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Coordination compounds based on the cluster anion $[Re_4Te_4(CN)_{12}]^{4-}$ and Zn^{2+} cation

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Three new coordination compounds $[\{Zn(H_2O)_2\}\{Zn(H_2O)_4\}Re_4Te_4(CN)_{12}]$ (**1**), $[Zn(en)_2(NH_3)_2][\{Zn(en)(NH_3)_2\}Re_4Te_4(CN)_{12}] \cdot H_2O$ (**2**), and $[\{Zn_2(dien)_3\}Re_4Te_4(CN)_{12}] \cdot 6H_2O$ (**3**) (dien is diethylenetriamine) were prepared by reactions of aqueous solutions of the tetrahedral cluster rhenium tellurocyanide complex $K_4[Re_4Te_4(CN)_{12}] \cdot 5H_2O$ with zinc dichloride in the presence of ammonia, ethylenediamine, and diethylenetriamine, respectively. Complex **1** has a three-dimensional structure with two types of the Zn atoms; complex **2** is ionic with the polymeric chain anion; complex **3** has a molecular structure. The structures of complexes **1**—**3** were determined by single-crystal X-ray diffraction analysis.

Key words: rhenium, tetrahedral chalcocyanide clusters, zinc, cyanide bridges, coordination polymers, polydentate amines, crystal structure.

Coordination compounds with polymeric structures attract rapt attention of the researchers. Until recently, mononuclear cyano complexes of transition metals have widely employed in the preparation of such compounds, because the ambidentate nature of the CN group gives rise to cyanide-bridged polymers.[1]

The successful development of simple and convenient methods for the synthesis of cluster chalcocyanide complexes of transition metals has given a new impetus to the evolution of the chemistry of these interesting compounds. Tetranuclear rhenium chalcocyanide complexes $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, or Te) belong to such objects.[2—4] The presence of 12 cyano groups in these anions substantially extends the metal abilities to coordinate with the cluster complex, yielding a broad spectrum of the resulting compounds.[4—7] The use of polydentate ligands that can block the coordination sites of metal atoms provides additional possibilities for the synthesis of various complexes with the desired dimension of the crystal structure.[8—12]

Here we present the data on the synthesis and structural study of three new complexes obtained in the cluster anion $[Re_4Te_4(CN)_{12}]^{4-}$—Zn^{2+} cation—n-donating ligand system.

Results and Discussion

We prepared three new cyanide-bridged complexes: $[\{Zn(H_2O)_2\}\{Zn(H_2O)_4\}Re_4Te_4(CN)_{12}]$ (**1**), $[Zn(en)_2(NH_3)_2][\{Zn(en)(NH_3)_2\}Re_4Te_4(CN)_{12}] \cdot H_2O$ (**2**), and $[\{Zn_2(dien)_3\}Re_4Te_4(CN)_{12}] \cdot 6H_2O$ (**3**) (dien stands for diethylenetriamine). The cluster complex $K_4[Re_4Te_4(CN)_{12}] \cdot 5H_2O$ (**4**) was used as the starting material for the synthesis of these three complexes. Complex **1** was prepared by pouring an aqueous solution of complex **4** and a solution of $ZnCl_2$ in aqueous ammonia. Complex **2** was obtained from a solution of $ZnCl_2$ in aqueous ammonia and ethylenediamine. Analogously, complex **3** was obtained from $ZnCl_2$ and diethylenetriamine. The structures of complexes **1**—**3** were established by single-crystal X-ray diffraction analysis.

The main building block of these complexes is the cluster anion $[Re_4Te_4(CN)_{12}]^{4-}$, whose structure is identical to its structure in the starting salt.[3] The Re—Re and Re—(μ_3-Te) distances in the cluster unit $\{Re_4Te_4\}$ vary as follows: Re—Re 2.8635(7)—2.8853(7) (**1**), 2.8566(15)—2.8814(15) (**2**), and 2.8587(4)—2.8826(4) Å (**3**); Re—(μ_3-Te): 2.6206(5)—2.6494(7) (**1**), 2.619(2)—2.654(2) (**2**), and 2.6237(5)—2.6450(5) Å (**3**).

