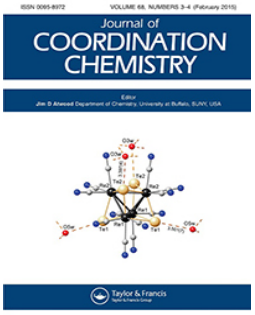

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Synthesis, crystal structure, and thermal stability of ionic cluster compounds $(phenH)_4[Re_4Q_4(CN)_{12}]\cdot nH_2O$ (Q = S, Se, $n = 6$; Q = Te, $n = 10$)

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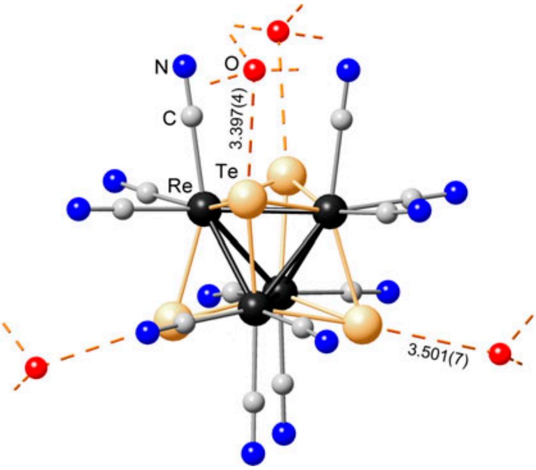

Three new salts of tetrahedral rhenium chalcocyanide cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, Te) and 1,10-phenanthroline-1-ium cations, $(phenH)_4[Re_4S_4(CN)_{12}]\cdot 6H_2O$ (**1**), $(phenH)_4[Re_4Se_4(CN)_{12}]\cdot 6H_2O$ (**2**), and $(phenH)_4[Re_4Te_4(CN)_{12}]\cdot 10H_2O$ (**3**), have been synthesized by reactions of $K_4[Re_4Q_4(CN)_{12}]\cdot nH_2O$ with 1,10-phenanthroline in the presence of Nd^{3+} in an acidic aqueous medium (pH 4). **1** and **2** exhibit similar 2-D layered supramolecular architectures based on hydrogen bonds between water molecules, CN-groups of cluster anions, and $phenH^+$ cations. The latter are involved in π–π and C–H$\cdots\pi$ stacking interactions, connecting the adjacent layers with each other. Complex **3** demonstrates a 3-D framework based on hydrogen bonds between water molecules and CN-groups, π–π and C–H$\cdots\pi$ interactions. Notably short O$\cdots$Te contacts of 3.40 and 3.50 Å are found in the structure of **3**. The thermal properties of **1–3** have been investigated by TG-DTG.

Keywords: Rhenium; Tetrahedral cluster complexes; Hydrogen bonding; Crystal structure; Thermal stability

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1. Introduction

Chemical and physical properties of the rhenium cluster complexes have been investigated over the past decades [1–5]. Along with these aspects, research has focused on the crystal chemistry of a variety of compounds based on rhenium clusters bearing cyanide ligands [6, 7]. Among them, the first complexes containing the tetranuclear chalcocyanide anions $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, Te) with the cubane-like cluster cores $\{Re_4Q_4\}^{8+}$ [8] were reported more than three decades ago. Their tetraphenylphosphonium salts $(Ph_4P)_4[Re_4Q_4(CN)_{12}]\cdot 3H_2O$ (Q = S, Se) were obtained by high-temperature reaction of $K_2[ReCl_6]$ with the molten mixture of KSCN (or KSeCN for Q = Se) and KCN [9]. Under mild conditions, the $[Re_4Q_4(CN)_{12}]^{4-}$ cluster complexes can be obtained more efficiently by reaction of insoluble but readily reactive cluster compounds $[Re_4Q_4(TeX_2)_4X_8]$ (synthesized by ampoule method at 350–550 °C; Q = S, Se, Te; X = Cl [10]; Q = Te, X = Br [11]) with excess of KCN in an aqueous medium [12, 13]. Indeed, this reaction results in substitution of all apical ligands in the starting compounds by cyanide. To date, a few ionic compounds containing $[Re_4Q_4(CN)_{12}]^{4-}$ cluster anions, and Cs^+ [14], K^+ [12, 13] and Ph_4P^+ [9, 15] cations have been synthesized and structurally characterized. In this article, we report the synthesis and characterization of three new ionic salts of the $[Re_4Q_4(CN)_{12}]^{4-}$ cluster anions and 1,10-phenanthroline-1-ium cations (*phen*H^+), the full formulas of which are as follows: (*phen*H)$_4[Re_4S_4(CN)_{12}]\cdot 6H_2O$ (**1**), (*phen*H)$_4[Re_4Se_4(CN)_{12}]\cdot 6H_2O$ (**2**), and (*phen*H)$_4[Re_4Te_4(CN)_{12}]\cdot 10H_2O$ (**3**).

2. Experimental

2.1. *Materials and instruments*

Starting cluster compounds $K_4[Re_4Q_4(CN)_{12}]\cdot nH_2O$ (Q = S, Se, $n = 6$; Q = Te, $n = 5$) were obtained by reactions of $[Re_4Q_4(TeBr_2)_4Br_8]$ with KCN, as described [12, 13]. KCN, $NdCl_3\cdot 6H_2O$, and 1,10-phenanthroline were used as purchased without purification. Elemental analysis was performed on a Euro EA3000 analyzer. IR spectra from 4000 to 400 cm^{-1} in KBr pellets were recorded on a Bruker Scimitar FTS 2000 spectrometer. Energy dispersion spectroscopy (EDS) was performed on an electron microscope Hitachi TM-3000 equipped by a Bruker Nano EDS analyzer. TG measurements from 25 to 650 °C were carried out on a Netzsch thermal analyzer TG 209 F1. The experiments were performed under helium flow (80 cm^3 min^{-1}) at 20 K min^{-1}; the sample mass was ~5.0 mg.

