Tetranuclear rhenium chalcogenide cluster complexes with a cubane core. Synthesis, structures, and properties

Yu. V. Mironov and V. E. Fedorov★

Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 4489. E-mail: fed@che.nsk.su

The results of studies of rhenium chalcogenide cluster complexes with the $[Re_4Q_4]$ cubane core, where Q = S, Se, or Te, are reviewed. Different approaches to the synthesis of these compounds are surveyed and their properties and structures are considered. Substitution reactions in the cluster core and replacements of terminal ligands are discussed. The formation of polymers consisting of the tetranuclear rhenium chalcogenide cyanide clusters as structural building blocks is considered.

Key words: cubane clusters, rhenium, chalcogenides, acido ligands, crystal structure, X-ray diffraction analysis.

Introduction

Tetranuclear cubane complexes are well known for most of transition metals.[1—5] These compounds contain the M_4Q_4 cubane cluster core as the main structural fragment, which can be represents as two interpenetrating M_4 and Q_4 tetrahedra. In the M_4Q_4 cluster cores, the chalcogenide ions S^{2-}, Se^{2-}, and Te^{2-} most often serve as the inner-sphere μ_3-ligands Q. The first (and until recently, the only) rhenium cubane clusters, *viz.*, the chalcogenide cyanide anionic complexes $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S or Se), have been prepared long ago.[6] However, considerable progress has been achieved in the chemistry of these compounds in the last few years owing primarily to our studies, which gave impetus to the present review.

The formal oxidation state of rhenium in tetranuclear cubane clusters is 4+ (d^3 configuration). Within the framework of the ion-covalent model, four metal atoms in the $[Re_4Q_4]^{8+}$ cubane cluster donate 16 electrons to form bonds with the ligands and the remaining 12 electrons in the Re_4 tetrahedron participate in the formation of the metal—metal bonds (two electrons per each edge of the tetrahedron). The formal bond order in the Re_4 tetrahedron is equal to unity. The most typical cubane cluster complexes have the stoichiometry $Re_4Q_4L_{12}$, where each rhenium atom is additionally coordinated by three outer-sphere ligands L. This structure of the complexes determines the pathways of chemical modifications of these compounds, which involve primarily the replacements of the most labile ligands L, the replacements of the ligands Q in the cluster core, and, finally, the replacements of the rhenium atoms by other metals to form heterometallic clusters. We examined all types of modifications of the rhenium cubane cluster complexes. The results of these studies lie at the basis of the present review.

Polymeric mixed telluride sulfide $Re_4(\mu_3\text{-}S)_4Te_4$

Two procedures for the preparation of $Re_4S_4Te_4$ (**1**) are known, *viz.*, heating of a mixture of the elements taken in a stoichiometric ratio Re : S : Te = 4 : 4 : 4 [7] and the reaction of hexanuclear rhenium telluride Re_6Te_{15} with elemental sulfur (Re_6Te_{15} : S = 1 : 6) at 900 °C.[8]

Initially, the structure of this compound was established from X-ray powder patterns by the Rietveld method.[7] Later on, the structure was refined by single-crystal X-ray diffraction analysis.[9] The structure of $Re_4S_4Te_4$ is shown in Fig. 1. Compound **1** is isostructural to the molybdenum and niobium chalcogenides of the general formula $M_4Q_4X_4$ (M = Mo or Nb; Q = S or Se; X = Cl, Br, or I).[1,2] The structure of $Re_4S_4Te_4$ is characterized by the presence of the tetrahedral Re_4 cluster whose triangular faces each are symmetrically coordinated by the sulfur atom to form the Re_4S_4 pseudocube (Re—Re, 2.785 Å; and Re—S, 2.337 Å). In addition, each rhenium atom is coordinated by three bridging Te atoms with the Re—Te bond lengths of 2.790 Å. The structure contains also the Te_4 fragment with the Te—Te distances in the range of 3.486—3.616 Å, which are substantially smaller than the sum of the van der Waals radii of the tellurium atoms. In the cubic lattice (space group

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 529—539, April, 2002.

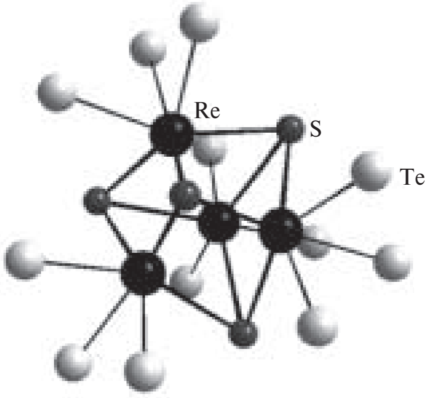


Fig. 1. Structure of the $Re_4S_4Te_{12/3}$ fragment in $Re_4S_4Te_4$ (here and in Figs. 3, 7, 8, 12a, and 13, the Re—Re bonds are omitted).

$F\bar{4}3m$), the Re_4S_4 and Te_4 cluster fragments alternate with each other to form the NaCl structural motif (Fig. 2). The structure of $Re_4S_4Te_4$ can also be considered as quasi-spinel. In the latter interpretation, the S and Te atoms serve as an anionic sublattice and the rhenium atoms are located in the octahedral cavities. The rhenium atoms are displaced from the centers of the S_3Te_3 octahedra toward each other to form the tetrahedral Re_4 cluster.

Phases with partial replacements in the cluster core, such as $Re_{4-x}Mo_xS_4Te_4$ ($0 < x < 2$) and $Re_3MoS_{4-y}Se_yTe_4$ ($0 < y < 1$), were prepared from the elements by the high-temperature synthesis.[7] The possibilities of the synthesis of a wider range of heterometallic clusters are limited due primarily to the electronic factors (non-isoelectronic replacement of rhenium by molybdenum), whereas the low degree of the replacement of sulfur by selenium is, most likely, determined by the size factors. Attempts to synthesize compounds with the stoichiometry $Re_4Se_4Te_4$ failed.

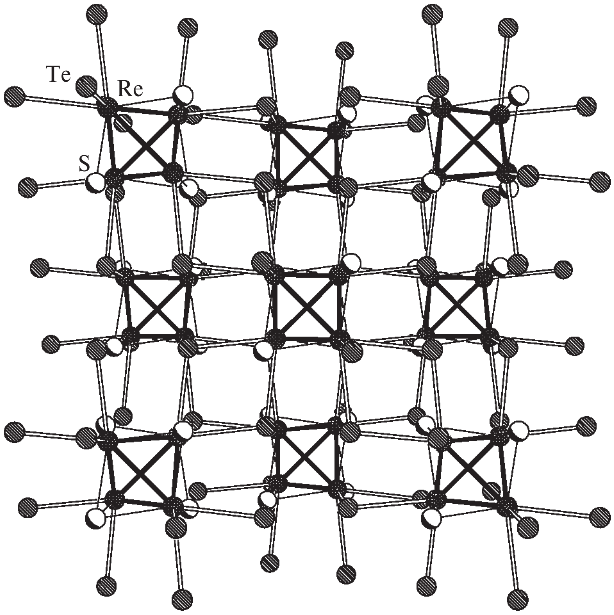


Fig. 2. Packing of the Re_4S_4 and Te_4 structural blocks in the lattice of $Re_4S_4Te_4$.

The electronic structures of the cubane clusters of the $Re_{4-x}Mo_xS_4Te_4$ series were studied by X-ray emission and X-ray electron spectroscopy in combination with quantum-chemical calculations.[10] It was found that the charge state of the rhenium atoms in $Re_4S_4Te_4$ is close to that of Re^{4+} and the charge states of the sulfur and tellurium atoms are similar to that of the chalcogenide ions, *i.e.*, this compound can be described by the ionic formula $Re_4^{4+}S_4^{2-}Te_4^{2-}$. The replacement of the rhenium atoms by the molybdenum atoms leads to a decrease in the number of valence electrons in the $[Re_{4-x}Mo_xS_4]$ cluster core, the charge states of the Re, S, and Te atoms being virtually unchanged. From this it follows that the number of electrons on the orbitals corresponding to the metal—metal bonds decreases. This effect agrees well with the results of calculations of the electronic structures by the EHT method, which demonstrated that the highest orbitals of the cluster core correspond to the M—M bonds.

