Synthesis and structures of new compounds based on tetrahedral rhenium chalcocyanide cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S or Se) and $[Cu(bipy)_2]^{2+}$ cations

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The reactions of the rhenium chalcocyanide cluster salts $K_4[Re_4Q_4(CN)_{12}]\cdot 6H_2O$ (Q = S or Se) with Cu^{2+} cations coordinated by the bidentate ligand 2,2′-bipyridyl (bipy) produced two new cluster compounds, $[Cu(NH_3)(bipy)_2]_2[Re_4S_4(CN)_{12}]\cdot bipy\cdot 3.25H_2O$ (**1**) and $[\{Cu(bipy)_2\}_2Re_4Se_4(CN)_{12}]\cdot bipy\cdot 8.5H_2O$ (**2**). The structures of these complexes were solved by X-ray diffraction. Compound **1** is ionic. Compound **2** is molecular. In the structures of both compounds, there are staking interactions between the $\{Cu(bipy)_2\}^{2+}$ cationic moieties and the solvate 2,2′-bipyridyl molecules.

Key words: rhenium, tetrahedral chalcocyanide clusters, copper, cyanide bridges, 2,2′-bipyridyl, crystal structure.

The development of facile and convenient procedures for the synthesis of chalcocyanide cluster complexes of early transition metals gave new impetus to the development of chemistry of these compounds. Considerable attention has been given to reactions of such complexes with 3d- and 4f-metal cations, interactions between which occur due to the ambident character of the CN ligand. Such complexes are of interest from the point of view of the design of materials with desired functional (magnetic, optical, electrochemical, *etc*.) properties. The tetranuclear rhenium chalcocyanide anionic complexes $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, or Te)[1,2] are very attractive objects of investigation. The presence of 12 cyano groups in such anions substantially extends the possibilities for coordination of metals (both transition and post-transition) by cluster complexes, resulting in a broad spectrum of the compounds.[3—6] One of ways of influencing the structure formation of such complex compounds is based on blocking the coordination sites of the metal atom by introducing ligands, which can compete with the nitrogen atoms of the CN ligands of cluster anions. Earlier, we have performed analogous studies for aliphatic polyamines, such as ethylenediamine (en),[7,8] diethylenetriamine (dien),[9] triethylenetetramine (trien),[10] and *threo*-tetraaminobutane.[11,12] The results of these studies demonstrated that low-dimensional (1D or 2D) coordination polymers are generally produced, although the formation of more complex structures is also possible.

In the present study, we synthesized and structurally characterized two new compounds prepared in systems containing the cluster anion $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S or Se), the Cu^{2+} cation, and 2,2′-bipyridyl (bipy).

Results and Discussion

We synthesized two new complexes $[Cu(NH_3)(bipy)_2]_2[Re_4S_4(CN)_{12}]\cdot bipy\cdot 3.25H_2O$ (**1**) and $[\{Cu(bipy)_2\}_2Re_4Se_4(CN)_{12}]\cdot bipy\cdot 8.5H_2O$ (**2**). The $K_4[Re_4Q_4(CN)_{12}]\cdot 6H_2O$ complexes (Q = S or Se) were used as the starting compounds. Compound **1** was prepared by slow evaporation of an aqueous ammonia mixture containing $K_4[Re_4S_4(CN)_{12}]\cdot 6H_2O$, $CuCl_2$, and bipy at room temperature. Compound **2** was prepared by counter diffusion of an aqueous solution of $K_4[Re_4Se_4(CN)_{12}]\cdot 6H_2O$ and an aqueous solution containing $CuCl_2$ and bipy in a U-shaped tube. The structures of compounds **1** and **2** were established by X-ray diffraction.

