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Hydrothermal Synthesis and Study of Compounds Based on Copper(I) Cyanide and Octahedral Rhenium Cyanohydroxo Cluster Complexes

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Abstract—Two new compounds, $Cs_2[Cu_2Re_6S_8(CN)_6]\cdot 3H_2O$ (**I**) and $(H_3O)_2[Cu\{Cu_2(\mu\text{-}CN)\}Re_6Se_8(CN)_6]\cdot 6.5H_2O$ (**II**), were synthesized under hydrothermal conditions from a mixture of CuCN and $Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$ or $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$, respectively. The reaction involves replacement of OH^- by CN^- and the formation of interpenetrating anionic framework through –CN–Cu–CN– bridges. The framework cavities accommodate counterions and water molecules. The obtained compounds were characterized by single crystal X-ray diffraction (CIF files CSD nos. 2048821 (**I**), 2048822 (**II**)), IR spectroscopy, and elemental analysis.

Keywords: hydrothermal synthesis, rhenium, chalcogens, octahedral cluster complex, copper, crystal structure

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INTRODUCTION

Cluster complexes with a $\{Re_6Q_8\}^{2+}$ core (Q = S, Se, Te) are most abundant among rhenium cluster compounds [1–4]. Recently, this series of compounds was supplemented with mixed-ligand cluster complexes $Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$ and $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$ [5, 6]. These compounds are of interest as they contain both relatively labile OH^- ligands, which can be replaced by organic or inorganic groups, and ambidentate CN^- ligands, which can form polymeric compounds of various dimensionality via –CN–M–CN– bridges, similar to rhenium hexacyanide cluster complexes with transition metals [7–11]. To date, ionic [5, 6, 12, 13], molecular [6, 14], and polymeric compounds [15] that contain mixed-ligand cluster anions and Ni(II) or Cu(II) cationic complexes with amines have been obtained. Attempts at the synthesis of compounds based on octahedral rhenium cyanohydroxo cluster complexes, CuCN, and 2,2'-bipyridine (Bipy), by analogy with hexacyanide complexes [16], resulted in the formation of one polymorph of the cyano-bridged copper(I) complex $[CuCN(Bipy)]_n$ [17]. Therefore, we made at attempt to synthesize new compounds under the same reaction conditions, but without Bipy. This resulted in the formation of two new coordination polymers, $Cs_2[Cu_2Re_6S_8(CN)_6]\cdot 3H_2O$ (**I**) and $(H_3O)_2[Cu\{Cu_2(\mu\text{-}CN)\}Re_6Se_8(CN)_6]\cdot 6.5H_2O$ (**II**).

EXPERIMENTAL

The starting cluster salts, $Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$ and $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$, were prepared by previously reported procedures [5, 6]; the other reagents were commercial chemicals.

Synthesis of I. A sealed glass tube filled with a mixture of $Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$ (100 mg, 0.051 mmol), CuCN (40 mg, 0.446 mmol), and distilled water (0.5 mL) was heated to 150°C, kept for 48 h, and cooled for 24 h. The final product represented a mixture of plate-like orange-red and needle white crystals. The white crystals were unreacted CuCN. The reaction products were washed with water on a paper filter and dried in air. The yield of the major product could not be determined due to the presence of white crystals. According to EDAX data, the element ratio in the sample was as follows: Cs : Cu : Re : S = 1.6 : 2 : 6 : 6.6.

IR (ν, cm^{-1}): 409 ν(ReS), 1075 $\nu(OH_{aq})$, 1598 $\delta(H_2O)$, 2114 and 2160 ν(CN), 3432 $\nu(OH^-)$.

Synthesis of II was carried out by a procedure similar to that used to prepare **I** (reactant amounts: $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$ (100 mg, 0.043 mmol), CuCN (0.446 mmol, 40 mg) and distilled water (0.4 mL)). Complex **II** was formed as red prismatic crystals, the yield of which could not be determined, since the amount of crystals was minor in rela-

tion to the total weight of the product. The isolated product looked like intergrown red and white crystals. According to EDAX data, the element ratio in the sample was as follows: Cu : Re : S = 2.8 : 6 : 6.9.