An interesting feature of the compounds of variable composition $Re_{4-x}Mo_xS_4Te_4$ is the appearance of metallic conductivity at $x \le 1$, which peaks at $x = 0.33$. In these compounds, the formation of the conduction band involving the partially occupied orbital was attributed to overlapping of the d orbitals corresponding to the M—M bonds with the p orbitals of the Te_4 tetrahedron.[10]

Molecular chalcogenide cubane cluster complexes

Rhenium chalcogenide halide cluster complexes of the general formula $Re_4Q_4(TeX_2)_4X_8$ were synthesized and structurally characterized for Q = S (**2**), Se (**3**), and Te (**4**) and X = Cl[11] and also for Q = Te and X = Br (**5**).[12] The tellurium-containing complex $Re_4(\mu_3\text{-}Te)_4(TeCl_2)_4Cl_8$ (**4**) was prepared by the reaction of $ReCl_5$ with elemental tellurium at 350 °C. Complexes **2** and **3** were synthesized by the reactions of $ReCl_5$ with mixtures of elemental tellurium and sulfur or selenium, respectively, at 400 °C. The reactions proceeded according to the following equations

$$4\,ReCl_5 + 9\,Te \longrightarrow Re_4(\mu_3\text{-}Te)_4(TeCl_2)_4Cl_8 + TeCl_4,$$

$$4\,ReCl_5 + 4\,Se + 5\,Te \longrightarrow Re_4(\mu_3\text{-}Se)_4(TeCl_2)_4Cl_8 + TeCl_4,$$

$$4\,ReCl_5 + 4\,S + 5\,Te \longrightarrow Re_4(\mu_3\text{-}S)_4(TeCl_2)_4Cl_8 + TeCl_4.$$

Rhenium telluride bromide cluster complex **5** was prepared[12] by heating the elements at 550 °C.

All compounds of composition $Re_4Q_4(TeX_2)_4X_8$ are isostructural and crystallize in the tetragonal system (space group $I\bar{4}$, the unit cell parameters are given in Table 1). Complexes each contain the $[Re_4Q_4]$ cubane cluster core formed by the virtually regular Re_4 tetrahedron all triangular faces of which are symmetrically coordinated by the bridging μ_3-Q ligands (Fig. 3). Each rhenium atom is additionally coordinated by two terminal X^- ligands and the neutral TeX_2 ligand. In these complexes, the Re—Re and Re—Q distances, on the average, increase in the series Re_4S_4, Re_4Se_4, and Re_4Te_4 (Table 2). An analogous regularity is also observed for the Re—Cl bond lengths (2.426(4)—2.443(4) Å in **2**, 2.444(7)—2.451(6) Å in **3**, and 2.474(3)—2.479(3) Å in **4**). In all three complexes, the Re—Te($TeCl_2$) bond has approximately the equal length (2.725(1), 2.725(2), and 2.709(1) Å, respectively).

The most interesting characteristic feature of these compounds is the presence of the neutral TeX_2 ligands (X = Cl or Br). The $TeCl_2$ and $TeBr_2$ molecules have long been known. They are unstable in the condensed state and were detected and structurally characterized only in the gas phase.[26,27] The data on the rhenium cluster complexes indicate that coordination with metal clusters stabilizes the TeX_2 molecules.

The tetranuclear rhenium chalcogenide chloride complex of composition $Re_4Q_4(TeCl_2)_4Cl_8$ under consideration along with the hexanuclear rhenium telluride chloride complex $[Re_6Te_6Cl_2](TeCl_2)_2Cl_4$ (see Ref. 28) are the first and the only presently known compounds containing the $TeCl_2$ ligand. The $TeBr_2$ ligand along with the tetranuclear rhenium telluride bromide cluster is present in two other rhenium telluride bromide complexes prepared recently, *viz.*, in the binuclear and hexanuclear rhenium telluride bromides of compositions $[Re_2Br_4(Te_2)(TeBr)_2(TeBr_2)_2]$ [29] and

Table 1. Principal crystallographic data for the tellurium-containing rhenium cluster complexes

Compound	Space group	*a*	*b*	*c*	α	β	γ	*V* /Å^3	Reference
		Å			deg				
$Re_4Te_8Cl_{16}$	$I\bar{4}$	10.742(4)		13.616(4)				1571.1(9)	11
$Re_4Te_8Br_{16}$	$I\bar{4}$	11.202(2)		13.935(3)				1748.6(6)	12
$Re_4Te_4Cl_8(DMF)_5$	$P\bar{1}$	11.820(4)	11.858(4)	14.274(5)	91.85(1)	107.27(1)	91.79(1)	1908(1)	13
$Cs_3(H)[Re_4Te_4Cl_{12}]\cdot4.33H_2O$	$C2$	26.403(8)	16.495(5)	11.744(3)		91.25(2)		5113.(2)	14
$K_4Re_4Te_4(CN)_{12}\cdot5H_2O$	$P\bar{1}$	12.515(1)	12.662(2)	13.036(1)	106.263(9)	108.627(9)	109.68(1)	1660.2(3)	15
$Cs_4Re_4Te_4(CN)_{12}\cdot4H_2O$	$I4_1/a$	15.468(2)		14.005(3)				3350.8(9)	16
$[Cu_4(OH)_4][Re_4Te_4(CN)_{12}]$	$I4_1/amd$	10.236(1)		28.25(1)				2960(1)	17
$Cu_2Re_4Te_4(CN)_{12}\cdot4H_2O$	*Imma*	10.190(3)	15.181(7)	18.953(7)				2932(2)	18
$Cd_2Re_4Te_4(CN)_{12}\cdot6H_2O$	*Imma*	10.684(1)	15.528(2)	19.118(3)				3171.7(7)	18
$[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}]\cdot\cdot3.4H_2O$	$P2_1/c$	19.572(3)	14.849(2)	23.576(3)		145.97(1)		3834.4(9)	19
$[Cd(NH_3)_5][Cd(NH_3)_3]$——$[Re_4Te_4(CN)_{12}]\cdot4H_2O$	$P\bar{1}$	12.726(2)	13.408(2)	13.918(2)	111.31(2)	116.77(2)	90.17(2)	1935.3(5)	19
$(NH_4)_4Re_4Te_4S_{20}\cdot8H_2O$	*Cmcm*	12.6463(7)	16.235(1)	19.804(1)				4065.92	20
$(Ph_4As)_4Re_4Te_4(NCS)_{12}$	$I4(1)/a$	28.286(6)		14.615(3)				11694(4)	21
$Re_4Se_4Te_4Cl_{16}$	$I\bar{4}$	10.831(3)		13.233(4)				1552.1(8)	11
$(Ph_4P)_4Re_4Se_4(NCS)_{12}$	$I4(1)/a$	28.191(3)		14.353(2)				11406(2)	21
$[PPh_4]_4[Re_4Se_4(CN)_{12}]\cdot3H_2O$	$P2_1/c$	15.45	24.18	28.60		106.6		10242	6
$K_4Re_4Se_4(CN)_{12}\cdot6H_2O$	$P\bar{1}$	12.459(3)	12.504(3)	13.079(3)	109.20(2)	107.30(2)	108.94(1)	1623.2(7)	18
$Mn_2Re_4Se_4(CN)_{12}\cdot6H_2O$	*Imma*	10.624(1)	14.999(2)	19.013(2)				3029.7(6)	18
$(Pr_4N)_2Re_4Se_4(MeCONH)_2Cl_8$	$P3_221$	12.726(1)		26.534(5)				3721.6(5)	22
$[Me_4N]_5[Me_2NH_2]_3[Re_4Se_4S_{20}]_2\cdot\cdot2.25H_2O$	$P2_1/c$	12.555(1)	38.397(4)	19.465(2)		93.135(2)		9369.80	20
$Re_4S_4Te_4$	$F4\bar{3}m$	10.044(3)						1013.1(8)	9
$Re_4S_4Te_4Cl_{16}$	$I\bar{4}$	10.823(3)		12.920(3)				1513.4(7)	11
$(Pr_4N)_2Re_4S_4(MeCONH)_2Cl_8$	$P3_221$	12.670(3)		26.09(1)				3627(2)	22
$(Ph_4P)_4Re_4S_4(NCS)_{12}$	$I4(1)/a$	28.235(7)		14.297(6)				11397(6)	21
$Cs_2K_2[Re_4S_4(CN)_{12}]\cdot2H_2O$	$P\bar{1}$	11.404(14)	11.81(2)	13.55(2)	68.33(5)	65.47(5)	71.67(5)	1515(3)	23
$[PPh_4]_4[Re_4S_4(CN)_{12}]\cdot3H_2O$	$P2_1/c$	15.43	24.12	28.54		106.8		10166	6
$[NH_4]_4[Re_4S_{22}]\cdot0.3NH_4Cl\cdot\cdot0.7H_2O$	$F4\bar{3}m$	15.181(3)						3498.7	24
$[NH_4]_4[Re_4S_{22}]\cdot2H_2O$	$F4\bar{3}m$	15.203(3)						3513.9	25