2.2. *Synthesis and characterization*

2.2.1. Synthesis of 1. $NdCl_3\cdot 6H_2O$ (0.070 g, 0.197 mM) and 1,10-phenanthroline (0.050 g, 0.278 mM) were dissolved in 5 mL of water under moderate heating. Concentrated hydrochloric acid was added dropwise to this mixture until the pH reached ~4, then the solution of $K_4[Re_4S_4(CN)_{12}]\cdot 6H_2O$ (0.050 g, 0.034 mM) in 5 mL of water was added. The resulting dark-brown solution was evaporated to a volume of 3 mL and cooled. Black crystals of **1** were formed, filtered off, and dried in air. Yield: 50 mg (73%). Anal. Calcd (%): C, 35.64; H, 2.39; N, 13.86. Found: C, 35.48; H, 2.40; N, 13.81. EDS found: Re : S = 4.0 : 3.9. IR (cm^{-1}, KBr pellet): ν(CN) 2152 (s), ν(ReS) 421 (m), ν(OH) 3479 (s), 3434 (s), 1616 (s), *phen*H$^+$: 3061 (m), 2926 (m), 1594 (s), 1541 (s), 1467 (m), 1412 (m), 1376 (m), 1284 (m), 1238 (m), 1190 (m), 882 (w), 847 (s), 775 (s), 718 (s), 619 (m).

2.2.2. Synthesis of 2. Black crystals of **2** were obtained using similar procedure, except that $K_4[Re_4Se_4(CN)_{12}]\cdot 6H_2O$ solution was used instead of the $K_4[Re_4S_4(CN)_{12}]\cdot 6H_2O$ solution; the quantities of all reagents were the same. Yield: 53 mg (80%). Anal. Calcd (%): C, 32.55; H, 2.19; N, 12.66. Found: C, 32.65; H, 2.26; N, 12.72. EDS found: Re : Se = 4.0 : 4.0. IR (cm^{-1}, KBr pellet): *ν*(CN) 2148 (s), *ν*(ReS) 423 (m), *ν*(OH) 3495 (s), 3430 (s), 1630 (s), *phen*H$^+$: 1594 (s), 1540 (s), 1493 (m), 1467 (m), 1412 (m), 1375 (m), 1283 (m), 1237 (m), 1190 (m), 882 (m), 848 (s), 775 (m), 718 (s), 618 (m).

2.2.3. Synthesis of 3. Black needle crystals of **3** were obtained using similar procedure, except that $K_4[Re_4Te_4(CN)_{12}]\cdot 5H_2O$ solution was used instead of the $K_4[Re_4S_4(CN)_{12}]\cdot 6H_2O$ solution; the quantities of all reagents were the same. Yield: 48 mg (71%). Anal. Calcd (%): C, 28.99; H, 2.27; N, 11.27. Found: C, 29.11; H, 2.40; N, 11.34. EDS found: Re: Te = 4.0 : 4.0. IR (cm^{-1}, KBr pellet): *ν*(CN) 2138 (s), 2130 (m), *ν*(ReS) 428 (m), *ν*(OH) 3377 (s), 1614 (s), *phen*H$^+$: 1594 (s), 1539 (s), 1467 (m), 1410 (m), 1375 (m), 1281 (m), 1233 (m), 1190 (m), 1139 (m), 880 (m), 850 (s), 776 (m), 718 (s), 618 (m).

2.2.4. Syntheses using a layering technique. For completeness, the reactions between neutral aqueous solutions of Nd^{3+} salt, *phen,* and $[Re_4Q_4(CN)_{12}]^{4-}$-containing salts were performed. Addition of Nd-phen solutions (2 : 1 or less) to solutions of $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se) gave no crystalline products even when a slow mixing (layering technique) was used. In the case of $[Re_4Te_4(CN)_{12}]^{4-}$, layering followed by cocrystallization yielded known polymeric compound (*phen*H)[{Nd(H$_2$O)$_2$(*phen*)$_2$}{Re$_4$Te$_4$(CN)$_{12}$}]·11H$_2$O [16]. The compound was synthesized in a thin glass tube constricted in the middle according to the following procedure. $NdCl_3\cdot 6H_2O$ (0.040 g, 0.112 mM) and 1,10-phenanthroline (0.020 g, 0.111 mM) were dissolved in 4 mL of water. This solution was then layered under 4 mL of an aqueous solution containing 0.020 g (0.011 mM) of $K_4[Re_4Te_4(CN)_{12}]\cdot 5H_2O$. Four days later, red-brown, needle-shaped crystals suitable for X-ray investigation were formed in the middle of the tube. The crystals were separated manually, washed with a small amount of distilled water, and dried on filter paper. Yield: 8 mg (40%). EDS found: Nd : Re : Te = 1.0 : 4.6 : 4.1. IR (cm^{-1}, KBr pellet): *ν*(CN): 2137s. All bands related to the organic ligand are observed. Anal. Calcd (%): C, 23.6; H, 2.1; N, 9.6. Found: C, 23.2; H, 2.1; N, 10.1.

