NEW COMPLEX COMPOUNDS BASED ON $[Re_6Te_8(CN)_6]^{4-}$ CLUSTER ANIONS AND $[M(dien)_2]^{2+}$ (M = Co²⁺ AND Cu²⁺) CATIONS: ADJUSTMENT OF THE CRYSTAL STRUCTURE BY THE BLOCKING OF COORDINATION SITES

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Three new octahedral ionic rhenium tellurocyanide cluster compounds $[Co(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (1), $[Cu(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (2), and $[Co(dien)_2]_3[Re_6Te_8(CN)_6]Br_2\cdot H_2O$ (3) (dien = diethylenetriamine) have been obtained by the diffusion of an ammonia solution of $Cs_4[Re_6Te_8(CN)_6]\cdot 2H_2O$ into a glycerol solution of $COCl_2\cdot 6H_2O$ (for 1 and 3) or $CuCl_2\cdot 2H_2O$ (for 2) in the presence of dien. The compounds have been characterized by single-crystal X-ray diffraction methods and by elemental analyses. **Keywords:** rhenium cluster, cyanide, transition-metal amine, X-ray structure.

INTRODUCTION

The chemistry of the chalcocyanide octahedral rhenium cluster complexes $[\text{Re}_6\text{Q}_8(\text{CN})_6]^4$ (Q = S, Se, Te) is in a stage of rapid development [1-14]. One of the important features of these complexes is the presence of terminal cyanide ligands. Owing to the ambidentate character of CN groups, the interaction of $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ anions with metal cations in aqueous solution leads to the formation of marginally soluble compounds with polymeric structures. In these reactions, the more nucleophilic nitrogen atoms of the cyano ligands replace the water molecules in the coordination spheres of the cations, resulting in the formation of Re–CN–M bridges. Generally, four or six such interactions occur and lead to the formation of extended polymeric arrays.

The use of chelating ligands rather than aqua species in such reactions can reduce the dimensionality of the resultant polymeric networks and lead to low-dimensional compounds. For example, we found that the presence of ethylenediamine (en) in reactions involving 3d transition-metal cations and $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ anions allowed us to obtain compounds with ionic, molecular, one-dimensional, and two-dimensional polymeric structures [15-17].

Other polydentate chelate ligands, such as triethylenetetramine [18], *N*,*N*'-ethylenebis(salicylideneaminato) [19, 20], octaethylporphyrinato dianion, tetraphenylporphyrinato dianion [21], and 1,2*S*,3*S*,4-tetraaminobutane [22] have been employed in similar reactions. With the last ligand, chiral polymer layers of composition $\{\{Cu(NH_3)(threo-tab)_2\} \{Cu(threo-tab)\}_2Re_6Q_8(CN)_6\}_{\infty\infty}$ (Q = S, Se) or $\{\{Cu(threo-tab)\}_2Re_6Te_8(CN)_6\}_{\infty\infty}$ are formed.

Here we describe the reactions between the $[Re_6Te_8(CN)_6]^{4-}$ cluster anion and Co^{2+} or Cu^{2+} cations in the presence of diethylenetriamine, a tridentate amine. Three new compounds, $[Co(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (1), $[Cu(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (2), and $[Co(dien)_2]_3[Re_6Te_8(CN)_6]Br_2\cdot H_2O$ (3) have been obtained and characterized by single-crystal X-ray diffraction methods and elemental analyses.

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EXPERIMENTAL

 $Cs_4[Re_6Te_8(CN)_6]\cdot 2H_2O$ was synthesized as described previously [23]. All other reagents were used as purchased. Elemental analyses of 1 and 2 for C, H, N (Carlo Erba 1106) were performed in the Laboratory of Microanalysis of the Institute of Organic Chemistry, Novosibirsk, Russia. Energy dispersive spectroscopy (EDS) for crystals of compound 3 was performed on an EDAX equipped Hitachi S-4500 field emission scanning electron microscope at the Northwestern University, Evanston, IL, USA.

Preparation of $[Co(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (1). In a 5 mm wide tube, a solution of 1.0 mg (0.35 µmol) of $Cs_4[Re_6Te_8(CN)_6]\cdot 2H_2O$ in 0.5 mL of 25% aqueous ammonia was allowed to diffuse into a solution of 3.5 mg (15 µmol) of $CoCl_2\cdot 6H_2O$ in 0.5 mL of glycerol to which 0.08 mL (750 µmol) of dien had been added. After one month, dark red-brown crystals suitable for an X-ray structure determination were obtained. The C, H, and N contents were determined by elemental analysis.

Found, %: C 9.3, H 1.9, N 8.6.

Calculated for [Co(dien)₂]₂[Re₆Te₈(CN)₆]·4H₂O, %: C 9.1, H 2.1, N 8.7.

Preparation of $[Cu(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O(2)$. 3.5 mg (20 µmol) of CuCl₂·2H₂O was employed in the procedure described for 1. After one month, dark red-brown crystals suitable for an X-ray structure determination were obtained. The C, H, and N contents were determined by elemental analysis.

