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Polymers Based on Anionic Octahedral Cluster Chalcocyanohydroxorhenium Complexes and Cations $[Cu(En)_2]^{2+}$

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Abstract—Polymer compounds $[Cu(En)_2(H_2O)_2][\{Cu(En)_2\}Re_6S_8(CN)_4(OH)_2] \cdot 5.5H_2O$ (**I**) and $[Cu(En)_2(H_2O)_2][\{Cu(En)_2\}Re_6Se_8(CN)_4(OH)_2] \cdot 5H_2O$ (**II**) are synthesized by the layering of an ammonia solution of $CuCl_2$ with ethylenediamine (En) on aqueous solutions of the corresponding octahedral cluster chalcocyanohydroxorhenium complexes. The compounds are characterized by IR spectroscopy and elemental and X-ray diffraction analyses.

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INTRODUCTION

Compounds containing octahedral cluster anions $[Re_6(\mu_3\text{-}Q)_8L_6]^{4-}$– (Q = S, Se, Te; L = CN^-, OH^-, and other) exhibit a wide range of chemical and physical properties, such as the ability to form coordination polymers, the possibility of redox transformations, and luminescence in both the solution and solid phase, which makes them an object of rapt attention of researchers [1–4]. In particular, the cluster anions containing cyanide ions as terminal ligands are well known playing the role of building blocks for the formation of polymer compounds built on CN—M—CN bridging interactions, where M is a transition 3*d* metal [1, 5–10]. The hydroxo complexes $[Re_6Q_8(OH)_6]^{4-}$ are also capable of forming OH-bridged coordination polymers with metal cations [11–13] and simultaneously they are convenient precursors for ligand exchange reactions, since the terminal OH^- ligands can fairly easily be replaced by other ligands, for example, carboxylic acid anions [14, 15]. We have recently synthesized mixed-ligand cluster anions with two types of terminal ligands: OH^- and CN^- [16, 17]. It was assumed that these chalcocyanohydroxo complexes can exhibit the properties of both cyano and hydroxo complexes. As a results of the studies of the reactivity of the chalcocyanohydroxo complexes in the reactions with 3*d* metals, molecular $([\{Cu(CH_3NH_2)_4\}_2\{Re_6Se_8(CN)_4(OH)_2\}]$ [16] and $[\{Ni(NH_3)_5\}_2\{Re_6Se_8(CN)_4(OH)_2\}] \cdot 6H_2O$ [18]) and ionic $([Cu(NH_3)_5]_2[Re_6Se_8(CN)_4(OH)_2] \cdot 8H_2O$ [16], $[Ni(En)_3]_2[Re_6S_8(CN)_4(OH)_2] \cdot 5.5H_2O$, and $[Ni(En)_3]_2[Re_6Se_8(CN)_4(OH)_2] \cdot 10H_2O$ [19]) compounds were synthesized. In this work, we studied the reactions of the anionic clusters $[Re_6Q_8(CN)_4(OH)_2]^{4-}$ (Q = S, Se) with $CuCl_2$ in the presence of ethylenediamine. Two new coordination polymers with the chain structure, $[Cu(En)_2(H_2O)_2][\{Cu(En)_2\}Re_6S_8(CN)_4(OH)_2] \cdot 5.5H_2O$ (**I**) and $[Cu(En)_2(H_2O)_2][\{Cu(En)_2\}Re_6Se_8(CN)_4(OH)_2] \cdot 5H_2O$ (**II**), were synthesized and characterized.

EXPERIMENTAL

The starting compounds $Cs_{2.75}K_{1.25}[Re_6Se_8(CN)_4(OH)_2] \cdot H_2O$ (**III**) and $Cs_{1.68}K_{2.32}[Re_6S_8(CN)_4(OH)_2] \cdot 2H_2O$ (**IV**) were synthesized according to earlier described procedures [16, 17], and other reagents were commercial. The ratio of heavy metals was determined by energy dispersive X-ray analysis (EDAX) using a JSM-6700F scanning electron microscope. IR spectra in the range from 4000 to 400 cm^{-1} were recorded for samples as KBr pellets on a Scimitar FTS 2000 FT-IR spectrometer. Elemental analyses to C, H, N, and S were carried out on a MICRO CORDER JM10 instrument.