2.3. *X-ray crystallography*

Crystal structures of the title compounds were solved by single-crystal X-ray diffraction analysis. Suitable crystals were selected from the mother liquors, fixed to the tips of glass fibers with epoxy resin, and mounted on a Bruker-Nonius X8 Apex 4 K CCD diffractometer (graphite monochromated MoKα radiation, $\lambda = 0.71073$ Å). The data were collected at 150(2) K by the standard technique. Data reduction and multi-scan absorption were carried out using SADABS [17]. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL software package [17]. All nonhydrogen atoms were refined anisotropically. Hydrogens of *phen*H$^+$ cations (except on nitrogen) were located geometrically and refined as riding. Hydrogens on N of *phen*H$^+$ were located in the electron density maps and refined as riding. Hydrogens of lattice water were not located. Crystallographic data and refinement details are given in table 1. The main bond distances and angles, as well as the parameters of hydrogen bonding and π–π and C–H···π stacking interactions, are listed in tables S1–S8 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.997719).

3. Results and discussion

3.1. *Synthesis*

Due to the ambidentate nature of apical cyano-groups, the $[Re_4Q_4(CN)_{12}]^{4-}$ cluster anions in combination with transition [18] or post-transition metal cations can be effectively used for construction of coordination polymers. Particularly, formation of polymeric compounds based on the tetranuclear rhenium cluster anions and 4f-metal cations have been studied over the past decade [19–21]. About 30 compounds containing Ln^{3+} (Ln = Eu, Gd, Tb, Dy, and other) were reported. In a typical synthetic procedure, aqueous solutions of $K_4[Re_4Q_4(CN)_{12}]\cdot nH_2O$ and $LnCl_3\cdot nH_2O$ were used. The acidic media (with HCl added) were used to prevent hydrolysis and precipitation of the $LnCl_3$ salts. The hydrolysis can also be prevented in neutral or basic media through addition of polydentate ligands, due to the formation of stable complex moieties. Investigation of the systems containing tetranuclear cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ and cationic lanthanide complexes with polydentate organic ligands started a few years ago. It was reported that in the systems containing the $[Re_4Te_4(CN)_{12}]^{4-}$, Nd^{3+}, and hexafluoroacetylacetonate (*hfac*), 2,2′-bipyridine (2,2′-*bpy*) or 1,10-phenanthroline (*phen*) as ligands, the formation of polymeric compounds (based on CN–Nd–NC bridges) is possible [16]. It is interesting to note that *phen* was found in the inner coordination sphere of Nd^{3+}, while *hfac* and 2,2′-*bpy* did not enter the structures.

The reactions between aqueous solutions of $[Re_4Q_4(CN)_{12}]^{4-}$-containing salts and Nd–*phen* cationic complexes occur very rapidly. X-ray amorphous brown solids are usually precipitated during these processes even when a slow mixing of reagents (layering technique) is used. In the present work, acidification of the reaction medium was supposed to slow these reactions and to prevent rapid formation of amorphous powders. It was found that even in moderate acidic environment (pH 4–5), the ionic salts **1–3** having four *phen*H$^+$ cations per cluster anion were crystallized in high yields. These salts can be easily dissolved under heating in the mother liquor and recrystallized. The control reactions carried out without the addition of $NdCl_3$ led to the rapid precipitation of amorphous powders having various amounts of phenanthroline (according to elemental analysis). Although the lanthanides are “hard” elements, which tend to bind preferably to “hard” O-donor ligands, the Ln^{3+} complexes with polydentate N-donor ligands are also known to possess good stability in aqueous solutions [22]. It can be assumed that the role of Nd^{3+} cations in formation of soluble crystalline products **1–3** resides in decreasing the reaction rate through formation of mixed-ligand complexes with *phen* and water. Accordingly, upon crystallization, the reversible dissociation of the $[Nd(H_2O)_x(phen)_y]^{3+}$ complexes followed by protonation of *phen* molecules may take place. This hypothesis can explain the solubility of **1–3** in the mother liquor, but it needs to be further studied using solution chemistry methods. Use of an acidic medium suppressed formation of coordination polymers similar to those described [16].

Table 1. Crystal data, data collection, and refinement parameters for **1–3.**

Empirical formula	$C_{60}H_{48}N_{20}O_6Re_4S_4$	$C_{60}H_{48}N_{20}O_6Re_4Se_4$	$C_{60}H_{56}N_{20}O_{10}Re_4Te_4$
Formula weight	2018.22	2205.82	2472.45
Crystal size (mm)	0.20 × 0.17 × 0.10	0.27 × 0.12 × 0.06	0.12 × 0.12 × 0.05
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2/n$	P-1	$C2/c$
a (Å)	12.1591(9)	11.6723(3)	28.7013(11)
b (Å)	11.7193(8)	12.2307(3)	15.4684(6)
c (Å)	22.090(2)	22.1430(5)	18.4912(8)
α (°)		93.4870(10)	
β (°)	93.667(2)	91.4560(10)	122.0610(10)
γ (°)		90.7480(10)	
Volume (Å^3)	3141.4(4)	3153.93(13)	6957.3(5)
Z	2	2	4
D_{Calcd} (g cm^{-3})	2.134	2.323	2.360
Absorption coeff. (mm^{-1})	7.884	10.029	8.652
F(0 0 0)	1920	2064	4567
θ range (°)	1.97–27.52	1.67–27.50	2.30–27.53
h, k, and l ranges	$-15 \le h \le 15$, $-15 \le k \le 12$, $-23 \le l \le 28$	$-15 \le h \le 15$, $-15 \le k \le 15$, $-17 \le l \le 28$	$-29 \le h \le 37$, $-17 \le k \le 20$, $-24 \le l \le 24$
Reflections collected	22,467	24,366	26,677
Unique reflections	7212	14,194	7983
Observed reflections [$I > 2\sigma(I)$]	6501	11,502	5901
Parameters refined	430	847	442
$R[F^2 > 2\sigma(F^2)]$	$R_1 = 0.0490$, $wR_2 = 0.1130$	$R_1 = 0.0335$, $wR_2 = 0.0710$	$R_1 = 0.0311$, $wR_2 = 0.0515$
$R(F^2)$ (all data)	$R_1 = 0.0562$, $wR_2 = 0.1151$	$R_1 = 0.0476$, $wR_2 = 0.0757$	$R_1 = 0.0590$, $wR_2 = 0.0646$
Goodness-of-fit on F^2	1.272	0.983	0.956
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	2.741, −4.151	1.803, −1.885	1.082, −0.912

