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Hydrothermal Synthesis and Crystal Structure of $[\{Ag_3(Bipy)_3(CN)\}_2Re_6Se_8(CN)_6]$

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Abstract—A supramolecular ensemble $[\{Ag_3(Bipy)_3(CN)\}_2Re_6Se_8(CN)_6]$ (**I**) is synthesized by the reaction of $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$ with $K[Ag(CN)_2]$ and 2,2'-bipyridine (Bipy) under the hydrothermal synthesis conditions. The crystal structure consists of polymer layers $[\{Ag_3(Bipy)_3(CN)\}_2Re_6Se_8(CN)_6]$. Inside the layer, each cluster core $\{Re_6Se_8\}^{2+}$ is linked with six Ag atoms via the CN bridge. Argentophilic interactions Ag···Ag (2.9035(6)–2.9697(5) Å) complete layer formation. π–π-Stacking interactions are observed both inside the layers and between the polymer layers. The synthesized compound is characterized by XRD (CIF file CCDC no. 2170365), IR spectroscopy, and elemental analysis.

Keywords: hydrothermal synthesis, rhenium, octahedral cluster complex, silver, crystal structure

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INTRODUCTION

The octahedral chalcocyanide cluster complexes $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se, Te) are the most representative among numerous known diverse cluster compounds of rhenium [1–9]. As a result of development of the chemistry of rhenium clusters, this series of compounds was supplemented by the heteroligand cluster anions *trans*-$[Re_6Q_8(CN)_{6-n}(OH)_n]^{4-}$ (Q = S, $n = 2, 4$ [10, 11]; Q = Se, $n = 2$ [12]). Similar compounds are interesting, because they contain both relatively labile OH^- ligands, which can be replaced by inorganic or organic ligands [10, 11], and ambidentate CN^- ligands capable of forming polymer compounds with transition metals of different dimensionality due to the –CN–M–CN– bridges [13]. At the same time, metal–metal interactions met in monovalent coinage metals can be considered as a method to increase dimensionality or enrich supramolecular topology [14–16]. The strength of these interactions is comparable with that of hydrogen bonds, which provides a possibility to strengthen desired frameworks [17, 18]. These interactions (for silver they are usually named argentophilic interactions) are met in many polynuclear complexes of Ag(I) [19–22]. A wide use of Ag(I) is due to its high affinity to donor ligands along with the flexible coordination number and geometry [23–25]. We have recently prepared the first examples of the compounds based on the anionic octahedral cluster chalcogenide rhenium complexes and monovalent complex cations of transition metals (Cu^+ and Ag^+) [26–31].

Continuing these investigations, here we studied the reaction of $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$ with $K[Ag(CN)_2]$ and Bipy.

EXPERIMENTAL

The starting cluster salt $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$ was synthesized using a previously described procedure [10], and other reagents were commercial (purity 99.5+%). Powder XRD patterns were recorded in 2θ ranges of 5°–60° on a Philips PW 1700 automated diffractometer (CuK_α radiation, λ = 1.54056 Å, graphite monochromator, internal silicon standard). The ratio of heavy metals was determined by energy dispersive X-ray analysis (EDAX) using a Bruker QUANTAX 70 analyzer of chemical composition on a Hitachi TM3000 desk scanning electron microscope. IR spectra in a range of 4000–400 cm^{-1} were recorded for samples as KBr pellets on a Bruker Vertex 80 FT-IR spectrometer. Elemental analyses for C, H, and N were carried out on a Euro EA 3000 analyzer instrument.

Synthesis of $[\{Ag_3(Bipy)_3(CN)\}_2Re_6Se_8(CN)_6]$ (I). A sealed glass ampule filled with a mixture of $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$ (50.0 mg, 0.022 mmol), $K[Ag(CN)_2]$ (25.7 mg, 0.129 mmol), 2,2'-bipyridine (20.2 mg, 0.129 mmol), and distilled water (0.5 mL) was heated to 150°C, hold for 48 h, and cooled down for 12 h. The product was isolated as orange orthorhombic crystals. The yield was 61.1 mg

Table 1. Crystallographic data and structure refinement parameters for compound **I**