Synthesis of compound I. A solution of $CuCl_2 \cdot 2H_2O$ (65 mg, 0.38 mmol) and ethylenediamine (0.07 mL, 1.05 mmol) in an aqueous ammonia (30%) solution (5 mL) in a glass tube was carefully layered on a solution of complex **IV** (20 mg, 0.01 mmol) in water (5 mL). The reaction afforded a red-brown finely crystalline powder. The powder was separated by filtration, washed with water, and dried on a paper filter. The yield was 12 mg (47%). The EDAX showed the following ratio of elements in the sample: Cu : Re : S = 1.16 : 6 : 7.89.

IR, ν, cm^{-1}: 973 $\delta_{rocking}(CH_2)$, 1037 $\nu(OH_{aq})$, 1577 $\delta(H_2O)$ and $\delta(NH_2)$, 2114 ν(CN), 3259 and 3292 $\nu_{as}(NH)$, 3438 $\nu(OH^-)$.

For $C_{12}H_{49}N_{12}O_{9.5}S_8Cu_2Re_6$

anal. calcd., %: C, 7.15; H, 2.45; N, 8.34; S, 12.73.

Found, %: C, 7.35; H, 2.30; N, 8.45; S, 13.10.

Synthesis of compound II was carried out similarly to complex **I** by the layering of a solution of $CuCl_2 \cdot 2H_2O$ (65 mg, 0.38 mmol) and ethylenediamine (0.07 mL, 1.05 mmol) in an aqueous ammonia (30%) solution (5 mL) on a solution of compound **III** (20 mg, 0.01 mmol) in water (5 mL). Needle-like red-brown crystals were isolated. The yield was 10 mg (49%). The EDAX showed the following ratio of elements in the sample: Cu : Re : Se = 1.92 : 6 : 7.83.

IR, ν, cm^{-1}; 970 $\delta_{rocking}(CH_2)$, 1030 $\nu(OH_{aq})$, 1573 $\delta(H_2O$ and $\delta(NH_2)$, 2100 ν(CN), 3242 and 3293 $\nu_{as}(NH)$, 3437 $\nu(OH^-)$.

For $C_{12}H_{48}N_{12}O_9Se_8Cu_2Re_6$

anal. calcd., %: C, 6.05; H, 2.03; N, 7.06.

Found, %: C, 6.23; H, 2.10; N, 7.12.

X-ray diffraction analysis. The structures of complexes **I** and **II** were determined using a standard procedure on a Bruker-Nonius X8 Apex automated four-circle diffractometer equipped with a CCD two-coordinate detector at 100(2) K for complex **I** and at 150(2) K for complex **II** (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). An absorption correction was applied empirically by the equivalent reflection intensities (SADABS) [20]. The crystal structures were solved by a direct method. The positions of the hydrogen atoms in the ethylenediamine molecules and hydroxide groups of the cluster anions were calculated geometrically and refined in the rigid body approximation. No hydrogen atoms of the water molecules were localized. The final refinement was performed by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms. All calculations were performed using the SHELXTL program package [20], and the figures were drawn using the DIAMOND program [21]. The crystallographic characteristics and details of diffraction experiments are given in Table 1. The coordinates of atoms and thermal parameters were deposited with the Cambridge Crystallographic Data Centre (961092 (**I**) and 961093 (**II**); www.ccdc.cam.ac.uk/data_request/cif) and are available from the authors.

RESULTS AND DISCUSSION

The interaction of the anionic octahedral chalcocyanohydroxo complexes $[Re_6Q_8(CN)_4(OH)_2]^{4-}$ (Q = S, Se) with an ammonia solution containing $CuCl_2$ and ethylenediamine was studied. Similar reactions have previously been studied comprehensively as applied to the cluster cyano complexes $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se, or Te) [1, 2, 5–8]. The compounds with different types of structures were synthesized and characterized: ionic structures in which the cluster does not interact directly with cations M^{2+} and molecular or polymer structures in which the $[Re_6Q_8(CN)_6]^{4-}$ ions act as building blocks coordinating through the nitrogen atoms of the apical CN^- ligands to the metal cations. The polymer compounds of the chalcohydroxo complexes $[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se) with the cationic copper complexes have recently been obtained in which the Cu atoms are not coordinated to the oxygen atoms of the OH^- ligands, but polymer formation due to the coordination of the transition metal cation by the chalcogen atoms from the cluster core occurred, which was not met earlier in the chemistry of octahedral chalcogenide clusters [12, 13]. Compounds **I** and **II** were synthesized according to a known procedure using a careful layering of solutions in a glass tube. In this work, an ammonia solution of $CuCl_2$ and ethylenediamine was layered on an aqueous solution of the corresponding cluster salt. Finely crystalline powders and then larger crystals used for X-ray diffraction analyses began to form already several minutes after mixing of the solutions.

