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A family of three-dimensional porous coordination polymers with general formula $(Kat)_2[\{M(H_2O)_n\}_3\{Re_6Q_8(CN)_6\}_2]\cdot xH_2O$ $(Q=S, Se;\ n=1.5, 2)$☆

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Abstract

The X-ray crystal structures of a series of new compounds $(H_3O)_2[\{Mn(H_2O)_{1.5}\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 19H_2O$ (**1**), $(Me_4N)_2[\{Co(H_2O)_{1.5}\}_3\{Re_6S_8(CN)_6\}_2]\cdot 13H_2O$ (**2**), $(Me_4N)_2[\{Co(H_2O)_{1.5}\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 3H_2O$ (**3**), $(Et_4N)_2[\{Mn(H_2O)_2\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 6.5H_2O$ (**4**), $(Et_4N)_2[\{Ni(H_2O)_2\}_3\{Re_6S_8(CN)_6\}_2]\cdot 6.5H_2O$ (**5**), and $(Et_4N)_2[\{Co(H_2O)_2\}_3\{Re_6S_8(CN)_6\}_2]\cdot 10H_2O$ (**6**) are reported. All six compounds are isostructural crystallizing in cubic $Im\bar{3}m$ space group with four formulae per unit cell. For compounds **1**, **3**–**5** the following parameters were found: (**1**) $a = 19.857(2)$ Å, $R1 = 0.0283$; (**3** at 150 K) $a = 19.634(1)$ Å, $R1 = 0.0572$; (**4**) $a = 20.060(2)$ Å, $R1=0.0288$; (**5**) $a=19.697(2)$ Å, $R1 = 0.0224$. The structures consist three-dimensional cyano-bridged framework formed by cyano cluster anions $[Re_6Q_8(CN)_6]^{4-}$, $Q = S$, Se and transition metal cations, $M^{2+} = Mn^{2+}$, Co^{2+}, Ni^{2+}. Water molecules and large organic cations Me_4N^+ and Et_4N^+ are included in cavities of this framework. Porosity of the framework, its ability to accommodate different cations and water molecules by little changes in the structure, as well as distortion of coordination framework under loss of water of crystallization is discussed.

Keywords: Rhenium; Octahedral cluster; Cyanide; Coordination framework; Transition metals

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1. Introduction

In recent years there has been a great deal of interest in the use of molecular species as precursors for the formation of organic and organic–inorganic materials [1–4]. Transition metal cyanides were widely used for these purposes. Ambidentate nature of CN^- and stability of cyanometallate complexes make transition metal cyanides convenient building blocks, while wide variety of coordination numbers (from two in $[Ag(CN)_2]^-$ to eight in $[Mo(CN)_8]^{4-}$) and of arrangement of metal centers favor to formation a diversity of coordination arrays (see e.g., reviews [5–7]). The most famous examples of these compounds are Prussian Blue and their analogues [8–10], and Hoffman clathrates [11–14]. 3D framework of Prussian Blue type compounds contains large cavities enough for including water molecules, large inorganic cations (up to Cs^+) and small neutral organic molecules. Zeolitic and ion exchange properties [15–17] as well as magnetic properties [18–20] of above compounds are well known.

Discovery of octahedral rhenium chalcocyanide complexes $[Re_6Q_8(CN)_6]^{4-}$ ($Q=S$, Se, Te) (Fig. 1) 5–8 years ago [21–24] have excited interest to them as to potential building blocks which are able to coordinate to metal cations forming extended cyano-bridged fragments $\cdots-NC-Re_6Q_8-CN-M-\cdots$ [25]. Since that time a numerous contributions from Long's group [26–28], Kim's [29–31] and ours [32–36], devoted to synthesis, structural studies and some properties of such compounds have appeared. Topological similarity of the

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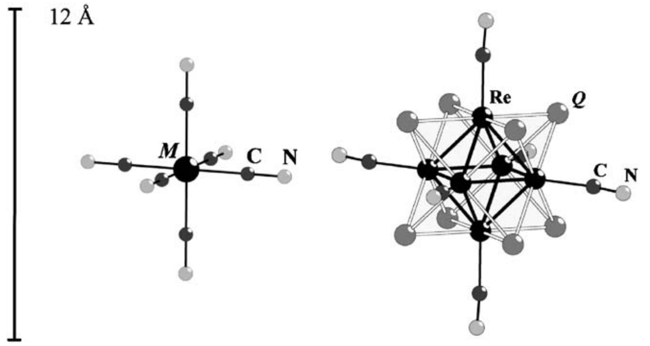

Fig. 1. Octahedral cyanide cluster complex $[Re_6Q_8(CN)_6]^{4-}$ (right) in comparison with mononuclear cyanide complex $[M(CN)_6]^{4-}$ (left).

cluster complexes $[Re_6Q_8(CN)_6]^{4-}$ and octahedral mononuclear cyanide complexes $[M(CN)_6]^{4-}$ allows to synthesize coordination polymers with crystal structures analogous to mononuclear cyanometallates [27,37] but with larger cavities, and channels due to larger size of cluster complexes.

In our first paper on cyanometallates based on cluster complexes [25], we reported synthesis of solids $Cs_2Mn_3[Re_6Se_8(CN)_6]_2 \cdot 15H_2O$ and $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2 \cdot 14.5H_2O$ from aqueous solutions. The structures include coordination frameworks built from $[Re_6Se_8(CN)_6]^{4-}$ and M^{2+}. In this paper, six new coordination solids with similar framework motif were obtained from aqueous solutions. When Me_4N^+ or Et_4N^+ was added to reaction mixture an inclusion of these cations into the framework was observed.

