Cluster Compounds

DOI: 10.1002/ange.200501911

$[Re_{12}CS_{17}(CN)_6]^{n-}$ ($n = 6, 8$): A Sulfido–Cyanide Rhenium Cluster with an Interstitial Carbon Atom**

Yuri V. Mironov, Nikolai G. Naumov,
Svetlana G. Kozlova, Sung-Jin Kim, and*
*Vladimir E. Fedorov**

The first compound with an octahedral sulfide–cyanide rhenium cluster, $KCs_3[Re_6S_8(CN)_6]$, was synthesized ten years ago.[1] Since then, the chemistry of chalcocyanide cluster complexes $[Re_6Q_8(CN)_6]^{n-}$ (Q = S, Se, Te; $n = 3, 4$) has developed intensively.[2–6] A remarkable feature of the $[Re_6Q_8(CN)_6]^{n-}$ complexes is their ability to coordinate the transition-metal and post-transition-metal atoms through ambidentate CN^- ligands. Such coordination leads to the formation of cyanide-bridged polymeric structures with various dimensionalities and architectures. Many complex compounds containing similar octahedral chalcocyanide clusters have now been synthesized and their crystal structures and properties studied in detail.[7]

The general approach for the synthesis of rhenium octahedral chalcocyanide complexes is to treat polymeric solids containing $\{Re_6Q_8\}$ cluster cores with molten KCN or NaCN. A similar method was applied to the synthesis of $[Re_6Te_8(CN)_6]^{4-}$ from $[Re_6Te_{15}]$[3,8] and $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se) by using $[Re_6Q_8Br_2]$[2] as precursors.

A few years ago,[9] it was found that ReS_2 and $ReSe_2$ react with molten KCN to form octahedral rhenium-cluster chalcocyanides with bridging S and Se_2 ligands in polymeric layered $K_4[\{Re_6S_8\}(CN)_4S_{4/2}]$ and chainlike $K_4[\{Re_6Se_8\}(CN)_4(Se_{2/2})_2]$ structures. Our further systematic study of phase formation in similar systems has culminated in the discovery of a unique rhenium sulfido–cyanide compound, $K_8[Re_{12}CS_{17}(CN)_6]$ (**1**), which contains a C-centered $\{Re_{12}\}$ cluster unit.

The diamagnetic compound **1** was prepared by treating ReS_2 with molten KCN with a mass ratio ReS_2/KCN of 1:2.[10] Single crystals suitable for a structural study were found in the reaction mixture and the single crystal structure of **1** has been solved by X-ray diffraction.[11] The cluster unit of **1** (Figure 1 a) consists of two $\{Re_6\}$ octahedra bonded by three μ_2-S bridges and one common μ_6-C atom. Each $\{Re_6\}$ cluster is capped by seven μ_3-S atoms and additionally by the centered μ_6-C ligand; thus, a typical octahedral cluster core analogous to $\{Re_6Q_8\}$ (i.e., $\{Re_6S_7C\}$) is formed. Through such bonding and coordination, we recognize trigonal μ_6-C-centered prisms, $\{Re_6C\}$, in which the triangle faces belong to two adjacent $\{Re_6\}$ octahedra. Six outward Re atoms (three from each $\{Re_6\}$ cluster unit) are coordinated by CN ligands.

