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New Method for the Synthesis of Octahedral Rhenium Chalcocyanide Cluster Complexes $[\{Re_6(\mu_3\text{-}Q)_8\}(CN)_6]^{4-}$ (Q = S, Se, Te)

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Abstract—A new method is proposed for the synthesis of the octahedral rhenium chalcocyanide cluster complexes $[\{Re_6(\mu_3\text{-}Q)_8\}(CN)_6]^{4-}$ (Q = S, Se, Te) using rhenium(IV) oxide as the starting compound. Among the synthesized compounds, the anhydrous cluster salt $K_4[\{Re_6Se_8\}(CN)_6]$ is characterized by X-ray diffraction analysis for the first time. The crystals are orthorhombic, space group *Pbcn*; a = 13.1386(13), b = 11.4941(8), c = 17.2990(16) Å, Z = 4, V = 2612.4(4) Å^3 (CIF file ICSD no. 434320). The crystal structure of $K_4[\{Re_6Se_8\}(CN)_6]$ represents a framework type packing based on the K^+ cations coordinated by the cyanide groups of the cluster anions $[\{Re_6Se_8\}(CN)_6]^{4-}$.

Keywords: rhenium, chalcogens, octahedral cluster complex, crystal structure

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INTRODUCTION

The compounds containing the octahedral cluster anion $[\{Re_6(\mu_3\text{-}Q)_8\}CN_6]^{4-}$ (Q = S, Se, Te) are characterized by a broad range of chemical and physical properties, such as long-lived luminescence [1, 2] in both the solid state and solution, the possibility of redox transformations [3, 4], the capability of forming coordination polymers [5–7], and X-ray contrast [8–10] due to which they are objects of rapt attention of researchers. In particular, the $Na_4[\{Re_6Te_8\}(CN)_6]$ complex was shown [10] to be a promising compound for a possible use as an X-ray contrast agent.

The rhenium chalcocyanide cluster complexes are presently prepared using known procedures. For example, the syntheses of the sulfide and selenide complexes occur in two stages, where octahedral chalcohalide $Re_6Q_8X_2$ is synthesized at 850°C at the first stage [11]. At the second stage, $Re_6Q_8X_2$ reacts with KCN at 600–650°C [12, 13]. Both stages are conducted in evacuated quartz ampules, and the whole synthesis takes 8.5 days. The telluride complex is also synthesized in two stages: the first stage is the synthesis of Re_6Te_{15} at 900°C [14], and the second stage is the reaction of Re_6Te_{15} with KCN at 700°C [15]. On the whole, the synthesis takes 17 days. Thus, the search for simpler and more convenient synthetic routes is an urgent task due to interesting and practically important properties of these compounds.

In this work, rhenium(IV) oxide was used for the first time as the initial compound in the synthesis of the octahedral rhenium chalcocyanide cluster complexes $[\{Re_6(\mu_3\text{-}Q)_8\}(CN)_6]^{4-}$ (Q = S, Se, Te). This method enables one to obtain these complexes at 600°C in one stage with a good yield within 48 h only, which is a doubtless advantage over the known methods. Among the synthesized compounds, the anhydrous cluster salt $K_4[\{Re_6Se_8\}(CN)_6]$ (**I**) was characterized by X-ray diffraction analysis for the first time.

EXPERIMENTAL

Rhenium oxide ReO_2 was obtained by the decomposition of NH_4ReO_4 at 400°C [16]. Other reagents were commercially available.

The ratio of heavy metals was determined by energy dispersive analysis (EDS) using a Hitachi TM3000 TableTop SEM bench scanning microscope and the Bruker QUANTAX 70 EDS equipment. Powder diffraction patterns were detected in a 2θ range of 5°–60° on a Philips PW 1700 automated diffractometer (CuK_α radiation, λ = 1.54056 Å, graphite monochromator, internal silicon standard). IR spectra were recorded in a range of 4000–400 cm^{-1} for samples as KBr pellets on a Bruker Vertex 80 spectrometer.