2. Experimental

2.1. Physical measurements

Elemental analyses for C, H, N, S (Carlo Erba 1106) were performed in the Laboratory of Microanalysis of the Institute of Organic Chemistry, Novosibirsk. Infrared spectra were measured on KBr disks with Bruker IFS-85 spectrometer. For determination of water the curves of mass losses and TGD curves of the compounds were recorded at the heating rate of 3°C/min (temperature range 20–300°C) in the atmosphere of an inert gas (Ar) with a TGD-7000 RH thermal analysis controller (Sinku-Riku, Japan). Magnetic measurements were performed using SQUID magnetometer Quantum Design, field 5 kOe. X-ray powder diffraction data (XPD) were obtained with Philips APD 1700 powder diffractometer with silicon as internal standard (step, 0.03°; sample time, 0.5 s; 2ϑ range, 5–60°; radiation, Cu*K*α).

2.2. Syntheses

Starting cluster compounds $Cs_3K[Re_6S_8(CN)_6] \cdot 2H_2O$ and $K_4[Re_6Se_8(CN)_6] \cdot 3.5H_2O$ were prepared from polymeric $Re_6S_8Br_2$ [38] and $Re_6Se_8Br_2$ [39]. All other reagents were employed as received. Individuality of crystalline powder samples was ascertained by X-ray powder diffractometry.

2.2.1. Preparation of $(H_3O)_2[\{Mn(H_2O)_{1.5}\}_3\{Re_6Se_8(CN)_6\}_2] \cdot 19H_2O$ (**1**)

The solution of $K_4[Re_6Se_8(CN)_6] \cdot 3.5H_2O$ [23] (1.00 g, 0.470 mmol) in 20 mL of water with acetic acid (pH 2–3) and the solution of $Mn(NO_3)_2 \cdot 6H_2O$ (0.357 g, 1.24 mmol) in 10 mL of H_2O were mixed and the mixture volume was reduced by slow evaporation to 1 mL. Crystals of product **1** were separated by filtration, washed with water and then air dried. Yield of **1**: 1.022 g (95%). X-ray: Sp. gr. $Im\bar{3}m$, $a = 19.857(2)$ Å. Found (Calcd.) for $C_{12}H_{53}N_{12}O_{25.5}Se_{16}Mn_3Re_{12}$, %: C, 3.40 (3.25); H, 0.90 (1.20); N, 4.11 (3.79); H_2O, 11.0 (10.7). IR(KBr), CN 2134 cm^{-1}. μ_{eff} (295 K) 17.85 μ_B (5.95 μ_B per Mn). Red–orange cube-like crystals can readily loose some water molecules. Partially dehydrated compound is crystallized in $R\bar{3}c$ space group and isostructural to $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2 \cdot 14.5H_2O$ [25].

2.2.2. Preparation of $(Me_4N)_2[\{Co(H_2O)_{1.5}\}_3\{Re_6S_8(CN)_6\}_2] \cdot 13H_2O$ (**2**)

The hot aqueous solution of 0.517 g (0.258 mmol) of $Cs_3K[Re_6S_8(CN)_6] \cdot 2H_2O$ [32] was added to 10 mL of hot aqueous solution of 0.045 g (0.292 mmol) of Me_4NBr and 0.092 g (0.388 mmol) of $CoCl_2 \cdot 6H_2O$ in 10 mL of H_2O and boiled for 1 h. Orange fine powder of **2** was filtered, washed with water and then air dried. Yield: quantitative. XPD: Sp. gr. $Im\bar{3}m$, $a = 19.513[5]$ Å. Found (Calcd) for $C_{40}H_{59}N_{14}O_{17.5}S_{16}Co_3Re_{12}$, %: C, 6.16 (6.49); H, 1.20 (1.61); N, 4.70 (5.30); H_2O 300°C, 8.3. IR (KBr), CN 2154 cm^{-1}. μ_{eff} (295 K) 14.61 μ_B (4.87 μB per Co).

2.2.3. Preparation of $(Me_4N)_2[\{Co(H_2O)_{1.5}\}_3\{Re_6Se_8(CN)_6\}_2] \cdot 3H_2O$ (**3**)

The hot aqueous solution of 0.550 g (0.259 mmol) of $K_4[Re_6Se_8(CN)_6] \cdot 3.5H_2O$ [23] in 10 mL was added to a hot aqueous solution of 0.045 g (0.292 mmol) of Me_4NBr and 0.092 g (0.388 mmol) of $CoCl_2 \cdot 6H_2O$ in 10 mL of H_2O and stirred for 1 h. Orange fine powder of **3** was filtered, washed with water and then air dried. X-ray: Sp. gr. $Im\bar{3}m$, $a = 19.634(1)$ Å. XPD: $a = 19.582[2]$ Å. Yield—0.525 g (95%). Found (Calcd) for $C_{20}H_{48}N_{14}O_{7.5}Se_{16}Co_3Re_{12}$, %: C, 6.16 (5.63); H, 1.15 (0.92); N, 4.70 (4.59); H_2O 197°C, 3.5. IR(KBr), CN 2140 cm^{-1}. μ_{eff} (295 K) 14.7 (4.90 μ_B per Co).