Table 2. Interatomic distances in the $[Re_4(\mu_3\text{-}Q)_4]$ cluster core

Compound	Re—Re/Å	Re—(μ_3-Q)/Å	Reference
	Q = Te		
$Re_4Te_4(TeCl_2)_4Cl_8$	2.783(1)—2.843(1)	2.602(1)—2.613(1)	11
$Cs_3(H)[Re_4Te_4Cl_{12}]\cdot 4.33H_2O$	2.848(2)—2.879(2)	2.587(2)—2.612(2)	14
$(Ph_4As)_4Re_4Te_4(SCN)_{12}$	2.864(2)—2.877(2)	2.626(2)—2.628(2)	21
$Re_4Te_4(TeBr_2)_4Br_8$	2.774(3)—2.831(3)	2.585(3)—2.605(4)	12
$Re_4Te_4Cl_8(DMF)_5$	2.846(2)—2.864(2)	2.588(2)—2.625(2)	13
$K_4Re_4Te_4(CN)_{12}\cdot 5H_2O$	2.862(2)—2.879(1)	2.625(2)—2.640(2)	15
$Cs_4Re_4Te_4(CN)_{12}\cdot 4H_2O$	2.876(1)—2.883(1)	2.641(1)—2.650(1)	16
$[Cu_4(OH)_4][Re_4Te_4(CN)_{12}]$	2.834(1)—2.857(1)	2.632(2)—2.636(1)	17
$Cu_2Re_4Te_4(CN)_{12}\cdot 4H_2O$	2.853(1)—2.863(1)	2.643(1)—2.655(1)	18
$Cd_2Re_4Te_4(CN)_{12}\cdot 6H_2O$	2.862(1)	2.635(2)—2.640(2)	18
$[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}]\cdot 3.4H_2O$	2.8540(6)—2.8767(7)	2.6230(8)—2.6469(8)	19
$[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]\cdot 4H_2O$	2.868(1)—2.878(1)	2.622(1)—2.645(1)	19
$[NH_4]_4Re_4Te_4(S_4)_2(S_3)_4\cdot 8H_2O$	2.8440(4)—2.9319(5)	2.6014(4)—2.6324(6)	20
	Q = Se		
$Re_4Se_4(TeCl_2)_4Cl_8$	2.737(2)—2.785(2)	2.433(3)—2.449(3)	11
$[Pr_4N]_2Re_4Se_4(MeCONH)_2Cl_8$	2.760(1), 2.813(2)—2.821(1)	2.419(2)—2.452(2)	22
$[Ph_4P]_4Re_4Se_4(SCN)_{12}$	2.799(2)—2.803(2)	2.443(3)—2.448(3)	21
$[PPh_4]_4[Re_4Se_4(CN)_{12}]\cdot 3H_2O$	2.805(5)	2.46(1)	6
$K_4Re_4Se_4(CN)_{12}\cdot 6H_2O$	2.798(1)—2.809(1)	2.460(2)—2.467(2)	18
$Mn_2Re_4Se_4(CN)_{12}\cdot 6H_2O$	2.798(2)	2.483(3)—2.492(2)	18
$[Me_4N]_5[Me_2NH_2]_3[Re_4Se_4S_{20}]_2\cdot 2.25H_2O$	2.7794(7)—2.8786(8)	2.433(1)—2.462(1)	20
	Q = S		
$Re_4S_4(TeCl_2)_4Cl_8$	2.706(1)—2.742(1)	2.332(4)—2.349(5)	11
$[Pr_4N]_2Re_4S_4(MeCONH)_2Cl_8$	2.754(2), 2.754(2)—2.760(1)	2.301(4)—2.340(5)	22
$[Ph_4P]_4Re_4S_4(SCN)_{12}$	2.762(3)—2.768(2)	2.353(8)—2.378(7)	21
$Re_4S_4Te_4$	2.784(1)	2.349(2)	9
$Cs_2K_2[Re_4S_4(CN)_{12}]\cdot 2H_2O$	2.736(3)—2.753(3)	2.329(7)—2.361(7)	23
$[PPh_4]_4[Re_4S_4(CN)_{12}]\cdot 3H_2O$	2.755(5)	2.34(1)	6
$[NH_4]_4[Re_4S_{22}]\cdot 0.3NH_4Cl\cdot 0.7H_2O$	2.764(3)	2.319(7)—2.463(12)	24
$[NH_4]_4[Re_4S_{22}]\cdot 2H_2O$	2.768(2)	2.324(5)—2.481(9)	25

$[Re_6Te_8(TeBr_2)_6]Br_2$.[28] Analogous telluride iodide ligands were found in a number of niobium and molybdenum cluster compounds[30—32] and in octahedral rhenium telluride iodide $Re_6Te_8(TeI_2)_6I_2$.[33]

The $Re_4Q_4(TeCl_2)_4Cl_8$ compounds are insoluble both in water and common organic solvents but very readily react with solutions of various compounds in water or organic solvents or with the solvents by themselves upon

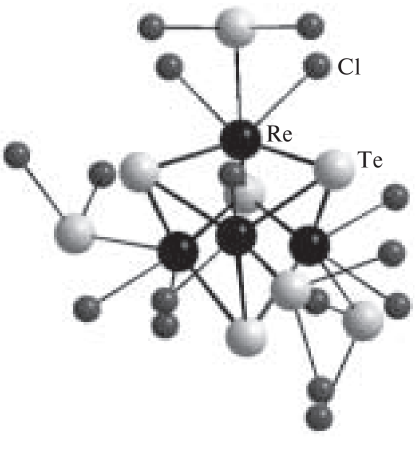
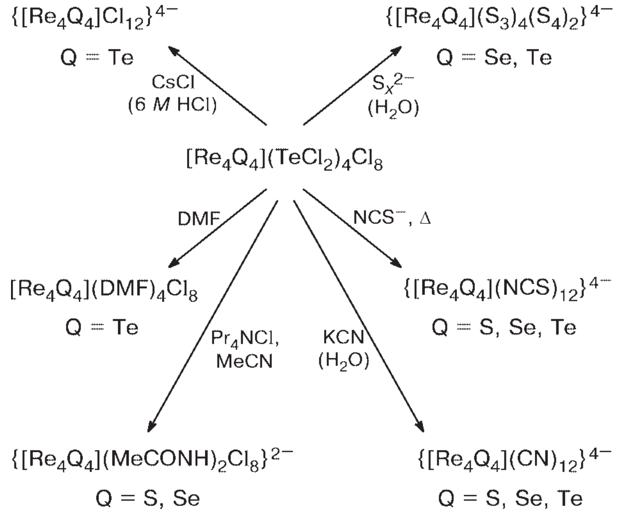


Fig. 3. Structure of the $[Re_4Te_4](TeCl_2)_4Cl_8$ complex.

Scheme 1



heating or even at room temperature. All such transformations proceed with the replacement of the outer-sphere ligands in the cluster complexes (see Scheme 1). All the reactions under consideration can formally be divided into two types: 1) reactions proceeding with the replacement of only the neutral $TeCl_2$ ligand; and 2) reactions proceeding with the replacement of all terminal ligands.

Compounds prepared by the replacement of the outer-sphere ligands in $Re_4Q_4(TeCl_2)_4Cl_8$

Molecular complex $Re_4(\mu_3\text{-}Te)_4(DMF)_4Cl_8 \cdot DMF$ (6). The $Re_4Te_4(TeCl_2)_4Cl_8$ compound slowly reacts with DMF to produce a new molecular complex of composition $Re_4(\mu_3\text{-}Te)_4(DMF)_4Cl_8 \cdot DMF$. The reaction formally leads to the replacement of the neutral $TeCl_2$ ligands by the neutral DMF molecules.

The structure of $Re_4(\mu_3\text{-}Te)_4(DMF)_4Cl_8 \cdot DMF$ was solved by single-crystal X-ray diffraction analysis (Fig. 4).[13] The complex contains the Re_4Te_4 cubane-like cluster fragment. In this fragment, each rhenium atom is additionally coordinated by two terminal Cl^- ligands and one neutral terminal ligand, *viz.*, the DMF molecule, which is bound to the rhenium atom through the oxygen atom (the Re—O distances are in the range of 2.11(2)—2.16(2) Å). The crystal structure contains the DMF molecules of solvation along with the $Re_4(\mu_3\text{-}Te)_4(DMF)_4Cl_8$ molecules.

Compounds with the anionic cluster complexes $(Pr_4N)_2Re_4Q_4(MeCONH)_2Cl_8$ (Q = S (7) or Se (8)). The reactions of the cluster complexes $Re_4Q_4(TeCl_2)_4Cl_8$ (Q = S or Se) with a boiling solution of Pr_4NCl in acetonitrile afforded the soluble ionic complexes $(Pr_4N)_2Re_4Q_4(MeCONH)_2Cl_8$ (Q = S or Se).[22] Interestingly, the reactions led to the transformation of the solvent (acetonitrile) molecules into the acetamide ligands and the replacement of all four neutral $TeCl_2$ ligands by two acetamide ligands, which were coordinated at the Re—Re bond of the tetrahedral metal cluster to give the cluster anion with a charge of 2−.

