

Electronic Switch in the Carbon-Centered $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{n-}$ Nanocluster

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Abstract An abrupt change in internuclear Re–Re distances between $\{\text{Re}_6\}$ subunits in the carbon-centered $[\text{Re}_{12}\mu_6\text{-CS}_{17}(\text{CN})_6]^{n-}$ complexes caused by the change of the oxidation state ($n = 6, 8$) is first theoretically shown to be possibly controlled by an external electric field. ^{13}C NMR signal is shown to change over ~ 400 ppm ($\sim 37\text{G}$) for $\mu_6\text{-C}$ atom together with n . Thereby, the metal cluster $[\text{Re}_{12}\mu_6\text{-CS}_{17}(\text{CN})_6]^{n-}$ can be considered as a perspective model of a molecular switch.

Keywords Switch · 12-Rhenium nanocluster · ^{13}C NMR · Electron localization function · DFT

Introduction

Molecular electronics has been a subject of growing interest in recent years [1]. As was shown, a mono-electronic transistor can be constructed on the basis of a single *p*-phenylenevinylene oligomer that can have a varied oxidation

state and is composed of five benzene rings connected by four double bonds [2]. Great opportunities are also associated with metal cluster complexes used as a basis for various nanodevices and molecular motors [3]. Metal cluster compounds are perspective elements of synthetic metals including superconductors. Some of them (e.g., Chevrel phases [4–6]) are characterized by high parameters of critical magnetic fields of superconductivity reaching 60 T. Structurally, the phases are characterized by metal bonds being formed between triangular faces of the neighboring octahedral units.

Recent research reported 12-rhenium cluster complexes $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{n-}$ ($n = 6, 8$) with a unique crystal structure and a reversible redox two-electron transformation $\{[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{6-} \leftrightarrow [\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}\}$ [7]. The complexes are dimers composed of two Re_6 octahedrons connected by rhenium atoms through the interstitial carbon with a trigonal-prismatic coordination, $\{\text{Re}_3(\mu_6\text{-C})\text{Re}_3\}$, and by three bridging sulfur atoms $\mu_2\text{-S}$ with corner coordination of rhenium atoms, $\{\text{Re}(\mu_2\text{-S})\text{Re}\}$. According to X-ray data, the change in the oxidation state of the complex is accompanied by substantial changes in internuclear distances ($\text{Re}^{\text{in}} - \text{Re}^{\text{in}} \sim 0.3 \text{ \AA}$) between two metal subunits $\{\text{Re}_6\}$, whereas inside $\{\text{Re}_6\}$ subunits interatomic distances Re–Re do not change more than for 0.01 \AA (Fig. 1). In other words, the two subunits $\{\text{Re}_6\}$ are closer to each other in $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{6-}$ than in $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}$.

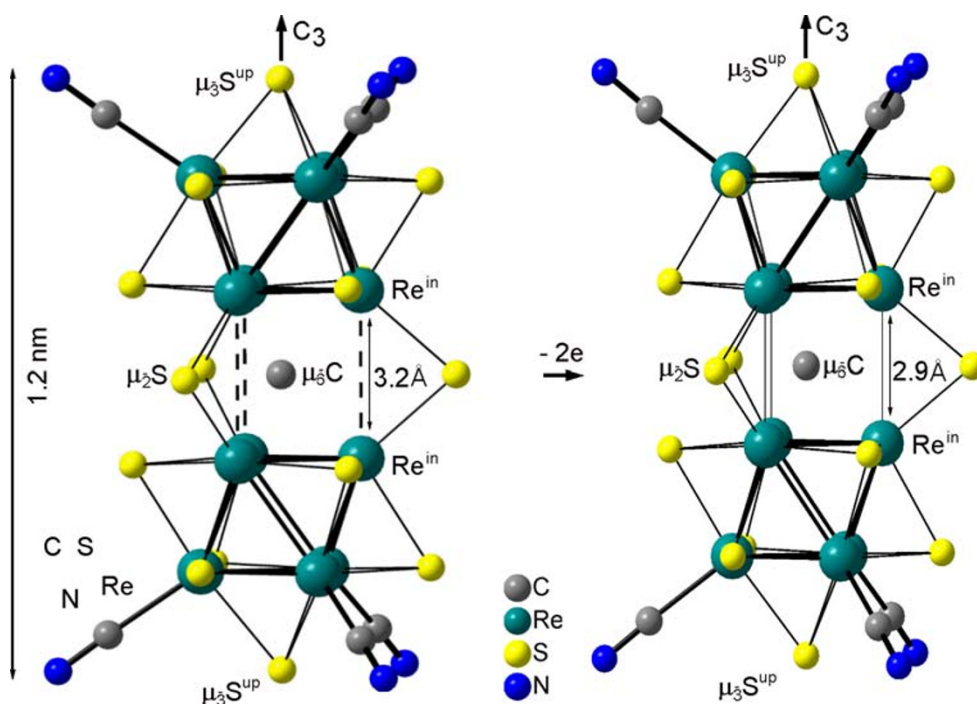
As is well known, a nanoscale device can be constructed from a molecule only if the molecule exhibits such electronic effects as rectification [8], amplification [9] or switching [10, 11]. Here, we study electronic effects in complexes $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{n-}$ ($n = 6, 8$) by NMR spectroscopy and quantum chemical method of electron localization function (ELF) [12, 13] and consider the effects as an evidence of molecular switching.

