Organometallic Chemistry

23-Electron Re_6 metal clusters: syntheses and crystal structures of $(Ph_4P)_3[Re_6S_8(CN)_6]$, $(Ph_4P)_2(H)[Re_6Se_8(CN)_6] \cdot 8H_2O$, and $(Et_4N)_2(H)[Re_6Te_8(CN)_6] \cdot 2H_2O$

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The cluster anions $[Re_6X_8(CN)_6]^{3-}$ (X = S, Se, or Te) containing 23 cluster valence electrons in the Re_6 octahedron were synthesized and isolated as salts with organic cations. The crystal structures of the $(Ph_4P)_3[Re_6S_8(CN)_6]$, $(Ph_4P)_2(H)[Re_6Se_8(CN)_6] \cdot 8H_2O$, and $(Et_4N)_2(H)[Re_6Te_8(CN)_6] \cdot 2H_2O$ clusters were solved by X-ray diffraction analysis. Removal of one electron has virtually no effect on the geometry and interatomic distances in the cluster anion but leads to a substantial change in the electronic spectrum and to an increase in stretching vibration frequencies ν_{CN} compared to those of the $[Re_6X_8(CN)_6]^{4-}$ anions.

Key words: rhenium, octahedral clusters, chalcogenide cyanide complexes, oxidation, crystal structure, X-ray diffraction analysis.

Chalcogenide octahedral cluster complexes containing the M_6X_8 cluster fragment are known for Mo, W, Re, Co, Fe, Cr, and other transition metals.[1—5] A large number of rhenium octahedral clusters were synthesized[6—10] among which are both polymeric compounds and molecular complexes. All these compounds contain 24 cluster valence electrons and possess diamagnetic properties.

In 1999, $(Bu_4N)_3Re_6Se_8Br_6$ containing 23 cluster valence electrons was synthesized.[11] Initially, this compound was described as $(Bu_4N)_3Re_6Se_7(SeH)Br_6$.[12] The ability of cluster anions to undergo reversible one-electron oxidation in solutions was revealed[13] in the studies of $[Re_6X_8(CN)_6]^{4-}$ (X = S, Se, or Te). Other examples of redox reactions of rhenium octahedral clusters were also reported.[14—17]

In the present study, we synthesized the cluster anions $[Re_6X_8(CN)_6]^{3-}$ (X = S, Se, or Te) as salts with organic cations, *viz.*, $(Ph_4P)_3[Re_6S_8(CN)_6]$ (**1**), $(Ph_4P)_2(H)[Re_6Se_8(CN)_6] \cdot 8H_2O$ (**2**), and $(Et_4N)_2(H)[Re_6Te_8(CN)_6] \cdot 2H_2O$ (**3**), and structurally characterized these complexes by X-ray diffraction analysis.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 799—803, May, 2002.

Table 1. Crystallographic characteristics and details of X-ray diffraction study of compounds **1—3**

Parameter	**1**	**2**	**3**
Molecular formula	$C_{78}H_{60}N_6P_3Re_6S_8$	$C_{54}H_{57}N_6O_8P_2Re_6Se_8$	$C_{22}H_{45}N_8O_2Re_6Te_8$
Molecular weight	2547.91	2702.67	2591.66
Crystal system	Triclinic	Monoclinic	Tetragonal
Space group	$P\bar{1}$	$P2_1/n$	$P4_2/mcm$
a/Å	13.838(3)	12.0827(6)	11.810(2)
b/Å	15.204(5)	20.284(1)	—
c/Å	19.858(5)	14.1464(7)	18.425(3)
α/deg	92.28(2)	—	—
β/deg	108.36(2)	96.144(1)	—
γ/deg	100.23(2)	—	—
V/Å^3	3881.7(18)	3447.2(3)	2569.8(7)
Z	2	2	2
ρ_{calc}/g cm^{-3}	2.180	2.604	3.349
μ/cm^{-1}	9.642	14.183	18.552
$2\theta_{max}$/deg	50	54	50
Number of measured/independent reflections, R_{int}	9294/8947, 0.0620	20253/7419, 0.0399	1848/1104, 0.0417
Number of parameters in the refinement	910	363	71
Number of reflections with $I > 2\sigma$	3042	4477	731
R_1 ($I > 2\sigma$)	0.0598	0.0296	0.0300
wR_2 (for all reflections)	0.1424	0.0668	0.0834