Crystals of **I** and **II** are isostructural. An insignificant variation of the hydrate composition of the studied single crystals is due to differences in site occupancies of the atoms of the water molecules, because these compounds tend to dehydration. The structures of cluster anions $[Re_6Q_8(CN)_4(OH)_2]^{4-}$ (Q = S, Se) in compounds **I** and **II** are similar to the structures of anions in the starting salts and other compounds containing these anions [7, 8, 16, 17, 22–24]. The structure of the anions is typical of octahedral chalcogenide clusters $[Re_6Q_8L_6]^m$ (Fig. 1). The Re_6 octahedron is surrounded by eight ligands μ_3-Q (Q = S, Se) localized at the vertices of the cube. In addition, four Re atoms are coordinated by the terminal CN^- ligands, and two other Re atoms are coordinated by the OH^- ligands arranged in the *trans* position relative to each other. The interatomic distances in the cluster anions of compounds **I** and **II** are given in Table 2 in comparison with the distances in the anions $[Re_6Q_8(CN)_4(OH)_2]^{4-}$, $[Re_6Q_8(CN)_6]^{4-}$, and $[Re_6Q_8(OH)_6]^{4-}$ in some known compounds.

Structures **I** and **II** include two crystallographically independent copper atoms (Cu(1) and Cu(2)), each having in the ligand environment two ethylenediamine molecules that occupy four coordination sites in one plane ($Cu-N_{En}$ 2.000(18)–2.052(14) Å in **I** and 1.962(15)–2.025(13) Å in **II**). The square coordination of the Cu(1) atoms is supplemented to a distorted octahedral one by the N atoms of the cyano groups of the cluster anions (Fig. 2a) due to which anionic polymer chains $[\cdots\{Cu(En)_2\}-CN-\{Re_6Q_8(CN)_2(OH)_2\}-CN\cdots]^{2-}$ directed along [110] are formed (Fig. 3). The $Cu-N_{CN}$ distances and $CuN_{CN}Re$ angles are 2.502(13) Å and 117.0(5)° in structure **I** and 2.567(13) Å and 115.4(4)° in compound **II**, respectively. The coordination environment of the Cu(2)

Table 1. Crystallographic characteristics and diffraction experimental and refinement details for structures **I** and **II**

Parameter	Value	
	I	**II**
FW	2014.39	2380.58
Crystal system	Triclinic	Triclinic
Space group	$P\overline{1}$	$P\overline{1}$
a, Å	8.3567(9)	8.6283(5)
b, Å	11.3924(11)	11.2905(8)
c, Å	11.6368(12)	11.8312(9)
α, deg	72.502(3)	73.885(4)
β, deg	85.880(2)	86.916(3)
γ, deg	82.654(2)	82.256(4)
V, Å^3	1047.3(2)	1097.02(13)
Z	1	1
ρ_{calcd}, g cm^{-3}	3.194	3.590
μ_{MoK_α}, mm^{-1}	18.709	24.112
Crystal size, mm	0.22 × 0.02 × 0.02	0.20 × 0.05 × 0.05
Data collection range θ, deg	1.84–27.59	2.2–27.56
Ranges h, k, l	$-10 \le h \le 10$, $-8 \le k \le 14$, $-11 \le l \le 15$	$-11 \le h \le 8$, $-14 \le k \le 13$, $-15 \le l \le 15$
Number of measured reflections	8369	8429
Number of independent reflections (R_{int})	4803 (0.0650)	5018 (0.0378)
Number of observed reflections ($I > 2\sigma(I)$)	2931	2798
Number of refined parameters	255	255
$F(000)$	917	1051
R ($F^2 > 2\sigma(F^2)$)	$R_1 = 0.0542$ $wR_2 = 0.0992$	$R_1 = 0.0487$ $wR_2 = 0.1105$
R (F^2 for all reflections)	$R_1 = 0.1119$ $wR_2 = 0.1127$	$R_1 = 0.1026$ $wR_2 = 0.1232$
Goodness-of-fit for	0.940	0.990
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	3.00/–2.16	2.33/–1.69

atoms is also supplemented to a distorted octahedron by the O atoms of the crystallization water molecules (Cu–O$_{aq}$ 2 2.532(14) and 2.534(10) Å in **I** and **II**, respectively). Thus formed cations $[Cu(En)_2(H_2O)_2]^{2+}$ (Fig. 2b) compensate the charge of the anionic chains $[\{Cu(En)_2\}Re_6Q_8(CN)_4(OH)_2]^{2-}$. The anionic chains, complex cations, and crystallization water molecules are joined by a system of hydrogen bonds O–H···O, O–H···N, N–H···O, and N–H···N involving the water molecules, hydroxide and cyanide ligands of the cluster anions, and coordinated ethylenediamine molecules (shortest distances O···O ~2.7, O···N ~2.9, and N···N ~3.2 Å). It should specially be mentioned that hydrogen bonds O–H···N between the terminal CN$^-$ and OH$^-$ ligands of the nearest cluster anions favor, to a significant extent, the linking of the chains between