IR (ν, cm^{-1}): 1064 $\nu(OH_{aq})$, 1575 $\delta(H_2O)$, 2152 ν(CN), 3416 $\nu(OH^-)$.

The ratio of heavy elements was determined by energy dispersive X-ray analysis (EDAX) using a EX-23000BU analyzer and a JSM-6700F scanning electron microscope.

IR spectra in the 4000–400 cm^{-1} range were measured for KBr pellets on a Scimitar FTS 2000 FTIR spectrometer. The samples were prepared using crystals of compounds **I** and **II** selected from the reaction mixture.

X-ray diffraction. The structures of compounds **I** and **II** were determined by a standard procedure on a Bruker-Nonius X8 Apex automated four-circle diffractometer equipped with a CCD array detector (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) at a temperature of 293(2) K for compound **I** and 173(2) K for compound **II**. The absorption corrections were applied empirically (using equivalent reflection intensities) by the SADABS software [18]. The crystal structure was solved by direct methods. The hydrogen atoms of water molecules were not located. The final refinement was carried out by full-matrix least squares method in the anisotropic approximation for all non-hydrogen atoms using unique reflections. All calculations were done by means of the SHELXL-2018/3 software [19]. The figures were performed using the DIAMOND software [20]. The crystallographic characteristics and X-ray diffraction experiment details are summarized in Table 1.

The atom coordinates and thermal parameters were deposited at the Inorganic Crystal Structure Database (CSD nos. 2048821 (**I**), 2048822 (**II**)) and are available from URL https://www.ccdc.cam.ac.uk/structures or from the authors.

RESULTS AND DISCUSSION

Copper(I) cyanide compounds were prepared using hydrothermal synthesis, which is a well elaborated method. A typical procedure was as follows: a sealed glass tube containing the reactants was heated and kept at a specified temperature. In both reactions we studied, the OH^- ligands of the cluster complex were replaced by CN^- ligands, giving rise to interpenetrating frameworks via the –CN–Cu–CN– bridges.

The IR spectrum of compound **I** exhibits CN^- stretching bands for the $[Re_6S_8(CN)_6]^{4-}$ cluster anion at 2114 and 2160 cm^{-1}. The 1075 and 3432 cm^{-1} bands refer to the stretching modes of H_2O. The H_2O bending modes are manifested at 1598 cm^{-1}. The 409 cm^{-1} band corresponds to the ReS stretching vibrations [21].

The IR spectrum of compound **II** shows stretching bands for H_2O molecules at 1064 and 3416 cm^{-1}. The H_2O bending modes are manifested at 1575 cm^{-1}. The 2152 cm^{-1} band is due to CN^- stretching modes of the $[Re_6Se_8(CN)_6]^{4-}$ cluster anion [21].

Compound **I** crystallizes in space group *Pnna* (orthorhombic system). The unit cell contains the $[Re_6S_8(CN)_6]^{4-}$ centrosymmetric cluster anion, the Cu^+ cation coordinated to this cluster anion, two H_2O molecules with occupancies of 1 and 0.5, and two Cs^+ cations, which counterbalance the negative charge of the framework polymer. The structure is formed by two interpenetrating frameworks, with Cs^+ cations and H_2O molecules being located in the cavities (Fig. 1). The Cs coordination environment is complex and consists of CN^-, μ_3-S, and H_2O oxygen atoms. The Cs(1) atoms are in the same plane as two neighboring cluster anions. The H_2O molecules and Cs(1) atom are in the perpendicular plane. The Cs(2) atoms are surrounded by three cluster anions and two H_2O molecules. All six CN^- ligands of the $[Re_6S_8(CN)_6]^{4-}$ cluster anions are involved in the coordination to copper. The Cu coordination number is three. The Cu coordination environment is formed by the cyanide N atoms of the cluster anions (Fig. 2). In turn, each cluster anion is bound to ten neighboring cluster anions: two in the *trans*-position and six in the equatorial plane (a cluster anion located in the *trans*-position to another one is bound to the latter via two copper cations, while two more anions are bound via one copper cation) (Fig. 3). Selected interatiomic distances, together with those for some other compounds are given in Table 2.