Parameter	Value
Empirical formula	$C_{68}H_{48}N_{20}Se_8Ag_6Re_6$
FW	3541.36
Crystal system	Triclinic
Space group	$P\overline{1}$
a, Å	13.8161(3)
b, Å	14.3229(3)
c, Å	19.0861(4)
α, deg	86.955(1)
β, deg	84.297(1)
γ, deg	88.279(1)
V, Å^3	3751.7(2)
Z	2
ρ_{calc}, g cm^{-3}	3.135
$\mu(MoK_\alpha)$, mm^{-1}	15.099
Crystal size, mm	0.10 × 0.08 × 0.04
Range of data collection over θ, deg	2.375–36.293
Ranges of *h*, *k*, *l*	$-23 \le h \le 23$ $-23 \le k \le 23$ $-31 \le l \le 31$
Number of measured reflections	93083
Number of independent reflections (R_{int})	36205 (0.0475)
Number of observed reflections ($I > 2\sigma(I)$)	27915
Number of refined parameters	219
F(000)	3200
R ($F^2 > 2\sigma(F^2)$)	$R_1 = 0.0361$ $wR_2 = 0.0721$
R (F^2 for all reflections)	$R_1 = 0.0548$ $wR_2 = 0.0861$
GOOF	1.024
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.615/–2.185

(80%). The EDAX method showed the ratio of elements in the sample Ag : Re : Se = 5.81 : 6 : 7.89.

IR (ν, cm^{-1}): 3086 w, 3074 w, 3059 w, 3032 w, 2124 s, 2077 s, 1589 s, 1576 s, 1564 s, 1483 m), 1469 s, 1435 s, 1311 m, 1279 m, 1244 m, 1213 w, 1151 m, 1097 w, 1055 w, 1039 sh, 977 w, 895 w, 758 s, 735 s, 650 m, 619 m.

For $C_{68}H_{48}N_{20}Se_8Ag_6Re_6$			
Anal. calcd., %	C, 23.06	H, 1.37	N, 7.91
Found, %	C, 23.2	H, 1.4	N, 8.0

XRD of a single crystal of compound **I** was carried out on a Bruker D8 Venture diffractometer equipped with a CMOS PHOTON III detector and an IμS 3.0 source (focusing Montel mirror optics, MoK_α radiation, λ = 0.71073 Å) at 150(2) K. An absorption correction was applied empirically from equivalent reflection intensities (SADABS) [32]. The crystal structure was solved by a direct method. The positions of the hydrogen atoms of the Bipy molecules were calculated geometrically and refined by the riding model. The final refinement was performed by full-matrix least squares in the anisotropic approximation for all non-hydrogen atoms. All calculations were performed using the SHELX-2018/3 software [33], and the figures were made using the DIAMOND program [34]. The crystallographic data and experimental and structure refinement details are given in Table 1.

The atomic coordinates and thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2170365; https://www.ccdc.cam.ac.uk/structures/) and can be obtained at request from the authors.

RESULTS AND DISCUSSION

The reaction of the anionic cluster rhenium complex $[Re_6Se_8(CN)_4(OH)_2]^{4-}$ with $K[Ag(CN)_2]$ and 2,2'-bipyridine (Bipy) was studied in this work. The synthesis procedures used by us for studying the reactions of the octahedral cluster rhenium complexes, for example, with Ni^{2+} [35–37], resulted in the formation of an X-ray amorphous powder. Compound $[\{Ag(Bipy)\}\{Ag_4(Bipy)_4(\mu\text{-}CN)\}\{Re_6Se_8(CN)_6\}]$ has recently been synthesized by the reaction involving $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$ with AgCN and Bipy under the hydrothermal conditions (and the compound was characterized). The compound represents a three-dimensional framework built of the cluster anions $[Re_6Se_8(CN)_6]^{4-}$ and two different types of Ag(I)-containing cations, mononuclear $\{Ag(Bipy)\}^+$, and tetranuclear $\{Ag_4(Bipy)_4(\mu\text{-}CN)\}^{3+}$, all of which are bound to each other via the cyanide bridges [27]. The supramolecular structure is maintained by the argentophilic interactions Ag···Ag but unexpectedly demonstrates a very restricted π–π-stacking interaction of the pyridine rings. The hydrothermal synthesis using $K[Ag(CN)_2]$ instead of AgCN results in the formation of compound **I** under similar conditions. The procedure of this method is the following: a glass ampule is filled with reagents, sealed, heated, and hold at a specified temperature.