Complex **1** contains two structurally different Zn(1) and Zn(2) cations with different coordination environments. The Zn(1) cation is surrounded by four N atoms of the CN groups and two O atoms of water molecules, thus forming a two-dimensional network with cluster fragments united through the Re—CN—Zn—NC—Re bridges (Fig. 1, *a*). The coordination sphere of Zn(1) is a virtually regular octahedron (point symmetry 2*m*). The Zn(2) cation is equally disordered over two crystallographically equivalent positions (0.5/0.5). The distance between these positions is too short (1.568(6) Å) for them to be occu-

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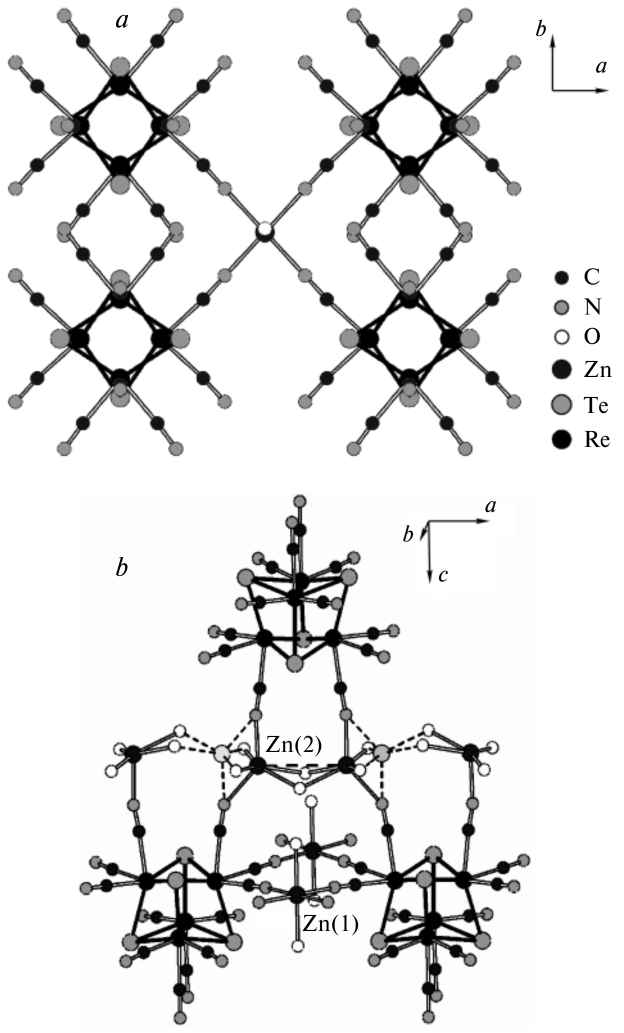

Fig. 1. Structure **1**: the nearest environment of the Zn(1) cation (*a*) and Zn(2)...Zn(2) dimers (*b*). The second disordered position of Zn(2) is colored gray.

pied simultaneously. The Zn(2) cations form dimers Zn(2)...Zn(2) with the nonbonding distance 3.717 Å. The Zn(2) atoms in dimers are coordinated with two water molecules as bridging ligands. The coordination environment of the Zn(2) atom includes two N atoms of the CN groups and four O atoms of water molecules arranged in a distorted octahedron (Fig. 1, *b*). The Zn(2) cations link two-dimensional networks together to produce a three-dimensional packing of complicated geometry. Structure **1** is similar to the earlier described complexes with other transition metals: $[\{Cu(H_2O)_2\}_2Re_4Te_4(CN)_{12}]$, $[\{Cd(H_2O)_4\}\{Cd(H_2O)_2\}_2Re_4Te_4(CN)_{12}]$, and $[\{Mn(H_2O)_4\}\{Mn(H_2O)_2\}_2Re_4Te_4(CN)_{12}]$.[4] In the study[6,7] of reactions of the cluster anion with ammine complexes of such metals as Cu, Cd, and Ni, we have found that complex formation in ammonia media follows a different pattern from the formation of aqua complexes. It has been suggested[7] that these complexes are intermediates in the formation of $[M_2(H_2O)_6Re_4Q_4(CN)_{12}]$. Thus, the polymeric complex **1** obtained in the present work is the missing unit to this scheme. It should be noted that complex **1** dissolves upon addition of ammonia and hence can be recrystallized with subsequent removal of the ammonia.