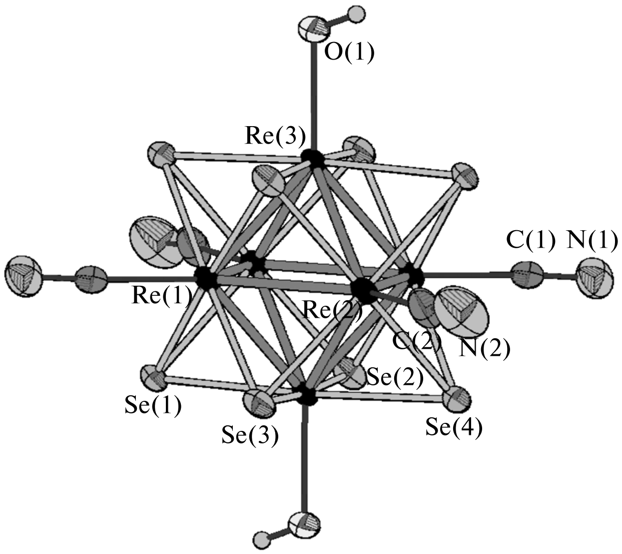

Fig. 1. Structure of the cluster anions in complexes **I** and **II** using $[Re_6Se_8(CN)_4(OH)_2]^{4-}$ in structure **II** as an example. Thermal ellipsoids of 30% probability are presented.

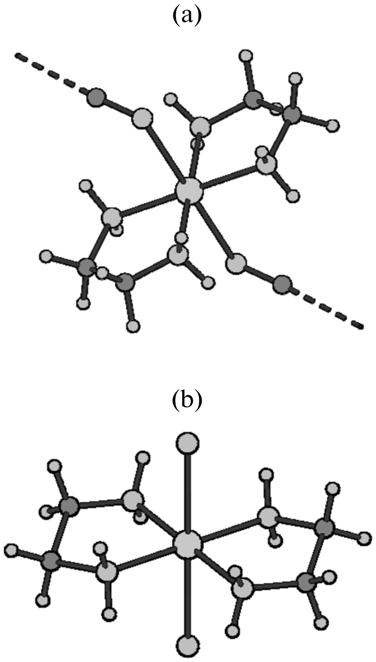

Fig. 2. Ligand environment of the (a) Cu(1) and (b) Cu(2) atoms.

each other (O···N 2.9302(18) Å in **I** and 2.9220(17) Å in **II**). This type of bonding of the cluster chalcocyanohydroxo complexes has recently been described [19]. The general view of structures **I** and **II** is presented in Fig. 4.

Thus, two new coordination polymers with the chain structure in the $[Re_6Q_8(CN)_4(OH)_2]^{4-}$–$[Cu(En)_2]^{2+}$ system (Q = S, Se) were isolated and structurally characterized in an aqueous-ammonia medium. Early described polymer compound $[\{Cu(H_2O)_{0.5}(En)_2\}\{Cu(En)_2\}Re_6Se_8(CN)_6] \cdot 3H_2O$ [9], whose chain structure similar to those of complexes **I** and **II** was obtained by studying the $[Re_6Se_8(CN)_6]^{4-}$–$[Cu(En)_2]^{2+}$ system in water. As can be seen from the composition, the main distinction of this complex from compounds **I** and **II** is the presence of the cationic fragment $\{Cu(H_2O)_{0.5}(En)_2\}^{2+}$ coordinated to the cluster anion through the nitrogen atom of the ambidentate CN group. It is known that in the similar $[Re_6Q_8(OH)_6]^{4-}$–$[Cu(En)_2]^{2+}$ system no compounds are formed in which the hydroxide ligands of the cluster anion would be coordinated to the Cu^{2+} ions [12]. This suggests that the formation of anionic chains $[\{Cu(En)_2\}Re_6Q_8(CN)_4(OH)_2]^{2-}$ together with isolated cations $[Cu(En)_2(H_2O)_2]^{2+}$ in compounds **I** and **II** is caused by the composition of the coordination sphere of the cluster anion, namely, by the presence of OH groups preventing the further coordination of the Cu^{2+} ions. Based on the obtained results, it can be concluded that the mixed-ligand cluster chalcocyanohydroxo complexes provide the possibility to synthesize compounds differed in structure from the compounds based on chalcocyanide and chalcohydroxide complexes.