3.2. *IR spectroscopy*

Complete IR spectra of **1–3** and the enlarged fragments in the range 2300–2000 cm^{-1} are shown in figures S1 and S2 (Supplemental data). The IR spectra of all previously reported hydrated salts $X_4[Re_4Q_4(CN)_{12}]\cdot nH_2O$ display only one CN stretch, despite the presence of two or more crystallographically independent CN-groups involved in hydrogen bonding (see for example $K_4[Re_4STe_3(CN)_{12}]\cdot 4H_2O$, $\nu(CN^-) = 2137\ cm^{-1}$ [12], and $K_4[Re_4Se_4(CN)_{12}]\cdot 6H_2O$, $\nu(CN^-) = 2157\ cm^{-1}$ [13]). We suppose that the energy of the $OH\cdots N$ hydrogen bonds is too small to have a visible influence on the CN stretch positions. Therefore, the presence of two bands in the IR spectrum of **3** is a quite unusual case. We have no acceptable explanation for this result.

The solid-state luminescence was also measured for **1–3**. In contrast to numerous octahedral $\{Re_6Q_8\}$ cluster complexes, photoluminescence was not observed for the reported tetranuclear species.

3.3. *Crystal structures*

In the structures of **1–3**, $[Re_4Q_4(CN)_{12}]^{4-}$ anions have a geometry similar to that in the starting and related compounds [12–15]. Therefore, the discussion of their geometrical characteristics has been omitted for the sake of brevity. Selected bond lengths and angles for cluster anions are given in the Supplemental data (tables S1–S3).

Compound **1** crystallizes in the monoclinic crystal system with the space group *P*2/*n* and two formula units per unit cell. The asymmetric unit contains half of $[Re_4S_4(CN)_{12}]^{4-}$, two *phen*H^+ cations, and three lattice water molecules (figure 1). All atoms occupy general positions. The structure consists of discrete ions and is stabilized by a complex system of hydrogen bonds (table S4). Each $[Re_4S_4(CN)_{12}]^{4-}$ uses eight CN-groups to form 12 relatively strong $O–H\cdots N_{CN}$ hydrogen bonds ($O\cdots N_{CN}$ distances 2.87–3.06 Å) with lattice water

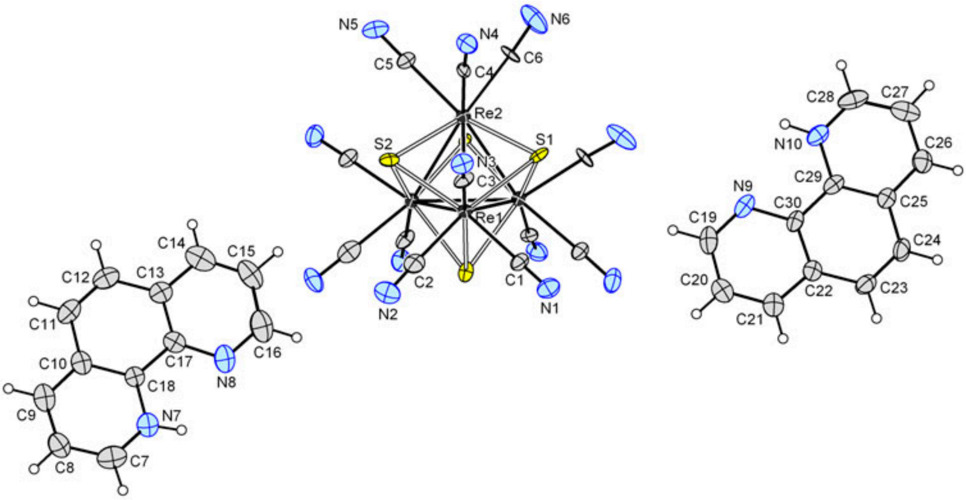

Figure 1. Thermal ellipsoid representation (at the 50% probability level) of the $[Re_4S_4(CN)_{12}]^{4-}$ anion and *phen*H^+ cations in **1**. Solvate water molecules are not shown for clarity. Unlabelled atoms of the anion are related by the symmetry operation: ½ − *x*, *y*, ½ − *z*.

molecules. The water molecules are involved in N_{phen}–H···O hydrogen bonds with *phen*H^+. The formation of O–H···N_{phen} hydrogen bonds, although possible, is unlikely because the water molecules provide all their hydrogens for the more favorable bonding with CN-groups of the cluster anions. Assignment of protons to *phen*H^+ was made through the analysis of short N_{phen}···O contacts and is not unambiguous. Hence, within at least one of the two crystallographically independent *phen*H^+ cations, the H^+ is probably disordered between two N sites, which makes the N_{phen}–H···O bonding scheme more complicated and raises the upper limit of the N_{phen}···O distances. The latter ranges from 2.73 to 3.00 Å. As a result of multiple hydrogen bonds, 2-D layers parallel to the (101) plane are formed (figure 2). Taking into account the large number of aromatic rings in the structure, one can anticipate the appearance of extensive π–π and C–H···π stacking interactions between *phen*H^+ cations. Indeed, the planes of *phen*H^+ are oriented almost parallel to each other (and perpendicular to the plane of a layer) that provides an effective interconnection of adjacent layers. The distances between the phenanthroline planes are 3.4 Å (figure S3, table S8).