Found, %: C 9.2, H 1.8, N 8.7.

Calculated for [Cu(dien)₂]₂[Re₆Te₈(CN)₆]·4H₂O, %: C 9.1, H 2.1, N 8.7.

Preparation of $[Co(dien)_2]_3[Re_6Te_8(CN)_6]Br_2 \cdot H_2O$ (3). In a similar manner, a solution of 1.0 mg (0.35 µmol) of $Cs_4[Re_6Te_8(CN)_6] \cdot 2H_2O$ in 0.5 mL of 25% aqueous ammonia solution to which 0.03 mL (585 µmol) of Br₂ had been added was layered on a solution of 3.5 mg (15 µmol) of CoCl₂·6H₂O and 0.08 mL (750 µmol) of dien in 0.5 mL of glycerol to afford dark red-brown crystals suitable for an X-ray structure determination.

EDS shows consistent Co:Re:Te:Br ratios of 1.5:3:4:1 for C₃₀H₈₀Br₂Co₃N₂₄ORe₆Te₈ (3).

X-ray diffraction analysis. Single-crystal X-ray diffraction data were collected at 153 K on a Bruker Smart-1000 CCD diffractometer with the program SMART [24]. Graphite-monochromatized Mo K_{α} radiation ($\lambda = 0.71073$ Å) was used. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in groups of 606 frames at ϕ settings of 0°, 90°, 180°, and 270°. The exposure times were 15 s/frame. Cell refinement and data reduction were carried out with the use of the program SAINT [24], and face-indexed absorption corrections were performed numerically with the use of the program XPREP [25]. The program SADABS [24] was then employed to make incident beam and decay corrections.

All structures were solved by means of the direct methods program SHELXS of the SHELXTL [25] suite of programs and were refined by full-matrix least-squares techniques with the use of the program SHELXL [25].

Details of the structural studies are summarized in Table 1. Crystallographic data in cif format for $[Co(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (1), $[Cu(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (2), and $[Co(dien)_2]_3[Re_6Te_8(CN)_6]Br_2\cdot H_2O$ (3) have been deposited as CCDC 258248 to 258250, respectively. These data may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK; fax: + 44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

Previously, we demonstrated that highly viscous glycerol solutions are effective in slowing the crystallization process [13, 16-18, 22]. This technique was utilized here to synthesize and crystallize $[Co(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (1),

	1	2	3
Empirical formula	$C_{22}H_{60}Co_2N_{18}O_4Re_6Te_8$	$C_{22}H_{60}Cu_2N_{18}O_4Re_6Te_8$	$\mathrm{C_{30}H_{80}Br_2Co_3N_{24}ORe_6Te_8}$
Formula weight	2896.74	2905.96	3267.79
Crystal system/space group	Triclinic, $P\overline{1}$	Triclinic, P1	Monoclinic, $P2_1/n$
<i>a</i> , Å	10.3720(6)	9.8387(7)	12.5974(8)
b, Å	11.9067(7)	11.3768(8)	12.0059(8)
<i>c</i> , Å	13.3095(8)	13.5832(10)	22.5936(15)
a (deg)	105.967(1)	103.960(1)	90
β (deg)	111.781(1)	108.665(1)	96.456(1)
γ (deg)	98.298(1)	100.826(1)	90
$V(\text{\AA}^3)/Z$	1410.5(1)/1	1338.6(2)/1	3395.5(4)/2
Calculated density, g/cm ³	3.410	3.605	3.196
μ , cm ⁻¹	174.89	186.03	159.51
Temperature, K	153	153	153
θ range (°)	1.85 to 29.03	1.67 to 28.91	1.77 to 28.93
<i>h</i> , <i>k</i> , <i>l</i> (min/max)	-14/14, -16/15, -17/18	-12/13, -15/15, -18/17	-19/17, -16/16, -30/30
Reflections collected	16937	16062	39693
Unique reflections / R_{int}	6705/0.0314	6343/0.0273	8402/0.0466
Parameters refined	270	271	340
$R1/wR2 \ (I > 2\sigma)$	0.0459/0.1163	0.0382/0.0875	0.0424/0.1044
R1/wR2 (all data)	0.0599/0.1263	0.0474/0.0917	0.0598/0.1154
GOOF	1.085	1.120	1.063
Largest peak/hole (eÅ ⁻³)	8.58/-1.71	8.97/-1.46	6.32/-2.26
CCDC deposition number	258248	258249	258250

TABLE 1. Crystal Data and Structure Refinements for $[Co(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (1),
 $[Cu(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (2), and $[Co(dien)_2]_3[Re_6Te_8(CN)_6]Br_2\cdot H_2O$ (3)

 $[Cu(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (2), and $[Co(dien)_2]_3[Re_6Te_8(CN)_6]Br_2\cdot H_2O$ (3) from the reactions of aqueous ammonia solutions of $Cs_4[Re_6Te_8(CN)_6]\cdot 2H_2O$ with glycerol solutions of $CoCl_2\cdot 6H_2O$ (for 1 and 3) and $CuCl_2\cdot 2H_2O$ (for 2) containing an excess of dien. All these syntheses are facile and provide quantitative yields.

