(3)
Cr3-Cr6	2.823(2)	Cr4-Cr5	2.582(3)
Cr4-Cr6	2.784(2)	Cr5-Cr6	2.773(2)
Cr6-Cr6′	2.948(3)		

Figure 1. ORTEP drawing and selected bond distances (Å) for $2{\cdot}2CH_2Cl_2$. Carbon atoms are omitted for clarity.

Cecconi et al. has reported a dodecanuclear cobalt cluster complex $[Co_{12}S_{16}(PEt_3)_{10}]^{2+}$ in which the disposition of atoms is similar to that in **2**.[6] In this complex, the intercluster Co–Co distance is shorter than the intracluster Co–Co distances. It has been indicated that the formation of the intercluster Co–Co bond stems from the spin coupling of the two unpaired electrons that localize at the metal atoms without triethylphosphine ligands.[7]

The Cr_6 octahedron of **1** is regular and all of the Cr–Cr distances are almost equal (av. 2.59 Å). In **2**, however, the four Cr–Cr distances between Cr6 and other four chromium atoms are larger (av. 2.79 Å) than the other eight Cr–Cr distances (av. 2.63 Å), and the Cr_6 octahedra are considerably distorted. The intercluster Cr–Cr distance between Cr6 and Cr6′ is 2.95 Å, which indicates some bonding interactions of bond order $n = 0.1$, where Pauling's equation is applied ($d(n) = d(1) - 0.6 \log n$, where $d(n)$ = 2.95 Å and $d(1)$ = 2.35 Å).[8] As there are 25 Cr–Cr distances in **2** and the number of CVE (cluster valence electron) is 40, the bond order for each Cr–Cr bonding should be smaller than that in **1** with 12 Cr–Cr distances and 20 CVE. In **2**, therefore, the intercluster bonding interaction between the chromium atoms is considered to cause the weakening and the elongation of the intracluster Cr–Cr6 bonds, and their distances are 0.2 Å longer than the Cr–Cr distances in **1**.

The cyclic voltammograms of the cluster complexes **1** and **2** in THF solution are shown in Figure 2. Complex **1** shows an

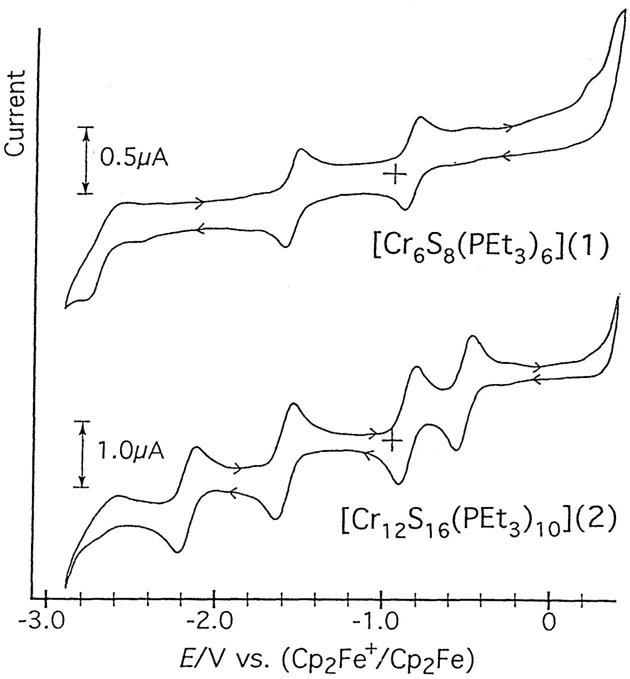


Figure 2. Cyclic voltammograms of **1** and **2** at platinum working electrode in 0.1 mol dm^{-3} Bu_4NClO_4-THF at a scan rate of 25 mV/s.

oxidation step at –0.86 V and a reduction step at –1.54 V, and complex **2** two oxidation steps at –0.86 V and –0.44 V and two reduction steps at –1.57 V and –2.12 V (vs. Cp_2Fe^+ / Cp_2Fe couple). All the waves are quasi-reversible and are assumed to be due to one-electron redox processes of a Cr_6S_8 cluster unit. Thus, the electrochemistry suggests that [$Cr_6S_8^+$– Cr_6S_8], [$Cr_6S_8^+$– $Cr_6S_8^+$], [$Cr_6S_8^-$– Cr_6S_8], and [$Cr_6S_8^-$– $Cr_6S_8^-$] are formed by the electrochemical redox reactions of **2**. Once one-electron redox reactions occur to a Cr_6S_8 cluster unit, the second redox reactions in another cluster unit are influenced by the change of the oxidation state of the first cluster unit. This indicates the existence of the intercluster electronic interaction between the two cluster units.[9] The difference of potentials between the first step and the second step is larger for the reduction processes (0.58 V for reduction and 0.35 V for oxidation). This shows that the electronic interaction between the two cluster units is larger in the reduced state [$Cr_6S_8^-$– Cr_6S_8] than in the oxidized state [$Cr_6S_8^+$– Cr_6S_8].

Complex **2** is paramagnetic. Temperature dependent paramagnetism suggests the antiferromagnetic interaction between the paramagnetic Cr_6 cluster units.[10]

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5 Crystal data for **2**•$2CH_2Cl_2$: formula $C_{62}H_{154}Cl_4Cr_{12}P_{10}S_{16}$, fw = 2488.4, space group $P\bar{1}$, a = 14.697(6) Å, b = 14.733(5) Å, c = 14.238(5) Å, α = 96.60(3)°, β = 109.77(3)°, γ = 65.69(3)°, V = 2643 Å^3, Z = 1, $D_{calcd.}$ = 1.563, R = 0.073, R_w = 0.057 for 7833 observed reflections ($|F_o| > 3\sigma(|F_o|)$; $6° < 2\theta < 55°$). The intensity data were collected by a Rigaku AFC-7R diffractometer with Mo Kα radiation at 207 K. In the crystal structure analyses, the positions of the chromium atoms were determined by direct methods (SHELXS86),[11] and other non-hydrogen atoms were located on Fourier maps (SHELXS76).[12] The full-matrix refinements were performed with programs SHELXS76 and ANYBLK.[13] Hydrogen atoms were not included in the refinements.

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