Compound **II** crystallizes in space group *C*2/*m* (monoclinic system). A unit cell contains half of the centrosymmetric $[Re_6Se_8(CN)_6]^{4-}$ cluster anion and three coordinated Cu^+ cations, two of which are disordered over two closely located positions. The disordered Cu^+ ions are coordinated to bridging CN^- groups. In addition, the unit cell contains eight independent positions occupied by H_2O molecules and H_3O^+ cations. The O atoms in these positions have partial occupancies. The exact location of H_3O^+ cations among these positions cannot be determined, while the number of the cations is dictated by the electroneutrality requirement. The coordination environment of the disordered closely located Cu(1) and Cu(2) atoms is a triangle consisting of two CN^- ligands of cluster anions and bridging CN^- ligand connecting the neighboring Cu(1) and Cu(2) atoms. This bridging CN^- ligand is disordered over two positions. The coordination environment of Cu(3) is linear and consists of two CN^- ligands of neighbor-

Table 1. Crystallographic characteristics and X-ray diffraction experiment and structure refinement details for **I** and **II**

Parameter	Value	
	I	**II**
M	1976.75	2267.78
System	Orthorhombic	Monoclinic
Space group	*Pnna*	*C2/m*
a, Å	15.9614(3)	18.7168(5)
b, Å	15.9522(3)	23.9787(9)
c, Å	10.9551(3)	8.9836(3)
β, deg		97.836(2)
V, Å^3	2789.4(2)	3994.2(2)
Z	4	4
ρ(calcd.), g cm^{-3}	4.707	3.771
μ(MoK_α), mm^{-1}	30.610	26.990
Crystal size, mm	0.12 × 0.10 × 0.06	0.18 × 0.12 × 0.12
Data collection range of θ, deg	3.41–27.46	2.78–30.57
Ranges of h, k, l	$-15 \le h \le 20$, $-20 \le k \le 17$, $-14 \le l \le 14$	$-26 \le h \le 14$, $-34 \le k \le 33$, $-12 \le l \le 12$
Number of measured reflections	20060	19023
Number of unique reflections (R_{int})	3214 (0.0350)	6238 (0.0251)
Number of observed reflections ($I > 2\sigma(I)$)	2661	5094
Number of refined parameters	155	219
F(000)	3416	3928
R ($F^2 > 2\sigma(F^2)$)	$R_1 = 0.0250$, $wR_2 = 0.0547$	$R_1 = 0.0265$, $wR_2 = 0.0776$
R (F^2 for all reflections)	$R_1 = 0.0348$, $wR_2 = 0.0571$	$R_1 = 0.0265$, $wR_2 = 0.0894$
GOOF	1.049	1.135
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	3.265/–3.439	4.274/–2.812