The absorption bands characteristic of chelate Bipy ligands predominate in the IR spectrum of compound **I**. The relatively weak absorption bands at 3086, 3074, 3059, 3032, 1483, 1469, and 1435 cm^{-1} are due to C–H vibrations involving aromatic hydrogen atoms. The absorption bands of variable intensity

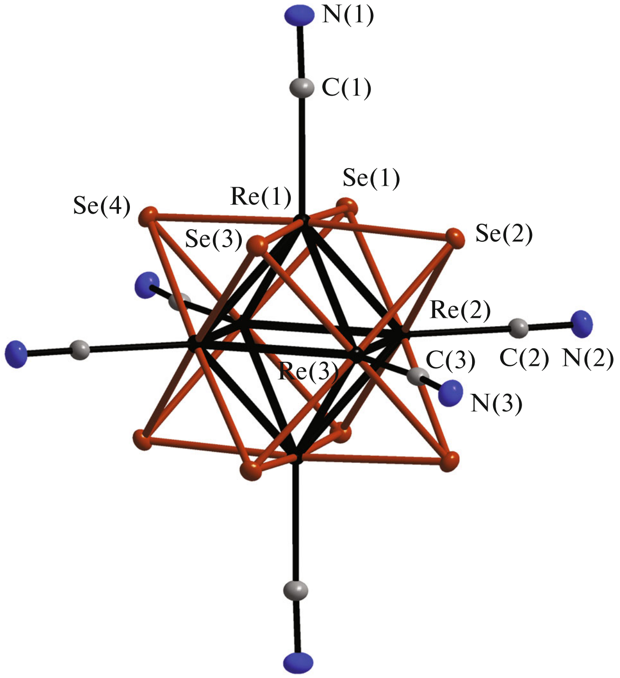

Fig. 1. Structure of the $[Re_6Se_8(CN)_6]^{4-}$ cluster anion. Thermal ellipsoids are given with 50% probability.

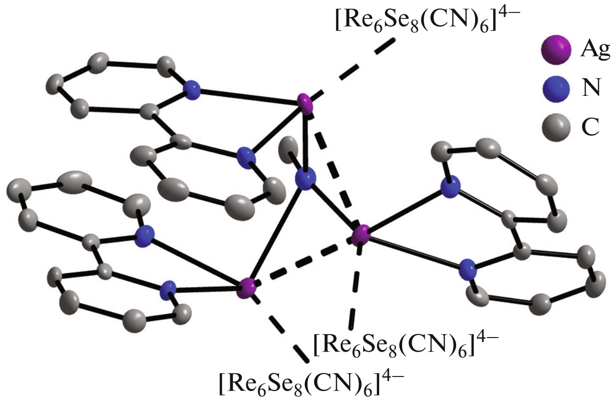

Fig. 2. Structure of the bridging $\{Ag_3(Bipy)_3(CN)\}^{2+}$ cationic complexes. Thermal ellipsoids are given with 50% probability.

about 1589, 1576, 1564, 1244, 1151, 894, and 650 cm^{-1} correspond to vibrations of the aromatic rings of the Bipy ligands. The vibration bands between 1213 and 977 cm^{-1} indicate the presence of Bipy. In addition, the bands in a range of 758–619 cm^{-1} can be considered as characteristic vibrations of coordinated Bipy ligands. The very strong band at 2124 cm^{-1} is attributed to stretching vibration frequencies of the bridging (Ag–CN–Re) CN^- ligand. The very strong band at 2077 cm^{-1} is assigned to stretching vibrations of the CN^- ligand coordinated to the Ag atom [38].