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Fig. 1 The structure of $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{n-}$ ($n = 8, 6$) complexes. Re^{in} are rhenium atoms in trigonal-prismatic coordination



Experimental Procedure

^{13}C NMR spectra were measured from the polycrystalline samples $\text{K}_8\text{Re}_{12}\text{CS}_{17}(\text{CN})_6 \cdot 20\text{H}_2\text{O}$ (I) and $\text{K}_6\text{Re}_{12}\text{CS}_{17}(\text{CN})_6$ (II) synthesized by precipitating $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}$ complexes from solutions [7]. ^{13}C NMR spectra of (I) and (II) enriched by ^{13}C were measured by Avance-400 spectrometer of BRUKER Bio-Spin in an ampoule for a rotor with the outer diameter 4 mm, the sample being rotated at the magic angle (MAS) at room temperature. The rotation rate was 7, 11 and 15 kHz. The duration of the stimulating 90° pulse was 5 μs , the accumulated amount was 200. The relaxation delay was 10 s. Tetramethylsilane (tms) was used as an external standard for the scale of chemical shifts.

Computational Details

Quantum-chemical study of the electronic structure of model systems $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{n-}$ ($n = 6, 8$) was carried out by a spin-restricted DFT method (code ADF2006 [14]) with model Hamiltonians of density functionals given by the sum of a local density functional LDA (VWN [15]) and a gradient exchange functional GGA (Becke [16] and Perdew [17]). The all-electron basis set of the TZP type, as included in the ADF2006 program, was used for all atoms. Geometry optimization was performed for D_{3h} point group; relativistic effects and spin-orbital interaction were taken into account with the zero-order relativistic approximation method ZORA [18]. ^{13}C NMR chemical shifts were

calculated by the method GIAO in view of scalar relativistic effects and spin-orbital interaction [19–21]. Interatomic interactions were studied by a quantum-chemical topological method “Electron localization function” (ELF) [13]. In this method, we analyze the function.

$$\text{ELF}(\vec{r}) = \frac{1}{1 + \left(\frac{D(\vec{r})}{D_h(\vec{r})}\right)^2},$$

$D_h(r)$ is the density of the Thomas–Fermi kinetic energy for the homogeneous electron gas, which acts as a normalizing multiplier; $D(r)$ is interpreted as excess density of the local kinetic energy of electrons (fermions) resulting from repulsion according to the Pauli principle relative to the density of the local kinetic energy of bosons [22]. The ELF is assumed to approximately 1 in the regions of space that are typical of the maximum localization of electron pairs with antiparallel spins (colored blue in our drawings). The ELF is 0.5 in the regions where the electron density is close to that of the homogeneous electron gas (green) and ~ 0 in the regions with delocalized electrons (red).