Results and Discussion

We found that the addition of an oxidizing agent (solutions of bromine in dichloromethane for **1** and in water for **2** and **3**) to solutions of the salts containing the $[Re_6X_8(CN)_6]^{4-}$ anions led to immediate oxidation of the latter accompanied by a change in the color. We used different procedures for transferring the $[Re_6X_8(CN)_6]^{3-}$ anions from a solution to the solid phase. Under the conditions described in the Experimental section, we prepared single crystals suitable for X-ray diffraction study.

All three crystal structures (Tables 1—4) belong to the ionic type (structures of the anions are shown in Fig. 1, and the crystal packings are presented in Fig. 2). In the crystals, both crystallographically independent anions of **1** and the anion of **2** occupy inversion centers. In the crystal of **3**, the anion occupies the position with the higher point symmetry (D_{2h}). All cluster anions contain the Re_6 octahedron whose faces each are μ_3-coordinated by the chalcogen atom X, the latter atoms forming the cube. Each Re atom is additionally coordinated by the apical CN group through the C atom. On the whole, the anions are structurally analogous to their nonoxidized $[Re_6X_8(CN)_6]^{4-}$ analogs.

The Re—Re and Re—X bond lengths in the series **1**, **2**, and **3** increase as the covalent radius of the chalcogen atom is increased (Table 5). The Re—C and C—N distances remain virtually unchanged in all the compounds under consideration.

Table 2. Selected bond lengths (d) and bond angles (ω) in the structure of **1**

Bond	d/Å
Re(1)—Re(2)	2.592(2)
Re(1)—Re(3)	2.602(2)
Re(1)—S(1)	2.410(9)
Re(1)—S(2)	2.39(1)
Re(1)—S(3)	2.402(9)
Re(1)—S(4)	2.41(1)
Re(1)—C(1)	2.04(2)
Re(2)—Re(3)	2.609(2)
Re(2)—S(1)	2.42(1)
Re(2)—S(2)	2.41(1)
Re(2)—S(3)	2.43(1)
Re(2)—S(4)	2.43(1)
Re(2)—C(2)	2.25(4)
Re(3)—S(1)	2.38(1)
Re(3)—S(2)	2.40(1)
Re(3)—S(3)	2.40(1)
Re(3)—S(4)	2.403(9)
Re(3)—C(3)	1.98(4)
Re(4)—Re(5)	2.597(3)
Re(4)—Re(6)	2.600(2)
Re(4)—S(5)	2.412(9)
Re(4)—S(6)	2.393(9)
Re(4)—S(7)	2.37(1)
Re(4)—S(8)	2.42(1)
Re(4)—C(4)	1.73(5)
Re(5)—Re(6)	2.597(3)
Re(5)—S(5)	2.38(1)
Re(5)—S(6)	2.39(1)
Re(5)—S(7)	2.37(1)
Re(5)—S(8)	2.42(1)
Re(5)—C(5)	2.20(4)
Re(6)—S(5)	2.41(1)
Re(6)—S(6)	2.40(1)
Re(6)—S(7)	2.38(1)
Re(6)—S(8)	2.40(1)
Re(6)—C(6)	2.06(4)
C(1)—N(1)	1.10(3)
C(2)—N(2)	1.12(4)
C(3)—N(3)	1.16(4)
C(4)—N(4)	1.35(5)
C(5)—N(5)	1.11(4)
C(6)—N(6)	1.20(4)

Angle	ω/deg
N(1)—C(1)—Re(1)	173(3)
N(2)—C(2)—Re(2)	170(4)
N(3)—C(3)—Re(3)	179(4)
N(4)—C(4)—Re(4)	174(3)
N(5)—C(5)—Re(5)	167(4)
N(6)—C(6)—Re(6)	164(4)

Table 3. Selected bond lengths (*d*) and bond angles (ω) in the structure of **2**