2.2.4. Preparation of $(Et_4N)_2[\{Mn(H_2O)_2\}_3\{Re_6Se_8(CN)_6\}_2] \cdot 6.5H_2O$ (**4**)

1 (0.200 g (0.045 mmol)) was stirred in 20 mL of hot 0.1 M aqueous solution of Et_4NBr for 2 h. Resulting orange powder was separated by filtration, washed with water and then air dried. Yield—quantitative. X-ray: Sp. gr. $Im\bar{3}m$, $a = 20.060(2)$ Å. XPD: $a = 20.180[1]$ Å. Found (Calcd) for $C_{28}H_{65}N_{14}O_{12.5}Se_{16}Mn_3Re_{12}$, %: C, 7.60 (7.83); N, 4.52 (4.56); H, 1.55 (1.53); H_2O 230°C, 5.9. IR(KBr), CN $2128\,cm^{-1}$. μ_{eff} (295 K) 17.61 μ_B (5.87 μ_B per Mn).

2.2.5. *Preparation of* $(Et_4N)_2[\{Ni(H_2O)_2\}_3\{Re_6S_8(CN)_6\}_2]\cdot 6.5H_2O$ (**5**)

The hot aqueous solution of 0.550 g (0.274 mmol) of $Cs_3K[Re_6S_8(CN)_6]\cdot 2H_2O$ [32] was added to 10 mL of hot aqueous solution of 0.057 g (0.271 mmol) of Et_4NBr and 0.100 g (0.402 mmol) of $Ni(CH_3COO)_2\cdot 4H_2O$ in 10 mL of H_2O and boiled for 1 h. Orange fine powder of **5** was filtered, washed with water and then air dried. Yield—0.467 g (93%). Sp. gr. $Im\bar{3}m$, $a = 19.697(2)$ Å. Found (Calcd) for $C_{28}H_{65}N_{14}O_{12.5}S_{16}Ni_3Re_{12}$, %: C, 8.98 (9.04); H, 1.85 (1.76); N, 5.17 (5.27); H_2O 250°C, 6.1. IR(KBr), CN $2164\,cm^{-1}$. μ_{eff} (295 K) 9.75 (3.25 μ_B per Ni).

2.2.6. *Preparation of* $(Et_4N)_2[\{Co(H_2O)_2\}_3\{Re_6S_8(CN)_6\}_2]\cdot 10H_2O$ (**6**)

The hot aqueous solution of 0.550 g (0.274 mmol) of $Cs_3K[Re_6S_8(CN)_6]\cdot 2H_2O$ [32] was added to 10 mL of hot aqueous solution of 0.057 g (0.271 mmol) of Et_4NBr and 0.096 g (0.402 mmol) of $CoCl_2\cdot 6H_2O$ in 10 mL of H_2O and boiled for 1 h. Orange fine powder of **6** was filtered, washed with water and then air dried. Yield—0.491 g (95%). Found (Calcd) for $C_{28}H_{76}N_{14}O_{16}S_{16}Ni_3Re_{12}$, %: C, 8.68 (8.88); H, 1.92 (2.02); N, 5.17 (5.18); H_2O 250°C, 8.5. IR(KBr), CN $2143\,cm^{-1}$. μ_{eff} (295 K) 14.85 μ_B (4.95 μ_B per Co).

2.2.7. *Single crystal growth*

Single crystal **1** for structural determination was obtained by slow cooling of hot aqueous solution of **1**. Compounds **3–5** have extremely low solubility, and therefore crystals suitable for X-ray single crystal analysis were grown by diffusion of reagents coming from opposite directions in U-tube filled with silica gel. To prepare of silica gel solution of 12.25 g of $Na_2SiO_3\cdot 9H_2O$ in 50 mL of water was titrated with 20 mL 1 M HCl under vigorous stirring. The resulting mixture was placed into U-tubes and allowed the gel to set for 2 days.

The aqueous solution of mixture of $R_4N^+_{(aq)}$ (0.1 M; R = Me, Et) and $[M(H_2O)_6]^{2+}_{(aq)}$ (0.1 M) and aqueous solution of $[Re_6Q_8(CN)_6]^{4-}_{(aq)}$ (0.1 M) were put into two sections of U-tube. Cross diffusion of reagents through silica gel for 4–6 weeks resulted in single crystals suitable for X-ray single crystal determination. Crystals were located in the middle part of U-tube. The following reagents were used: for **3**: Me_4NBr, $CoCl_2\cdot 6H_2O$, $K_4[Re_6Se_8(CN)_6]\cdot 3.5H_2O$; for **4**: Et_4NBr, $Mn(NO_3)_2\cdot 6H_2O$, $K_4[Re_6Se_8(CN)_6]\cdot 2H_2O$; for **5**: Et_4NBr, $Ni(CH_3COO)_2\cdot 4H_2O$, $Cs_3K[Re_6S_8(CN)_6]\cdot 2H_2O$. Octahedral or cubic crystals can be easily separated from silica gel manually. X-ray powder diffraction and IR spectroscopy revealed identity of these crystals with powder samples.

2.3. *Structural studies of compounds* **1**, **3–5**

Details of structure determinations for compounds **1**, **3–5** are given in Table 1. Crystal data were collected by standard technique on Enraf-Nonius CAD4 (**1**, **4**, **5**) and Siemens SMART CCD (**3**) diffractometers. Absorption corrections were applied using several azimutal scan curves for compounds **1**, **4**, **5** and SADABS [40] program for compound **3**. Structures were solved by direct methods and refined by full-matrix least-squares method on F^2 using SHELX-97 program set [41]. Hydrogen atoms were not located.