Results and Discussion

It was found out that both structure and ^{13}C NMR spectra change dramatically depending on the oxidation state (n) of the complex $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{n-}$ (Fig. 2). According to the obtained data, the reduction/oxidation of the complex $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{n-}$ is accompanied by the change of ^{13}C

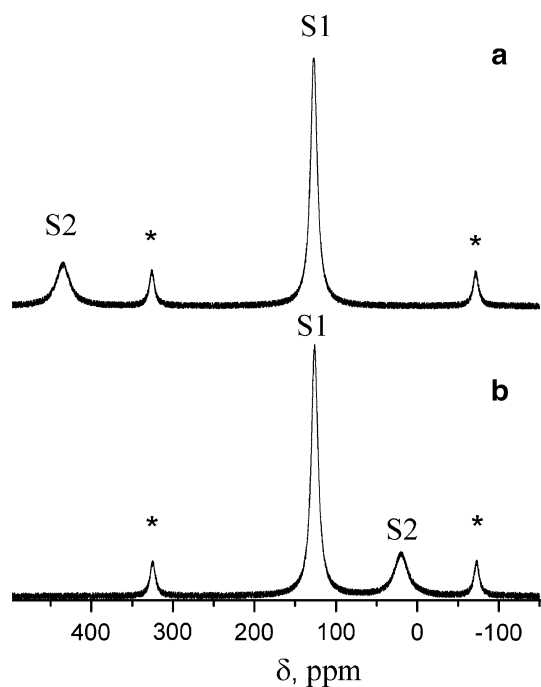


Fig. 2 ^{13}C MAS NMR spectrum of $\text{K}_6\text{Re}_{12}\text{CS}_{17}(\text{CN})_6$ (a) and $\text{K}_8\text{Re}_{12}\text{CS}_{17}(\text{CN})_6 \cdot 20\text{H}_2\text{O}$ (b). S1 is the NMR signal of CN-groups, S2 is the NMR signal of the atom $\mu_6\text{-C}$. Satellite signals are marked by *. Rotation rate is 15 kHz

NMR signal from $\mu_6\text{-C}$ for 415 ppm (or $\sim 37\text{G}$) that substantially exceeds chemical shifts due to the change of the distances between carbon–transition metal [23]. Besides, there is obviously a fundamental difference between the electrically conductive properties of the complexes since the chemical shift is caused by induced electric currents to arise in the complexes in an external magnetic field [24].

Quantum-chemical DFT calculations show a good agreement with the data of X-ray-structural analysis [7, 25] and NMR data (Table 1). The fact suggests a high reliability of the model of electronic structure of complexes $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{n-}$ ($n = 6, 8$) received at the DFT level.

The energy gaps between the highest occupied and the lowest unoccupied molecular orbitals (HOMO-LUMO gap) are 1.05 eV ($n = 6$) and 1.31 eV ($n = 8$), respectively [25]. The difference between the energy gaps and

Table 1 Measured and calculated values of isotropic NMR chemical shifts (δ , ppm) in the $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{n-}$ complexes ($n = 6, 8$)

Complexes	δ (exp)	δ (cal) ^a
$[\text{Re}_{12}^{13}\text{CS}_{17}(\text{CN})_6]^{6-}$	435 ± 1	388
$[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{6-}$	127 ± 1	151.3
$[\text{Re}_{12}^{13}\text{CS}_{17}(\text{CN})_6]^{8-}$	20 ± 1	66.8
$[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}$	126 ± 1	165.0

^a Calculated absolute isotropic chemical shielding $\sigma_{\text{tms}} = 177.4$ ppm, and $\delta = \sigma_{\text{tms}} - \sigma_{\text{substance}}$

distance between the two subunits $\{\text{Re}_6\}$ also suggests different resistance of the molecular complexes [26]. Note that according to Kozlova et al. [25], HOMO orbital is characterized by some bonding interaction between Re atoms from different subunits $\{\text{Re}_6\}$ in the complex $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{6-}$ and by antibonding interaction in $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}$.