Compound **I** crystallizes in the space group $P\overline{1}$ (triclinic crystal system). The independent part of the unit cell contains two fragments of the layered coordination polymer $[\{Ag_3(Bipy)_3(CN)\}_2Re_6Se_8(CN)_6]$. The coordination polymer is formed from the $[Re_6Se_8(CN)_6]^{4-}$ cluster anion (Fig. 1) and bridging $\{Ag_3(Bipy)_3(CN)\}^{2+}$ cationic complexes (Fig. 2). The steric structure of the cluster anion in compound **I** is similar to those in other related complexes [10, 27, 39]. The rhenium atoms form an octahedron, selenium atoms are coordinated to its faces via the μ_3 mode, and each rhenium atom is additionally coordinated by the CN^- ligand through the carbon atom. The bond lengths in the cluster core are compared with the data for other complexes containing the $[Re_6Se_8(CN)_6]^{4-}$ cluster core (Table 2). The structure contains two crystallographically independent bridging cationic complexes $\{Ag_3(Bipy)_3(CN)\}^{2+}$ in which the Bipy ligand is coordinated to each Ag atom via the chelate mode. In addition, each Ag atom is linked with the cluster core via the CN^- bridge. The Ag–Ag argentophilic interactions (2.9035(6), 2.9233(5), 2.9312(6), 2.9697(5) Å) contribute to the overall structural stabilization of the discussed fragment: they join three Ag atoms into a chain to form the polymer layer (Fig. 3). The bond lengths are well consistent with the doubled empirical covalent radius of the Ag atom (3.06 Å) and only slightly exceed the distance between the atoms in metallic silver (2.886 Å). The AgAgAg angles are 97.248(15)° and 97.341(15)°. The terminal CN^- ligand is located between these three Ag atoms. The shortest $Ag-N_{CN}$ distances are 2.118(5) and 2.150(5) Å, and the distances from the ultimate Ag atoms to N_{CN} are equal to 2.465(5)–2.591(5) Å. The structure exhibits the π–π-stacking interactions both inside the cationic fragment and between the adjacent nearest cationic fragments inside the polymer layer and between the layers (Fig. 4). The distance between the centers of the aromatic rings inside the cationic fragment is somewhat longer (4.121–4.211 Å) than that between the layers (3.710–3.842 Å). Together they form a nearly straight line along the *b* axis. The distance between the centers of the aromatic rings of the nearest cationic fragments inside the layer is 3.654 Å. Thus, the supramolecular ensemble consisting of the polymer layers perpendicular to the *a* axis is formed due to the π–π-stacking interactions. The structure is closely packed.

To conclude, the reaction of $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$ with $K[Ag(CN)_2]$ and Bipy under the hydrothermal synthesis conditions results in the substitution of the OH^- ligands by CN^- and formation of cationic fragments and compound $[\{Ag_3(Bipy)_3$-

Table 2. Selected geometric characteristics of complex **I** and some known compounds

Compound	*d*, Å			
	Re–Re	Re–(μ_3-Q)	Re–C	Ag/Cu–N
I	2.6281(2)–2.6421(2)	2.5076(4)–2.5299(5)	2.100(4)–2.123(4)	2.118(5)–2.591(5)
$Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2]\cdot H_2O$ [10]	2.6160(2)–2.6239(2)	2.518(2)–2.532(2)	2.01(2)–2.05(2)	
$K_4[Re_6Se_8(CN)_6]\cdot 3.5H_2O$ [39]	2.624(1)–2.642(1)	2.516(1)–2.538(1)	2.09(2)–2.12(2)	
$[\{Cu(Bipy)(\mu\text{-}CN)Cu(Bipy)\}_2\{Cu(Bipy)\}_2Re_6Se_8(CN)_6]$ [26]	2.6306(2)–2.6420(2)	2.5107(4)–2.5385(4)	2.106(4)–2.110(4)	1.844(4)–2.118(4)
$[\{Ag(Bipy)\}\{Ag_4(Bipy)_4(\mu\text{-}CN)\}Re_6Se_8(CN)_6\}]$ [27]	2.6285(4)–2.6386(4)	2.5171(7)–2.5309(7)	2.096(6)–2.118(7)	2.111(7)–2.577(5)

$(CN)\}_2Re_6Se_8(CN)_6]$, being the supramolecular ensemble in which the argentophilic interactions form the polymer layer and the π–π-stacking interactions bind the closest layers between each other. The replacement of polymer AgCN (as the source of Ag(I)) by the anionic $[Ag(CN)_2]^-$ complex results in a cardinal difference in the reaction products with the octahedral rhenium cluster complex.