All the structures appeared to be disordered. Positions of the disordered water molecules, H_3O^+ and R_4N^+ (R = Me, Et) cations were found on difference electron density maps. The site occupancies were set using information about short contacts between the peaks, refined thermal parameters and chemical analysis data. All compounds have isostructural frameworks and the same atom labeling scheme. The site occupancy for atom O(1) in **1**, **3** was set to 50% according to the short O(1)…O(1)′ contacts (ca. 2 Å). Highly disordered R_4N^+ cations occupy only 1/3 of their positions according to the charge balance and chemical analysis data. Thermogravimetric method gave larger water content compared with structural data in all compounds.

Final atomic coordinates are given in Supplementary (Tables 1–4), selected bond lengths and angles in Table 2.

Framework volumes were calculated using KPACK program [42], 200 test points per 1 Å^3 and the following atomic radii (Å): C, 1.71; N, 1.55; S, 1.80; Se, 2.0; Re, 1.37; Co, Mn, Ni, 1.35.

3. Results and discussion

3.1. *Synthesis of compounds* **1–6**

Coordination polymeric solids **1–6** have been obtained in similar way from reactions of aqueous solution containing Kat^+, $[Re_6Q_8(CN)_6]^{4-}$ and M^{2+}. According to X-ray single crystal and powder data the compounds possess one type of coordination framework, and demonstrate diffractograms which are indexed in cubic $Im\bar{3}m$ space group. Crystals **1** have been obtained from aqueous solution at slow evaporation and with pH 3. Individuality of the phase was proved by XPD. These crystals are unstable in air. We have observed a framework distortion after the crystals were kept for

Table 1
Crystallographic data for compounds $(H_3O)_2[\{Mn(H_2O)_{1.5}\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 19H_2O$ (**1**), $(Me_4N)_2[\{Co(H_2O)_{1.5}\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 3H_2O$ (**3**), $(Et_4N)_2[\{Mn(H_2O)_2\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 6.5H_2O$ (**4**), and $(Et_4N)_2[\{Ni(H_2O)_2\}_3\{Re_6S_8(CN)_6\}_2]\cdot 6.5H_2O$ (**5**)

	1	**3**	**4**	**5**
Formula	$C_{12}H_{53}Mn_3N_{12}O_{25.50}Re_{12}Se_{16}$	$C_{20}H_{48}Co_3N_{14}O_{7.50}Re_{12}Se_{16}$	$C_{28}H_{65}Mn_3N_{14}O_{12.50}Re_{12}Se_{16}$	$C_{28}H_{65}N_{14}Ni_3O_{12.50}Re_{12}S_{16}$
Formula weight	4436.24	4261.13	4460.52	3721.43
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group, Z	$Im\bar{3}m$, 4	$Im\bar{3}m$, 4	$Im\bar{3}m$, 4	$Im\bar{3}m$, 4
a (Å)	19.857(2)	19.634(1)	20.060(2)	19.697(2)
V (Å^3)	7830(1)	7568.8(7)	8072(1)	7642(1)
ρ_{calc} (g cm^{-3})	3.763	3.739	3.670	3.235
μ (mm^{-1})	26.426	27.468	25.622	20.124
Diffractometer	Enraf-Nonius CAD4	Smart CCD detector	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Temperature (K)	298	150	293	293
Crystal size (mm)	$0.24\times0.24\times0.36$	$0.11\times0.11\times0.11$	$0.16\times0.16\times0.12$	$0.16\times0.18\times0.19$
$2\theta_{max}$ (deg)	60	61.3	52	50
Reflections total/unique	4598/1113	29376/1129	3090/784	2924/680
R_{int}	0.1027	0.0593	0.0677	0.0488
$R(F)$, w$R(F^2)$ for $F_{obs}\geqslant 4\sigma(F)$	0.0283, 0.0512	0.0572, 0.1069	0.0288, 0.0526	0.0224, 0.0487
$R(F)$, w$R(F^2)$ for all data	0.0832, 0.0549	0.0622, 0.1081	0.0855, 0.0579	0.0545, 0.0509
GOOF for all data	0.744	1.515	0.686	0.778

Table 2
Main bond distances and angles for compounds **1**, **3–5**

	1 M = Mn, Q = Se	**3** M = Co, Q = Se	**4** M = Mn, Q = Se	**5** M = Ni, Q = S
Bonds				
Re(1)–Re(1)#1	2.6233(8)	2.6308(9)	2.625(1)	2.598(1)
Re(1)–Re(1)#2	2.6266(8)	2.6376(9)	2.629(1)	2.599(1)
Re(1)–Q(1)	2.519(1)	2.525(1)	2.522(2)	2.416(3)
Re(1)–Q(1)#3	2.520(1)	2.528(2)	2.517(2)	2.412(4)
Re(1)–Q(2)	2.509(2)	2.522(2)	2.499(3)	2.395(5)
Re(1)–C(1)	2.11(1)	2.10(2)	2.13(2)	2.12(2)
M(1)–N(1)	2.18(1)	2.10(2)	2.20(2)	2.05(1)
M(1)–O(1)	2.22(4)	2.08(4)	2.19(4)	2.04(3)
M(1)–O(2)	2.29(3)	2.18(6)	2.26(3)	2.17(3)
C(1)–N(1)	1.15(1)	1.16(2)	1.11(2)	1.16(2)
Angles				
N(1)–C(1)–Re(1)	177(1)	180(2)	177(2)	175(2)
C(1)–N(1)–M(1)	168(1)	166(2)	167(2)	170(2)

Symmetry transformations used to generate equivalent atoms: #1: z,x,y; #2: $-z+1/2,-x+1/2,-y+1/2$; #3:$-y+1/2,-z+1/2,-x+1/2$.