Synthesis of $K_4[\{Re_6S_8\}(CN)_6]$ (I). A mixture of ReO_2 (0.150 g, 0.69 mmol), KCN (0.239 g, 3.68 mmol), and elemental S (0.029 g, 0.92 mmol) was thoroughly triturated in a mortar and sealed in an evacuated quartz ampule. The ampule was heated to 600°C within 5 h, kept at this temperature for 40 h, and cooled with a rate

Table 1. Experimental X-ray diffraction details and selected crystallographic data for compound **II**

Parameter	Value
Empirical formula	$C_6N_6Se_8K_4Re_6$
FW	2061.40
Crystal system	Orthorhombic
Space group	*Pbcn*
a, Å	13.1386(13)
b, Å	11.4941(8)
c, Å	17.2990(16)
V, Å^3	2612.4(4)
Z	4
ρ_{calcd}, g/cm^3	5.241
μ, mm^{-1}	39.483
F(000)	3504
Crystal sizes, mm	0.15 × 0.15 × 0.05
Ranges of indices *h*, *k*, *l*	$-17 \le h \le 12$, $-14 \le k \le 14$, $-22 \le l \le 18$
Measured reflections	15025
Independent reflections	2960
R_{int}	0.0890
Reflections with $I > 2\sigma(I)$	2377
R, $I > 2\sigma(I)$	$R_1 = 0.0397$, $wR_2 = 0.0776$
R, all reflections	$R_1 = 0.0553$, $wR_2 = 0.0822$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	3.041/–3.010

of 50°C/h. The reaction products were dissolved in water (50 mL), refluxed, and filtered. The solution was evaporated to 5 mL, and ethanol (50 mL) was added. A precipitate that formed was filtered off, washed with a $C_2H_5OH–H_2O$ (1 : 1) mixture, and dried in air. The yield of compound **I** was 0.155 g (80%).

EDS: K : Re : S = 3.9 : 6.0 : 8.3. IR (ν, cm^{-1}): 2107 ν(CN).

Synthesis of $K_4[\{Re_6Se_8\}(CN)_6]$ (II) was similar to that of compound **I** from ReO_2 (0.150 g, 0.69 mmol), KCN (0.239 g, 3.68 mmol), and elemental Se (0.073 g, 0.92 mmol). The yield of compound **II** was 0.158 g (65%).

EDS: K : Re : Se = 4.3 : 6.0 : 7.9. IR (ν, cm^{-1}): 2120 ν(CN).

Synthesis of $K_4[\{Re_6Te_8\}(CN)_6]$ (III) was similar to that of compound **I** from ReO_2 (0.150 g, 0.69 mmol), KCN (0.239 g, 3.68 mmol), and elemental Te (0.117 g, 0.92 mmol). The yield of compound **III** was 0.154 g (55%).

EDS: K : Re : Te = 4.2 : 6.0 : 8.1. IR (ν, cm^{-1}): 2085 ν(CN).

X-ray diffraction analysis. A single crystal of compound **II** was selected directly from the reaction mixture after the end of the synthesis. An X-ray diffraction experiment was carried out on a Bruker-Nonius X8 Apex automated diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). An absorption correction was applied semiempirically by intensities of equivalent reflections (SADABS) [17]. The structure was solved by a direct method and refined by full-matrix least squares for F^2 in the anisotropic approxi-

Table 2. Selected bond lengths in compound **II**

Bond	d, Å	
	range	average
Re–Re	2.6225(7)–2.6402(7)	2.634(7)
Re–Se	2.5013(13)–2.5383(12)	2.522(11)
Re–C	2.106(12)–2.132(11)	2.117(11)
C–N	1.143(15)–1.160(15)	1.151(7)

mation for non-hydrogen atoms (SHELXL) [18]. The figures were drawn using the DIAMOND program [19]. The X-ray diffraction experimental details and selected crystallographic data are presented in Table 1. Selected bond lengths are given in Table 2.

The coordinates of atoms and other parameters for the structure of compound **II** were deposited with the Fachinformationszentrum Karlsruhe Inorganic Crystal Structure Database (ICSD no. 434320; crysdata@fiz-karlsruhe.de).

RESULTS AND DISCUSSION

In this work, we proposed a new method for the synthesis of the rhenium cluster complexes containing $[\{Re_6Q_8\}(CN)_6]^{4-}$ anions. The method consists of the preparation of rhenium chalcocyanide cluster complexes by the reaction of rhenium(IV) oxide, potassium cyanide, and the corresponding chalcogen at 600°C. This temperature was determined experimentally as optimum for the synthesis. The temperature increase to 650°C results in the explosion of the ampule, whereas at a lower temperature the yield of the reaction product decreases considerably. The reaction time was varied in a range of 12–72 h, and its optimum value (from the viewpoint of the maximum yield) was determined as equal to 48 h.