Complex **2** is ionic, being composed of the complex cation *cis*-$[Zn(en)_2(NH_3)_2]^{2+}$ and the polymeric anion with the simplest monomer unit $[\{Zn(en)(NH_3)_2\}Re_4Te_4(CN)_{12}]^{2-}$ (Fig. 2). The Zn atoms in the cation and the anion are both in the octahedral environment. The zinc(II) atom in the complex cation *cis*-$[Zn(NH_3)_2(en)_2]^{2+}$ is coordinated to two ammonia and two ethylenediamine molecules; the Zn(1)—N(NH_3 and NH_2) range from 2.095(18) to 2.393(16) Å.

In the anionic fragment of complex **2**, the cluster anions $[Re_4Te_4(CN)_{12}]^{4-}$ are linked together by the CN bridging ligands through the $[Zn(NH_3)_2(en)]^{2+}$ cations to form infinite zigzag chains with repeating units $[\{Zn(NH_3)_2(en)\}Re_4Te_4(CN)_{12}]^{2-}$. The coordination polyhedron of the Zn atom in the anionic fragment with the coordination number (C.N.) 6 is a distorted octahedron made up of two N atoms of the bidentate ethylenediamine ligand, two N atoms of ammonia molecules, and two N atoms of the CN ligands, the cyanide N atoms being *cis* to each other (see Fig. 2). The Zn(2)—N(NH_3, NH_2 and CN) bond lengths range from 2.04(2) to 2.37(2) Å.

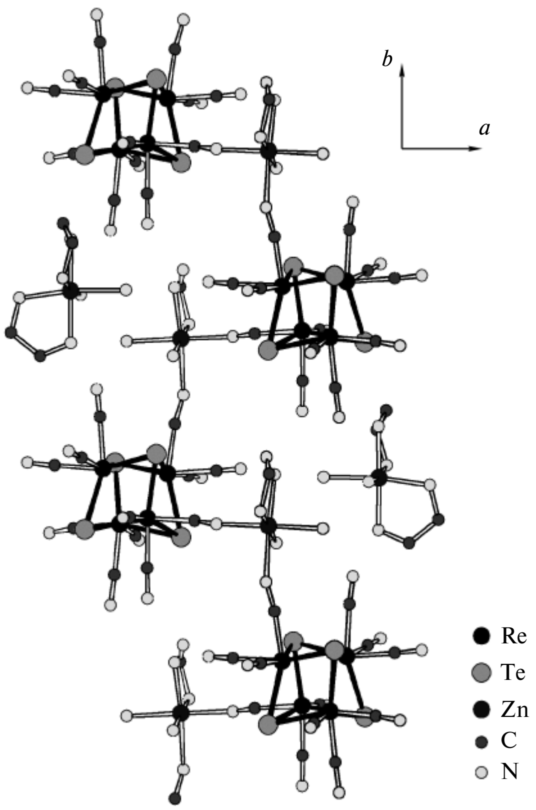

Fig. 2. Fragment of structure **2**.

The structure of the polymer chains in complex **2** appreciably differs from previously studied[6,7,9] chain structures based on the cluster anion $[Re_4Te_4(CN)_{12}]^{4-}$.

Molecular complex **3** can be formulated as a coordination compound of the complex cation $[Zn_2(dien)_3]^{4+}$ with the cluster anion $[Re_4Te_4(CN)_{12}]^{4-}$, both the Zn atoms being coordinated to the N atoms of the CN ligands attached to different Re atoms of the cluster anion (Fig. 3). The Zn atoms in this cation differ in coordination environment. The Zn(1) cation is in a distorted octahedral environment formed by three N atoms of one dien ligand, two amino groups of another dien ligand connecting the Zn(1) and Zn(2) atoms, and the N atom of the bridging CN ligand (Zn(1)—N 2.122(1)—2.276(1) Å). The coordination polyhedron of the Zn(2) cation is a trigonal bipyramid (C.N. = 5) with two terminal amino groups of the dien ligand and one amino group of the bridging dien ligand in the equatorial plane (Zn(1)—N(NH_2) 2.054(1)—2.069(1) Å). The axial positions are occupied by the medium amino group of the dien ligand (Zn(1)—N (NH) 2.216(1) Å) and the N atom of the bridging CN ligand (Zn(1)—N(CN) 2.124(1) Å). This structure resembles earlier described[9] complexes $[\{Cu_2(dien)_3\}Re_4Q_4(CN)_{12}]\cdot nH_2O$ (Q = Se and Te) with a similar complex cation $\{Cu_2(dien)_3\}^{4+}$; however, in contrast to structure **3**, the cluster anion is coordinated through only one CN group and the resulting C.N. for both Cu atoms is five.