1 to 2 h, the crystals were partially dehydrated. Fig. 2 shows two powder diffractograms for the fresh (Fig. 2a) and "aged" (Fig. 2b) products; the pattern b is referred to trigonal coordination framework. The position of the band of bridging CN valent vibration has been shifted from 2134 to 2129 cm^{-1}. The latter value is equal to that of valence ν_{CN} stretch vibration [43] for trigonal crystals $Cs_2Mn_3[Re_6Se_8(CN)_6]_2\cdot 15H_2O$ [25]. "Aged" sample can also be prepared by evaporating of aqueous solution containing $K_4Re_6Se_8(CN)_6\cdot 3.5H_2O$ and $Mn(NO_3)_2\cdot 6H_2O$ in equimolar ratio, with pH 6.

The addition of Et_4NBr to the aqueous solution containing $[Re_6Se_8(CN)_6]^{4-}$ and Mn^{2+} results in formation of orange fine powder, corresponding to the compound **4**. In a similar manner, analogous fine powder samples have been obtained for **2**, **3**, **5**, and **6** with yields close to quantitative. Due to low solubility, the crystals for X-ray structural studies were grown by cross-slow diffusion of aqueous solution in silica gel. XPD reveals correspondence of intensities, positions of reflexes and unit cell parameter a values in experimental and calculated powder diffractograms. The analogous structure of coordination framework for compounds **2** and **6** was ascertained by powder diffractometry; unit cell dimensions calculated from powder data, $a = 19.513[5]$ Å (**2**) and $a = 19.582[2]$ Å (**3**) are quite similar, irrespective to sulfur or selenium in cluster complex.

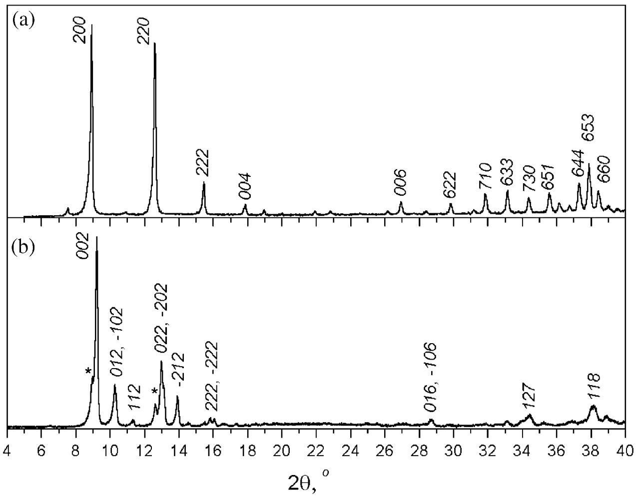

Fig. 2. Powder diffraction patterns of sample $(\mathrm{H_3O})_2[\{\mathrm{Mn(H_2O)_{1.5}}\}_3\{\mathrm{Re_6Se_8(CN)_6}\}_2]\cdot 19\mathrm{H_2O}$ (**1**) freshly obtained (pattern *a*) and "aged" (pattern *b*). Remarks marked with * on (b) are attributed to phase **1**.

Coordination of CN ligands to metal centers leads to shift ν_{CN} stretch vibrations to higher frequency compared with non-coordinated CN ligands in $[\mathrm{Re}_6Q_8(\mathrm{CN})_6]^{4-}$ anions. The values were 2143–2164 cm^{-1} for compounds with $[\mathrm{Re_6S_8(CN)_6}]^{4-}$ (2115 cm^{-1} for non-coordinated anion) and 2128–2140 cm^{-1} for compounds with $[\mathrm{Re_6Se_8(CN)_6}]^{4-}$ (2108 cm^{-1} for non-coordinated anion).

3.2. Description of the crystal structures

All the compounds have similar structural motif, namely, coordination polymeric framework $\{M_3[\mathrm{Re}_6Q_8(\mathrm{CN})_6]_2\}^{2-}_{3\infty}$. N atoms of cyano groups of four different $[\mathrm{Re}_6Q_8(\mathrm{CN})_6]^{4-}$ anionic complexes are coordinated to transition metal cation M^{2+}. In the structures **1**, **3**–**5** asymmetric unit of coordination framework includes Re1, *Q*1, *Q*2, C1, N1, *M*1, O1, and O2 (Fig. 3, the labelling scheme is the same for **1**, **3**–**5**). In the framework each cluster complex forms six cyanobridges to six metal cations M^{2+}. Coordination environment of M^{2+} consists of four nitrogen atoms placed near one plane. Additionally, M^{2+} cations are coordinated by one water molecule or two water molecules in *trans*-position (a discussion on the number of coordinated water molecules is as follows). Fragment of the crystal structure of **1** and its simplified presentation are given in Fig. 4, showing the transition metal cation–cluster anion binding. Such fragments form extended three-dimensional structure (Fig. 4a). The selected cubes are linked to neighboring ones in such a way that each cluster complex is shared by two cubes (Fig. 5). So, three *fac*-cyanogroups of cluster complex belongs to one cube, the rest (three) belong to neighboring cube. One can see that each M^{2+} cation is linked to four clusters, and each cluster is linked to six M^{2+} cations. This type of binding results in formation of negatively charged framework $\{M_3[\mathrm{Re_6Se_8(CN)_6}]_2\}^{2-}_{3\infty}$, Re–CN–*M* fragments being nearly linear (Table 2). Fig. 6a represents extended fragment of the framework, in nine adjusting cubes.