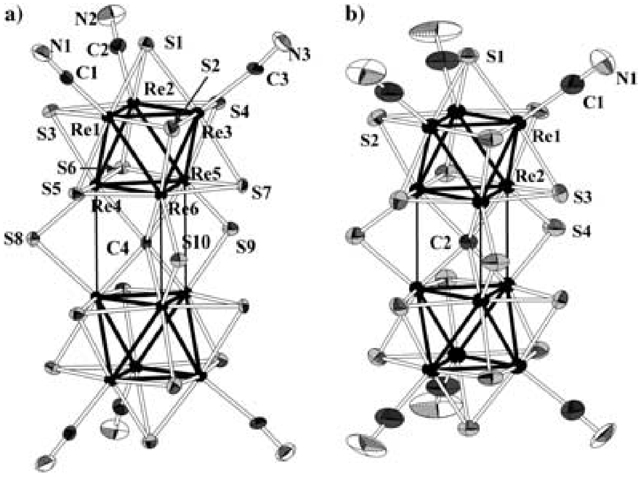

Figure 1. a) Structure of the $[Re_6(\mu_6\text{-}C)S_{17}(CN)_6]^{8-}$ ion in **1**. b) Structure of $[Re_6(\mu_6\text{-}C)S_{17}(CN)_6]^{6-}$ anion in **3**. For average bond lengths and angles, see Table 1. (Displacement ellipsoids are drawn at the 50% probability level.)

The Re–Re interatomic distances in the $\{Re_6S_7C\}$ fragments are comparable with those of $\{Re_6S_8\}$ cluster cores; their mean values are 2.595 Å for Re^{outer}–Re^{outer}, 2.591 Å for Re^{inner}–Re^{inner}, and 2.622 Å for Re^{outer}–Re^{inner} (see Table 1). These values are within the range for Re–Re single bonds observed in octahedral rhenium clusters (in $[Re_6(Q_8(CN)_6]^{4-}$ mean Re–Re distances are 2.599, 2.633, and 2.684 Å for Q = S, Se, and Te, respectively[7a]).

In the trigonal-prismatic $\{Re_6C\}$ units, the long Re···Re separations are 3.1576(17), 3.1722(17), and 3.1740(17) Å. Re–(μ_3-S) bond lengths range from 2.401(6) to 2.445(6) Å. These separations are comparable with those found in other $Re_6S_8L_6$ cluster units, for example $[Re_6S_8(CN)_6]^{4-/3-}$[4] and $[Re_6S_8Br_6]^{4-}$,[12] and polymeric $K_4[\{Re_6S_8\}(CN)_4S_{4/2}]$[9] and $Li_4[\{Re_6S_8\}S_{6/2}]$.[13] The mean Re–(μ_2-S) bond length of **1**, 2.425 Å is close to Re–S bond lengths found in numerous Bronger phases.[14] Re–(μ_6-C) bond lengths in the trigonal prism, $\{Re_6C\}$, range from 2.16(2) to 2.21(2) Å.

Dissolution of **1** in water resulted in fast oxidation of the $[Re_{12}CS_{17}(CN)_6]^{8-}$ ion and formation of the $[Re_{12}CS_{17}(CN)_6]^{6-}$

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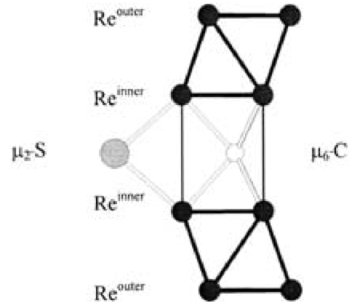
[*] Prof. S.-J. Kim
Department of Chemistry
Ewha Womans University
Seoul 120-750 (Korea)
Fax: (+82) 2-3277-2384
E-mail: sjkim@ewha.ac.kr

Dr. Y. V. Mironov, Dr. N. G. Naumov, Dr. S. G. Kozlova,
Prof. V. E. Fedorov
Nikolaev Institute of Inorganic Chemistry
Siberian Branch of the Russian Academy of Sciences
3, Acad. Lavrentiev pr., 630090 Novosibirsk (Russia)
Fax: (+7) 3833-309489
E-mail: yuri@che.nsk.su

[**] This work was supported by the Russian Foundation for Basic Research (grants 05-03-08090 and 05-03-32123), the International Cooperation Research Program of the Ministry of Science & Technology of Korea (grant M60403000099-04A0100-02310), and the Division of Chemistry and Sciences on Materials of RAS (project No. 15 of Program 4.1). The authors are grateful to the Boreskov Institute of Catalysis SB RAS for an opportunity to use the ADF program.