To confirm the composition of the cluster anions in compounds **I–III**, the latter were transformed into the corresponding salts $Cs_2Co[\{Re_6S_8\}(CN)_6] \cdot 2H_2O$ [12], $K_4[\{Re_6Se_8\}(CN)_6] \cdot 3.5H_2O$ [13], and $Cs_4[\{Re_6Te_8\}(CN)_6] \cdot 2H_2O$ [15] with the known characteristics of the crystal structures. The powder diffraction patterns detected for the indicated complexes (Fig. 1) are well consistent with the theoretical patterns calculated from the structural data.

As indicated earlier, the major amount of compounds **I–III** was isolated by crystallization from aqueous solutions. However, in the case of compound **II**, it turned out possible to isolate a single crystal suitable for X-ray diffraction analysis directly from a mixture of products of the high-temperature ampule synthesis.

The structure of the cluster anion $[\{Re_6Se_8\}(CN)_6]^{4-}$ in compound **II** is similar to the structure of this anion in the known hydrated complex $K_4[\{Re_6Se_8\}(CN)_6] \cdot 3.5H_2O$ (**IV**) and in a series of other representatives of cyanocluster complexes of the $[\{Re_6Q_8\}(CN)_6]^{n-}$ type [12, 13, 15]. An octahedron of the rhenium atoms is coordinated by the selenium atoms (via the μ_3 mode) forming a cube around the octahedron. The terminal cyanide ligands form an external coordination octahedron. The main bond lengths in the cluster anion $[\{Re_6Se_8\}(CN)_6]^{4-}$ (Table 2) are typical of the cluster fragment $\{Re_6Se_8\}$ in other structures [13, 20, 21]. The packing of anions in the structure of compound **II** along the crystallographic axes *a* and *c* is shown in Fig. 2. The cationic moiety of the compound is presented by the potassium ions localized in three crystallographically nonequivalent positions with the coordination number 6. The coordination environment of the potassium cations consists of the nitrogen atoms of the CN groups and μ_3-Se atoms of the cluster fragment $\{Re_6Se_8\}$. The K–N and K–Se bonds have typical lengths of 2.704–3.303 and 3.365–3.8208 Å, respectively.

It seemed interesting to compare the crystallographic characteristics of complex **II** with the known published data for compound **IV** (space group $P\bar{1}$, $Z = 4$, $a = 13.582(4)$, $b = 16.279(5)$, $c = 16.701(4)$ Å, $\alpha = 115.05(2)°$, $\beta = 103.05(2)°$, $\gamma = 105.06(2)°$, $V = 2983(2)$ Å^3). The absence of water molecules in compound **II** results in the enhancement of symmetry, a denser packing of the anions in the crystal lattice, and, correspondingly, a smaller unit cell volume. The cell is compressed along the crystallographic axes *a* and *b* and elongates along the *c* axis.

To conclude, we proposed the new simple method for the synthesis of the rhenium cluster complexess containing the $[\{Re_6Q_8\}(CN)_6]^{4-}$ anions. This result is significant, because rhenium cluster complexes of the $Re_6Q_8L_6$ type (Q = S, Se; L are various inorganic and organic ligands) exhibit luminescence in a range of ~550–1000 nm with microsecond lifetimes (phosphorescence) and are interesting for the photodynamic therapy, a novel procedure in antitumor therapy. In

