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Original Scientific Article

Synthesis of Molecular Dodecanuclear Carbon-centered Rhenium Cluster $Re_{12}CS_{17}$ and its Conducting Properties[†]

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Abstract. The unique dodecanuclear cluster compound $Re_{12}CS_{17}$ was prepared and studied by X-ray, complex impedance method and density functional theory (DFT). The compound is amorphous, possesses semiconducting properties. Computer simulations showed that the Re and S atoms at the external borders of the neighboring molecules $Re_{12}CS_{17}$ can form sufficiently strong Re···S intermolecular bonds, similar to the Mo···S intermolecular bonds of cuboctahedron Mo_6S_8 molecules in the Chevrel phases. (doi: 10.5562/cca1973)

Keywords: rhenium cluster, Chevrel phase, DFT, conductivity

INTRODUCTION

The interest to the cluster chalcogenides of transition metals (M = Mo, Re, *etc.*) is associated with the prospects of their use for the development of superconducting solenoids, cathode materials, molecular "machines", *etc.*[1] The most famous representatives of cluster chalcogenides are Chevrel phase type MMo_6Q_8 (Q = S, Se), based on the parent structure Mo_6Q_8.[1] Detailed studies of the lower chalcogenides of molybdenum have shown that in these systems, in addition to octahedral clusters Mo_6Q_8, larger clusters of Mo_9Q_{11} and $Mo_{12}Q_{14}$ may be generated; these clusters can be viewed as the condensation products of Mo_6 octahedra *via* common triangular faces.[2] Cluster chemistry of rhenium is very similar to the chemistry of molybdenum. Thus, in addition to well-known octahedral complexes with the cluster core $\{Re_6Q_8\}$, some condensed complexes like $[Re_9Se_{11}Br_6]^{2-}$ and $K_6[Re_{12}CS_{17}(CN)_6]$ were obtained too.[3,4] Last complex is considered as promising monomolecular switch.[5,6]

Drawing an analogy between the crystallochemical properties of chalcogenide cluster complexes of molybdenum and rhenium, it is interesting to note the following examples. The reaction of Mo_6Se_8 with molten KCN leads to the complex $K_6[Mo_6Se_8(CN)_6]$, which recalls a complex $K_6[Re_{12}CS_{17}(CN)_6]$. These two chalcocyanide complexes of molybdenum and rhenium can be conventionally written as $[Mo_6Se_8]\cdot 6KCN$, and $[Re_{12}CS_{17}]\cdot 6KCN$. Similar description of these complexes suggests that if Mo_6Se_8 exists as a neutral stable phase, perhaps, $Re_{12}CS_{17}$ can exist too. This idea was the basis for developing a method of synthesis of rhenium cluster molecular complex $Re_{12}CS_{17}$ without terminal ligands, in order to obtain a molecular switch.

For realization of this idea the reactions of successive substitution of terminal ligands in the basic complex $K_6[Re_{12}CS_{17}(CN)_6]$ were carried out using following steps: $K_6[Re_{12}CS_{17}(CN)_6] \rightarrow K_6[Re_{12}CS_{17}(OH)_6] \rightarrow [Re_{12}CS_{17}(H_2O)_6] \rightarrow [Re_{12}CS_{17}(OH)_6]$.

EXPERIMENTAL AND CALCULATIONS

Synthesis

Synthesis of $Re_{12}CS_{17}$ was carried out using two-steps procedure.

Step 1. *Synthesis of* $[Re_{12}CS_{17}(H_2O)_6]\cdot 4H_2O$. 0.1 M aqueous solution of H_2SO_4 was added dropwise to aqueous solution of $K_6[Re_{12}CS_{17}(OH)_6]\cdot 4H_2O$ (400 mg, 0.128 mmol) until bleaching solution. Black precipitate was deposited. The solution was decanted, the precipitate was washed with water and dried in air. Yield: 370

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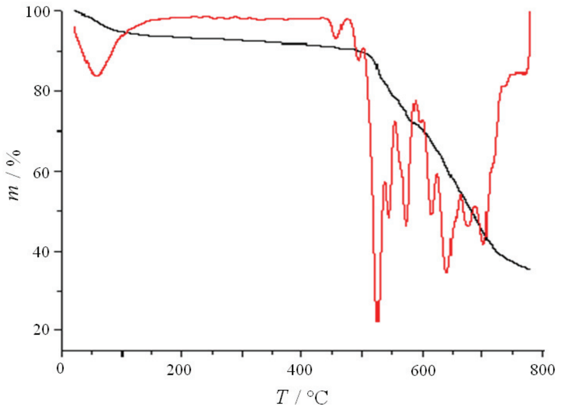

Figure 1. Thermogravimetric curves of $[Re_{12}CS_{17}(H_2O)_6]\cdot 4H_2O$.

mg. EDS: Re:S = 12.0:16.9. The presence of potassium in the solid was not found. Number of water molecules was determined according to thermogravimetric analysis (Figure 1). On the thermogram in the range from 25 to 150° C a single broad endothermic peak was recorded, which corresponds to the mass loss of 6.1 %. Such a mass (6.1 % = 177 amu) corresponds to the loss of about 10 water molecules per molecule of the cluster complex. The calculation shows that in a cluster complex with empirical formula $[Re_{12}CS_{17}(H_2O)_6]$, $w(H_2O) = 3.7$ %.