Table 1: Experimental and calculated interatomic distances [Å] and angles [°] in the clusters $[Re_{12}(\mu_6\text{-}C)S_{17}(CN)_6]^{n-}$.



	Experimental			Calculated		
	$n=8$	$n=6$	$\Delta^{[a]}$	$n=8$	$n=6$	$\Delta^{[a]}$
$Re^{outer}-Re^{outer}$	2.595	2.600	+0.005	2.687	2.664	−0.023
$Re^{inner}-Re^{inner}$	2.591	2.692	+0.101	2.641	2.739	+0.098
$Re^{inner}-Re^{outer}$	2.622	2.630	+0.008	2.700	2.688	−0.012
$Re^{inner}-Re^{inner}$ (in prism)	3.168	2.901	−0.267	3.290	2.976	−0.314
$Re^{inner}-\mu_6\text{-}C$	2.179	2.126	−0.053	2.243	2.171	−0.072
$Re^{inner}-\mu_2\text{-}S$	2.425	2.378	−0.047	2.452	2.392	−0.060
$Re^{inner}\text{-}\mu_2\text{-}S\text{-}Re^{inner}$	81.6	75.2	−6.4	84.30	76.94	−7.36

[a] Difference between values for anions with $n=8$ and $n=6$.

ion, which was isolated as a diamagnetic potassium or cesium salt—$K_6[Re_{12}CS_{17}(CN)_6]\cdot 20\,H_2O$ (**2**) or $Cs_6[Re_{12}CS_{17}(CN)_6]$ (**3**); single crystals of **2** and **3** were obtained by recrystallization of **1** from aqueous solutions.

Crystal structures of **2** and **3** contain the $[Re_{12}CS_{17}(CN)_6]^{6-}$ cluster unit (Figure 1b). The removal of two electrons from the $[Re_{12}CS_{17}(CN)_6]^{8-}$ ion leads to remarkable changes in the interatomic distances of the cluster, and at the same time, the interatomic distances in the trigonal prism, $\{Re_6C\}$, are most sensitive to these redox transformations. For example, in the $[Re_{12}CS_{17}(CN)_6]^{8-}$ ion, the Re···Re distances are 3.168 Å while in the oxidized complex, $[Re_{12}CS_{17}(CN)_6]^{6-}$, they are shortened to 2.902 Å. The mean bond lengths in these anions are presented in Table 1. These changes in interatomic distances are in a good agreement with DFT calculations for $[Re_{12}CS_{17}(CN)_6]^{8-}$ and $[Re_{12}CS_{17}(CN)_6]^{6-}$ ions with idealized D_{3h} symmetry.

The most surprising feature in these compounds is the presence of a carbon atom inside the cluster unit of the product. Its origin may be explained by the partial decomposition of KCN. If that is the case, a nitrogen atom might also be found in the cluster unit. However, X-ray diffraction studies did not identify the μ_6 interstitial atom. Therefore we studied by NMR spectroscopy solids enriched with ^{13}C and ^{15}N isotopes. Several samples of **2** were synthesized from $K^{13}CN$ and $KC^{15}N$ starting materials. The ^{13}C NMR spectrum of **2** (Figure 2) displays two signals at $\delta = 127$ and 435 ppm with relative intensities close to 6:1. The signal at $\delta = 127$ ppm corresponds to coordinated CN ligands whereas the signal at $\delta = 435$ ppm may be attributed to the interstitial carbon atom.[15]

The potassium salt of **2** readily dissolves in water and methanol, which allowed us to study its properties by solution-chemistry methods. The ESI mass spectrum (positive mode) of a solution of **2** in a mixture of water and acetonitrile is shown in Figure 3. The most intense peak corresponds to the dicationic $\{K_8Re_{12}CS_{17}(CN)_6\}^{2+}$ ($m/z = 1630.35$, 100%).