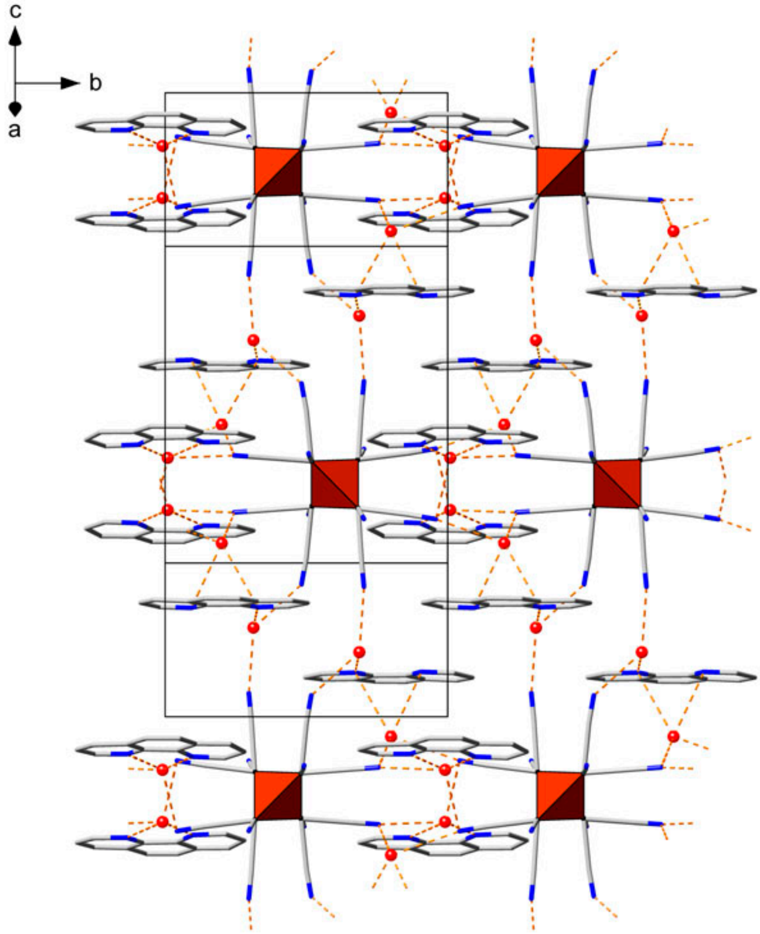

Figure 2. (101) Projection of a layer in the structure of **1**, showing hydrogen bonding (dashed lines) between $[Re_4S_4(CN)_{12}]^{4-}$, *phen*H^+, and H_2O molecules. Cluster anions are depicted as tetrahedra with sulfur omitted for clarity.

Compound **2** crystallizes in the triclinic crystal system with space group *P*-1 and two formula units per unit cell. Although **2** has the same chemical composition (except for the Se in place of S) as that of **1** and similar unit cell metrics, it exhibits lower symmetry (triclinic) and is not isostructural with **1**. Consequently, the asymmetric unit of **2** consists of the whole $[Re_4Se_4(CN)_{12}]^{4-}$ anion, four *phen*H^+ cations and six lattice waters. All atoms occupy general positions. The differences between the structures of **1** and **2** are minimal and are only reflected in some geometrical characteristics. The 2-D layers are extended parallel to the (011) plane and have topology almost identical to that of **1** (figure 3). The $O\cdots N_{CN}$ and $N_{phen}\cdots O$ distances vary in the intervals 2.87–3.13 and 2.72–3.13 Å, respectively (table S5). The *phen*H^+ planes are oriented almost parallel to each other (perpendicular to the layer). The distances between the planes are 3.4 Å (figure S3, table S8). In our opinion, the reasons for nonisostructurality between **1** and **2** can be explained as the cumulative effect of subtle changes in the system of weak interactions (hydrogen bonds, π–π and