Thus, we synthesized and structurally characterized three new cyanide-bridged complexes based on the tetrahedral anionic cyano complex of rhenium, Zn^{2+} cations, and N-donating ligands from solutions of ammonia. The presented data supplement previous data obtained for such metals as Cu, Ni, and Cd.

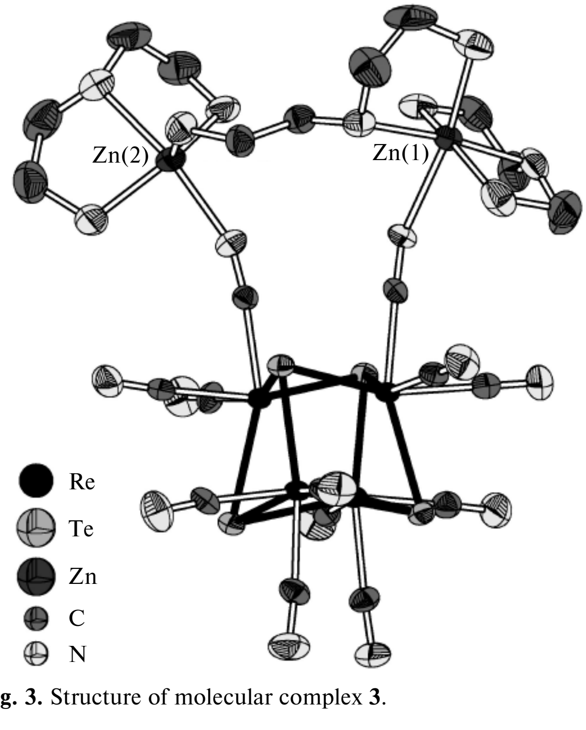

Fig. 3. Structure of molecular complex **3**.

Experimental

The starting complex $K_4[Re_4Te_4(CN)_{12}]\cdot 5H_2O$ was synthesized by the reaction of $Re_4Te_4(TeCl_2)_4Cl_8$ (prepared from $ReCl_5$ and elemental Te[13]) with an aqueous solution of KCN.[3] Other reagents were commercially available. IR spectra were recorded on a Bruker IFS-85 FTIR spectrometer. Elemental analysis was carried out on a Carlo Erba 1106 instrument.

Dodecacyano-μ₃-telluridotetrarhenium(Re—Re){tetraaquazinc(II)}{diaquazinc(II)}, $[\{Zn(H_2O)_2\}\{Zn(H_2O)_4\}Re_4Te_4(CN)_{12}]$ (1). An aqueous 25% NH_3 (5 mL) containing $ZnCl_2$ (0.084 g, 0.062 mmol) was added to a solution of $K_4[Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (0.01 g, 0.006 mmol) in water (5 mL). The resulting solution was concentrated in an open beaker at room temperature for two weeks. The dark crystals that formed were separated from a white precipitate by decantation with two to three portions of water, filtered off, and dried in air. The yield was 0.009 g (77%). IR, ν_{CN}/cm^{-1}: 2175 s, 2141 s.

Dodecacyano-μ₃-telluridotetrarhenium(Re—Re){diammineethylenediaminezincate(II)}diamminebisethylenediaminezinc(II) monohydrate, $[Zn(NH_3)_2(en)_2][\{Zn(NH_3)_2(en)\}Re_4Te_4(CN)_{12}]\cdot H_2O$ (2). An aqueous 25% NH_3 (5 mL) containing $ZnCl_2$ (0.042 g, 0.031 mmol) and ethylenediamine (0.025 mL, 0.37 mmol) was added to a solution of $K_4[Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (0.005 g, 0.003 mmol) in water (3 mL). The resulting solution was concentrated at room temperature for four weeks. The crystals that formed were filtered off and dried in air. The yield was 0.0038 g (65%). IR, ν_{CN}/cm^{-1}: 2162 m, 2135 s.