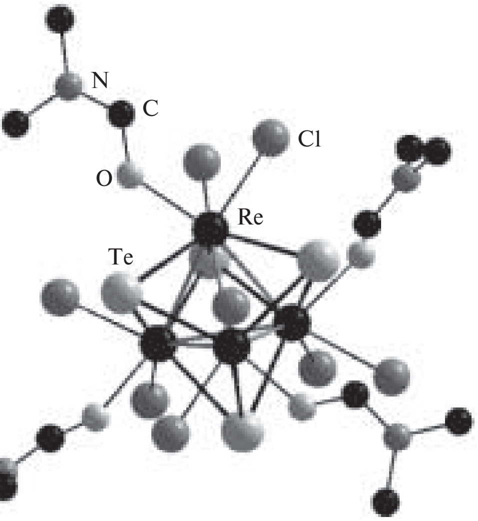


Fig. 4. Structure of $Re_4Te_4(DMF)_4Cl_8$ in the $Re_4Te_4(DMF)_4Cl_8 \cdot DMF$ complex.

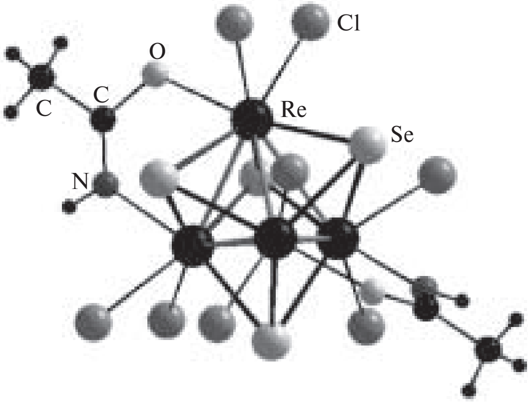


Fig. 5. Structure of the $[Re_4Se_4(MeCONH)_2Cl_8]^{2-}$ anion.

The structures of both complexes were solved by single-crystal X-ray diffraction analysis[22] (Fig. 5). Compounds **7** and **8** are isostructural and have the crystallographic symmetry $\bar{3}$. In both complexes, the Re_4 tetrahedron is distorted because of the presence of two shorter Re—Re bonds resulting from coordination of the bidentate $(MeCONH)^-$ ligands at these bonds. In these complexes, the Re—Re bonds coordinated by the acetamide ligands have close lengths, whereas the other Re—Re bonds differ in the length (see Table 2). Each rhenium atom is coordinated by two terminal chlorine atoms (Re—Cl distances are in the ranges of 2.395(5)—2.413(5) (**7**) and 2.419(6)—2.438(6) Å (**8**)) and the oxygen or nitrogen atom of the bridging acetamide ligand (the Re—O and Re—N bond lengths are 2.13(1) (**7**), 2.12(2) (**8**) and 2.14(1) (**7**), 2.10(2) Å (**8**), respectively). The C—O and C—N bond lengths in the $(MeCONH)^-$ ligand (1.27(2) (**7**), 1.32(3) (**8**) and 1.29(2) Å (**7**), 1.26(3) Å (**8**), respectively) have close values and are very close to those found in acetamide complexes of platinum.[34]

The presence of the acetamide ligands was confirmed by IR and NMR spectroscopy. The $(Pr_4N)_2Re_4S_4(MeCONH)_2Cl_8$ complex was also characterized by mass spectrometry. The transformation of acetonitrile into acetamide in the coordination sphere of the metal atom, which takes place in alkaline solutions, is well known for platinum complexes.[34,35]

Complex containing the $[Re_4Te_4Cl_{12}]^{4-}$ cluster fragment. Yet another example of the replacement of the $TeCl_2$ ligands is the reaction of $Re_4Te_4(TeCl_2)_4Cl_8$ with CsCl in a 6 *M* solution of hydrochloric acid.[14] Rhenium telluride chloride was dissolved on reflux followed by

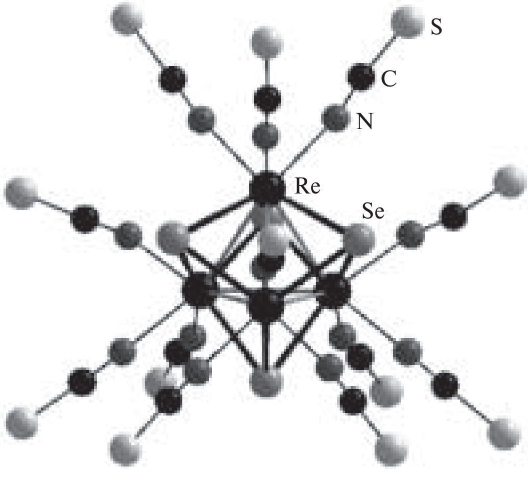


Fig. 6. Structure of the $[Re_4Se_4(SCN)_{12}]^{4-}$ anion.

crystallization of black crystals of the diamagnetic salt $Cs_3(H)[Re_4Te_4Cl_{12}] \cdot 4.33H_2O$. According to the X-ray diffraction data, the complex contains only three Cs^+ atoms, whereas the charge of the cluster fragment is 4+, which was confirmed by the data from additional physicochemical studies. No redox processes were revealed for this cluster throughout the accessible range.

Rhenium chalcogenide rhodanide complexes. Rhenium chalcogenide rhodanide complexes containing the $[Re_4Q_4(NCS)_{12}]^{4-}$ cluster anion were readily generated in the reactions of the molecular rhenium clusters of composition $Re_4Q_4(TeCl_2)_4Cl_8$ (Q = S, Se, or Te) with a melt of KSCN.[21] The reactions were accompanied by the replacement of all terminal ligands (Cl^- and $TeCl_2$) with the rhodanide ligands.

Three compounds, *viz.*, $(Ph_4P)_4Re_4S_4(NCS)_{12}$ (**9**), $(Ph_4P)_4Re_4Se_4(NCS)_{12}$ (**10**), and $(Ph_4As)_4Re_4Te_4(NCS)_{12}$ (**11**), were studied by X-ray diffraction analysis. The structure of the cluster anion is shown in Fig. 6.

All compounds are isostructural. They involve the $[Re_4Q_4]^{8+}$ cubane cluster fragment containing the virtually regular Re_4 tetrahedron. Each triangular face of this tetrahedron is symmetrically coordinated by the chalcogenide ligand Q. The Re—Re and Re—Q distances are given in Table 2. All rhenium atoms are coordinated by the N atoms of three terminal NCS^- ligands; the Re—N distances are 2.07(3)—2.14(2) (**9**), 2.07(3)—2.18(2) (**10**), and 2.09(2)—2.14(2) Å (**11**). Such a typical coordination was also found in molybdenum, tungsten, and niobium chalcogenide rhodanide cluster complexes, which have been characterized earlier.[36—38]

The most interesting feature of the above-described reactions is the retention of the $[Re_4Se_4]$ and $[Re_4Te_4]$ cluster cores in the reactions performed in the presence of an excess of NCS^- anions as the potential source of sulfur. This is, apparently, associated with high kinetic stability of the cubane cluster fragments. We emphasize this characteristic feature because the reactions of selenium-containing cubane complexes of W or Nb performed under analogous conditions led to the replacement of the selenium atoms by the sulfur atoms of the NCS^- ligands.[39] Selenide rhodanide complexes of these metals can be prepared only by the exchange reactions in solutions.[40] It should be noted that $(Ph_4As)_4Re_4Te_4(NCS)_{12}$ is the first representative of telluride rhodanide clusters of transition metals.

Molecular complexes with polysulfide ligands. Among tetranuclear rhenium cubane clusters, chalcogenide complexes with polysulfide ligands are of considerable interest. Previously, only two such compounds, *viz.*, $[NH_4]_4[Re_4S_4(S_3)_6] \cdot 0.3NH_4Cl \cdot 0.7H_2O$ (**12**)[24] and $[NH_4]_4[Re_4S_4(S_3)_6] \cdot 2H_2O$ (**13**),[25] have been described in the literature. We synthesized two new complexes, *viz.*, $[Me_4N]_5[Me_2NH_2]_3[Re_4Se_4(S_3)_4(S_4)_2]_2 \cdot 2.25H_2O$ (**14**) and $(NH_4)_4[Re_4Te_4(S_3)_4(S_4)_2] \cdot 8H_2O$ (**15**),[20] containing both the polysulfide ligands and the selenium- or tellurium-containing Re_4Q_4 clusters (Q = Se or Te). Compounds **12** and **13** were prepared by heating a solution of NH_4ReO_4 with an aqueous solution of ammonium polysulfide. The cluster fragment consists of the Re_4 tetrahedron. Each face of the tetrahedron is coordinated by the μ_3-S ligand, and each edge is coordinated by the bridging S_3 ligand (Fig. 7). In the Re_4 tetrahedron, the Re—Re and Re—(μ_3-S) distances are 2.763 and 2.319 Å, respectively. The Re_2S_3 fragments adopt an envelope conformation with the S—S distances of 2.140 Å.