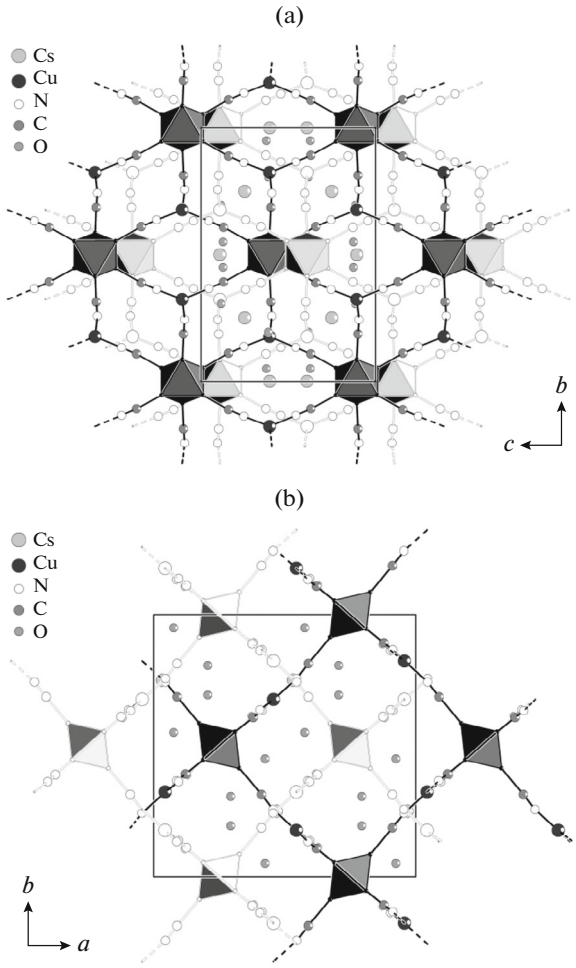

Fig. 1. General view of the structure of $Cs_2[Cu_2Re_6S_8(CN)_6]\cdot 3H_2O$ along the *a* axis (a) and along the *c* axis (b), H_2O molecules and Cs^+ cations are shown for one unit cell; the interpenetrating framework is shown in white, and the $\{Re_6S_8\}^{2+}$ cluster cores are depicted as octahedra.

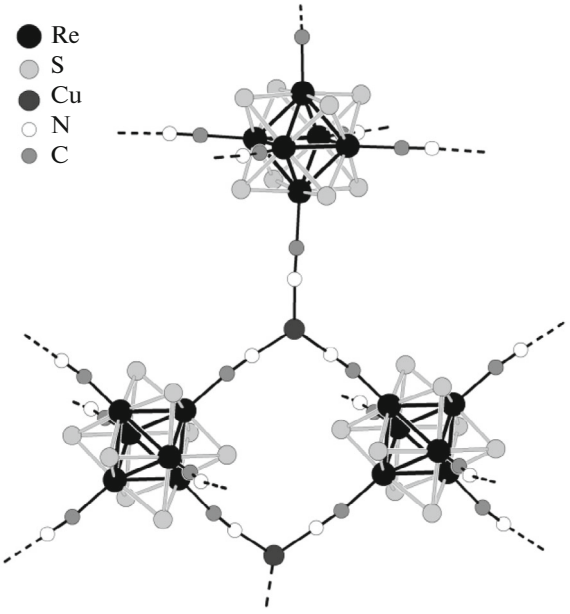

Fig. 2. Fragment of $[Cu_2Re_6S_8(CN)_6]^{2-}$.

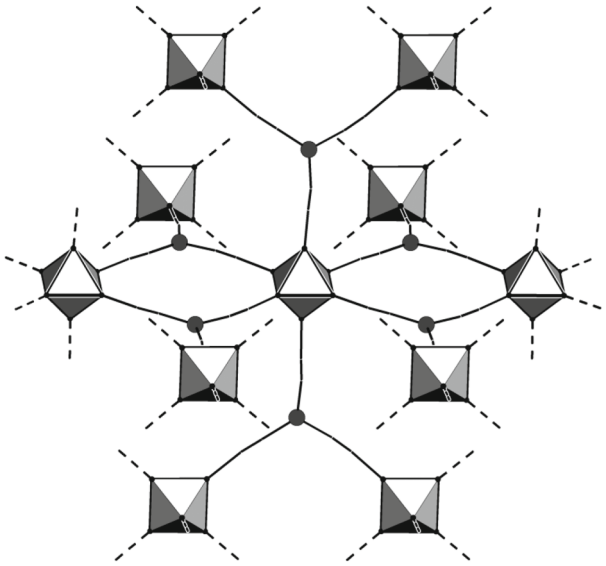

Fig. 3. Schematic of the $[Cu_2Re_6S_8(CN)_6]^{2-}$ fragment of the framework; the $[Re_6S_8(CN)_6]^{4-}$ cluster complexes are depicted as octahedra with copper atoms at the nodes.