This type of framework can be described as (4,6)-connected net according to the nomenclature used in review [44]. The nodes are: 4—metal cations M^{2+} in planar square environment of four nitrogen atoms of the cluster complexes, and 6—cluster complexes being coordinated to metal cations via six cyanogroups octahedrally arranged.

Two oxygen atoms, O1 and O2, of water molecules in *trans* positions complete the coordination sphere of M^{2+}. The *M*1 atoms together with O1 form linear fragment *M*–O···O–*M* with the crystallographic

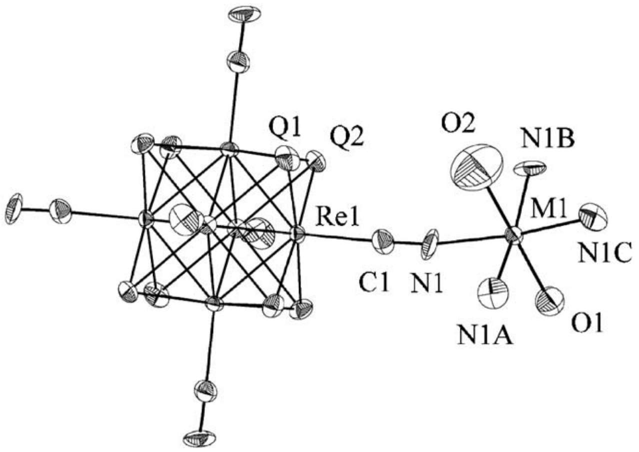

Fig. 3. Asymmetric unit of coordination framework $[\{M(\mathrm{H_2O})_n\}_3\{\mathrm{Re}_6Q_8(\mathrm{CN})_6\}_2]^{2-}_{3\infty}$. The atoms are represented at 50% probability level.

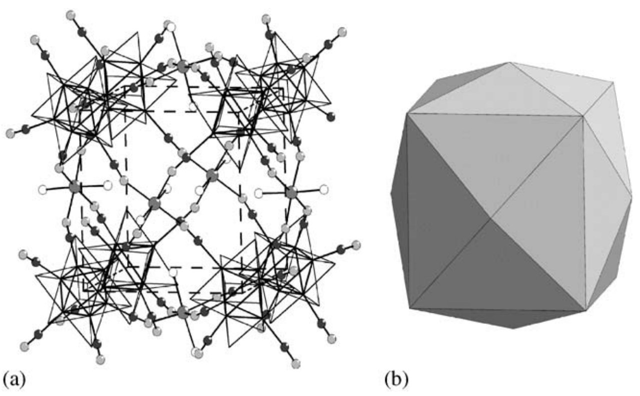

Fig. 4. (a) The coordination of transition metal cations by cluster anions in compounds **1**–**6**. The circles of Re and *Q* are omitted for clarity. The bonds to μ_3-*Q* ligands are shown by thin lines. The selected cube of cluster anions is shown by dashes. (b) Simplified presentation of the selected cube. The centers of cluster anions are the cube's vertices; the centers of *M* atoms are the vertices which are capping the cube's faces.

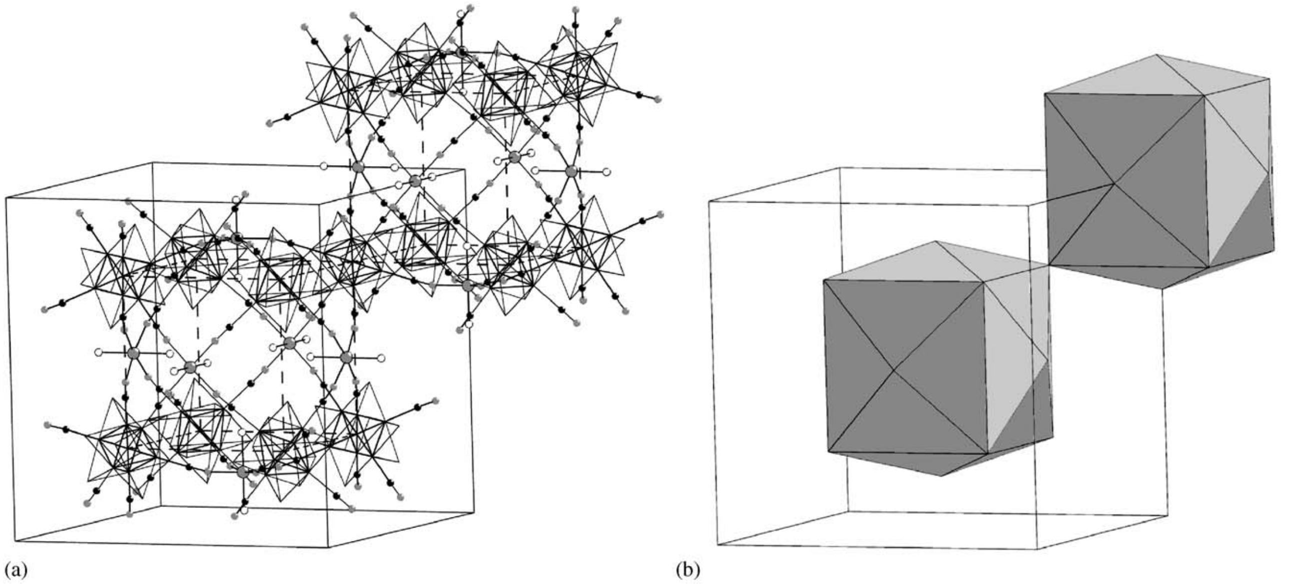

Fig. 5. Fragment of coordination framework $[M(H_2O)_n\}_3\{Re_6Q_8(CN)_6\}_2]^{2-}_{3\infty}$. (a) Stacking of two adjacent cubes via shared cluster complex; (b) presentation of the same in cubes (see text).