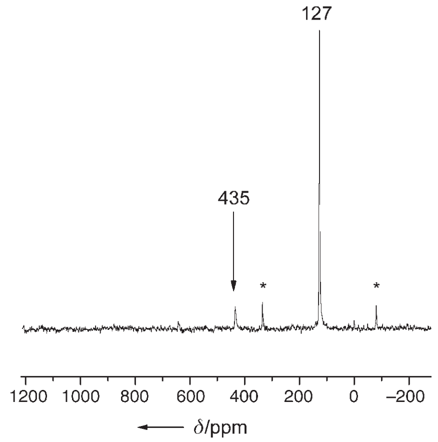


Figure 2. ^{13}C MAS NMR spectrum of **2.** Satellite signals are marked by asterisks.

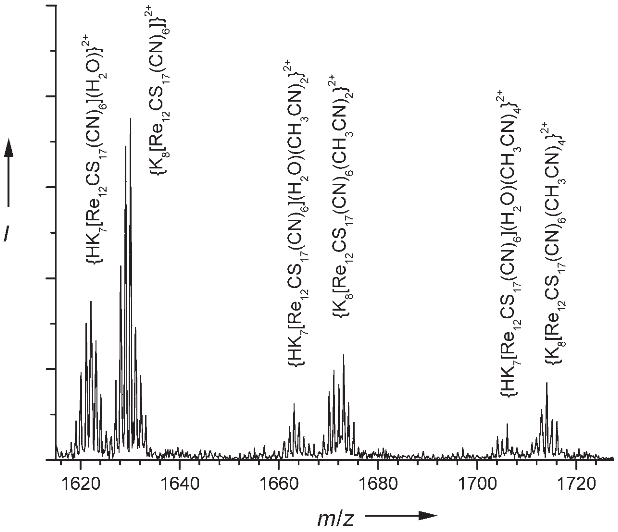


Figure 3. ESI mass spectrum of **2** in a H_2O/CH_3CN solution.

The spectrum contains also two sets of less intense peaks: one set can be attributed to adducts with acetonitrile, $\{K_8Re_{12}CS_{17}(CN)_6(CH_3CN)_n\}^{2+}$, $n = 2$ ($m/z = 1671.38$, 35%), $n = 4$ ($m/z = 1712.40$, 24%), $n = 6$ ($m/z = 1753.40$, 17%); the other set belongs to a protonated species, $\{(H_3O)K_7Re_{12}CS_{17}(CN)_6(CH_3CN)_n\}^{2+}$.

Cyclic voltammograms for aqueous solutions of **2** show two quasi-reversible waves: the $[Re_{12}CS_{17}(CN)_6]^{6-}$ ion exhibits its one reduction wave with the $[Re_{12}CS_{17}(CN)_6]^{6-/8-}$ couple centered at $E_{1/2} = -0.56$ V ($\Delta E = 200$ mV). The negative value of this potential is consistent with the fact that $K_8[Re_{12}CS_{17}(CN)_6]$ is not stable in aqueous solution but rapidly converts into the $[Re_{12}CS_{17}(CN)_6]^{6-}$ ion. The voltammogram for a solution of $[Re_{12}CS_{17}(CN)_6]^{6-}$ has one oxidation wave at $E_{1/2} = 0.70$ V ($\Delta E = 100$ mV). This wave corresponds to further oxidation of the $[Re_{12}CS_{17}(CN)_6]^{6-}$ ion, which was confirmed by chemical oxidation with bromine. Isolation and characterization of this oxidized anion is in progress.