Compounds **1** and **2** contain the cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$, where Q = S or Se, respectively. The structures of the $[Re_4Q_4(CN)_{12}]^{4-}$ anions are analogous to their structures in the starting salts and other compounds, which contain the same anions. The cluster fragment $\{Re_4Q_4\}$ has a distorted cubic structure composed of two interpenetrating Re_4 and Q_4 tetrahedra. The chalcogen (S or Se) atoms are capping μ_3-ligands and are located above the Re_3 triangles almost symmetrically. Each metal atom is additionally coordinated by three terminal CN^- ligands through the carbon atoms. The Re—Re and Re—(μ_3-Q) distances in the cluster cores of com-

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pounds **1** and **2** are in ranges 2.7504(3)—2.7704(4) (**1**), 2.7955(5)—2.8076(5) (**2**) and 2.3481(13)—2.3991(13) (**1**), 2.4625(7)—2.4751(7) (**2**) Å, respectively, and are consistent with the distances found in other compounds containing analogous cluster fragments.

The structure of compound **1** consists of $[Cu(NH_3)(bipy)_2]^{2+}$ cations and $[Re_4S_4(CN)_{12}]^{2-}$ anions. In the $[Cu(NH_3)(bipy)_2]^{2+}$ cationic fragment, the copper(II) atom is coordinated by four nitrogen atoms of two 2,2′-bipyridyl molecules and one ammonia molecule (Fig. 1). Analysis of the Cambridge Structural Database (CSD V.5.25) demonstrated that the coordination polyhedron of the copper atoms in most of the cationic fragments $[Cu(bipy)_2L]$ (L is a monodentate ligand) is a trigonal bipyramid as, for example, in the related compound $[\{Cu(NH_3)(bipy)_2\}(BF_4)_2$.[13] However, the coordination polyhedron of the copper atoms in compound **1** is intermediate between a distorted square pyramid, whose base is formed by the N(5) atom of the ammonia molecule, the N(31) and N(32) atoms of one bipyridyl molecule, and the N(41) atom of another bipyridyl molecule (another nitrogen atom, N(42), of the latter bipyridyl molecule is apical), and a trigonal bipyramid, in which the triangular base is formed by the N(31) and N(42) atoms of different bipyridyl molecules and the N(5) atom of the ammonia molecule. The Cu—N bond lengths and the N—Cu—N angles are given in Table 1.

The structure of compound **2** (Fig. 2) contains one independent cluster anion $[Re_4Se_4(CN)_{12}]^{4-}$ linked to two cationic fragments $[Cu(bipy)_2]^{2+}$ through CN groups coordinated to different rhenium atoms. The cluster anion is involved in the formation of the molecular complex of composition $[\{Cu(bipy)_2\}_2Re_4Se_4(CN)_{12}]$. The coordination polyhedron of each copper atom (coordination number is 5) is a trigonal bipyramid formed by four nitrogen atoms of two different bipyridyl molecules and the nitrogen atom of the cluster anion (Cu—N bond lengths and N—Cu—N bond angles are given in Table 1).

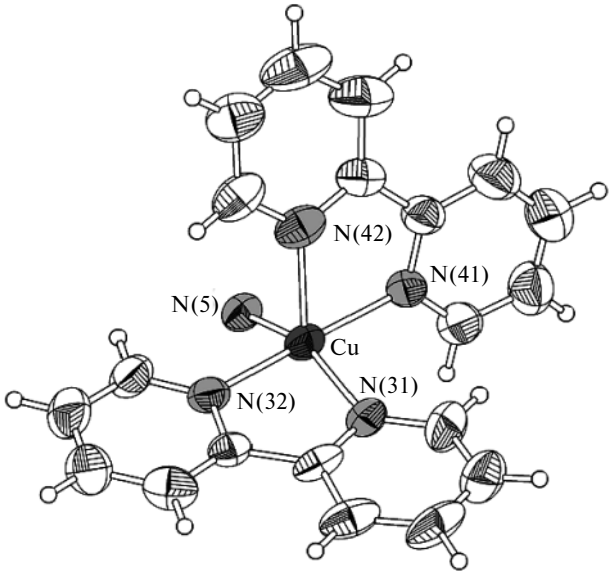

Fig. 1. Structure of the $[Cu(NH_3)(bipy)]^{2+}$ cation in the crystal structure of compound **1** (displacement ellipsoids are drawn at the 50% probability level).