Complexes **14** and **15** containing two types of polysulfide ligands, *viz.*, S_3 and S_4, were prepared by the reactions of rhenium chalcogenide halides $Re_4Q_4(TeCl_2)_4Cl_8$ (Q = Se or Te) with an aqueous solution of ammonium polysulfide. The reactions started already at room temperature. However, with the aim of bringing the reactions to completion and obtaining crystals, the reaction

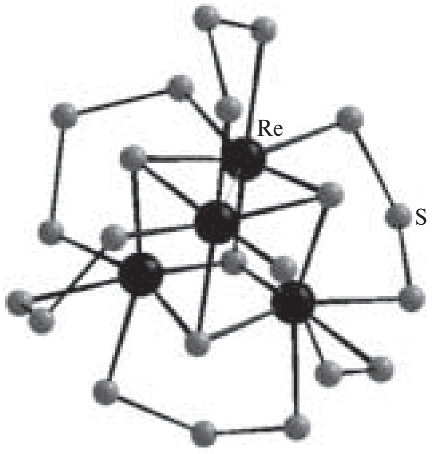


Fig. 7. Structure of the $\{[Re_4S_4](S_3)_6\}^{4-}$ anion.

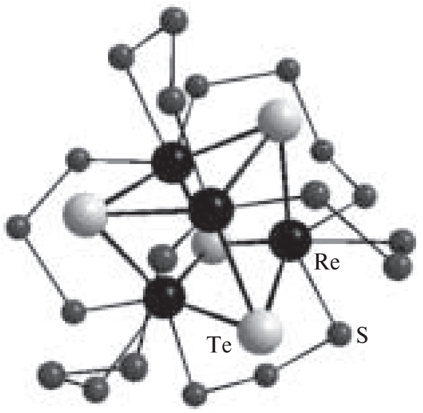


Fig. 8. Structure of the $\{[Re_4Te_4](S_4)_2(S_3)_4\}^{4-}$ anion.

mixtures were kept at 60 °C for 3—4 h and then slowly cooled. The structures of both complexes were solved by single-crystal X-ray diffraction analysis. Both complexes contain the $[Re_4Q_4]$ cluster fragment. The rhenium atoms are coordinated at the edges of the Re_4 tetrahedron through four bidentate polysulfide S_3 ligands and two S_4 ligands (Fig. 8). The S_4 ligands are in the *trans* positions with respect to each other. In complexes **14** and **15**, the S—S distances in the polysulfide ligands (2.042(6)—2.105(8) Å 2.000(5)—2.069(6) Å, respectively) are typical of complexes with such ligands.[41]

Chalcogenide cyanide complexes. Complex cyanides of transition metals occupy a special place among a wide variety of inorganic compounds. It is these cyanide complexes that were used for formulating the major concepts of the coordination chemistry. Due to a number of useful properties, these compounds are widely used in inorganic and analytical chemistry and chemical technology. Recently, it has been demonstrated that high-temperature molecular magnets can be created on the basis of cyanide materials.[42] Inorganic cyanides were surveyed in recent excellent reviews.[43,44] However, these investigations concerned primarily with mononuclear complexes.

Recently, a series of chalcogenide cyanide cluster complexes of composition $[M_4X_4(CN)_{12}]^{n-}$, where M = Mo, W; X = S, Se, or Te, were prepared.[23,45—47] The first niobium cubane complex was also synthesized and structurally characterized.[48]

The chalcogenide cyanide complexes $[Re_4Q_4(CN)_{12}]^{4-}$ containing the $[Re_4Q_4]$ cubane cluster fragment (Q = S or Se) were first synthesized by the reaction of K_2ReCl_6 with KSCN (KSeCN).[6] Both compounds were structurally characterized as the $[PPh_4]_2[Re_4Q_4(CN)_{12}]\cdot3H_2O$ salts (Q = S (**16**) or Se (**17**)) and remained for long the only known rhenium complexes of this type. More recently, the thiocyanide cluster anion $[Re_4S_4(CN)_{12}]^{4-}$ was prepared along with the rhombic tetranuclear cluster anion $[Re_4(\mu_3\text{-}S)_2(\mu\text{-}SO_2)_4(CN)_{10}]^{8-}$ by the reaction of Re_2S_7 with an aqueous solution of KCN.[49] The $[Re_4S_4(CN)_{12}]^{4-}$ complex was also synthesized by the reaction of the trinuclear $Re_3S_7Br_7$ cluster with an aqueous solution of KCN at room temperature.[23] Upon the addition of CsCl to the resulting solution, crystals of composition $Cs_2K_2[Re_4S_4(CN)_{12}]$ (**18**) precipitated in 78% yield. Recently, we have developed a new universal procedure for the preparation of the $[Re_4Q_4(CN)_{12}]^{4-}$ complexes, where Q = S, Se, or Te. The potassium salts $K_4[Re_4Q_4(CN)_{12}]$ (Q = Se (**19**) or Q = Te (**20**)) were synthesized by the reactions of $Re_4Q_4(TeCl_2)_4Cl_8$ with KCN in water.[15,18] The cesium salt $Cs_4[Re_4Te_4(CN)_{12}]\cdot4H_2O$ (**21**) crystallized upon the addition of CsCl to an aqueous solution of $K_4[Re_4Te_4(CN)_{12}]\cdot5H_2O$.[16]

In recent years, a series of new rhenium cyanide clusters were prepared and structurally characterized. These compounds can be divided into two types: 1) salts with island structures, which are formed upon crystallization of the cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, or Te) together with the non-coordinating cations, such as K^+ or Cs^+, and organic cations; and 2) polymeric complexes formed upon crystallization of chalcogenide cyanide cluster anions with transition metal cations.

All compounds contain the $[Re_4Q_4(CN)_{12}]^{4-}$ anion whose structure is shown in Fig. 9. The rhenium atoms form a tetrahedron and the chalcogen atoms are μ_3-coordinated. Each metal atom possesses three terminal CN ligands, which are coordinated through the carbon atoms. In the K^+ and Cs^+ salts of the telluride complexes, the Re—Re distances in the Re_4 tetrahedron have virtually equal values. These distances are somewhat shorter in the selenide complexes and even more shorter in the sulfide complexes (see Table 2).

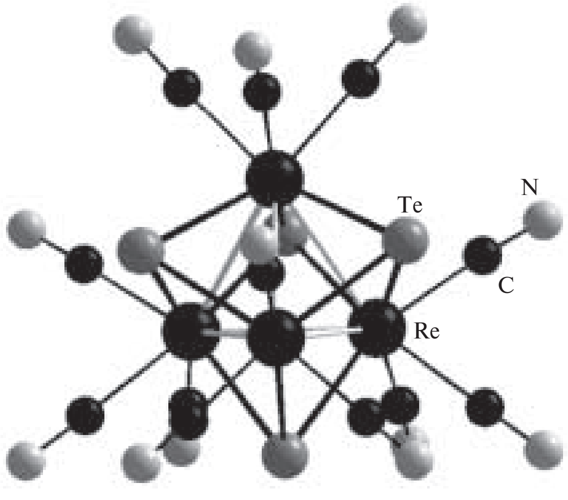


Fig. 9. Structure of the $[Re_4Te_4(CN)_{12}]^{4-}$ anion.

Compounds of rhenium chalcogenide cyanide clusters with transition metals

Since compounds containing the chalcogenide cyanide cluster anions and transition metal cations are poorly soluble in usual solvents, the preparation of their single crystals calls for special procedures among which counter diffusion in silica gel proved to be the method of choice. Most of single-crystalline samples of these compounds were synthesized by this method.

The complicated cluster complex $[Cu_4(\mu_3\text{-}OH)_4][Re_4(\mu_3\text{-}Te)_4(CN)_{12}]$ (**22**) was prepared by the reaction of aqueous solutions of $K_4[Re_4Te_4(CN)_{12}]$ and $CuCl_2$.[17] The reaction was carried out by counter diffusion of the solutions in a gel based on sodium silicate. The structure of the complex was solved by single-crystal X-ray diffraction analysis. The crystal structure of complex **22** consists of layers formed from the $[Cu_4(\mu_3\text{-}OH)_4]^{4+}$ cations and $[Re_4Te_4(CN)_{12}]^{4-}$ cluster anions (Fig. 10, *a* and *b*). Eight of twelve CN ligands of the cluster anion are coordinated to the copper atoms in the layer. The remaining four CN^- ligands are directed perpendicular to the layer and are bound to the hydroxo groups of the cations lying in the adjacent layers through hydrogen bonds (the N...O bond length is 2.82 Å) (Fig. 10, *a*). In the structure of **22**, the layers are arranged so that they form the classical four-layer packing (...ABCDA...) (Fig. 10, *b*).

The geometric characteristics of the cluster anion are close to those of the above-discussed K^{+-} and Cs^+ salts. In the $[Cu_4(\mu_3\text{-}OH)_4]^{4+}$ cation, four copper atoms and four OH^- anions form a cubane-type complex with two short (2.99 Å) and four long (3.18 Å) Cu—Cu contacts. The coordination polyhedron of the copper atom is a distorted square pyramid with two oxygen atoms and two nitrogen atoms located in the base of the pyramid and one oxygen atom in the axial position. On the whole, the $[Cu_4(\mu_3\text{-}OH)_4]$ cluster in this compound is structurally similar to the analogous fragments found in $[Cu_4(OH)_4(SO_3CF_3)_2(N(py)_3)_4]\cdot[SO_3CF_3]_2\cdot C_3H_6O$ [50] and $[Cu(bpy)OH]_4(PF_6)_4$.[51] The substantial difference is that the copper atom in the two latter complexes is coordinated by six donor atoms of the ligands, whereas the copper atom in the rhenium complex is coordinated only by five atoms. Besides, the Cu_4 clusters in the copper complexes are more substantially distorted from the ideal tetrahedron than the cluster in the rhenium complex prepared by us.