Bond	*d*/Å	Bond	*d*/Å
Re(1)—Re(2)	2.638(1)	Re(2)—Se(4)	2.519(1)
Re(1)—Re(3)	2.636(1)	Re(2)—C(2)	2.119(9)
Re(1)—Se(1)	2.511(1)	Re(3)—Se(1)	2.520(1)
Re(1)—Se(2)	2.524(1)	Re(3)—Se(2)	2.529(1)
Re(1)—Se(3)	2.521(1)	Re(3)—Se(3)	2.527(1)
Re(1)—Se(4)	2.514(1)	Re(3)—Se(4)	2.523(1)
Re(1)—C(1)	2.091(8)	Re(3)—C(3)	2.086(8)
Re(2)—Se(1)	2.527(1)	C(1)—N(1)	1.166(9)
Re(2)—Se(2)	2.529(1)	C(2)—N(2)	1.148(10)
Re(2)—Se(3)	2.515(1)	C(3)—N(3)	1.155(9)

Angle	ω/deg	Angle	ω/deg
Re(1)—C(1)—N(1)	176.9(7)	Re(3)—C(3)—N(3)	178.1(7)
Re(2)—C(2)—N(2)	178.8(9)		

Table 4. Selected bond lengths (*d*) and bond angles (ω) in the structure of **3**

Bond	*d*/Å	Bond	*d*/Å
Re(1)—Re(2)	2.676(1)	Re(2)—Te(1)	2.687(2)
Re(1)—Te(1)	2.708(2)	Re(2)—Te(2)	2.691(2)
Re(1)—Te(2)	2.682(2)	Re(2)—C(2)	2.09(2)
Re(1)—C(1)	2.09(5)	C(1)—N(1)	1.19(5)
Re(2)—Re(2)	2.677(2)	C(2)—N(2)	1.15(3)

Angle	ω/deg	Angle	ω/deg
N(1)—C(1)—Re(1)	179.995(3)	N(2)—C(2)—Re(2)	178(2)

A comparison of the interatomic distances (see Tables 2—5) in the $[Re_6X_8(CN)_6]^{3-}$ and $[Re_6X_8(CN)_6]^{4-}$ cluster anions (see, for example, the review[10]) demonstrated that the removal of one cluster valence electron