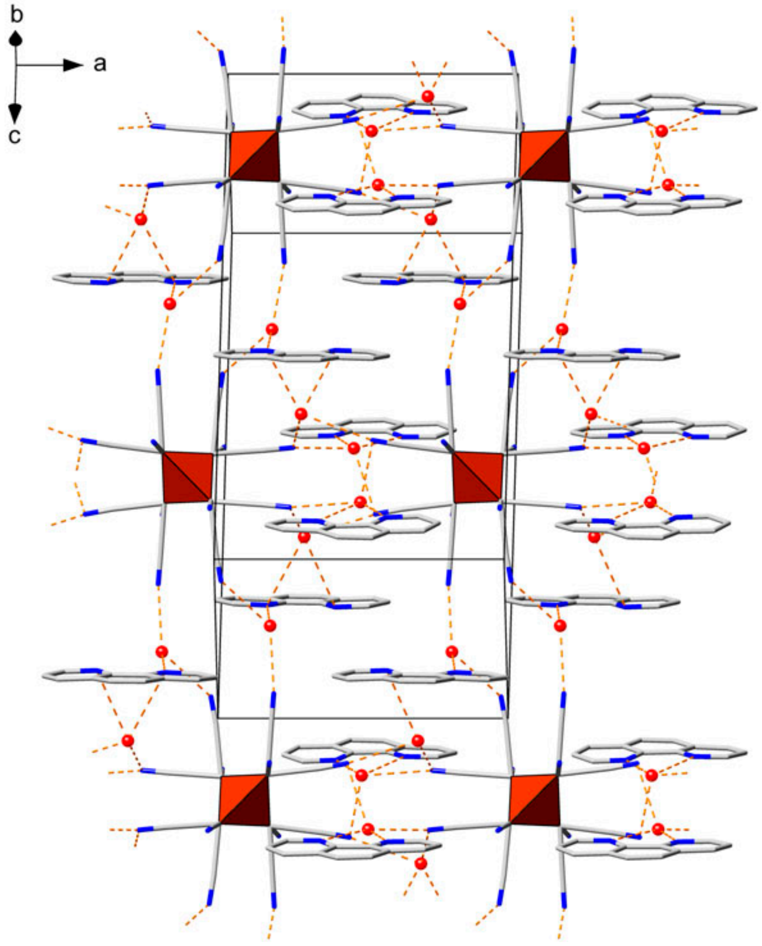

Figure 3. (011) Projection of a layer in the structure of **2**, showing hydrogen bonding (dashed lines) between $[Re_4Se_4(CN)_{12}]^{4-}$, *phen*H^+, and H_2O molecules. Cluster anions are depicted as tetrahedra with selenium omitted for clarity. Note the distortion of the structure caused by lower symmetry as compared to **1**.

C–H···π interactions) which arose from the different chalcogen atoms in the $\{Re_4Q_4\}$ cluster cores. The structures of **1** and **2** show no $H_2O\cdots H_2O$ hydrogen bonds typical of hydrates.

Compound **3** crystallizes in the monoclinic crystal system with space group *C*2/*c* and four formula units per unit cell. The asymmetric unit contains half of the cluster anion $[Re_4Te_4(CN)_{12}]^{4-}$ (the other half is generated by a two-fold axis), two *phen*H$^+$ cations, and five lattice waters. All atoms are in general positions. The structure of **3** differs significantly from those of **1** and **2**; it exhibits a rather complicated 3-D supramolecular architecture based on weak interactions. In contrast to the structures of **1** and **2**, it includes all types of hydrogen bonding possible between the $[Re_4Te_4(CN)_{12}]^{4-}$ anions, *phen*H$^+$ cations, and lattice water molecules (figure 4, table S6). In particular, the $[Re_4Te_4(CN)_{12}]^{4-}$ anion has each of its CN-groups involved in a hydrogen bond with a water molecule ($O\cdots N_{CN}$ distances 2.80–2.91 Å). A large number of O–H···O hydrogen bonds between water molecules are observed with O···O distances ranging from 2.76 to 2.86 Å. The *phen*H$^+$ cations form N_{phen}–H···O hydrogen bonds with water molecules; the $N_{phen}\cdots O$ distances fall in the narrow interval 2.67–2.69 Å. O–H···N_{phen} bonds are probably not present in the structure, but their existence cannot be completely ruled out. The *phen*H$^+$ cations are stacked by four in relatively separate groups due to the π–π and C–H···π interactions with mean interplanar distance of 3.5 Å (figure S4, table S8).

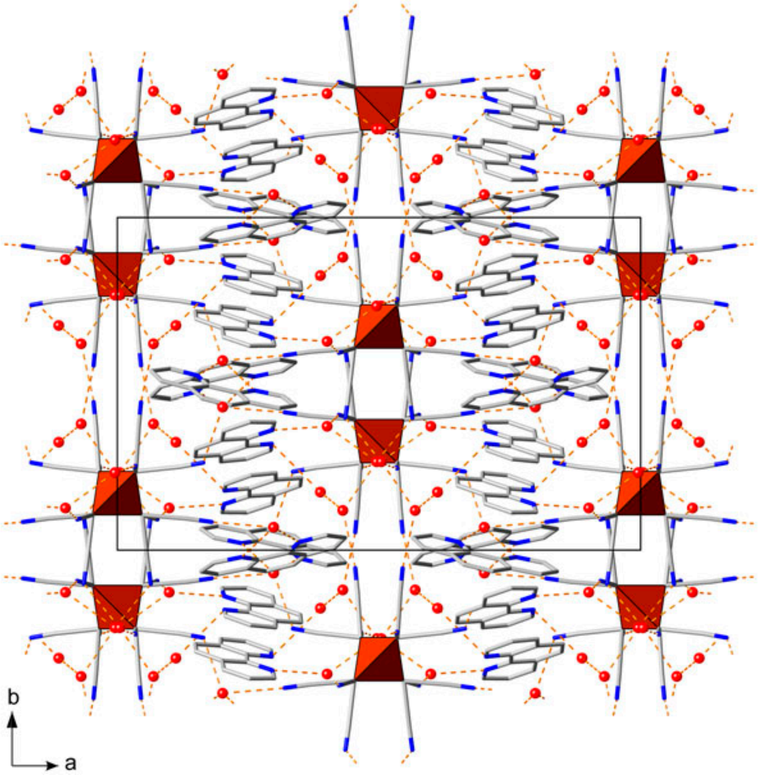

Figure 4. Fragment of the hydrogen-bonded 3-D framework of **3**. $[Re_4Te_4(CN)_{12}]^{4-}$ anions are depicted as tetrahedra with tellurium omitted for clarity.