Recently, it was demonstrated[18] that the reaction of $K_4[Re_4Te_4(CN)_{12}]$ with the use of a $CuCl_2$ solution in 1 *M* hydrochloric acid instead of a neutral aqueous solution of $CuCl_2$ afforded the cluster complex of composition $Cu_2[Re_4Te_4(CN)_{12}]\cdot 4H_2O$ (**23**). According to the results of single-crystal X-ray diffraction analysis, the structure of **23** contains two copper cations, which have different coordination environments. The coordination polyhedron about the Cu(1) atom is a distorted octahedron formed by four nitrogen atoms of the CN groups and two oxygen atoms of the water molecules. This co-

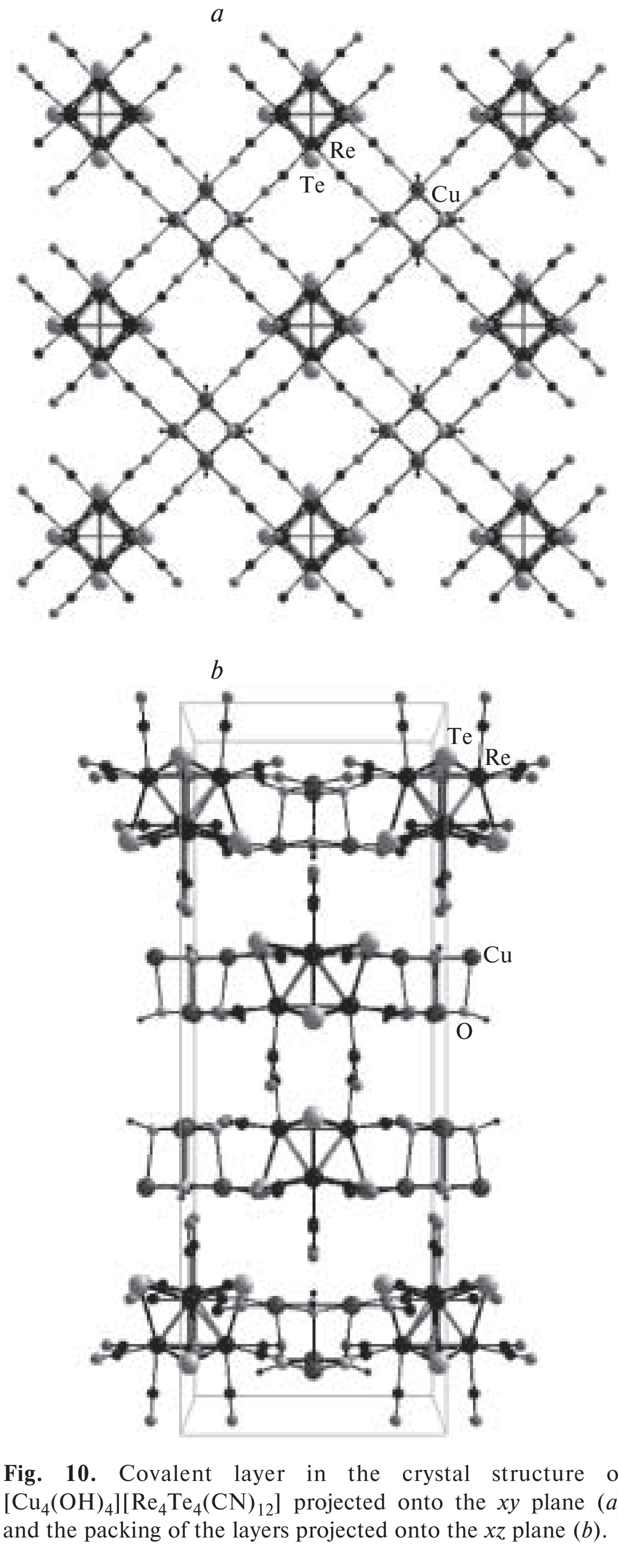


Fig. 10. Covalent layer in the crystal structure of $[Cu_4(OH)_4][Re_4Te_4(CN)_{12}]$ projected onto the *xy* plane (*a*) and the packing of the layers projected onto the *xz* plane (*b*).

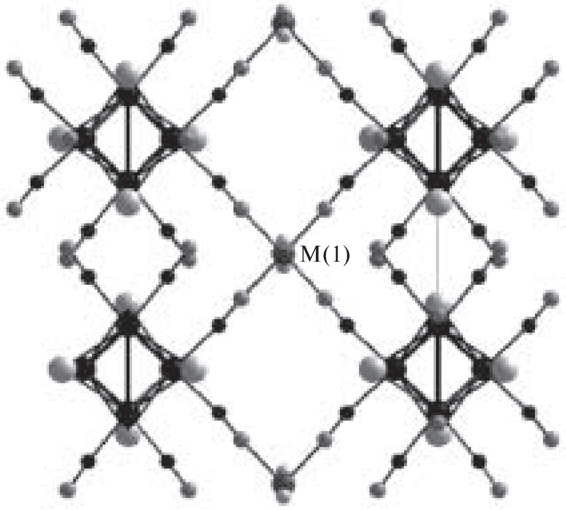


Fig. 11. Coordination environment of the M(1) cations in $M_2[Re_4Q_4(CN)_{12}] \cdot nH_2O$.

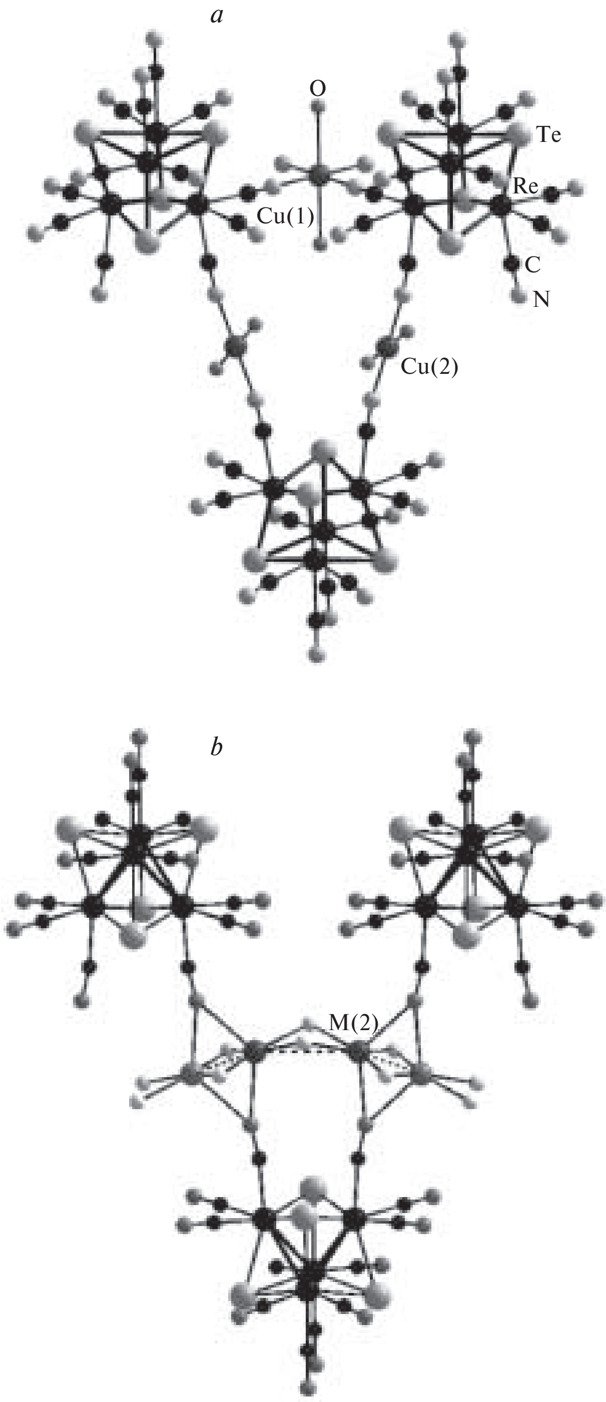


Fig. 12. Coordination environments of the Cu(2) (*a*) and M(2) (M = Mn or Cd) cations (*b*) in the $M_2[Re_4Q_4(CN)_{12}] \cdot nH_2O$ compounds. One of statistical positions of the M(2) cation is represented by a pale-colored ball.

ordination gives rise to a two-dimensional network in which the cluster fragments are linked through the Re—C≡N—Cu—N≡C—Re bridges (Fig. 11). The Cu(2) atom has a planar-square environment formed by two nitrogen atoms of the CN groups and two oxygen atoms of the water molecules (Fig. 12, *a*). Such a coordination is typical of copper. It was found in many Cu^{2+} complexes with organic ligands.[52] The Cu(2) cations link the two-dimensional networks to form a three-dimensional packing with a complicated geometry.