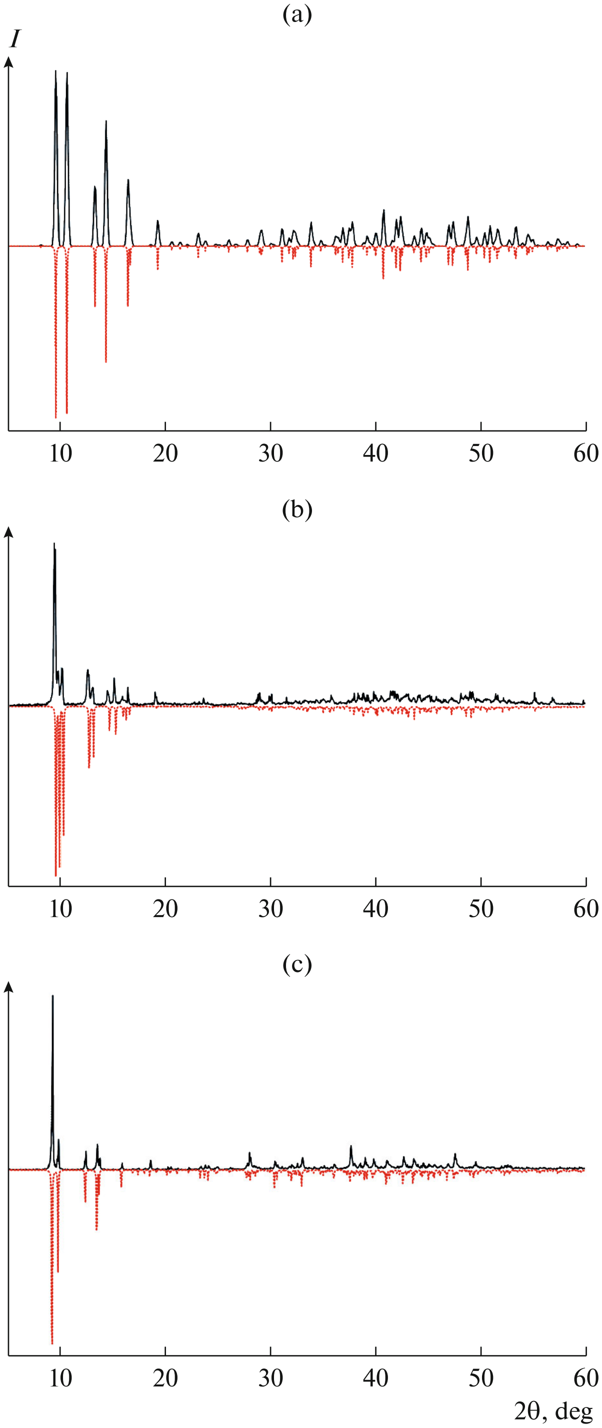

Fig. 1. Experimental powder X-ray diffraction patterns (solid line) of compounds (a) $Cs_2Co[\{Re_6S_8\}(CN)_6] \cdot 2H_2O$, (b) $K_4[\{Re_6Se_8\}(CN)_6] \cdot 3.5H_2O$, and (c) $Cs_4[\{Re_6Te_8\}(CN)_6] \cdot 2H_2O$ compared to the patterns calculated from the single crystal structures (dash).

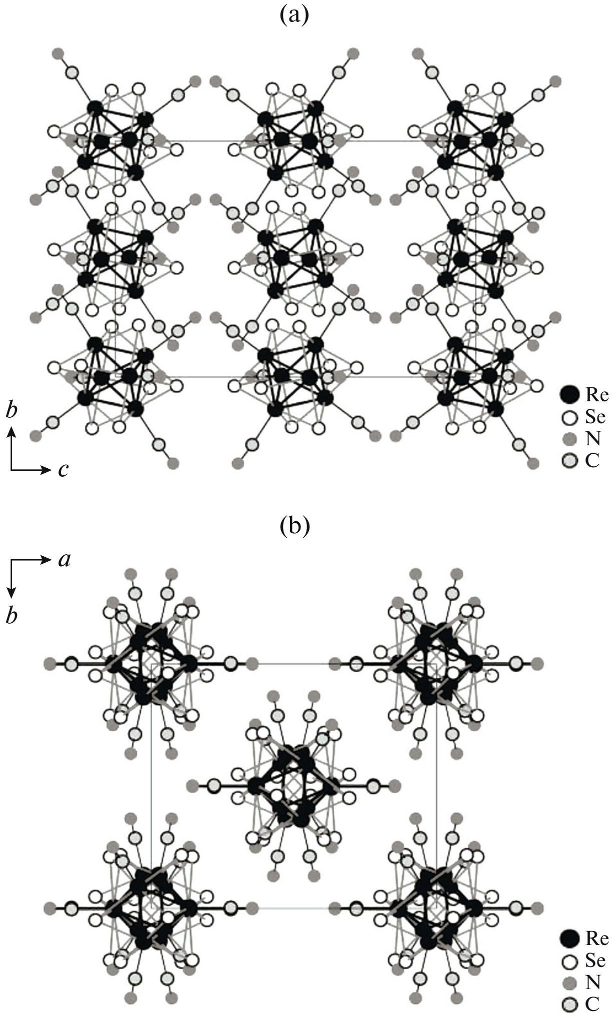

Fig. 2. Packing of anions $[\{Re_6Se_8\}(CN)_6]^{4-}$ in the structure of compound **II**: views along the crystallographic axes (a) *a* and (b) *c*.

addition, these complexes manifest high X-ray contrast due to a high local concentration of heavy atoms in a small volume (for example, the volume of the cluster core $\{Re_6Q_8\}$ is ~1 nm^3) due to which they are excellent candidates for the application in the areas associated with X-ray contrast.

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