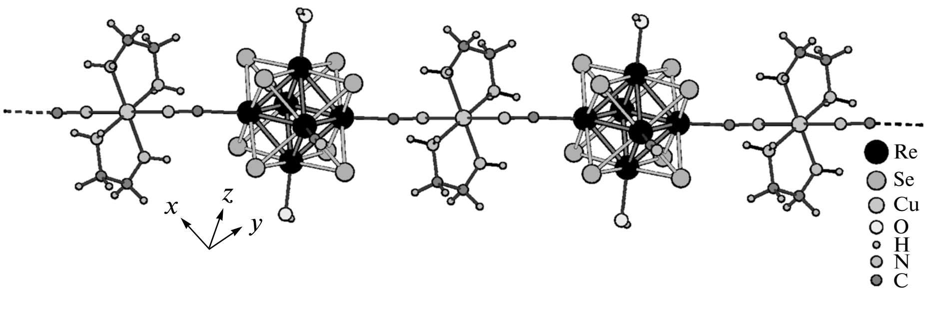

Fig. 3. Fragment of the polymer chain $[\{Cu(En)_2\}Re_6Q_8(CN)_4(OH)_2]^{2-}$.

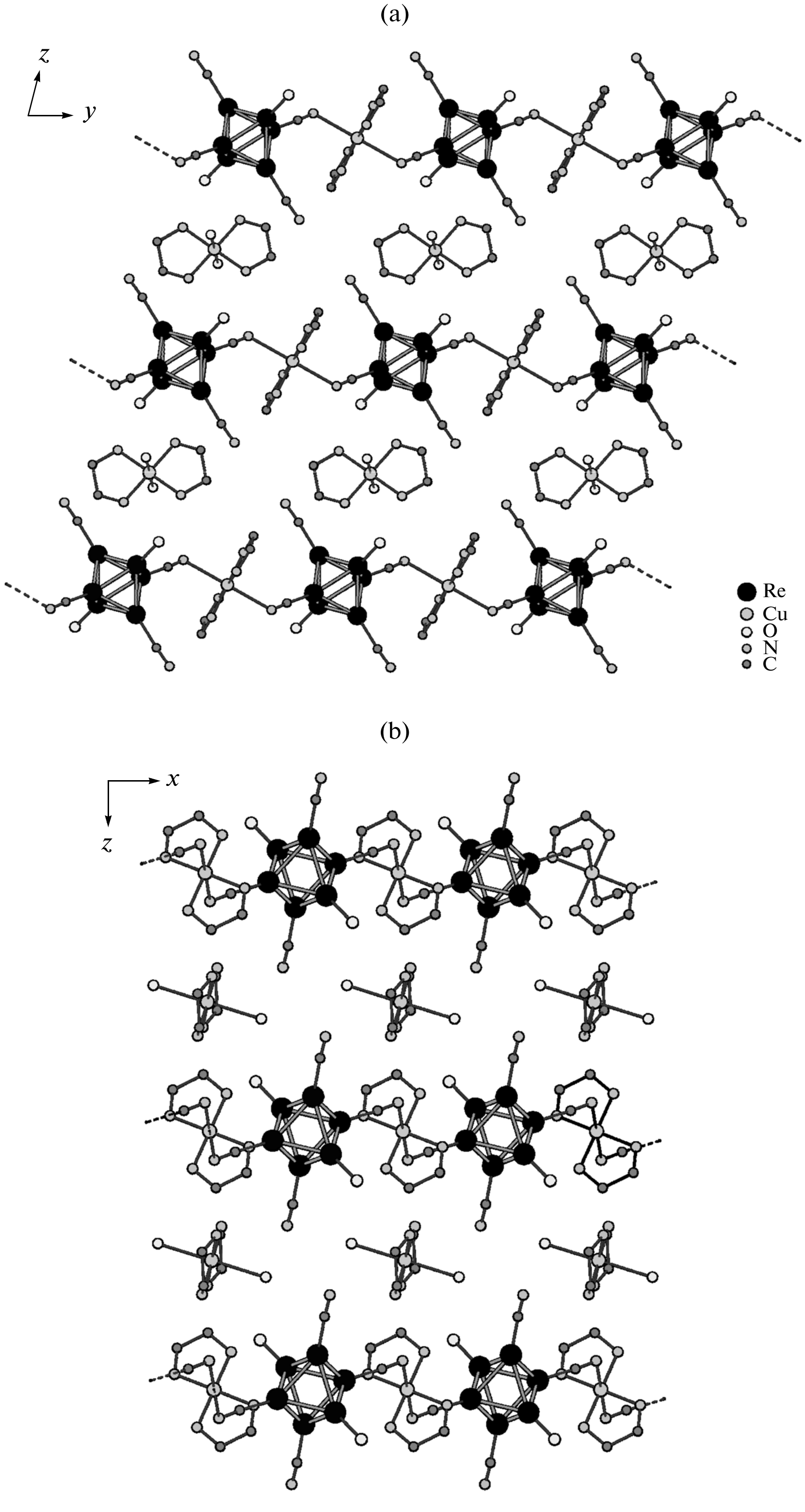

Fig. 4. General view of structures **I** and **II** along the axes (a) *x* and (b) *y*. Chalcogen and hydrogen atoms and solvate water molecules are omitted.

Table 2. Main geometric characteristics of the cluster anions $[Re_6Q_8(CN)_4(OH)_2]^{4-}$, $[Re_6Q_8(CN)_6]^{4-}$, and $[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se) in complexes **I** and **II** and in some known compounds

Compound	*d*, Å		
	Re–Re	Re–(μ_3-Q)	Re–O, Re–C
I	2.5917(9)–2.698(9)	2.394(4)–2.434(5)	2.068(10), 2.098(16), 2.10(2)
II	2.113(9)–2.6365(8)	2.5133(14)–2.533(18)	2.092(8), 2.053(16), 2.082(15)
IV [17]	2.5967(6)–2.6114(8)	2.408(2)–2.429(2)	2.068(6), 2.101(8)–2.132(9)
III [16]	2.6160(11)–2.6239(12)	2.518(2)–2.532(2)	2.110(14), 2.01(2)–2.05(2)
$[Cu(NH_3)_5]_2[Re_6Se_8(CN)_4(OH)_2] \cdot 8H_2O$ [16]	2.6198(6)–2.6311(6)	2.5140(12)–2.5327(11)	2.068(8), 2.100(10)–2.103(11)