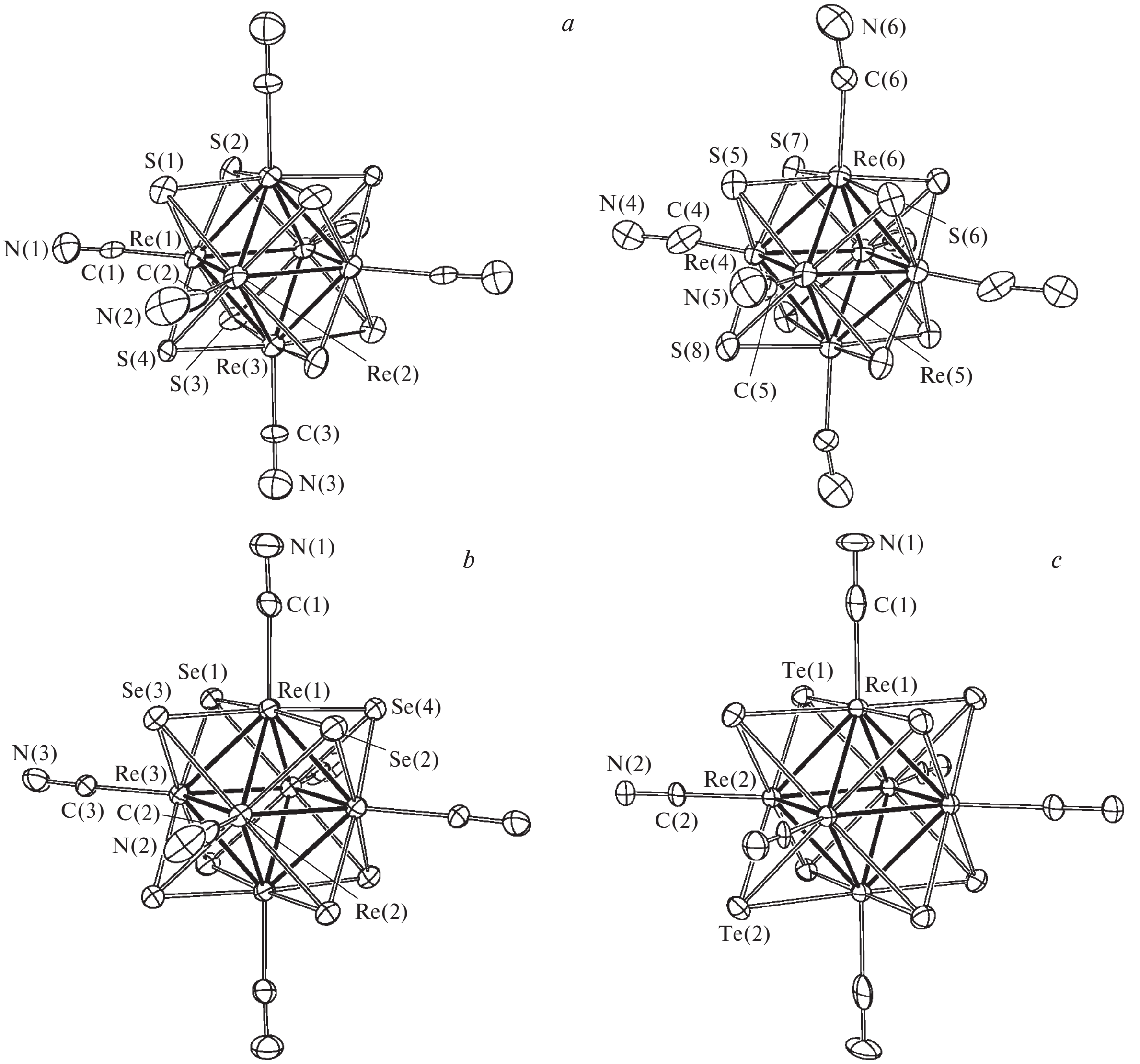

Fig. 1. Structures of the $[Re_6X_8(CN)_6]^{3-}$ anions in compounds **1** (*a*), **2** (*b*), and **3** (*c*) (thermal ellipsoids with the 50% probability).