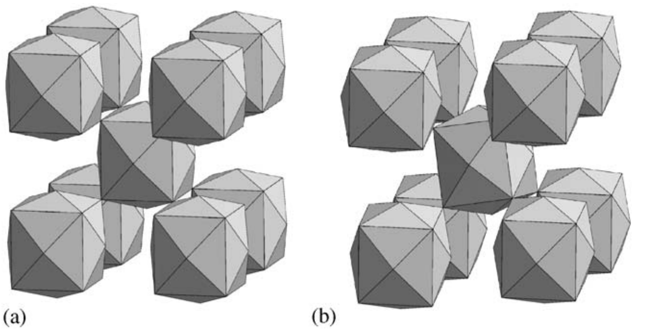

Fig. 6. Formal presentation of coordination frameworks in the structures **1**, **3–5** (a) and $Cs_2Mn_3[Re_6Se_8(CN)_6]_2 \cdot 15H_2O$ or $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2 \cdot 14.5H_2O$ (b).

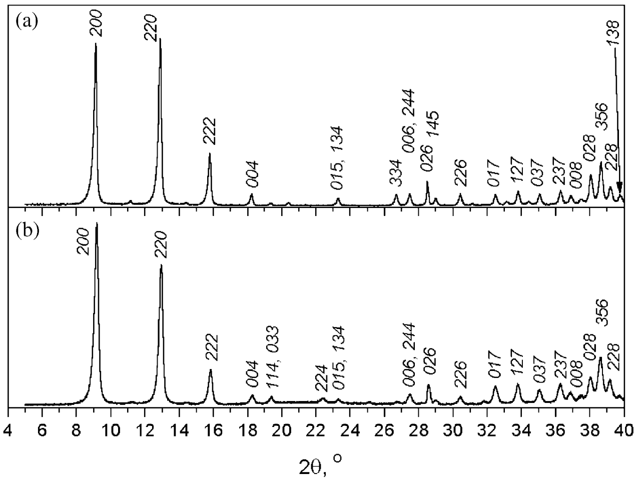

Fig. 7. XPD patterns for $(Me_4N)_2[\{Co(H_2O)_{1.5}\}_3\{Re_6Q_8(CN)_6\}_2] \cdot nH_2O$ (a: $Q = S$, 2; b: $Q = Se$, 3).

$mmm(D_{2h})$ symmetry. The shortest $M^{2+} \cdots M^{2+}$ distance in those fragments in **1** and **3** are 6.354 and 6.206 Å, respectively. The normal M–O distances are ca. 2.1 Å and the O⋯O distance forced to be 6.3–2.1–2.1 = 2.1 Å, which is too short for O⋯O contact. Actually distances between O1⋯O1 positions are 1.92 and 2.05 in **1** and **3**, respectively. Taking into account all the above-mentioned the O1 atom occupancy of 50% in **1** and **3** was assumed. Therefore, we formulated compounds **1**, **2** and **3** as containing 1.5 H_2O coordinated molecules per metal cation M^{2+}. In the structures of **4** and **5** the $M^{2+} \cdots M^{2+}$ distances become larger, 7.276 and 7.122 Å, resulting in normal O1⋯O1 contacts 2.89 and 3.05 Å, respectively. For structures **4** and **5** there is enough space to have two coordinated water molecules per Mn^{2+} (Ni^{2+}) and full occupancy of O1 position.

Solvate water molecules and charge compensating cations Me_4N^+ in **2** and **3**, Et_4N^+ in **4** and **5** are located between cubes shown in Fig. 4a. In contrast to heavy atoms and coordinated water oxygens O1 and O2, organic cations and crystallization water molecules are strongly disordered and have large thermal parameters. In the case of **1**, H_3O^+ presence of cations was assumed. This conclusion was based on the preparation condition (pH level 3), magnetic data, absence of potassium (by chemical and structural analyses) and stoichiometry of framework.

3.3. Discussion of synthesis

Based on our experimental observations, symmetry of the structure is governed mainly by nature of additional cations Kat^+ and pH level of reaction mixture.

Table 3
Volume characteristics of 3D frameworks in $[Re_6Q_8(CN)_6]^{4-}$ salts.