In compound **2**, the coordination mode of the cation to the cluster anion is similar to that found earlier in the $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]\cdot 5H_2O$ compound. In the lat-

Table 1. The Cu—N bond lengths (d) and N—Cu—N bond angles (ω) in the cationic fragments of the $[Cu(NH_3)(bipy)_2]_2[Re_4S_4(CN)_{12}]\cdot bipy\cdot 3.25H_2O$ (**1**) and $[\{Cu(bipy)_2\}_2Re_4Se_4(CN)_{12}]\cdot bipy\cdot 8.5H_2O$ (**2**) compounds

1		**2**		**2**	
Bond	d/Å	Bond	d/Å	Bond	d/Å
Cu(1)—N(32)	2.014(5)	Cu(1)—N(61)	1.997(5)	Cu(2)—N(72)	1.981(5)
Cu(1)—N(41)	2.015(5)	Cu(1)—N(52)	2.012(5)	Cu(2)—N(82)	1.985(5)
Cu(1)—N(5)	2.019(5)	Cu(1)—N(13)	2.036(5)	Cu(2)—N(21)	2.024(5)
Cu(1)—N(31)	2.033(5)	Cu(1)—N(51)	2.061(5)	Cu(2)—N(71)	2.082(5)
Cu(1)—N(42)	2.189(6)	Cu(1)—N(62)	2.106(5)	Cu(2)—N(81)	2.085(5)
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
N(32)—Cu(1)—N(41)	172.8(2)	N(61)—Cu(1)—N(52)	176.4(2)	N(72)—Cu(2)—N(82)	176.1(2)
N(32)—Cu(1)—N(5)	94.8(2)	N(61)—Cu(1)—N(13)	92.9(2)	N(72)—Cu(2)—N(21)	91.5(2)
N(41)—Cu(1)—N(5)	91.9(2)	N(52)—Cu(1)—N(13)	90.5(2)	N(82)—Cu(2)—N(21)	92.4(2)
N(32)—Cu(1)—N(31)	81.0(2)	N(61)—Cu(1)—N(51)	96.7(2)	N(72)—Cu(2)—N(71)	80.8(2)
N(41)—Cu(1)—N(31)	93.8(2)	N(52)—Cu(1)—N(51)	80.1(2)	N(82)—Cu(2)—N(71)	97.1(2)
N(5)—Cu(1)—N(31)	155.2(2)	N(13)—Cu(1)—N(51)	127.4(2)	N(21)—Cu(2)—N(71)	129.0(2)
N(32)—Cu(1)—N(42)	98.3(2)	N(61)—Cu(1)—N(62)	79.8(2)	N(72)—Cu(2)—N(81)	97.4(2)
N(41)—Cu(1)—N(42)	78.3(2)	N(52)—Cu(1)—N(62)	100.1(2)	N(82)—Cu(2)—N(81)	80.3(2)
N(5)—Cu(1)—N(42)	99.2(2)	N(13)—Cu(1)—N(62)	114.3(2)	N(21)—Cu(2)—N(81)	119.0(2)
N(31)—Cu(1)—N(42)	105.6(2)	N(51)—Cu(1)—N(62)	118.3(2)	N(71)—Cu(2)—N(81)	112.0(2)