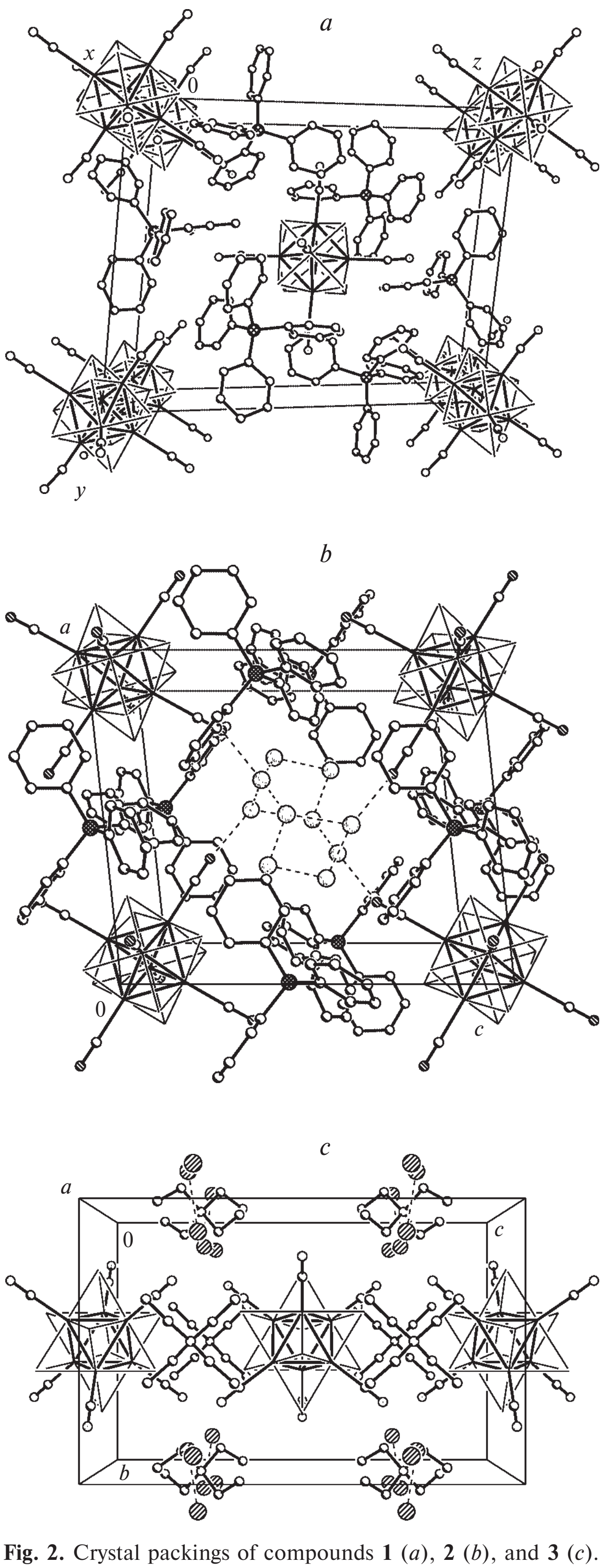

Fig. 2. Crystal packings of compounds **1** (*a*), **2** (*b*), and **3** (*c*). The hydrogen bonds between the oxygen atoms of the H_2O molecules and the N atoms of the CN groups are indicated by dashed lines.

Table 5. Principal interatomic distances (ranges and meanvalues) (Å) in the cluster anions of compounds **1—3**

Compound	Re—Re	Re—X	Re—C	C—N
1[a]	2.599(6)	2.407(13)	2.09(12)	1.13(2)
	2.591—2.609	2.383—2.431	1.98—2.25	1.10—1.16
1[b]	2.601(4)	2.395(17)	2.00(21)	1.22(11)
	2.597—2.609	2.369—2.419	1.73—2.20	1.11—1.35
2	2.636(5)	2.522(6)	2.10(16)	1.16(8)
	2.629—2.644	2.511—2.529	2.09—2.12	1.15—1.17
3	2.680(8)	2.691(8)	2.09(1)	1.16(2)
	2.675—2.698	2.682—2.708	2.09—2.10	1.15—1.19

[a] Compound **1**, the anion 1. [b] Compound **1**, the anion 2.

has virtually no effect on the geometry of the cluster. The Re—Re distance averaged over two independent $[Re_6S_8(CN)_6]^{3-}$ anions of compound **1** (2.600 Å) is equal to that found in $Cs_2Co[Re_6S_8(CN)_6] \cdot 2H_2O$ (2.600 Å). The average Re—Re distance in the $[Re_6Se_8(CN)_6]^{3-}$ anion in compound **2** (2.636 Å) is somewhat longer than that found in $K_4[Re_6Se_8(CN)_6] \cdot 4H_2O$. However, the increase in this distance is smaller than the difference between the average Re—Re distances in two independent anions in the same structure. The average metal—metal distance in the $[Re_6Te_8(CN)_6]^{3-}$ anion (2.680 Å) in compound **3** is close to the corresponding distances in the $[Re_6Te_8(CN)_6]^{4-}$ anion (2.684 Å) in the structure of $Cs_4[Re_6Te_8(CN)_6] \cdot 2H_2O$.[18] The volume of the Re_6 octahedra also remains unchanged, *i.e.*, the skeleton of the cluster anion is very rigid and is virtually insensitive to removal of one of the 24 cluster valence electrons unlike the octahedral cluster complexes with other transition metals.[19]

At the same time, the rhenium—chalcogen distances in all three oxidized anions are somewhat shorter than those found in the 24-electron cluster anions. The distances are decreased by 0.01, 0.004, and 0.012 Å for the thio, selenium, and tellurium anions, respectively. Within the framework of the ionic model, this decrease in the distances can be related to an increase in the average charge on the Re atoms on going from $Re^{III}{}_6$ to $Re^{III}{}_5Re^{IV}$.