Consequently, the compound obtained can be described by the formula $[Re_{12}CS_{17}(H_2O)_6]\cdot 4H_2O$, subject to the special feature of coordination of cluster core. Resulting anhydrous compound $Re_{12}CS_{17}$ is stable up to 400 °C.

Step 2. *Synthesis of $Re_{12}CS_{17}$*. 300 mg (0.103 mmol) $[Re_{12}CS_{17}(H_2O)_6]\cdot 4H_2O$ was placed in a glass boat and held for 2 hours at 250 °C in a tube furnace under vacuum. A black crumbly powder is formed. Yield: 280 mg. EDS: Re:S = 12.0:17.0. IR (KBr) ν/cm^{-1}: 411. According to X-ray diffraction study the bulk phase of the cluster compound $Re_{12}CS_{17}$ is amorphous. As evidence that the substance contains the Re_{12}-fragment the proper hydroxocomplex has been synthesized starting from $Re_{12}CS_{17}$. For this, 0.2 g $Re_{12}CS_{17}$ was dissolved in boiling KOH solution. The solution was evaporated until the onset of crystallization and cooled. The precipitated crystals were filtered and the precipitate was dried in air. Yield: 0.185 g (85 %).

X-ray Analysis

The structure of compound $K_6[Re_{12}CS_{17}(OH)_6]\cdot 9H_2O$ is solved by X-ray single crystal diffraction analysis. Single crystals suitable for XRD analysis were selected manually from reaction product. X-ray diffraction data (a = 14.1085 (7) Å, c = 14.1784 (7) Å, V = 2444.1 (2) Å^3, Z = 2, space group $P_{6\,3/m}$, ρ_{calc} = 4.4375 g/cm^3) were obtained at 150 K by the standard four-circle diffractometer Bruker-Nonius X8 Apex (MoKα radiation, graphite monochromator, a two-coordinate CCD-detector). According to crystal structure data the resulting hexahydroxocomplex is described by formula $K_6[Re_{12}CS_{17}(OH)_6]\cdot 9H_2O$. The structure of the cluster core in this compound is the same as that in cluster complex $K_6[Re_{12}CS_{17}(OH)_6]\cdot 4H_2O$ described previously, the main interatomic distances correspond to known values for this cluster anion.[7] The slight discrepancy is observed at distances of Re–O: 2.063(9) Å is in the compound synthesized here and 2.091(14) Å in published previously.[7] We should also note a slight difference in the unit cell parameters. The reason for these discrepancies, we associate with a different number of water molecules in the structure of compounds.

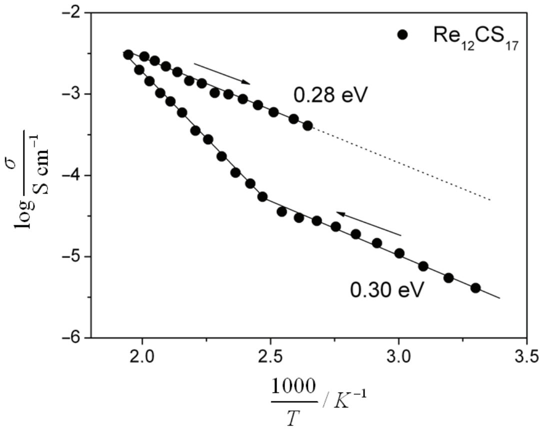

Figure 2. Temperature dependence of the conductivity of the pelletized sample $Re_{12}CS_{17}$.

Electrical Measurements

$Re_{12}S_{17}$ conductivity measurements were carried out on pelletized samples, pressed under a pressure of 400 MPa with pressed into silver electrodes. Conductivity measurements were performed by two-electrode scheme in forevacuum (6.67 Pa) at temperatures of 20 to 200 ºC on an alternating current with a precision measuring electrical parameters of the Hewlett Packard HP 4284A in the frequency range from 20 Hz to 1 MHz. Conductivity values were calculated from the frequency dependence of conductivity by the method of complex impedance.