Formula	Space group	Unit cell volume V (Å^3)	Framework volume V_F (Å^3)[a]	Non-framework volume V_U (Å^3)[b]	V_F/V	Reference
$(Et_4N)_2[\{Ni(H_2O)_2\}_3\{Re_6S_8(CN)_6\}_2]\cdot 6.5H_2O\cdot$ (**5**)	$Im\bar{3}m$	7642	3083	4559	0.403	This work
$(Et_4N)_2[\{Mn(H_2O)_2\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 6.5H_2O$ (**4**)	$Im\bar{3}m$	8072	3534	4538	0.438	This work
$(H_3O)_2[\{Mn(H_2O)_2\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 8.5H_2O$ (**1**)	$Im\bar{3}m$	7830	3548	4282	0.453	This work
$(Me_4N)_2[\{Co(H_2O)_{1.5}\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 3H_2O$ (**3**)	$Im\bar{3}m$	7569	3535	4033	0.467	This work
$Cs_2Mn_3[Re_6Se_8(CN)_6]_2\cdot 15H_2O$	$R\bar{3}c$	7106	3526	3580	0.496	[25]
$(H_3O)_2[\{Mn(H_2O)_2\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 8.5H_2O$	$R\bar{3}c$	6824	3518	3306	0.516	[25]

[a] V_F is the volume of $[M_3[Re_6Q_8(CN)_6]_2]_3^{2-}$ framework per one unit cell.

[b] $V_U = V - V_F$. V_U indicates volume in the unit cell not occupied by coordination framework.

The interaction of $K_4[Re_6Se_8(CN)_6]$ with $Mn(NO_3)_2$ at pH level 6 results in the formation of $(H_3O)_2[\{Mn(H_2O)_2\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 14.5H_2O$ isostructural to $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2\cdot 14.5H_2O$ with trigonal symmetry. Addition of acid solution to reaction mixture (down to pH = 3) leads to precipitation $(H_3O)_2[\{Mn(H_2O)_{1.5}\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 19H_2O$ (**1**) with cubic symmetry. Crystals of this phase are rather unstable in air and readily lose solvent water giving partially dehydrated compound $(H_3O)_2[\{Mn(H_2O)_2\}_3\{Re_6Se_8(CN)_6\}_2]\cdot 14.5H_2O$.

The addition of Me_4N^+ or Et_4N^+ cations to reaction mixtures containing $[Re_6Q_8(CN)_6]^{4-}$ (Q = S or Se) and appropriate metal cation M^{2+} results in incorporation of these cations and in quick precipitation of neat solids **2**–**6** characterized by cubic symmetry (XPD patterns for powder samples **2** and **3** are presented in Fig. 7).

This incorporation takes place regardless the pH of solutions, used alkali cations and molar ratio of reactants. This fact confirms that inclusion of Me_4N^+ or Et_4N^+ cations in cavities of framework increases the stability of cubic phases **2**–**6.**

In contrast to compound **1** crystalline powder samples of **2**–**6** are quite stable. Heating of powder samples **2**–**6** in argon atmosphere resulted in release solvent water molecules at temperatures 100–150°C while the coordination framework was retained up to 300°C according to powder diffraction data (e.g., for sample **2** see Supplementary material) and infrared spectra. So, we suppose that cubic framework is stable to heating in this range of temperature.

Probably, Et_4N^+ cation is the largest that could be adopted by this framework. Attempt to increase the cation size to Pr_4N^+ results in cleavage of two of four M–N bonds and formation of chain structure of $(Pr_4N)_2M[Re_6S_8(CN)_6]\cdot 4H_2O$ [45]. For comparison, framework based on the mononuclear hexacyanometallate anions can adopt Cs^+ cations only, and is cleaved by introducing Me_4N^+ cation [46].

3.4. Framework porosity

The packing motif of above compounds is close to that found in $Cs_2Mn_3[Re_6Se_8(CN)_6]_2\cdot 15H_2O$ and $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2\cdot 14.5H_2O$ [25], in which cations and cluster anions form similar fragment $(M(H_2O)_2)_6[Re_6Se_8(CN)_6]_8$ with the same stoichiometry. Main difference between the structures is that the selected cubes in $Cs_2Mn_3[Re_6Se_8(CN)_6]_2\cdot 15H_2O$ and $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2\cdot 14.5H_2O$ are tilted in relation to neighboring cubes (Fig. 6b) resulting in symmetry reduction from $Im\bar{3}m$ to $R\bar{3}c$. This deformation leads to remarkable decrease in unit cell volume and non-framework volume, while the framework volume is not varying significantly (Table 3). Difference between unit cell volumes of compounds consists up to 18% in the case of compound **4** and $(H_3O)_2Co_3[Re_6Se_8(CN)_6]_2\cdot 14.5H_2O$, while the non-framework volume increases to 27% in this case.

4. Conclusion

In conclusion, we have synthesized and structurally characterized the 3D polymeric framework $[M_3\{Re_6Q_8(CN)_6\}_2]^{2-}_{3\infty}$ formed by large cluster anions $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se) and transition metal cations M^{2+} ($M^{2+} = Mn^{2+}$, Co^{2+}, Ni^{2+}) with different counter ions and crystallization water content. This framework is able to incorporate H_3O^+, Cs^+, Me_4N^+ and Et_4N^+ cations. This incorporation does not affect the framework connectivity but affects their symmetry: H_3O^+—containing framework may be cubic or trigonal; Cs^+—only trigonal; Me_4N^+ and Et_4N^+ force formation of cubic framework. H_3O^+—containing cubic crystals losing part of crystallization water transform to trigonal sample. For the framework obtained, unit cell volume and the volume free of coordination framework varies up to 18% and 27%, respectively.

Supplementary materials

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC_218204–218207. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary material includes powder diffraction patterns for sample **2** (a) freshly obtained; and (b) for heated to 300°C; atomic coordinates with site occupancies, and equivalent (isotropic) thermal parameters for compounds **1**, **3–5**; mass loss curves up to 300°C for compounds **2** and **3**.

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