The results of X-ray diffraction study and the data from elemental analysis demonstrate that the compounds under consideration differ in the organic cation : anion ratio. The $(Ph_4P)_3[Re_6S_8(CN)_6]$ compound contains three cations, whereas $(Ph_4P)_2(H)[Re_6Se_8(CN)_6] \cdot 8H_2O$ and $(Et_4N)_2(H)[Re_6Te_8(CN)_6] \cdot 2H_2O$ possess only two organic cations per anion. The Re_6X_8 cluster core must contain 22 cluster valence electrons without considering protons. However, the magnetic susceptibility measurements for the oxidized thio, seleno, and telluro complexes and the ESR spectra of the thio and seleno complexes showed that these compounds contain one unpaired electron each.[20] According to the data from electrochemical studies, the cluster anion undergoes one-electron oxidation.

Oxidation of the $[Re_6X_8(CN)_6]^{4-}$ cluster anions led to a change in the electronic spectra of these compounds. The visible region of the spectra has intense bands (at 530, 600, and 735 nm for X = S, Se, and Te, respectively), and the long-wavelength region has broad absorption bands (at 915, 875, and 992 cm^{-1} for X = S, Se, and Te, respectively). The similarity of the electronic absorption spectra of the oxidized thio, seleno, and telluro complexes indicates that all three cluster anions have close electronic structures.

According to the above-mentioned data, the charges of the cluster anions in all the compounds under consideration are –3. The $(Ph_4P)_2(H)[Re_6Se_8(CN)_6] \cdot 8H_2O$ and $(Et_4N)_2(H)[Re_6Te_8(CN)_6] \cdot 2H_2O$ compounds were prepared in aqueous media at pH 1—3. Apparently, these compounds possess a proton as an additional H_3O^+ cation. However, our attempts to reveal the H atoms of the H_2O molecules in the crystal structures failed due, apparently, to the difficulties associated with the location of the hydrogen atoms from electron density syntheses in the presence of the heavy rhenium and chalcogen atoms.

Experimental

The IR spectra were recorded on a Bruker IFS 85 spectrometer. The electronic absorption spectra were measured in the range of 300—1100 nm on a Specord M-40 spectrophotometer.

The X-ray powder diffraction patterns were measured on a Philips APD 1700 diffractometer (Cu-Kα radiation, graphite monochromator, 2θ = 5—60°, scan step 0.02°, accumulation for 1 s) at ~20 °C. The X-ray powder patterns are in good agreement with the single-crystal X-ray diffraction data.

The magnetic susceptibilities (χ) of the complexes were measured on a Quantum Design MPMS-5S SQUID magnetometer in the temperature range of 2—300 K in the magnetic fields up to 10 kE. The paramagnetic susceptibilities were corrected for the diamagnetic contribution of the ions according to the Pascal scheme.

Synthesis of $(Ph_4P)_3[Re_6S_8(CN)_6]$ (1). The $(Ph_4P)_4[Re_6S_8(CN)_6]$ salt was prepared by the addition of a solution of tetraphenylphosphonium chloride to an aqueous solution of $K_4[Re_6S_8(CN)_6]$.[21] A 0.23 *M* Br_2 solution (0.345 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise with stirring to a solution containing $(Ph_4P)_4[Re_6S_8(CN)_6]$ (535 mg, 0.185 mmol) in DMF (5 mL). Then diethyl ether (50 mL) was added dropwise with stirring. The red-orange precipitate of $(Ph_4P)_3[Re_6S_8(CN)_6]$ was filtered off on a glass filter, washed with ehtanol, and dried. The yield was 410.7 mg (87%). Found (%): C, 37.97; S, 9.81; P, 4.65; N, 3.08; H, 2.55. $C_{78}H_{60}N_6P_3Re_6S_8$. Calculated (%): C, 36.77; S, 10.07; P, 3.65; N, 3.30; H, 2.37. IR: 2137 cm^{-1} (CN). The UV-Vis, λ_{max}/nm: 326, 429 sh, 471, 530, 915; μ_{eff} = 2.01 μB (298 K). Single crystals were obtained upon storage of an acetonitrile solution of compound **1** in air for 2 days after which red-orange crystals suitable for X-ray diffraction analysis were obtained.