The study of the electronic density by the method of electron localization function (ELF) revealed weak exchange interactions ($\text{ELF} \sim 0.3$) between $\mu_6\text{-C}$ and $\mu_2\text{-S}$ in the complex $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{6-}$, the interaction almost disappears in the complex $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}$ [25]. The interaction can affect the structural properties, since even weak localization of electron pairs with antiparallel spins between two positively charged Re atoms should result in some reduction of the distances between subunits $\{\text{Re}_6\}$. Therefore, the internuclear distances $\text{Re}^{\text{in}} - \text{Re}^{\text{in}}$ can be changed if we somehow succeed to weaken or strengthen this interaction.

We placed hypothetical point charges Q in the plane $\{(\mu_6\text{-C}) - (\mu_2\text{-S})_3\}$ at the distance $\sim 5 \text{ \AA}$ from $\mu_2\text{-S}$ atoms of $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}$ complex (Fig. 3) and calculated ELF distribution maps. Various charges Q and their various positions around $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}$ complex were tried. The most demonstrative impact of the external electric field was seen for $Q = \pm 25e$. The modeled point charge $Q = \pm 25e$ creates on the $\mu_2\text{-S}$ atom an

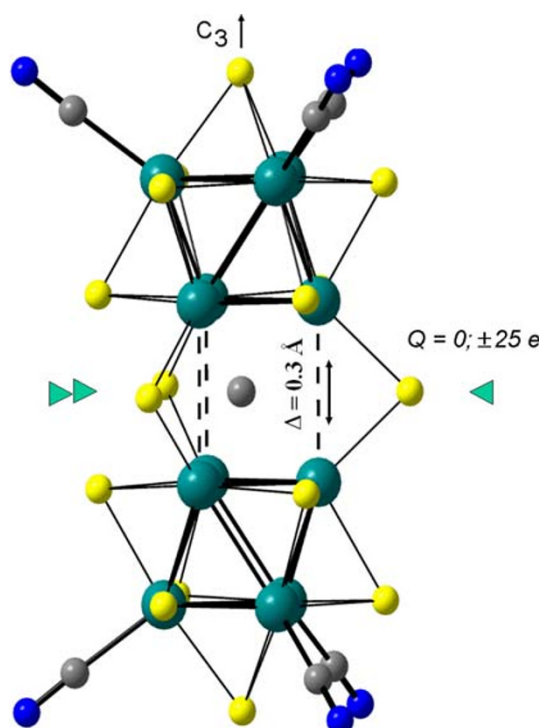
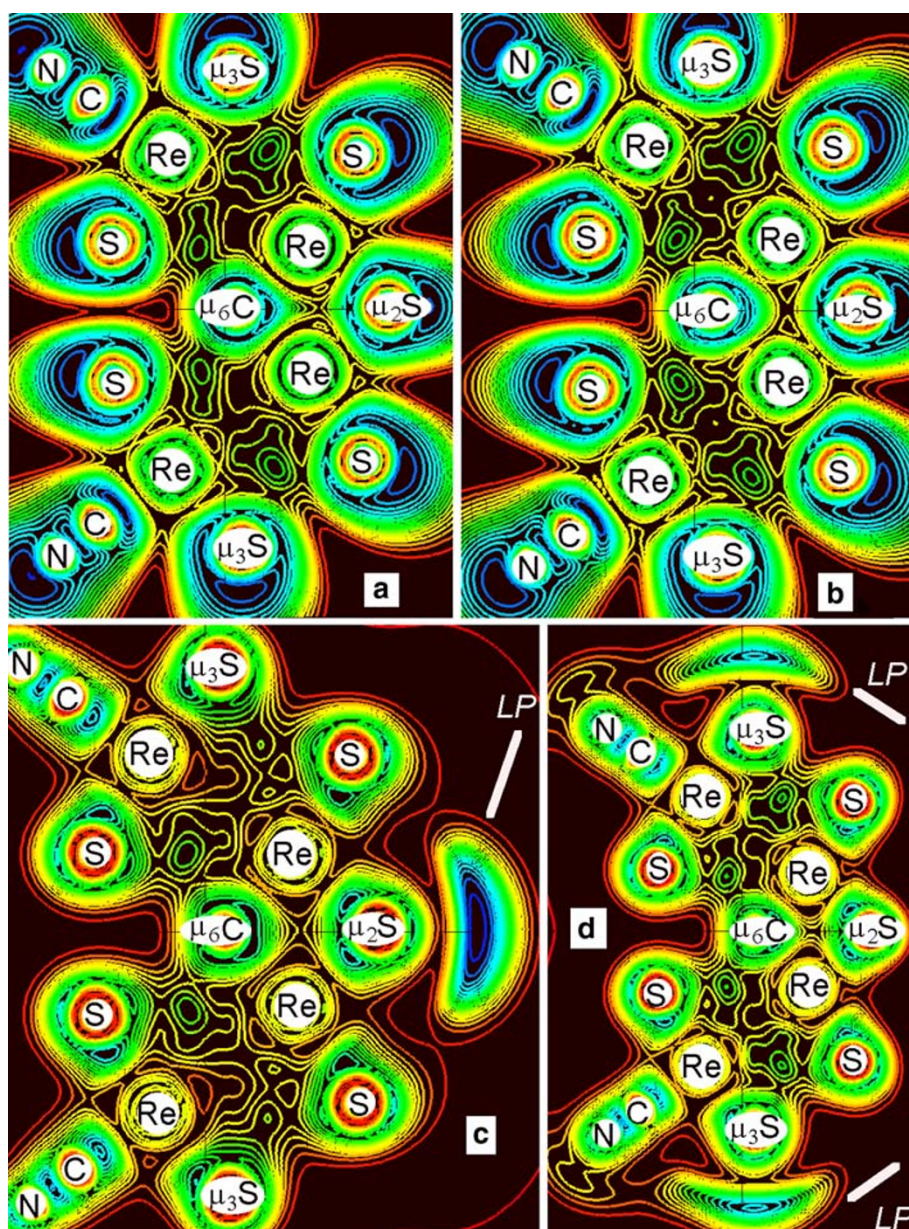


