

## New Rhenium Octahedral Cluster Sulfido-cyanide Chain Polymer: The Synthesis and Crystal Structure of $\text{Cs}_4[\{\text{Re}_6\text{S}_8\}(\text{CN})_4\text{S}_{2/2}]$

N. G. Naumov,\* S.-J. Kim,†\* A. V. Virovets, Y. V. Mironov, and V. E. Fedorov

Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3, Acad. Lavrentiev pr., Novosibirsk, 630090, Russia. \*E-mail: naumov@che.nsk.su

†Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea. \*E-mail: sjkim@ewha.ac.kr

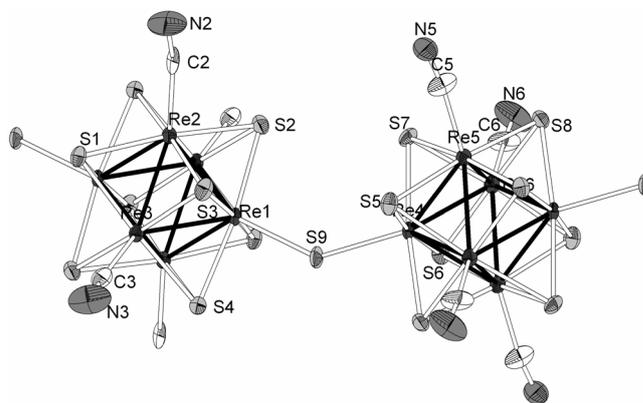
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The chemistry of rhenium octahedral cluster chalcogenides demonstrates a rich diversity of types of chain-like, layered and framework structures as well as bridging ligands between clusters. The clusters can be connected via  $\mu_3$  inner ligands of cluster units,<sup>1</sup> apical halogenide ligands,<sup>2</sup> complex telluride  $\text{Te}_6$  or  $\text{Te}_7$ <sup>3,4</sup> and halogen-telluride  $\text{Te}_8\text{Q}_{18}^{2-}$  groups,  $\text{Q}=\text{Cl}$ ,  $\text{Br}^3$ , chalcogenides, dichalcogenide and trichalcogenide ligands.<sup>5-7</sup> The latter family described by Prof. W. Bronger (so called “Bronger phases”) seems to be most numerous and complete family of polymeric rhenium octahedral cluster chalcogenides with various bridges and connectivity between clusters. For example,  $\text{Li}_4\text{Re}_6\text{S}_{11}$ <sup>7</sup> contains  $\text{Re}_6\text{S}_8$  cluster units connected by six bridging  $m_2$  sulfido ligands that gave  $\text{Li}_4[\{\text{Re}_6\text{S}_8^i\}(\text{S})^{a-a}_{6/2}]_{\infty}$  framework according to Schafer notation.<sup>8</sup>

Recently it was shown that reaction of  $\text{ReS}_2$  with KCN at elevated temperature leads to formation an unique layered compound  $\text{K}_4\text{Re}_6\text{S}_{10}(\text{CN})_2$ .<sup>9</sup> In this polymer the  $\text{Re}_6\text{S}_8$  units are linked into two-dimensional grids by sharing four apical sulphide ligands. Additionally two “trans” rhenium atoms in cluster core are coordinated by terminal cyano-groups. Thus, crystallographic formula of this compound may be written according to Schafer notation as  $\text{K}_4[\{\text{Re}_6\text{S}_8^i\}(\text{CN})_2(\text{S})^{a-a}_{4/2}]_{\infty}$ . From formal point of view this compound could be presented as cleavage of two  $\text{Re}-\mu_2\text{S}-\text{Re}$  bridges in  $[\{\text{Re}_6\text{S}_8^i\}(\text{S})^{a-a}_{6/2}]$  and substitution of them by terminal cyano-ligands. In present work we report the synthesis and crystal structure of new chain polymer  $\text{Cs}_4[\{\text{Re}_6\text{S}_8^i\}(\text{CN})_4(\text{S})^{a-a}_{2/2}]_{\infty}$  which is the next member of a series  $\text{M}_4[\{\text{Re}_6\text{S}_8^i\}(\text{CN})_{2x}(\text{S})^{a-a}_{(6-2x)/2}]$ , where M is alkali metal. This compound was obtained with high yield by high temperature reaction of  $\text{ReS}_2$  with KCN in presence of CsCl excess.<sup>10</sup>