Quantum-chemical Analysis

Analysis of the intermolecular interactions carried out by numerical simulation of the binding of two molecules $Re_{12}CS_{17}$ using known data about the location of molecules in Mo_6S_8 Chevrel phases.[1] The density functional theory method was used with software package ADF2008.[8] Analysis of interatomic interactions were carried out using a topological method of "Atoms in the molecule" (AIM).[9] For the analysis of electron density by AIM program was used DGrid 4.5.[10]

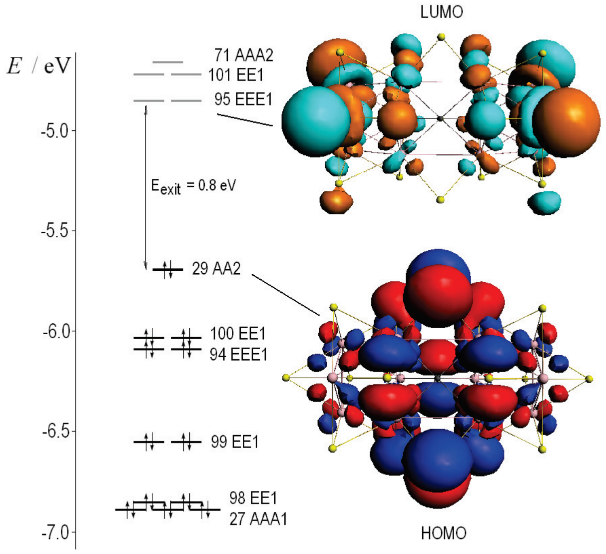

Figure 3. Energy levels of MOs for $Re_{12}CS_{17}$. Estimated image of bonding highest occupied molecular orbital (HOMO) and of antibonding lowest unoccupied molecular orbital (LUMO).

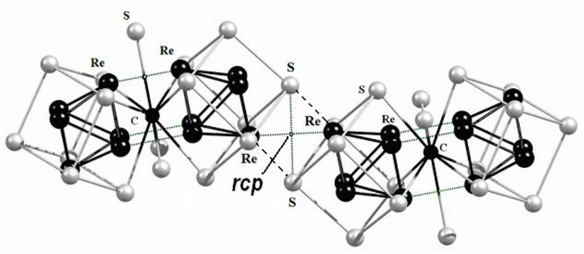

Figure 4. The structure of two interacting molecules $Re_{12}CS_{17}$ (simulation results).

DISCUSSION

According to conductivity study, tablet samples of $Re_{12}CS_{17}$ have stable semiconducting properties at temperatures below 400 K (Figure 2). The experimental value of conduction activation energy E_{act}, determined from the Arrhenius dependence of $\sigma = (A/T)\cdot\exp(E_{act}/kT)$ is the $E_{act} = 0.28 \pm 0.02$ eV. The obtained value of ≈ 3 times less energy-electron excitation calculated for the cluster molecule $Re_{12}CS_{17}$ ($E_{exc} = 0.8$ eV) (Figure 3). This result may reflect the fact that the experimental E_{act} is not connected with the one-electron excitation of molecules, and the measured value of the barrier corresponds to the activation energy of electron hopping on the intermolecular contacts Re···Re. At temperatures above 400 K an irreversible increase in conductivity, due to, apparently, with the dehydration of compounds that might partially hydrated during storage in air. Most likely, water molecules are located close to the cations and block electron transfer between them. When dehydration opens a path of electron transfer, this leads to an increase in conductivity on the order. At the same time, the intermolecular distance cation-cation decreases, which leads to a slight decrease in the conduction activation energy E_{act} from 0.30 to 0.28 eV.

Computer simulations showed that the Re and S atoms at the external borders of the neighboring molecules $Re_{12}CS_{17}$ can form sufficiently strong intermolecular bonds Re···S (Figure 4), similar to the intermolecular bonds of Mo···S cuboctahedron Mo_6S_8 molecules in the Chevrel phases.[1] The binding energy between two molecules Mo_6S_8 is –1.71 and –1.55 eV for the two molecules $Re_{12}CS_{17}$. Topological quantum analysis of the intermolecular interaction of molecules Mo_6S_8 and $Re_{12}CS_{17}$ showed that the interactions are a four-center and are characterized by a ring critical point (rcp) with density of energy –0.37 and –0.53 eV Å^{-3}, respectively. The emergence of one-dimensional zigzag chains $Re_{12}CS_{17}$–$Re_{12}CS_{17}$, as well as chains of atoms –S–S–S– in the amorphous sulfur, can explain the absence of X-ray reflections of the bulk phase of the compound.

CONCLUSION

Molecular cluster complex of composition $Re_{12}CS_{17}$ with stable semiconducting properties is synthesized for the first time. The structure of the $Re_{12}CS_{17}$ is identified as amorphous. It is shown that the molecule $Re_{12}CS_{17}$ can form a bound state, like the molecules Mo_6S_8 in Chevrel phases. It is assumed that this sample can be used as a basis for creating monomolecular electrical device.

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