Density functional theory (DFT) calculations[16] performed on the complexes $[Re_{12}CS_{17}(CN)_6]^{6-}$ and $[Re_{12}CS_{17}(CN)_6]^{8-}$ gave bond energies of −309.2 and −285.1 eV, respectively. For the $[Re_{12}CS_{17}(CN)_6]^{6-}$ complex, the $13a_2'$ highest occupied molecular orbital (HOMO) consists predominantly of S and 3p orbitals ($\approx 80\,\%$) with a small contribution from the Re 5d orbitals. There is no contribution from the μ_6-C states (Figure 4). The HOMO orbital of $[Re_{12}CS_{17}(CN)_6]^{8-}$ ($31a_2''$) consists of mainly Re 5d orbitals, the μ_6-C $2p_z$ orbital, and μ_2-S $3p_z$ orbitals. In prismatic $\{Re_6C\}$, short Re−Re and Re−(μ_6-C) contacts have bonding character while long Re···Re contacts along edges of the prism are strongly antibonding. Thus the removal of two electrons from the HOMO of complex **1** results in significant changes in the interatomic distances of cluster anions, mainly within the $\{Re_6C\}$ prism (Table 1). Removal of electrons elongates the Re^{inner}−Re^{inner} bond and contracts the long prismatic Re···Re contacts and the Re−(μ_6-C) bond due to the strong antibonding nature of Re···Re interaction. The calculated HOMO–LUMO gap is 1.08 eV for the $[Re_{12}CS_{17}(CN)_6]^{6-}$ ion and 1.44 eV for the $[Re_{12}CS_{17}(CN)_6]^{8-}$ ion. One interesting feature of the cluster is the position of $31a_2''$ orbital, which strongly depends on the charge of anion (Figure 4) and correlates with the length of the Re···Re interactions.

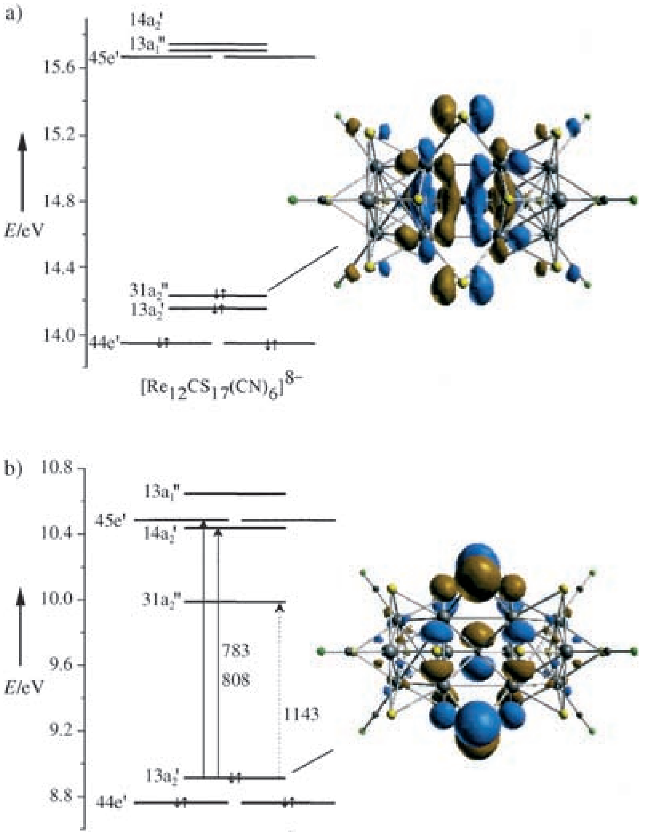


Figure 4. Calculated energy level diagrams and HOMO orbitals: a) $[Re_{12}CS_{17}(CN)_6]^{8-}$: The $31a_2''$ MO is shown perpendicular to the C_3 axis. Calculated charges: Re^{inner} (+0.083), Re^{outer} (+0.054), μ_6-C (−0.209). b) $[Re_{12}CS_{17}(CN)_6]^{6-}$: The $13a_2'$ MO is shown perpendicular to the C_3 axis. Arrows represent the forbidden (dotted) and allowed (solid) electronic transitions. Calculated charges: Re^{inner} (+0.090), Re^{outer} (+0.049), μ_6-C (−0.212).