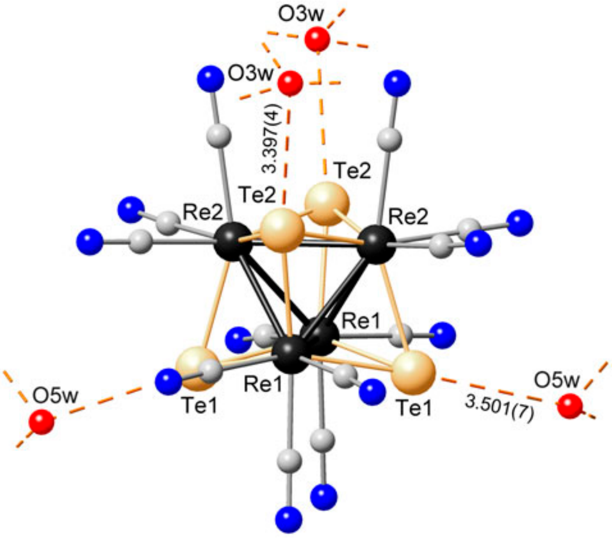

Figure 5. Close-up view of the arrangement of H_2O molecules around $[Re_4Te_4(CN)_{12}]^{4-}$ in the structure of **3**, distinguishing close O···Te contacts (dashed lines). Distances are given in Å.

The most interesting feature of the structure of **3** is the close contacts between telluride ligands of the cluster anions and water molecules, which may indicate the presence of weak hydrogen bonding interactions. Each $[Re_4Te_4(CN)_{12}]^{4-}$ is involved in four such contacts with the O···Te distances of 3.40 and 3.50 Å (figure 5), shorter than the sum of the corresponding van der Waals radii (3.6 Å [23]). A literature survey shows that similar O···Te contacts are observed, although rarely, in the structures of various organic/inorganic tellurides which contain crystal waters or other polar solvent molecules. For instance, in the structure of $(Ph_4P)_2Te_4{\cdot}2MeOH$ [24], the methanol molecules are attached through weak hydrogen bonds (O···Te 3.585(7) Å) to both ends of the zigzag polyanion Te_4^{2-}. In a series of hydrated tellurostannates which contain $[SnTe_4]^{4-}$ [25], the O···Te interactions are characterized by values of 3.5–3.7 Å. Finally, the structures of $[K_2(MeOH)_6][PPh_4]_2[Sn_2Te_6]$, $[AsPh_4][TePh(H_2O)_{0.5}]$, and $[AsPh_4]_2[Te_4(H_2O)_2]$ [26] demonstrate O···Te distances falling in the intervals 3.48–3.58, 3.65–3.74, and 3.63–3.70 Å, respectively. Therefore, the O···Te distance of 3.40 Å in **3** is the shortest of those reported in the literature to date. This can be explained by the extensive hydrogen bonding in the structure of **3**, resulting in close approach of some water molecules to the telluride ligands (packing effects), and/or by the electron density distribution around the telluride ligands bridging three less electronegative Re ions.

3.4. *Thermogravimetric data*

To confirm the water content and investigate the thermal behavior of **1–3**, thermogravimetric analysis was employed. As seen in figure 6, the decomposition of **1–3** proceeded in three main stages. In the first stage, the water molecules are lost. The corresponding temperature ranges are 35–125, 45–160, and 30–130 °C for **1–3**, respectively. The total mass losses in this step (5, 4.5, and 7%) correlate well with the amounts of water found by X-ray