Synthesis of $(Ph_4P)_2(H)[Re_6Se_8(CN)_6]{\cdot}8H_2O$ (2). The $(Ph_4P)_4[Re_6Se_8(CN)_6]$ salt was prepared by adding a solution of Ph_4PCl to an aqueous solution of $K_4[Re_6Se_8(CN)_6]$.[22] Then a solution of Br_2 in CH_2Cl_2 (0.1 mmol) was added to a solution of the $(Ph_4P)_4[Re_6Se_8(CN)_6]$ salt (0.200 g, 0.061 mmol) in DMF (10 mL). Isopropyl alcohol (10 mL) and water were successively added until crystallization started. After separation of the crystals, the filtrate was kept in a refrigerator. After one day, the green crystals that precipitated were filtered off, washed with isopropyl alcohol and ether, and dried in air. The yield was 0.095 g (57%). Found (%): C, 24.00; P, 2.17; N, 3.10; H, 2.20. $C_{54}H_{57}N_6O_8P_2Re_6Se_8$. Calculated (%): C, 23.77; P, 2.27; N, 3.08; H, 2.11. IR: 2130 cm^{-1} (CN). UV-Vis, λ_{max}/nm: 330, 447 sh, 540, 600, 875; μ_{eff} = 1.90 μB (298 K).

Synthesis of $(Et_4N)_2(H)[Re_6Te_8(CN)_6] \cdot 2H_2O$ (3). A 0.188 *M* Br_2 solution (0.282 mmol) in water (1.5 mL) was added dropwise with stirring to an aqueous solution (5 mL) containing $Cs_4[Re_6Te_8(CN)_6] \cdot 2H_2O$ (600 mg, 0.21 mmol).[18] Then an aqueous solution containing Et_4NBr (2.24 mmol, 470 mg) and ethanol (200 mL) was added. The dark-brown precipitate that formed was filtered off, washed with ethanol, and dried in air. The yield was 446 mg (82%). Found (%): C, 10.00; N, 4.25; H, 2.00. $C_{22}H_{45}N_8O_2Re_6Te_8$. Calculated (%): C, 10.20; N, 4.32; H, 1.75. IR: 2098 cm^{-1} (CN). UV-Vis, λ_{max}/nm: 309, 337 sh, 412, 500 sh, 735, 992; μ_{eff} = 1.96 μB (298 K).

Single crystals of **3** were prepared by slow counter diffusion of aqueous solutions containing the oxidized $[Re_6Te_8(CN)_6]^{3-}$ anion and the Et_4N^+ cation in a U-shaped tube filled with agarose gel (pH 1—2). After ~20 days, crystals suitable for X-ray diffraction study grew in the gel.

X-ray diffraction study of single crystals of compounds 1—3 was carried out according to a standard procedure on an automated Enraf-Nonius CAD4 diffractometer at ~20 °C (for **1** and **3**) and on a Siemens AXS diffractometer equipped with a 1K CCD detector at –90 °C (**2**) (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator). The crystallographic characteristics and details of X-ray diffraction study are given in Table 1. The absorption corrections were applied using azimuthal scan curves (**1** and **3**) or semiempirically based on the intensities of equivalent reflections (**2**). The structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 using the SHELX97 program package.[23] The hydrogen atoms of the organic cations were placed in geometrically calculated positions and refined within the framework of the rigid-body model. The positions of the hydrogen atoms of the water molecules were not revealed. The refinement of the occupancy demonstrated that the O atom of the solvate H_2O molecule in the structure of **3** occupies the crystallographic position by 50%.

The atomic coordinates of compounds **1—3** were deposited with the Cambridge Structural Database (CCDC 170981 and CCDC 170982) and can be obtained from the authors.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 99-03-32789) and INTAS (Grant 2000-00689). N. G. Naumov acknowledges the INTAS for the scholarship for young scientists.

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Received October 8, 2001;
in revised form February 26, 2002