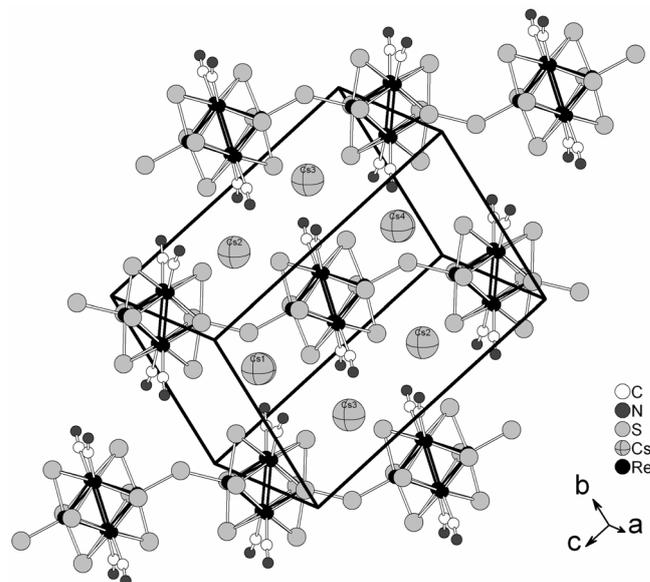
X-ray structural analysis<sup>11,12</sup> revealed that compound  $\text{Cs}_4[\text{Re}_6\text{S}_8(\text{CN})_4\text{S}_{2/2}]$  is built from octahedral rhenium cluster units  $\{\text{Re}_6\text{S}_8\}$ . All atoms in the unit cell are lying in general Wyckoff  $2i$  positions. Six crystallographically independent rhenium atoms and eight sulfur atoms form two centrosymmetric cluster units  $\text{Re}_6(\mu_3-\text{S})_8$  (Figure 1). Interatomic distances  $\text{Re}-\text{Re}$  are: mean: 2.606[9] Å, min-max: 2.5924(11) ÷ 2.6201(11) Å that are comparable within the  $\text{Re}-\text{Re}$  single bonds usually observed in octahedral rhenium clusters with  $\text{Re}_6(\mu_3-\text{S})_8$  cluster cores, e.g. in  $\text{Li}_4\text{Re}_6\text{S}_{11}$ ,<sup>7</sup> in  $\text{K}_4[\text{Re}_6\text{S}_{10}(\text{CN})_2]$ <sup>9</sup>



**Figure 1.** Two independent  $\text{Re}_6\text{S}_8$  cluster units bridged by  $\mu_2\text{-S}$  ligand in the structure of  $\text{Cs}_4[\text{Re}_6\text{S}_8(\text{CN})_4\text{S}_{2/2}]$ .

and in  $\text{Cs}_3\text{K}[\text{Re}_6\text{S}_8(\text{CN})_6]$ .<sup>13</sup>  $\text{Re}-\mu_3-\text{S}$  vary from 2.384(6) to 2.422(6), mean 2.406(10) Å. These values are also typical for  $\text{Re}_6(\mu_3-\text{S})_8$  cluster unit.

These cluster units are linked via two *trans*- $\mu_2\text{-S}$  ligands to form the infinite chains running along  $a$  axis (Figure 2). The



**Figure 2.** Crystal packing in the structure of  $\text{Cs}_4[\text{Re}_6\text{S}_8(\text{CN})_4\text{S}_{2/2}]$ .

bridge is bent with Re-( $\mu_2$ -S)-Re angle 137.6(3)° and Re- $\mu_2$ -S distances are equal to 2.400(5) and 2.402(5) Å. The mean Re-C (2.16 Å) and C-N (1.08 Å) bond distances have their typical values. These chains are packed in *bc* plane in pseudo-hexagonal manner with Cs<sup>+</sup> cations allocated between them. Cesium atoms are located in general positions which are fully occupied. Each cluster unit is surrounded by 12 Cs atoms forming slightly distorted cubo-octahedron. The cesium cations make contacts with both  $\mu_3$ - and  $\mu_2$ -S ligands and with C and N atoms of CN ligands with distances Cs-S of 3.47–3.82 Å, Cs-C of 3.41–3.58 Å, Cs-N of 3.10–3.85 Å. No Cs/K mixing was found according to structural analysis and EDAX.

Comparison of 1D structure in the title compound with 2D in K<sub>4</sub>[Re<sub>6</sub>S<sub>10</sub>(CN)<sub>2</sub>] and 3D in Li<sub>4</sub>[Re<sub>6</sub>S<sub>11</sub>] demonstrated notable elongation of Re- $\mu_2$ -S bonds from ~2.40 to ~2.49 Å with increase of number Re- $\mu_2$ -S bridges. In the same time the Re- $\mu_2$ -S-Re fragment seems to be flexible, angle on S varying from 118.8(2) in Cs<sub>4</sub>[Re<sub>6</sub>S<sub>9</sub>(CN)<sub>4</sub>] to 152.8(5) in Li<sub>4</sub>[Re<sub>6</sub>S<sub>11</sub>].