The absorption bands in the visible region of the electronic spectrum of $[Re_{12}CS_{17}(CN)_6]^{6-}$ are in good agreement with the calculated electronic structure. According to symmetry rules for D_{3h} symmetry, the electron–dipole transitions from occupied $13a_2'$ to the next unoccupied $14a_2'$ and $45e'$ levels are allowed. Energies of calculated transitions (Figure 4) are close to the observed absorption band at 740 nm; very weak absorption at 1150 nm may be attributed to the forbidden $13a_2' \rightarrow 31a_2''$ transition.

A simple valence electron count shows that in the $[Re_{12}CS_{17}(CN)_6]^{8-}$ ion the rhenium atoms have a charge of +3.[17] Accordingly, the $[Re_{12}CS_{17}(CN)_6]^{6-}$ ion contains slightly oxidized rhenium atoms ($Re^{3.17+}$), which correlate with charges of rhenium atoms calculated by DFT.

Vibrational spectra of the complexes display CN valence stretch vibrations and group vibrations associated with the $\{Re_{12}CS_{17}\}$ cluster core. The bands at 403–406 cm^{-1} may be attributed to ReS stretching. The decrease of anion charge leads to increase of CN stretching vibrations (from $\tilde{\nu} = 2114$ for **1** to 2120 cm^{-1} for **3**). This change is less than that for the $[Re_6S_8(CN)_6]^{4-/3-}$ octahedral ions for which the difference is about 18 cm^{-1} (ν(CN): $\tilde{\nu} = 2119$ cm^{-1} for $[Re_6S_8(CN)_6]^{4-}$ with 24 electrons per $\{Re_6\}$ cluster and 2137 cm^{-1} for $[Re_6S_8(CN)_6]^{3-}$ with 23 electrons per $\{Re_6\}$ cluster).[4,7b] The group of lines in the range 640 to 950 cm^{-1} may be assigned to "breathing" vibrations of the $\{Re_{12}C\}$ cluster core.

Several dodecanuclear cluster chalcogenide complexes of Co, Mo, W, and Re were described earlier.[18–22] However, the bonding in all of these clusters is different from that in the clusters described above: two octahedral $\{M_6Q_8\}$ units are bridged by a $\{M_2Q_2\}$ rhomblike Chevrel phase. The formation of atom-centered trigonal prisms has been found in some related anions with interstitial atoms—$[W_6(\mu_6\text{-}Q)Cl_{18}]^{n-}$ (Q = C, $n = 0$–3; Q = N, $n = 1$–3),[23] $[Nb_6(\mu_6\text{-}S)Br_{17}]^{3-}$ [24]—and in polymeric chalcohalides of niobium $]Nb_6(\mu_6\text{-}S)I_9]_\infty$[25] and molybdenum $[Mo_6(\mu_6\text{-}Se)I_6Se]_\infty$.[26] There are many other clusters, for example carbonyl compounds, with interstitial atoms around which atom-centered trigonal prisms are formed.

In summary, we have synthesized novel cluster complexes with a unique structure that may represent a new family of $\{Re_{12}\}$ clusters. The presence of terminal cyano ligands favors the use of these anions as building blocks for the formation of cyano-bridged polymeric materials such as those of the $[Re_6Q_8(CN)_6]^{4-}$ family.[7] Ions larger than $[Re_6S_8(CN)_6]^{4-}$, such as $[Re_{12}CS_{17}(CN)_6]^{n-}$ ions, may give polymers with larger voids and high porosity.