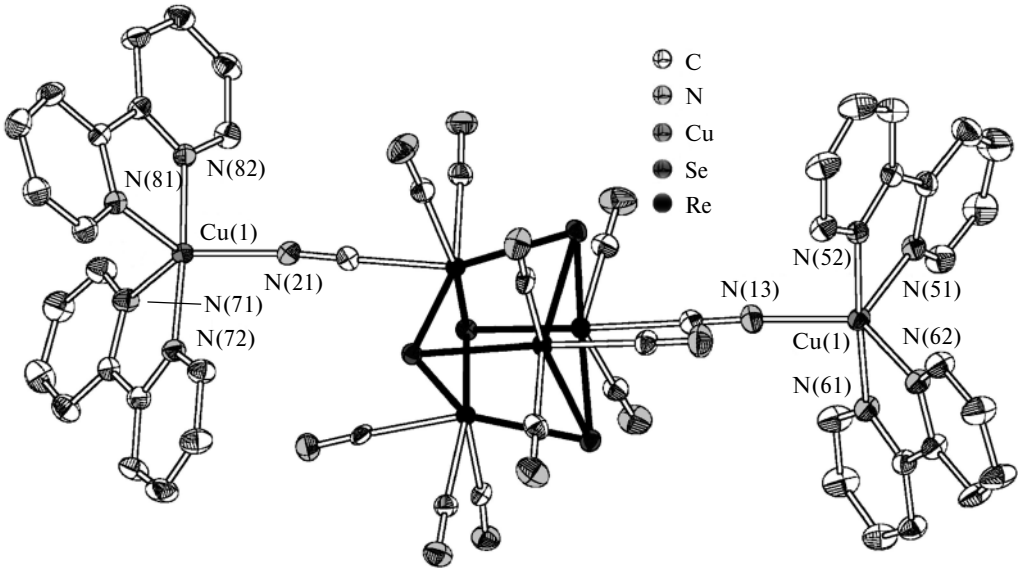

Fig. 2. Structure of molecular complex **2** (displacement ellipsoids are drawn at the 50% probability level).

ter compound, the cluster anion $[Re_4Te_4(CN)_{12}]^{4-}$ is linked to two cationic fragments $[Cu(en)_2]^{2+}$, which also deviate in opposite directions from the mean plane of the metal cluster.[8] By contrast, the cationic fragments $[Cu(trien)]^{2+}$ and $[Cu(NH_3)(dien)]^{2+}$ linked to the cluster anions in the $[\{Cu(trien)\}_2Re_4Q_4(CN)_{12}]\cdot nH_2O$ (Q = Se[14] or Te[10]) and $[\{Cu(NH_3)(dien)\}_2Re_4Se_4(CN)_{12}]\cdot 2.5H_2O$ compounds, respectively, are mutually perpendicular.

The structures of compounds **1** and **2** each contain one solvate 2,2′-bipyridyl molecule located virtually parallel to one of the coordinated 2,2′-bipyridyl molecules. The distances between two π systems are ~3.2 Å (for compound **1**) and ~3.5 Å (for compound **2**), which may be indicative of the presence of a π—π interaction between the conjugated systems of the coordinated and free bipyridyl molecules (stacking interactions).

Experimental

The starting $K_4[Re_4Q_4(CN)_{12}]\cdot 6H_2O$ compounds (Q = S or Se) were synthesized by the reaction of $Re_4Q_4(TeCl_2)_4Cl_8$ with KCN in water according to a procedure described earlier[1] for $K_4[Re_4Se_4(CN)_{12}]\cdot 6H_2O$. The $Re_4Q_4(TeCl_2)_4Cl_8$ clusters (Q = S or Se) were synthesized by the reaction of $ReCl_5$ with a mixture of elemental Te and S or Se.[15] Other reagents were commercial products.

An agarose gel was prepared as follows: agarose (1.5 g) was dissolved in water (100 mL) on heating. Then U-shaped tubes were filled with this solution and the tubes were kept for one day.

The IR spectra were recorded on a Bruker IFS-85 Fourier-transform IR spectrometer. Elemental analysis was carried out on a Carlo Erba 1106 instrument.