Two cluster complexes with other transition metals, *viz.*, $Cd_2[Re_4Te_4(CN)_{12}] \cdot 6H_2O$ (**24**) and $Mn_2[Re_4Se_4(CN)_{12}] \cdot 6H_2O$ (**25**), which are isostructural to copper complex **23**, were prepared and structurally characterized. The structures of both compounds also contain two different types of transition metal cations, *viz.*, M(1) and M(2). The coordination polyhedron about the M(1) cation is analogous to that described for the copper complex. However, the M(2) cation has a somewhat different environment. In the crystal structures of complexes **24** and **25**, the M(2) cations are disordered over two crystallographically equivalent positions with equal occupancies (0.5/0.5). In accordance with the coordination requirements of Cd^{2+} and Mn^{2+}, this cation is surrounded by two nitrogen atoms of the CN groups and four oxygen atoms of the water molecules (a distorted octahedron). In addition, these cations are linked in dimers to which two bridging water molecules and one cluster anion are coordinated (Fig. 12, *b*).

Two new tetrahedral rhenium telluride cyanide complexes, *viz.*, $[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}] \cdot 3.4H_2O$ (**26**) and $[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}] \cdot 4H_2O$ (**27**), were prepared by the reactions of $K_4Re_4Te_4(CN)_{12}$ with solutions of $NiCl_2$ and $CdSO_4$, respectively, in concentrated aqueous ammonia.[19] According to the X-ray diffraction data, two $[Ni(NH_3)_5]^{2+}$ cations in the structure of **26** are coordinated to the same Re atom through the nitrogen atoms of the CN ligands of the cluster $[Re_4Te_4(CN)_{12}]^{4-}$ anion (Fig. 13). Hence, each Ni atom is coordinated by five N atoms of the NH_3 molecules (the

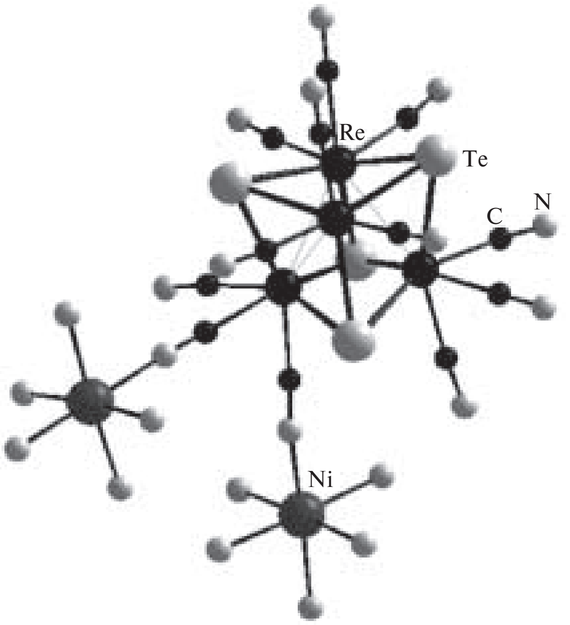


Fig. 13. Structure of the molecular complex $[Ni(NH_3)_5]_2Re_4Te_4(CN)_{12}$ (**26**).

Ni—N distances are in the range of 2.081(9)—2.150(9) Å) and one nitrogen atom of the CN^- ligand (the Ni—N distances are 2.067(8) and 2.097(8) Å).

Another rhenium telluride cyanide complex, $[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]$ (**27**), contains two types of cations, *viz.*, the terminal $[Cd(NH_3)_5]^{2+}$ cation and the bridging $[Cd(NH_3)_3]^{2+}$ cation. The Cd atom of each $[Cd(NH_3)_5]^{2+}$ cation (Fig. 14, *a*) is coordinated by five N atoms of the NH_3 molecules (the Cd—N distances are in the range of 2.29(3)—2.47(4) Å) and one N atom of the CN^- ligand of the cluster fragment (the Cd—N distance is 2.43(3) Å). The Cd atom in each $[Cd(NH_3)_3]^{2+}$ cation (Fig. 14, *b*) is coordinated by three N atoms of the NH_3 molecules (the Cd—N distances are in the range of 2.25(2)—2.39(2) Å) and three N atoms of the CN^- ligands belonging to three cluster complexes (the Cd—N distances are 2.358(18)—2.42(2) Å) to form a chain structure in which each cluster anion $[Re_4Te_4(CN)_{12}]^{4-}$ is coordinated by the terminal $[Cd(NH_3)_5]^{2+}$ ligand.

Complex **27** can be considered as an intermediate between the molecular complex of the $[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}]\cdot3.4H_2O$ type and the framework complex $Cd_2[Re_4Te_4(CN)_{12}]\cdot6H_2O$. Like the $Cd_2[Re_4Te_4(CN)_{12}]\cdot6H_2O$ complex, compound **27** contains two types of cations. The formation of the framework complex may be readily conceived as a result of the replacement of one ammonia molecule by CN and the replacement of the remaining NH_3 molecules by water molecules both in the $[Cd(NH_3)_5]^{2+}$ and $[Cd(NH_3)_3]^{2+}$ cations.

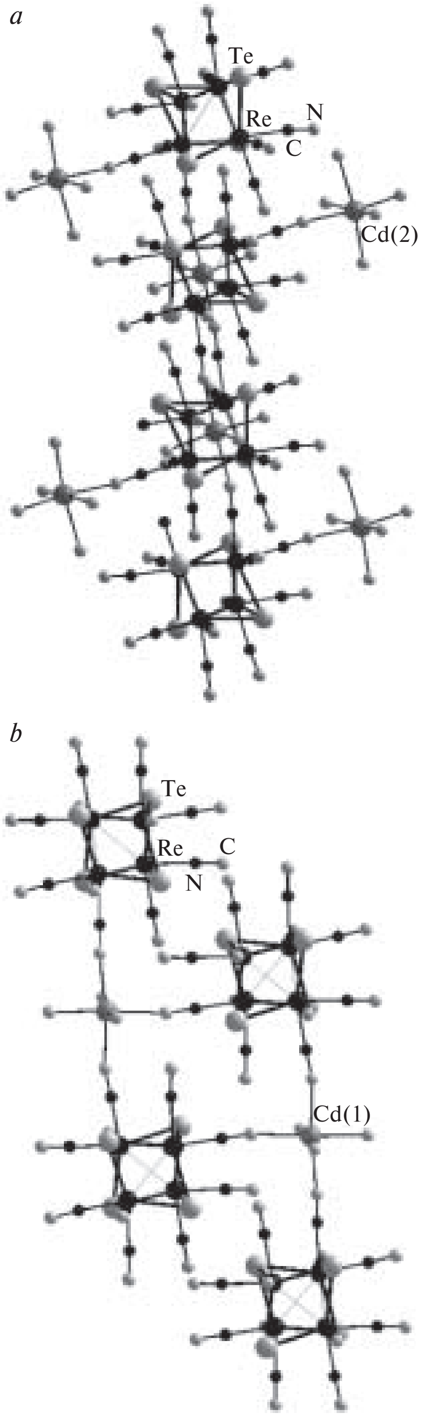


Fig. 14. Structure of the $[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]$ complex (**27**): *a*, coordination of the $[Cd(NH_3)_5]^{2+}$ cation to the cluster anion; *b*, the formation of infinite chains consisting of the cluster anions linked by the bridging $[Cd(NH_3)_3]^{2+}$ cations (the $[Cd(NH_3)_5]^{2+}$ cations are omitted).

Conclusion

To summarize, the tetranuclear rhenium cubane cluster complexes can be arbitrarily classed into three types:

1) compounds prepared by the high-temperature solid-phase synthesis; among these compounds are $Re_4S_4Te_4$ (polymeric structure) and $Re_4Q_4(TeX_2)_4X_8$ (molecular complexes);

2) compounds of different types prepared by the exchange reactions of the neutral TeX_2 or all terminal ligands in the $Re_4Q_4(TeX_2)_4X_8$ complexes;

3) cyanide-bridged polymeric chalcogenide cyanide complexes with cations of 3d transition and post-transition metals.

Based on the data on the chemical properties of tetranuclear rhenium chalcogenide cluster complexes with the cubane core, it can be stated that:

1. The replacements in metal clusters producing the heterometallic $Re_{4-x}M_x$ clusters can, apparently, be carried out only by high-temperature reactions.

2. The replacements of the inner-sphere ligands Q in the Re_4Q_4 cluster core also proceed at high temperature; the replacements occur according to the rule, which is well known in the coordination chemistry, *i.e.*, the replacement proceeds most readily upon the attack of more nucleophilic ligands (for example, in the series $Te \rightarrow Se \rightarrow S$).