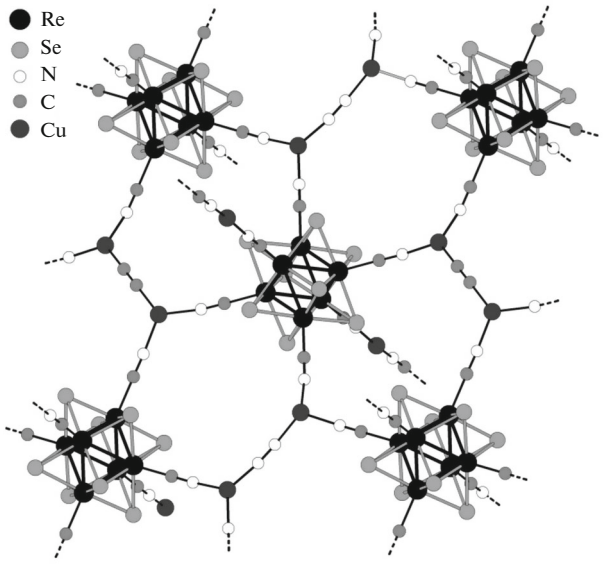

Fig. 4. Fragment of $[Cu\{Cu_2(\mu\text{-}CN)\}Re_6Se_8(CN)_6]^{2-}$.

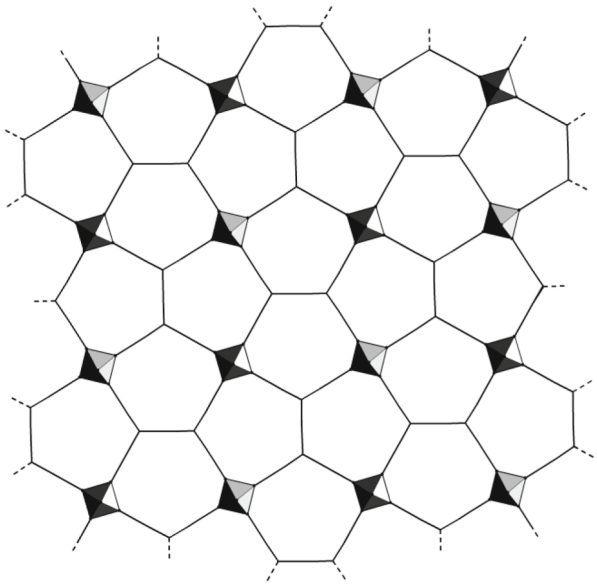

Fig. 5. Schematic of the fragment of the layer formed by $\{Cu_2(\mu\text{-}CN)\}^+$ and cluster anions in **II**. The $\{Re_6Se_8\}^{2+}$ cluster cores are depicted as octahedra.

