Cluster Compounds

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

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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.

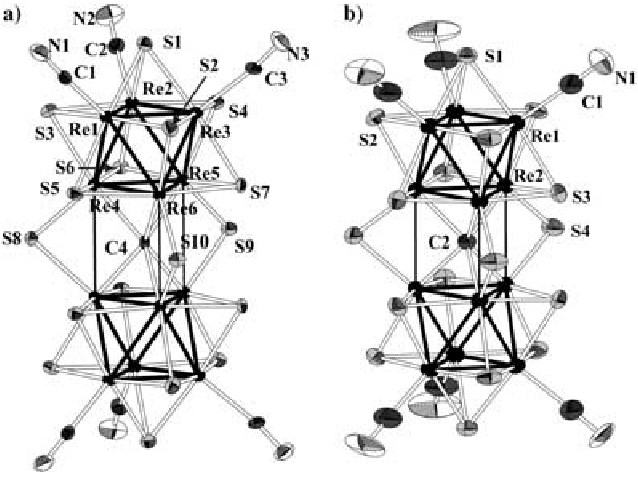

Figure 1. a) Structure of the $[Re_6(\mu_6\text{-}C)S_{17}(CN)_6]^{8-}$ ion in **1**. b) Structure of $[Re_6(\mu_6\text{-}C)S_{17}(CN)_6]^{6-}$ anion in **3**. For average bond lengths and angles, see Table 1. (Displacement ellipsoids are drawn at the 50% probability level.)

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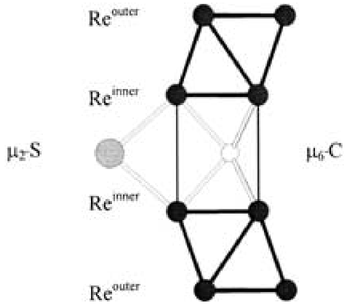
Table 1: Experimental and calculated interatomic distances [Å] and angles [°] in the clusters $[Re_{12}(\mu_6\text{-}C)S_{17}(CN)_6]^{n-}$.



	Experimental			Calculated		
	$n=8$	$n=6$	Δ[a]	$n=8$	$n=6$	Δ[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}–μ$_6$-C	2.179	2.126	−0.053	2.243	2.171	−0.072
Re^{inner}–μ$_2$-S	2.425	2.378	−0.047	2.452	2.392	−0.060
Re^{inner}-μ$_2$-S-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$_6$C}, 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 %). 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, $\{(H_3O)K_7Re_{12}CS_{17}(CN)_6(CH_3CN)_n\}^{2+}$.

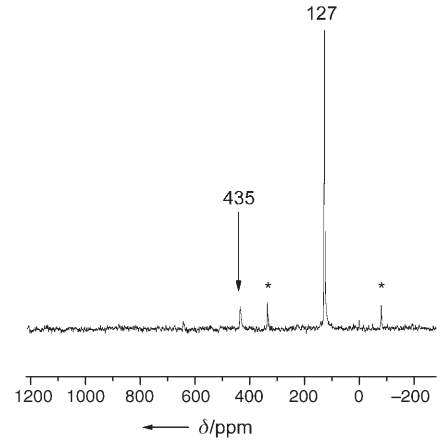


Figure 2. ^{13}C MAS NMR spectrum of **2**. Satellite signals are marked by asterisks.