We have found that in the reaction of ReS<sub>2</sub> with molten KCN/CsCl mixture an increase in temperature up to 750–800 °C suppresses a formation of the title compound and favors formation of a compound with composition Cs<sub>8</sub>[Re<sub>12</sub>CS<sub>17</sub>(CN)<sub>6</sub>]. The last compound is the cesium analog of K<sub>8</sub>[Re<sub>12</sub>CS<sub>17</sub>(CN)<sub>6</sub>] salt having twelve nuclear rhenium cluster with interstitial  $\mu_6$  carbon atom. The dissolution of this compound in hot water followed partial oxidation of cluster anion resulted in formation of Cs<sub>6</sub>[Re<sub>12</sub>CS<sub>17</sub>(CN)<sub>6</sub>] reported very recently.<sup>14</sup> The identity was confirmed by comparison of UV-Vis spectra and X-ray powder diffraction patterns.<sup>15</sup>

It is interesting to note that chain-like compound Cs<sub>4</sub>[Re<sub>6</sub>S<sub>8</sub>(CN)<sub>4</sub>S<sub>2/2</sub>] obtained can be dissolved by heating in aqueous solution of KCN, and at the same time monomeric [Re<sub>6</sub>S<sub>8</sub>(CN)<sub>6</sub>]<sup>4-</sup> anion is formed.

Thus, high temperature chemistry of rhenium chalcogenides still demonstrates fascinating variety of new thermodynamically stable compounds at variation of reaction conditions (temperature, stoichiometry, presence of additional cations, etc.).<sup>6,16</sup> The title compound completes a homologous series of octahedral cluster anions [Re<sub>6</sub>S<sub>8</sub>S<sub>6/2</sub>]<sup>4-</sup>, [Re<sub>6</sub>S<sub>8</sub>(CN)<sub>2</sub>S<sub>4/2</sub>]<sup>4-</sup>, [Re<sub>6</sub>S<sub>8</sub>(CN)<sub>4</sub>S<sub>2/2</sub>]<sup>4-</sup> and [Re<sub>6</sub>S<sub>8</sub>(CN)<sub>6</sub>]<sup>4-</sup> which could be described as consequent cleavage of Re- $\mu_2$ S-Re bridges and substitution of bridged sulphur atoms by terminal cyanoligands.

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- The mixture of ReS<sub>2</sub> (0.200 g, 0.799 mmol), KCN (0.200 g, 3.07 mmol) and CsCl (0.300 g, 1.78 mmol) were heated in evacuated quartz tube at 650 °C for 48 hrs. After cooling down the dark red single crystals for X-ray analysis were selected from reaction mixture. The reaction product was washed with water and dried on air. Yield: 0.255 g (93.8%). According to XRD pattern, polycrystalline sample did not contain any additional peaks. IR (KBr), cm<sup>-1</sup>: 399, 406, 414, 2117. Energy dispersive analysis showed absence of noticeable amounts of K and Cl in crystals and adequate agreement of Cs:Re:S ratio to structural data.
- Crystal data for Cs<sub>4</sub>[Re<sub>6</sub>S<sub>8</sub>(CN)<sub>4</sub>S<sub>2/2</sub>]: C<sub>4</sub>Cs<sub>4</sub>N<sub>4</sub>Re<sub>6</sub>S<sub>9</sub>, M = 2041.46, red plate, 0.064 × 0.047 × 0.022 mm<sup>3</sup>, triclinic, space group P-1 (No. 2), a = 9.9153(6), b = 10.0002(5), c = 15.1053(10) Å, α = 102.347(3), β = 107.685(3), γ = 101.744(2)°, V = 1334.71(14) Å<sup>3</sup>, Z = 2, D<sub>calc</sub> = 5.080 g/cm<sup>3</sup>, Bruker X8Apex CCD detector, MoKα radiation, λ = 0.71073 Å, T = 293(2)K, 2θ<sub>max</sub> = 55.0°, 13209 reflections collected, 5953 unique (Rint = 0.0420). The structure was solved and refined using the programs SHELXS-97 and SHELXL-97<sup>12</sup> respectively. Final GooF = 1.164, R1 = 0.0544, wR2 = 0.1581, R indices based on 4766 reflections with I > 2σ(I) (refinement on F<sup>2</sup>), 244 parameters, 0 restraints. Lp and absorption corrections applied, μ = 33.181 mm<sup>-1</sup>.
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- Experimental data for Cs<sub>6</sub>[Re<sub>12</sub>CS<sub>17</sub>(CN)<sub>6</sub>]: EDAX: Cs:Re:S = 5.9 : 12 : 16.2; XRD: hexagonal, a = 9.73(1), c = 14.63(5) Å, UV-Vis (aqueous solution), mn: 330 (s), 360 (s), 445 (sh), 505 (m), 605 (sh), 735 (w).
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