Experimental Section

ReS_2 was prepared from Re and S in an evacuated quartz tube at 650 °C. Commercially available reagent-grade KCN was used. UV/Vis spectra were recorded on Shimatzu 3101PS spectrometer. IR spectra in KBr pellets were recorded on a Bruker Scimifar FTS 2000 spectrometer in the range 4000–375 cm^{-1}. Electrospray mass-spectrometric measurements were performed in the positive-ion mode on a Q-Tof Ultima Global mass spectrometer.

1: ReS_2 (1 g, 0.004 mol) and KCN (2 g, 0.03 mol) were heated in an evacuated quartz tube at 750 °C for 48 h. After the reaction mixture had cooled, single crystals suitable for X-ray analysis were selected. The product was washed with dry methanol to remove excess KCN. A suspension of unconverted ReS_2 was removed by decantation with methanol. Yield: 0.65 g (60 %). IR (KBr): $\tilde{\nu} = 383$ (w), 403, 417 (sh), 619 (w), 641, 720 (w), 755 (w), 912 (w), 2114 cm^{-1}.

2: As for **1**, ReS_2 (1 g, 0.004 mol) and KCN (2 g, 0.03 mol) were heated in an evacuated quartz tube at 750 °C for 48 h. The reaction mixture was then dissolved in water (50 ml) and filtered. The filtrate was heated under reduced pressure until the volume was about 5 mL and the resulting solution was allowed to cool. The hexagonal plate crystals that formed were isolated by filtration and dried in air. Yield: 0.76 g (80 %). UV/Vis: $\lambda(\varepsilon) = 330$ (9100), 360 (6500), 445 (2240 sh), 505 (1400), 605 (310 sh), 735 (175), 1150 nm ($\approx 10\ L\,mol^{-1}\,cm^{-1}$). IR (KBr): $\tilde{\nu} = 406$, 639, 719 (w), 757 (w), 882, 2116 cm^{-1}.

3: Compound **3** was obtained by precipitation: CsCl (1 g, 0.006 mol) was added to an aqueous solution of **2**, obtained as above, to give **3** in quantitative yield. Single crystals were grown by diffusion of methanol into a dilute aqueous solution of **3**. IR (KBr): $\tilde{\nu} = 382$ (w), 405, 643, 721 (w), 764 (w), 939, 2120 cm^{-1}.

Received: June 2, 2005

Keywords: cluster compounds · cyanides · density functional calculations · electronic structure · rhenium

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[10] The reaction of ReS_2 with KCN has been studied in the temperature range from 650 to 800 °C by using different ReS_2/KCN ratios. We found that for mass ratios of ReS_2/KCN from 1:2 to 1:20 the main product of the reaction was $K_8[Re_{12}CS_{17}(CN)_6]$. To understand the conditions that yield $[Re_{12}CS_{17}(CN)_6]^{8-}$, $KCs_3[Re_6S_8(CN)_6]$ was used as the starting material. It was found that $[Re_6S_8(CN)_6]^{4-}$ transforms into $[Re_{12}CS_{17}(CN)_6]^{8-}$ if the temperature rises to between 700 and 800 °C. Furthermore, the reaction of $[Re_6S_8Br_2]$ with KCN at high temperature also gave the $[Re_{12}CS_{17}(CN)_6]^{8-}$ cluster , whereas below 650 °C $[Re_6S_8(CN)_6]^{4-}$ formed. These data indicate that $[Re_{12}CS_{17}(CN)_6]^{8-}$ cluster is thermodynamically stable within the 650 to 800 °C range.