3. The Re_4Q_4 cluster cubane core is a stable fragment and is remained unchanged (with retention of composition and structure) upon chemical transformations of one complex into another.

4. The outer-sphere ligands L are most reactive, their high lability allows one to perform numerous substitution reactions by methods of solution chemistry under standard conditions.

This study was financially supported by the INTAS (Grant 00-00689).

References

1. V. E. Fedorov, V. K. Evstaf´ev, S. D. Kirik, and A. V. Mishchenko, *Zh. Neorg. Khim.,* 1981, **26**, 2701 [*J. Inorg. Chem. USSR*, 1981, **26** (Engl. Transl.)].
2. C. Perrin, R. Chevrel, and M. Sergent, *C. R. Acad. Sci.*, 1975, **C280**, 949.
3. S. Harris, *Polyhedron*, 1989, **8**, 2843.
4. R. H. Holm, *Adv. Inorg. Chem.*, 1992, **38**, 1.
5. T. Shibakhara, *Coord. Chem. Rev.*, 1993, **123**, 73.
6. M. Laing, P. M. Kiernan, and W. P. Griffith, *J. Chem. Soc.*, *Chem. Commun.*, 1977, 221.
7. V. E. Fedorov, Yu. V. Mironov, V. P. Fedin, and Yu. I. Mironov, *Zh. Strukt. Khim.,* 1994, **35**, 146 [*J. Struct. Chem.*, 1994, **35** (Engl. Transl.)].
8. V. E. Fedorov, Yu. I. Mironov, Yu. V. Mironov, N. G. Naumov, U.-Hyon Paek, and S. C. Shin, *Zh. Neorg. Khim.,* 1998, **43**, 1916 [*Russ. J. Inorg. Chem.*, 1998, **43** (Engl. Transl.)].
9. V. E. Fedorov, Yu. V. Mironov, V. P. Fedin, H. Imoto, and T. Saito, *Acta Crystallogr.*, 1996, **C52**, 1065.
10. G. F. Khudorozhko, E. A. Kravtsova, L. N. Mazalov, V. E. Fedorov, L. G. Bulusheva, I. P. Asanov, G. K. Parygina, and Yu. V. Mironov, *Zh. Strukt. Khim.,* 1996, **37**, 901 [*J. Struct. Chem.*, 1996, **37** (Engl. Transl.)].
11. Y. V. Mironov, T. E. Albrecht-Schmitt, and J. A. Ibers, *Inorg. Chem.*, 1997, **36**, 944.
12. E. S. Lang, U. Abram, and J. Strähle, *Z. Anorg. Allg. Chem.*, 1996, **622**, 251.
13. Y. V. Mironov, T. E. Albrecht-Schmitt, D. M. Smith, and J. A. Ibers, *Z. Kristallogr.*, *New Crystal Structures*, 2001, **216**, 517.
14. Yu. V. Mironov, Dr. Sc. (Chem.) Thesis, Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 2000, 242 pp. (in Russian).
15. Yu. V. Mironov, A. V. Virovets, S. B. Artemkina, and V. E. Fedorov, *Zh. Strukt. Khim.,* 1999, **40**, 374 [*J. Struct. Chem.*, 1999, **40** (Engl. Transl.)].
16. Y. V. Mironov, T. E. Albrecht-Schmitt, and J. A. Ibers, *Z. Kristallogr.-New Crystal Structures*, 1997, **212**, 308.
17. Y. V. Mironov, A. V. Virovets, S. B. Artemkina, and V. E. Fedorov, *Angew. Chem.*, *Int. Ed. Engl.*, 1998, **37**, 2507.
18. Y. V. Mironov, A. V. Virovets, W. S. Sheldrick, and V. E. Fedorov, *Polyhedron*, 2001, **20**, 969.
19. Y. V. Mironov, O. Oeckler, A. Simon, and V. E. Fedorov, *Eur. J. Inorg. Chem.*, 2001, 2751.
20. Y. V. Mironov, M. A. Pell, T. E. Albrecht-Schmitt, and J. A. Ibers, *Inorg. Chem.*, 2001, **40**, 5472.
21. Y. V. Mironov, *Polyhedron*, 2000, **19**, 437.
22. Y. V. Mironov, *Eur. J. Inorg. Chem.*, 1999, 997.
23. V. P. Fedin, M. R. J. Elsegood, W. Clegg, and A. G. Sykes, *Polyhedron*, 1996, **15**, 485.
24. A. Müller, E. Krickemeyer, and H. Bögge, *Angew. Chem.*, *Int. Ed. Engl.*, 1986, **25**, 272.
25. A. Müller, E. Krickemeyer, and H. Bögge, *Z. Anorg. Allg. Chem.*, 1987, **554**, 61.
26. L. Fernholt, A. Haaland, H. V. Volden, and R. Kniep, *J. Mol. Struct.*, 1985, **128**, 29.
27. M. T. Rogers and R. A. Spurr, *J. Am. Chem. Soc.*, 1947, **69**, 2102.
28. Y. V. Mironov, M. A. Pell, and J. A. Ibers, *Inorg. Chem.*, 1996, **35**, 2709.
29. J. Beck and K. Müller-Buschbaum, *Eur. J. Inorg. Chem.*, 1999, 839.
30. A. Leist and W. Tremel, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 235.
31. V. P. Fedin, V. E. Fedorov, H. Imoto, and T. Saito, *Polyhedron*, 1997, **16**, 995.
32. V. P. Fedin, H. Imoto, and T. Saito, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1559.
33. V. P. Fedin, V. E. Fedorov, H. Imoto, and T. Saito, *Polyhedron*, 1997, **16**, 1615.
34. A. Erxleben, I. Mutikainen, and B. Lippert, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3667.
35. F. D. Rochon, P. C. Kong, and R. Melanson, *Inorg. Chem.*, 1990, **29**, 1352.
36. V. P. Fedin, M. N. Sokolov, A. V. Virovets, N. V. Podberezskaya, and V. E. Fedorov, *Polyhedron*, 1992, **11**, 2973.

37. A. Müller, V. P. Fedin, E. Diemann, H. Bögge, E. Krickemeyer, D. Solter, A. M. Giuliani, R. Barbieri, and P. Adler, *Inorg. Chem.*, 1994, **33**, 2243.
38. V. P. Fedin, M. N. Sokolov, A. V. Virovets, N. V. Podberezskaya, and V. E. Fedorov, *Polyhedron*, 1992, **11**, 2395.
39. V. P. Fedin, A. Müller, K. Khegechvailer, M. N. Sokolov, and V. E. Fedorov, *Zh. Neorg. Khim.,* 1994, **39**, 1663 [*Russ. J. Inorg. Chem.*, 1994, **39** (Engl. Transl.)].
40. V. P. Fedin, M. N. Sokolov, A. V. Virovets, N. V. Podberezskaya, and V. E. Fedorov, *Inorg. Chim. Acta*, 1998, **269**, 292.
41. D. Coucouvanis, *Adv. Inorg. Chem.*, 1998, **45**, 1.
42. S. Ferlay, T. Mallah, R. Ouahes, P. Veillet, and M. Verdaguer, *Nature*, 1995, **378**, 701.
43. A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Acad. Press, London, 1976.
44. W. P. Fehlhammer and M. Fritz, *Chem. Rev.*, 1993, **93**, 1243.
45. V. P. Fedin, I. V. Kalinina, A. V. Virovets, N. V. Podberezskaya, and A. G. Sykes, *J. Chem. Soc.*, *Chem. Commun.*, 1998, 237.
46. V. P. Fedin, I. V. Kalinina, D. G. Samsonenko, Y. V. Mironov, M. N. Sokolov, S. V. Tkachev, A. V. Virovets, N. V. Podberezskaya, M. R. J. Elsegood, W. Clegg, and A. G. Sykes, *Inorg. Chem.*, 1999, **38**, 1956.
47. V. P. Fedin, A. V. Virovets, D. G. Samsonenko, I. V. Kalinina, and D. Yu. Naumov, *Izv. Akad. Nauk, Ser. Khim.*, 2000, **49**, 18 [*Russ. Chem. Bull.*, *Int. Ed.*, 2000, **49**, 19].
48. V. P. Fedin, I. V. Kalinina, A. V. Virovets, N. V. Podberezskaya, I. S. Neretin, and Y. L. Slovokhotov, *J. Chem. Soc.*, *Chem. Commun.*, 1998, 2579.
49. A. Müller, E. Krikemeyer, H. Bögge, H. Ratajczak, and A. Armatage, *Angew. Chem.*, 1994, **106**, 800.
50. P. L. Dedert, T. Sorrell, T. J. Marks, and J. A. Ibers, *Inorg. Chem.*, 1982, **21**, 3506.
51. J. Sletten, A. Sorensen, M. Julve, and Y. Journaux, *Inorg. Chem.*, 1990, **29**, 5054.
52. F. H. Allen and O. Kennard, *Chemical Design Automation News.*, 1993, **8**, 1, 31.

Received July 20, 2001;
in revised form December 14, 2001