Dodecacyano-μ₃-telluridotetrarhenium(Re—Re){trisdiethylenetriaminedizinc(II)} hexahydrate, $[\{Zn_2(dien)_3\}Re_4Te_4(CN)_{12}]\cdot 6H_2O$ (3). An aqueous 25% NH_3 (5 mL) containing $ZnCl_2$ (0.046 g, 0.034 mmol) and diethylenetriamine (0.033 mL, 0.25 mmol) was added to a solution of $K_4[Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (0.005 g, 0.003 mmol) in water (3 mL). The resulting solution was concentrated at room temperature for four weeks. The red needle-like crystals that formed were filtered off and dried in air. The yield was 0.004 g (80%). Found (%): C, 11.9; H, 2.7; N, 13.1. $C_{24}H_{51}N_{21}O_6Re_4Te_4Zn_2$. Calculated (%): C, 13.6; H, 2.4; N, 13.9. IR, ν_{CN}/cm^{-1}: 2170 m, 2132 s.

X-ray diffraction analysis. Crystallographic and X-ray diffraction data for the determination of crystal structures **1**, **2**, and **3** were collected on Bruker SMART CCD, Enraf Nonius CAD4, and Bruker-Nonius X8APEX CCD diffractometers, respectively, at room temperature according to a standard procedure (in all cases, Mo-*K*α radiation, λ = 0.71073 Å, graphite monochromator). An absorption correction was applied from the crystal faces with the XPREP program (for complex **1**),[14] from five azimuthal scan curves (**2**), and semiempirically with consideration of the intensities of equivalent reflections with the SADABS program (**3**).[14]

The structures were solved by the direct method with the use of electron-density difference maps. The coordinates and anisotropic thermal parameters of the structural models were refined by the full-matrix least-squares method with the SHELX-97 program package.[15,16] Water H atoms were not located; the positions of hydrogen atoms in the polyamine molecules for

Table 1. Crystallographic data for $[\{Zn(H_2O)_2\}\{Zn(H_2O)_4\}Re_4Te_4(CN)_{12}]$ (**1**), $[Zn(en)_2(NH_3)_2][\{Zn(en)(NH_3)_2\}Re_4Te_4(CN)_{12}] \cdot H_2O$ (**2**), and $[\{Zn_2(dien)_3\}Re_4Te_4(CN)_{12}] \cdot 6H_2O$ (**3**)

Parameter	**1**	**2**	**3**
Molecular formula	$C_{12}H_{12}N_{12}O_6Re_4Te_4Zn_2$	$C_{18}H_{38}N_{22}ORe_4Te_4Zn_2$	$C_{24}H_{51}N_{21}O_6Re_4Te_4Zn_2$
Molecular mass	1806.28	1964.64	2115.80
Crystal sizes/mm	0.14×0.12×0.02	0.30×0.25×0.10	0.09×0.085×0.01
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Imma*	$P2_1/c$	$P2_1/n$
a/Å	10.4112(10)	16.926(3)	13.7462(3)
b/Å	15.3544(14)	15.168(3)	15.9435(5)
c/Å	18.840(2)	16.333(3)	22.7372(7)
β/deg		105.63(3)	95.735(1)
V/Å^3	3011.8(5)	4038.2(14)	4958.2(2)
Z	4	4	4
ρ_{calc}/g cm^{-3}	3.984	3.231	2.834
μ/mm^{-1}	21.427	15.993	13.043
Ranges of *hkl* indices	$-13 \le h \le 6$, $-20 \le k \le 20$, $-25 \le l \le 24$	$-20 \le h \le 19$, $-18 \le k \le 0$, $0 \le l \le 19$	$-9 \le h \le 19$, $-23 \le k \le 24$, $-34 \le l \le 33$
Transmission factors	0.1534 0.6739	0.37471 0.64221	0.0300 0.3554
Number of measured/independent reflections	9198/1972	7345/7074	47372/17312
R_{int}	0.0400	0.0579	0.0538
Number of parameters refined	113	462	550
R ($I > 2\sigma$)	$R_1 = 0.0236$, $wR_2 = 0.0537$	$R_1 = 0.0639$, $wR_2 = 0.1273$	$R_1 = 0.0381$, $wR_2 = 0.0724$
R (all reflections)	$R_1 = 0.0271$, $wR_2 = 0.0545$	$R_1 = 0.1201$, $wR_2 = 0.1515$	$R_1 = 0.0867$, $wR_2 = 0.0836$

structures **2** and **3** were determined geometrically. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Center. Selected crystallographic parameters and a summary of data collection are given in Table 1.

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