$[\{Cu(CH_3NH_2)_4\}_2Re_6Se_8(CN)_4(OH)_2]$ [16]	2.6153(18)–2.6261(9)	2.512(2)–2.533(3)	2.13(3), 2.01(5)–2.12(4)
$[Cu(NH_3)(Trien)]_2[Re_6S_8(CN)_6] \cdot 7H_2O$ [22]	2.5953(8)–2.6071(8)	2.396(2)–2.417(2)	2.114(9)
$[Cu(NH_3)(Trien)]_2[Re_6Se_8(CN)_6]$ [22]	2.5253(10)–2.6396(7)	2.5155(10)–2.5338(11)	2.104(10)
$[Ni(NH_3)_2(En)_2]_2[\{Ni(NH_3)_4\}Re_6Se_8(CN)_6]Cl_2 \cdot 2H_2O$ [7]	2.6270(7)–2.6330(3)	2.5247(8)–2.5275(8)	2.08(1)–2.104(9)
$[\{Cu(H_2O)_{0.5}(En)_2\}Cu(En)_2\}Re_6Se_8(CN)_6] \cdot 3H_2O$ [8]	2.624(2)–2.647(2)	2.505(4)–2.542(4)	2.06(4)–2.18(4)
$K_4[Re_6S_8(OH)_6] \cdot 8H_2O$ [23]	2.5846(8)–2.5906(9)	2.407(4)–2.420(3)	2.07(1)–2.09(1)
$Cs_4[Re_6S_8(OH)_6] \cdot 6H_2O$ [24]	2.5873(5)–2.5995(5)	2.401(2)–2.440(2)	2.063(5)–2.086(5)
$K_4[Re_6Se_8(OH)_6] \cdot 8H_2O$ [23]	2.6085(6)–2.6155(6)	2.527(1)–2.545(1)	2.081(6)–2.088(6)
$Cs_4[Re_6Se_8(OH)_6] \cdot 8H_2O$ [24]	2.6103(11)–2.6210(12)	2.522(2)–2.560(2)	2.059(9)–2.092(9)

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