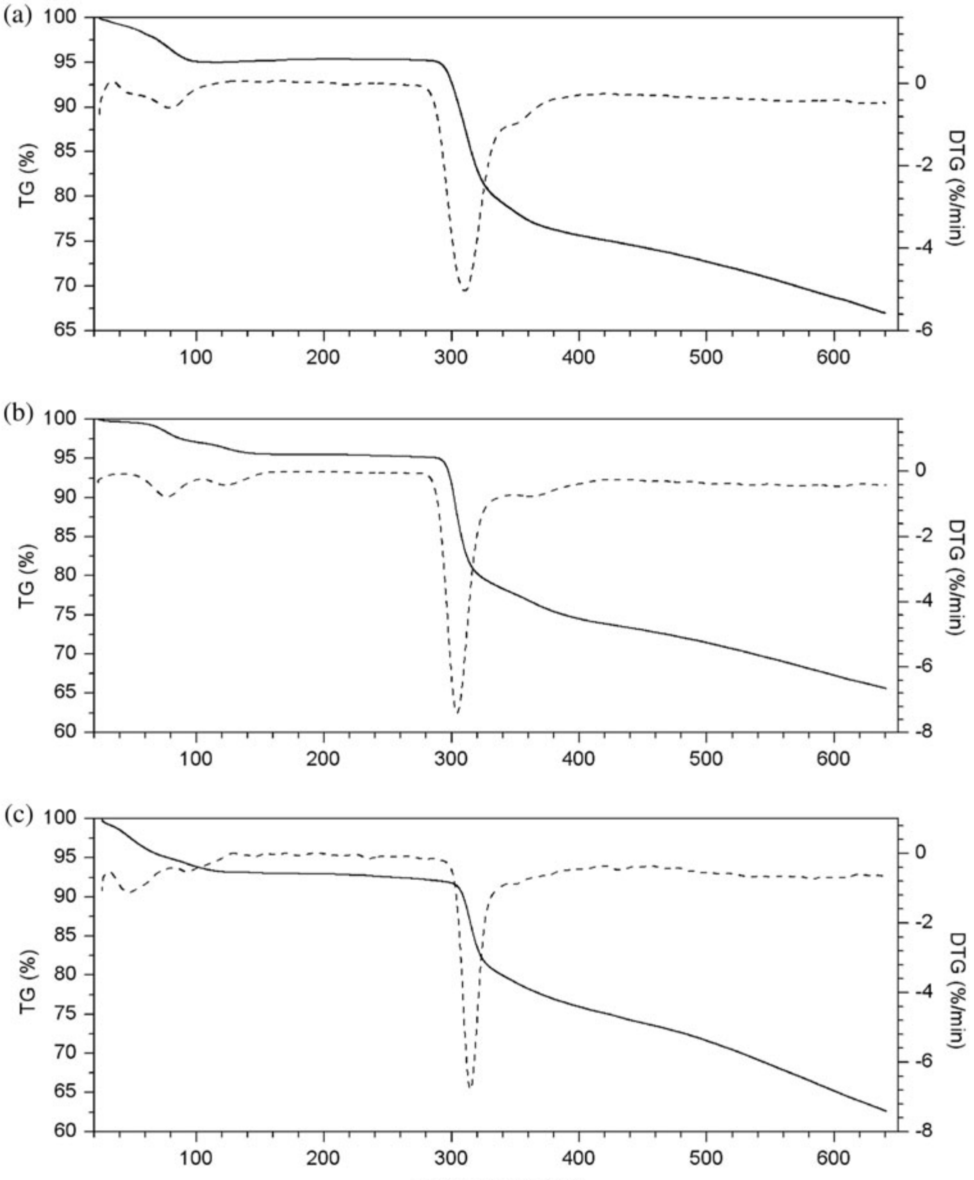

Figure 6. TG and DTG diagrams for (a) **1**, (b) **2**, and (c) **3**.

crystallography and elemental analyses (5.3, 4.9, and 7.2%, respectively). After removal of water, the compounds show no decomposition to 280 °C. The second stage corresponds to decomposition of organic part of the compounds. The most intensive mass loss starts at 275, 280, and 290 °C for **1–3**, respectively. The decomposition rates at this stage are rather different for the structurally related **1** and **2** (compare maximum rates of 5.0% min^{-1} at 310 °C for **1** and 7.4% min^{-1} at 304 °C for **2**). Maximum weight loss rate for **3** is

6.8% min^{-1} at 315 °C. The period of intensive decomposition is finished at 410 °C for **1** and 420 °C for **2** and **3**. At these temperatures, the total mass losses are 25, 26, and 25%, which correspond to decomposition of 2.2, 2.7, and 2.3 phenanthroline molecules for **1–3**, respectively. In addition, from the DTG curves, it is found that there are two consecutive steps in the first and the second stages, respectively, but there are no clear plateaus in the TG curves, indicating that the intermediates are unstable. The last stage is characterized by a permanent mass reduction until the end of the experiments (650 °C) and surely proceeds above this temperature. This stage is most likely associated with pyrolysis and carbonization of the rest of the phenanthroline molecules accompanied by decomposition of the cluster core. The residual weight losses at 650 °C are 32, 35, and 38%, which correspond to the decomposition of 3.0, 3.7, and all four phenanthroline molecules for **1–3**, respectively. These values cannot be attributed only to decomposition of phenanthroline, because it is not clear how much organic carbon remains in the crucible in the elementary form and as rhenium carbide. Thus, one can see that although all three compounds have generally similar structures stabilized by hydrogen bonds and π–π interactions, the behavior of their thermal decomposition is not uniform. Finally, it is worth noting that the related polymeric compound (*phen*H)[$\{\mathrm{Nd(H_2O)_2}(phen)_2\}\{\mathrm{Re_4Te_4(CN)_{12}}\}$]$\cdot 11\mathrm{H_2O}$ [16] showed similar decomposition. The removal of water from the voids is observed at 20–120 °C. The weight loss of 8.2% corresponds exactly to 11 water molecules per formula unit. After this, there is a slow weight loss of 2.6% that could be associated with the loss of coordinated water, which is then followed by a permanent mass reduction until the temperature reaches 580 °C. The latter is most likely associated with the decomposition of phenanthroline molecules.

4. Conclusion

Three new ionic complexes of $[\mathrm{Re_4Q_4(CN)_{12}}]^{4-}$ (Q = S, Se, and Te) and 1,10-phenanthroline-1-ium cations (*phen*H^+) have been synthesized and characterized. Addition of Nd^{3+} to the reaction mixtures was used. The latter appeared to be the key factor which directed the formation of **1–3** instead of precipitation of amorphous solids of variable composition. It is assumed that the influence of Nd^{3+} on the formation of **1–3** resides in decreasing the reaction rate through formation of mixed-ligand complexes $[\mathrm{Nd(H_2O)}_x(phen)_y]^{3+}$. Compounds **1–3** display supramolecular architectures based on hydrogen bonds between lattice water molecules, *phen*H^+ cations, and CN-groups of the cluster anions. The π–π and C–H···π stacking interactions play a significant role in the stabilization of the structures. The structure of **3** reveals close O···Te contacts between water molecules and telluride ligands of the cluster anions, indicating weak hydrogen bonds. The O···Te distance of 3.40 Å in **3** is the shortest distance of this type reported to date.

Supplementary material

The complete crystallographic data for **1–3** have been deposited with the Cambridge Crystallographic Data Center under the reference numbers CCDC 992521–992523, respectively. These data can be obtained free of charge from CCDC via www.ccdc.cam.ac.uk/data_request/cif.

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