[Amminebis(2,2′-bipyridyl)copper(II)dodecacyanotetra-μ$_3$-sulfidotetrarhenate(Re—Re)] 2,2′-bipyridyl solvate hydrate, $[Cu(NH_3)(bipy)_2]_2[Re_4S_4(CN)_{12}]\cdot bipy\cdot 3.25H_2O$ (1). A mixture of $CuCl_2\cdot 2H_2O$ (20 mg, 0.12 mmol) and 2,2′-bipyridyl (37 mg, 0.24 mmol) in water (10 mL) was heated for 30 min, after which the color of the solution changed from blue to turquoise-colored. Then an aqueous ammonia solution (5 mL) containing $K_4[Re_4S_4(CN)_{12}]\cdot 6H_2O$ (10 mg, 0.007 mmol) was added, and the reaction mixture was slowly concentrated at room temperature for 3 days. The dark crystals that precipitated were filtered off and dried in air. Compound **1** was obtained in a yield of 5 mg (78%). IR, ν_{CN}/cm^{-1}: 2158 s.

[Dodecacyanotetra-μ$_3$-selenidotetrarhenium(Re—Re)-bis{bis(2,2′-bipyridyl)copper(II)}] 2,2′-bipyridyl solvate hydrate, $[\{Cu(bipy)_2\}_2Re_4Se_4(CN)_{12}]\cdot bipy\cdot 8.5H_2O$ (2). One arm of a U-shaped tube containing an agarose gel was filled with an aqueous solution (3 mL) containing $CuCl_2\cdot 2H_2O$ (10 mg, 0.06 mmol) and 2,2′-bipyridyl (18 mg, 0.14 mmol), and another arm was filled with an aqueous solution (3 mL) of $K_4[Re_4Se_4(CN)_{12}]\cdot 6H_2O$ (5 mg, 0.003 mol). After five weeks, dark large crystals were formed at the place, where the solutions contacted each other. The crystals suitable for X-ray diffraction study were selected manually. IR, ν_{CN}/cm^{-1}: 2177 w, 2146 s.

X-ray diffraction study. The crystallographic and X-ray diffraction data for crystals of **1** and **2** were obtained according to a standard procedure at room temperature on an automated Bruker—Nonius X8APEX CCD single-crystal diffractometer (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator). Semiempirical absorption corrections were applied based on the intensities of equivalent reflections using the SADABS program.[16]

The structures were solved by direct methods followed by calculations of difference Fourier maps and refinement of the positional and anisotropic thermal displacement parameters for the structural models by the full-matrix least-squares method using the SHELX-97 program package.[17,18] The positions of the hydrogen atoms in the water molecules were not located. The positions of the hydrogen atoms in the bipy molecules were calculated geometrically. The X-ray data collection and refinement statistics are given in Table 2.

Table 2. Crystallographic data for the $[Cu(NH_3)(bipy)_2]_2[Re_4S_4(CN)_{12}]\cdot bipy\cdot 3.25H_2O$ (**1**) and $[\{Cu(bipy)_2\}_2Re_4Se_4(CN)_{12}]\cdot bipy\cdot 8.5H_2O$ (**2**) compounds

Parameter	**1**	**2**
Molecular formula	$C_{62}H_{46.50}Cu_2N_{24}O_{3.25}Re_4S_4$	$C_{62}H_{57}Cu_2N_{22}O_{8.50}Re_4Se_4$
Molecular weight	2179.85	2434.02
Crystal dimensions/mm	0.08×0.07×0.06	0.26×0.14×0.12
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
a/Å	20.5950(12)	12.561(2)
b/Å	15.5139(10)	15.108(3)
c/Å	24.6009(16)	19.511(4)
α/deg		85.476(7)
β/deg	99.666(2)	89.685(7)
γ/deg		86.033(7)
V/Å^3	7748.6(8)	3682.2(12)
Z	4	2
ρ_{calc}/mg cm^{-3}	1.869	2.195
μ/mm^{-1}	6.928	9.161
$2\theta_{max}$/deg	62.96	66.66
Transmission factors	0.6072	0.1992
	0.6813	0.4061
Number of measured/independent reflections,	35406/14038	48051/14835
R_{int}	0.0357	0.0225
Number of observed reflections	9211	13913
Number of parameters in refinement *R* ($I > 2\sigma$)	476	914
R_1	0.0433	0.0291
wR_2	0.1162	0.0689
R (all data)		
R_1	0.0784	0.0317
wR_2	0.1255	0.0682

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