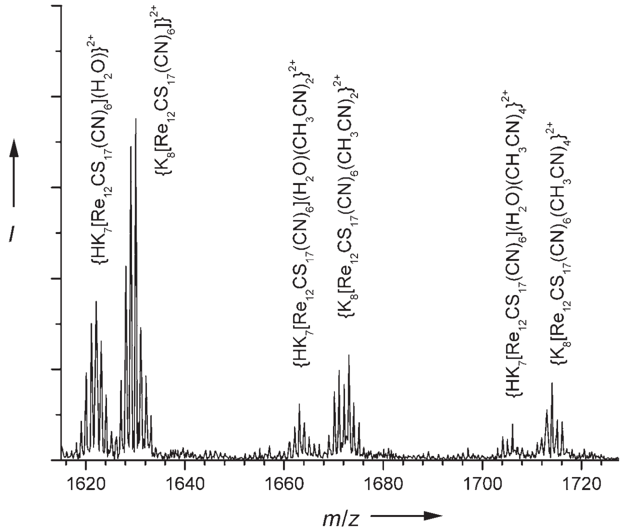


Figure 3. ESI mass spectrum of **2** in a H_2O/CH_3CN solution.

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.

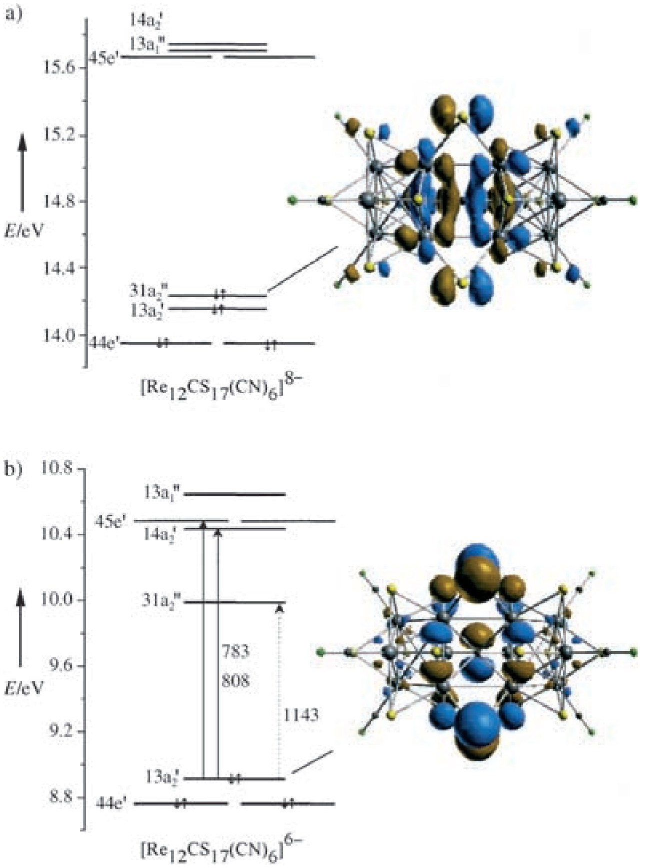


Figure 4. Calculated energy level diagrams and HOMO orbitals: a) $[Re_{12}CS_{17}(CN)_6]^{8-}$: The $31a_2''$ MO is shown perpendicular to the C_3 axis. Calculated charges: Re^{inner} (+0.083), Re^{outer} (+0.054), μ_6-C (−0.209). b) $[Re_{12}CS_{17}(CN)_6]^{6-}$: The $13a_2'$ MO is shown perpendicular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

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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, $\beta = 119.777(1)°$, $V = 2141.5(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 5.056\ g\,cm^{-3}$, $\mu = 35.381\ mm^{-1}$, $2.55 < \theta < 28.21°$, $T = 293(2)$ K, face-indexed absorption correction (transmission coefficient: 0.0831, 0.4598). Reflections: 13 011 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, $Z = 2$, $\rho_{calcd} = 4.119\ g\,cm^{-3}$, $\mu = 26.427\ mm^{-1}$, $2.16 < \theta < 28.24°$, $T = 293(2)$ K, face-indexed absorption correction (transmission coefficient: 0.1436, 0.5044). Reflections: 16 972 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, $Z = 1$, $\rho_{calcd} = 5.190\ g\,cm^{-3}$, $\mu = 35.407\ mm^{-1}$, $2.42 < \theta < 28.18°$, $T = 293(2)$ 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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