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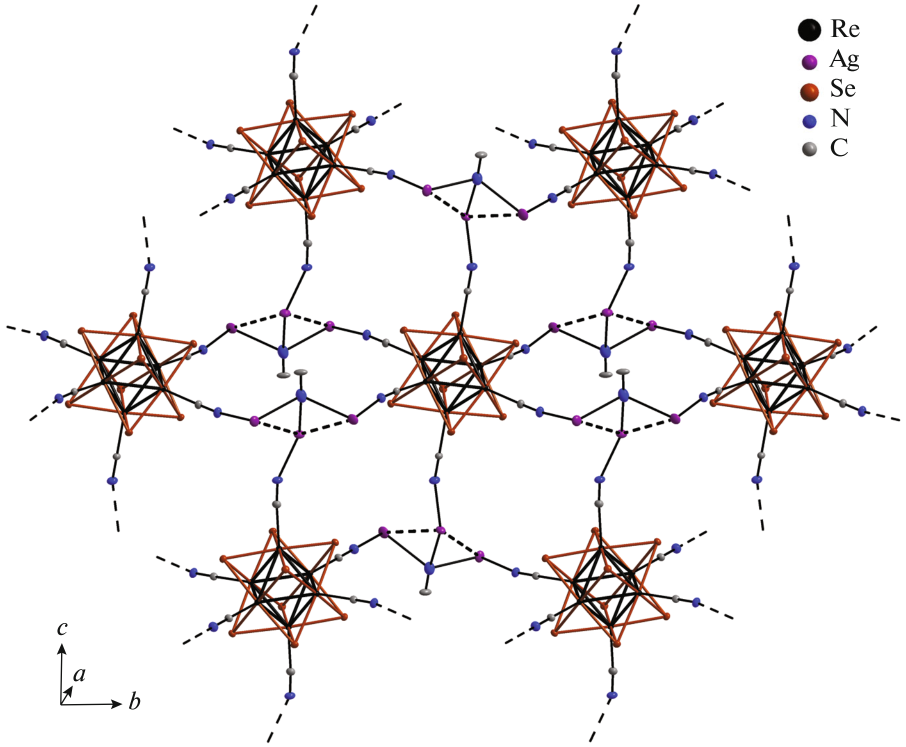

Fig. 3. Fragment of the polymer layer in compound **I** (Bipy molecules are omitted for clarity).

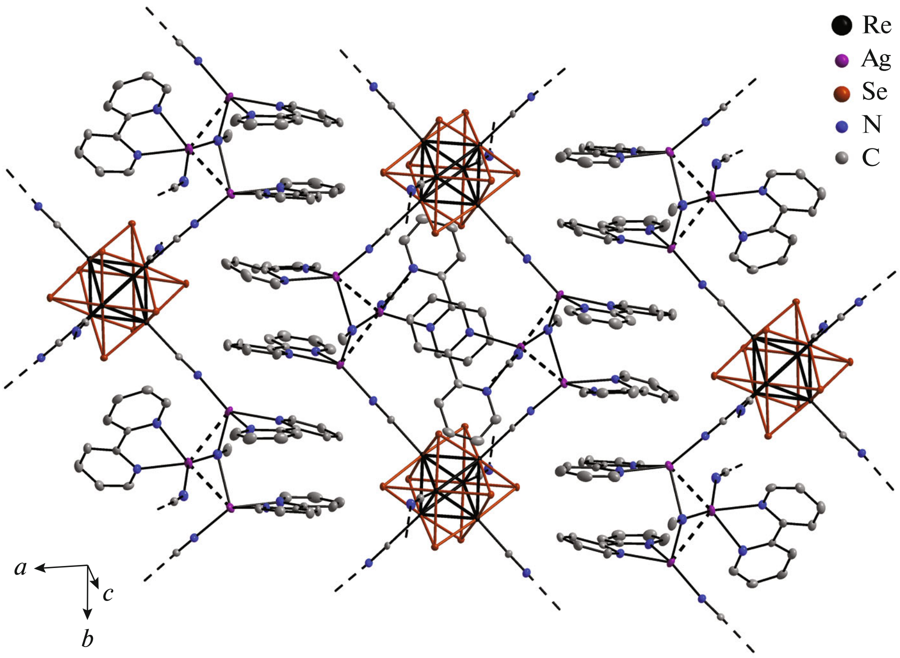

Fig. 4. Fragment of the $[\{Ag_3(Bipy)_3(CN)\}_2Re_6Se_8(CN)_6]$ supramolecular ensemble. Hydrogen atoms are omitted for clarity.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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