Fig. 3 Hypothetic charges Q (green triangles) on the plane containing three atoms $\mu_2\text{-S}$ and the atom $\mu_6\text{-C}$

Fig. 4 ELF distribution maps for $[\text{Re}_6\text{CS}_{17}(\text{CN})_6]^{n-}$ complex (cutting plane $\text{Re}-(\mu_2\text{-S})-\text{Re}-(\mu_6\text{-C})$): **a** $n = 6$, $Q = 0$; **b** $n = 8$, $Q = 0$; **c** $n = 8$, $Q = +25$, arrow (*LP*) points to the attractors of electronic lone pair; **d** $n = 8$, $Q = -25$, arrows (*LP*) point to the attractors of electronic lone pairs



electrostatic potential $\sim 10^{-9}$ V which is 10–100 times higher than typical an electrostatic potentials created by the atoms inside the complexes. As can be seen, the electrostatic field of a point charge (especially, a negative charge) reinforces the exchange interaction between $\mu_6\text{-C}$ and $\mu_2\text{-S}$ atoms. As mentioned earlier, $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{6-}$ is characterized by increased exchange interaction between $\mu_6\text{-C}$ and $(\mu_2\text{-S})_3$. Therefore, the magnification of exchange interaction between $\mu_6\text{-C}$ and $(\mu_2\text{-S})_3$ in the complex $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}$ should result in its ionization and reduction in the distances between $\{\text{Re}_6\}$ subunits. In fact, the increased localization of electronic lone pairs observed at the sulfur atoms in the positions $\mu_3\text{-S}^{\text{up}}$ ($Q = -25e$) and $\mu_2\text{-S}$ ($Q = +25e$) can signify the

beginning of the oxidation process ($[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-} \rightarrow [\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{6-}$) (Fig. 4).

Conclusions

Thereby, the oxidation state and the distances between $\{\text{Re}_6\}$ subunits in the $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}$ complexes and, therefore, the electron properties of the system are shown to be controlled by an external electric field. We believe that the ON condition with higher conductivity corresponds to the complex $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{6-}$, since NMR spectroscopy reveals the strongest paramagnetic currents induced by external magnetic field. The state can be achieved by

applying external electric field in the plane containing three atoms μ_2 -S and the atom μ_6 -C of the complex $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-}$. Similarly, OFF state should result from turning off the field. We believe that the system is an example of a monomolecular switch.

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