[11] X-ray structural analyses: Bruker SMART CCD diffractometer with area detector, graphite monochromator, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), SHELX-97 program[27] for structure solution (direct methods) and refinement (full-matrix least-squares on F^2). **1**: $C_7K_8N_6Re_{12}S_{17}$ ($M_r = 3260.35$), crystal size $0.14 \times 0.13 \times 0.03$ mm, monoclinic, space group $P2_1/m$, $a = 9.1806(11)$, $b = 29.210(2)$, $c = 9.2006(8)$ Å, $\beta = 119.777(1)^\circ$, $V = 2141.5(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 5.056\ g\,cm^{-3}$, $\mu = 35.381\ mm^{-1}$, $2.55 < \theta < 28.21^\circ$, $T = 293(2)$ K, face-indexed absorption correction (transmission coefficient: 0.0831, 0.4598). Reflections: 13011 collected, 4890 unique ($R_{int} = 0.0512$), 3756 observed ($I > 2\sigma(I)$). There were 239 parameters refined with $R = 0.0619$ ($I > 2\sigma(I)$), $wR_2 = 0.1693$ (all data), GOF = 1.107, residual electron density: +4.889/−4.827 e Å^{-3}. **2**: $C_7H_{40}K_6N_6O_{20}Re_{12}S_{17}$ ($M_r = 3542.47$), crystal size $0.12 \times 0.12 \times 0.03$ mm, hexagonal, space group $P6_3/mmc$, $a = 10.8843(8)$, $c = 27.840(4)$ Å, $V = 2856.3(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 4.119\ g\,cm^{-3}$, $\mu = 26.427\ mm^{-1}$, $2.16 < \theta < 28.24^\circ$, $T = 293(2)$ K, face-indexed absorption correction (transmission coefficient: 0.1436, 0.5044). Reflections: 16972 collected, 1383 unique ($R_{int} = 0.0384$), 1236 observed ($I > 2\sigma(I)$), 82 parameters refined with $R = 0.0263$ ($I > 2\sigma(I)$), $wR_2 = 0.0589$ (all data), GOF = 1.107, residual electron density: +1.643/−2.408 e Å^{-3}. **3**: $C_7Cs_6N_6Re_{12}S_{17}$ ($M_r = 3746.34$), crystal size $0.09 \times 0.09 \times 0.01$ mm, hexagonal, space group $P\bar{6}2m$, $a = 9.7270(15)$, $c = 14.629(3)$ Å, $V = 1198.7(4)$ Å^3, $Z = 1$, $\rho_{calcd} = 5.190\ g\,cm^{-3}$, $\mu = 35.407\ mm^{-1}$, $2.42 < \theta < 28.18^\circ$, $T = 293(2)$ K, face-indexed absorption correction (transmission coefficient: 0.1428, 0.6760). Reflections: 7284 collected, 1105 unique ($R_{int} = 0.0672$), 913 observed ($I > 2\sigma(I)$), 59 parameters refined with $R = 0.0340$ ($I > 2\sigma(I)$), $wR_2 = 0.0915$ (all data), GOF = 1.046, residual electron density: +2.391/−1.234 e Å^{-3}. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-415476–415478.

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[15] To determine isotropic chemical shifts of carbons the ^{13}C magic-angle spinning (MAS) NMR measurements were made by using a BRUKER Bio-Spin Avance 400 MHz solid-state NMR spectrometer. The spinning rate was 20 kHz, the π/2 pulse duration was 5 s, the relaxation delay was 10 s. About 200 free induction decays were accumulated at room temperature. TMS was used as a reference. The ^{15}N NMR spectrum contained one sharp signal at 311 ppm (relative to NH_3), which corresponds to coordinated cyano ligands. No signal attributable to an interstitial nitrogen atom was found. The diamagnetic properties of

compounds **1**–**3** indicated the presence of an interstitial atom with an even number of electrons.

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[17] It is interesting to note that in rhenium cluster chemistry there are several types of cluster in which the rhenium atoms have a +III oxidation state; besides $[Re_{12}CS_{17}(CN)_6]^{8-}$, there are three well-known cluster complexes, namely, dinuclear $[Re_2X_8]^{2-}$ with quadruple Re–Re bond, trigonal $[Re_3X_{12}]^{3-}$ with double Re–Re bonds, and octahedral $[Re_6Q_8X_6]^{4-}$ with single Re–Re bonds (X = halide ions).

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