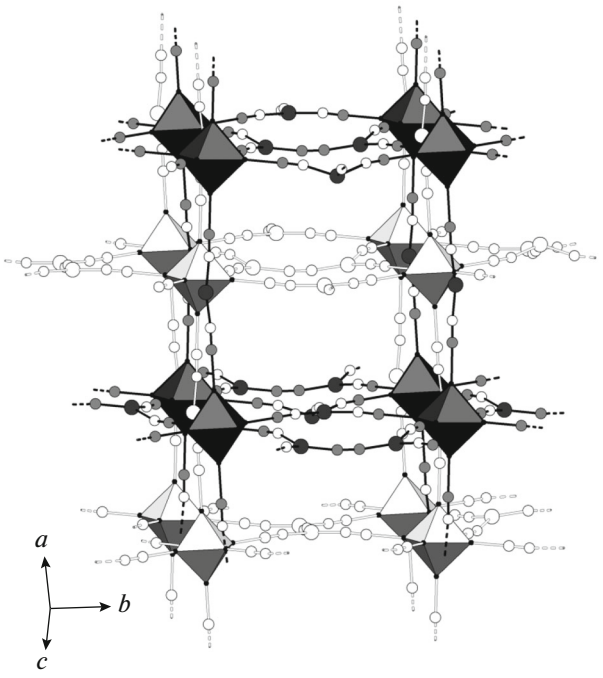

Fig. 6. General view of the structure of $(H_3O)_2[Cu\{Cu_2(\mu\text{-}CN)\}Re_6Se_8(CN)_6]\cdot 6.5H_2O$; the interpenetrating framework is shown in white, and the $\{Re_6Se_8\}^{2+}$ cluster cores are depicted as octahedra.

ing cluster anions (Fig. 4). The cluster anions and $\{Cu_2(\mu\text{-}CN)\}^+$ form layers (Fig. 5), which are connected into a framework via Cu(3) cations. There are two such frameworks in the structure, which interpenetrate (Fig. 6). The cavities of the interpenetrating frameworks contain H_2O molecules and H_3O^+ cations.

This communication reports the first study of the octahedral cyanohydroxo rhenium chalcogenide cluster complexes with CuCN. The hydrothermal synthe-

Table 2. Selected geometric characteristics in the prepared and some known compounds

Compound	*d*, Å				Ref.
	Re–Re	Re–(μ_3-Q)	Re–C	Cu–N	
I	2.5861(6)–2.6056(4)	2.390(2)–2.4154(2)	2.098(8)–2.110(8)	1.910(7)–1.933(7)	This work
II	2.6238(4)–2.6295(4)	2.5152(7)–2.5265(8)	2.080(8)–2.096(7)	1.835(6)–1.944(8)	This work
$Cs_{2.67}K_{1.33}[Re_6S_8(CN)_2(OH)_4]\cdot 4H_2O$	2.5810(2)–2.5860(1)	2.407(3)–2.406(4)	2.07(3)		[5]
$Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$	2.6160(2)–2.6239(2)	2.518(2)–2.532(2)	2.01(2)–2.05(2)		[6]
$Cs_3K[Re_6S_8(CN)_6]$	2.601(1)–2.611(1)	2.402(4)–2.593(3)	2.725(2)		[22]
$K_4[Re_6Se_8(CN)_6]\cdot 3.5H_2O$	2.624(1)–2.642(1)	2.516(1)–2.538(1)	2.09(2)–2.12(2)		[23]
$[\{Cu(Bipy)_2(\mu\text{-}CN)Cu(Bipy)\}_2Re_6S_8(CN)_6]\cdot Bipy\cdot 2H_2O$	2.6005(2)–2.6035(2)	2.4004(8)–2.4146(8)	2.109(3)–2.126(4)	1.909(4)–2.100(3)	[16]
$[\{Cu(Bipy)\}_2(\mu\text{-}CN)][\{Cu(Bipy)\}_3Re_6S_8(CN)_6]$	2.6016(2)–2.6101(2)	2.4040(9)–2.4212(9)	2.106(4)–2.119(4)	1.848(4)–2.138(3)	[16]
$[\{Cu(Bipy)(\mu\text{-}CN)Cu(Bipy)\}_2\{Cu(Bipy)\}_2Re_6Se_8(CN)_6]$	2.6306(2)–2.6420(2)	2.5107(4)–2.5385(4)	2.106(4)–2.110(4)	1.844(4)–2.118(4)	[16]

sis affords interpenetrating frameworks, the cavities of which are occupied by cations, counterbalancing negative charge, and H_2O molecules. The difference between the framework structures may be due to the slight difference between the linear sizes of cluster complexes caused by the difference in chalcogen atoms and the CN : OH ratio.

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