All three compounds have been characterized by single-crystal X-ray diffraction methods. $[Co(dien)_2]_2[Re_6Te_8(CN)_6] \cdot 4H_2O$ (1) and $[Cu(dien)_2]_2[Re_6Te_8(CN)_6] \cdot 4H_2O$ (2) are isostructural, crystallizing with one formula unit in the triclinic space group $P\overline{1}$ (Table 1); $[Co(dien)_2]_3[Re_6Te_8(CN)_6]Br_2 \cdot H_2O$ (3) crystallizes with two formula units in the monoclinic space group $P2_1/n$ (Table 1).

The geometry of the $[\text{Re}_6\text{Te}_8(\text{CN})_6]^{4-}$ anion in these structures is similar to that found in the starting compound and related complexes [6, 13, 15-19, 23]. The six Re atoms in the Re₆ cluster form an almost ideal octahedron. The Re–Re bond distances vary from 2.6781(5) Å to 2.6841(4) Å in 1, from 2.6847(4) Å to 2.6996(4) Å in 2, and from 2.6766(5) Å to 2.6915(4) Å in 3. The chalcogen atoms cap each triangular face of the Re₆ octahedron. The Re–Te bonds range from 2.6831(5) Å to 2.6977(6) Å in 1, from 2.6881(5) Å to 2.7137(5) Å in 2, and from 2.6648(7) Å to 2.7093(7) Å in 3. Each Re atom is coordinated by a terminal CN ligand. The Re–C distances range from 2.083(8) Å to 2.106(10) Å in 1, from 2.091(6) Å to 2.111(7) Å in 2, and from 2.093(9) Å to 2.099(10) Å in 3; the C–N distances range from 1.095(11) Å to 1.154(10) Å in 1, from 1.131(8) Å to 1.149(8) Å in 2, and from 1.155(12) Å to 1.165(12) Å in 3. The anions in all three compounds have crystallographically imposed $\overline{1}$ symmetry.

In compounds 1 and 2, there is one crystallographically independent $[M(dien)_2]^{2+}$ cation (M = Co in 1, Cu in 2). The Co atom in the $[Co(dien)_2]^{2+}$ cation is octahedrally coordinated (Fig. 1). The Co–N distances vary from 2.129(8) Å to



Fig. 1. Ligand environment of Co1 in **1**. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted.



Fig. 2. Ligand environment of Cu1 in **2**. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted.



Fig. 3. Ligand environment of Co1 (a) and Co2 (b) in 3. Displacement ellipsoids are drawn at the 30% probability level. H atoms are omitted.

2.218(7) Å. The Cu atom in the $[Cu(dien)_2]^{2+}$ cation in **2** has a distorted square-pyramidal environment (Fig. 2). Three N atoms of one dien ligand and one N atom from a second dien ligand form four short bonds in the base of the pyramid. The Cu–N distances in the base of the pyramid vary from 2.007(6) Å to 2.039(6) Å. A second N atom of the second dien ligand coordinates at the apical position at a distance of 2.312(6) Å.

There are two crystallographically independent $[Co(dien)_2]^{2+}$ cations in the structure of compound **3**. The Co atoms in these are octahedrally coordinated (Fig. 3). The Co1–N distances vary from 2.152(9) Å to 2.190(8) Å; the Co2–N distances range from 2.120(10) Å to 2.159(10) Å. The $[Co2(dien)_2]^{2+}$ cation has crystallographically imposed $\overline{1}$ symmetry.

The crystal structures of $[Co(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (1), $[Cu(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (2), and $[Co(dien)_2]_3[Re_6Te_8(CN)_6]Br_2\cdot H_2O$ (3) are shown in Figs. 4, 5, and 6, respectively. Because the dien ligands occupy all the coordination sites of the *3d* transition-metal cations in compounds 1-3 (Figs. 1-3), the resultant compounds with $[Re_6Te_8(CN)_6]^{4-}$ anions are ionic, rather than polymeric; the ions are not bonded covalently to one another as they were in a



Fig. 4. View down [100] of the crystal packing in $[Co(dien)_2]_2[Re_6Te_8(CN)_6] \cdot 4H_2O$ (1). H atoms on the water molecules and dien ligands have been omitted for clarity.



Fig. 5. View down [100] of the crystal packing in $[Cu(dien)_2]_2[Re_6Te_8(CN)_6]\cdot 4H_2O$ (2). H atoms on the water molecules and dien ligands are not shown.



Fig. 6. View down [100] of the crystal packing in $[Co(dien)_2]_3[Re_6Te_8(CN)_6]Br_2 \cdot H_2O$ (3). H_2O molecules and H atoms on the dien ligands have been omitted for clarity.

large number of compounds of chalcocyanide cluster anions and transition metal cations studied earlier. Rather, an extensive system of weak hydrogen bonds joins the ions to one another and to the water molecules of crystallization. The shortest interactions of a given type include N–H···N hydrogen bonds between NH₂ and CN groups (N···N distance of 2.97 Å in 1, 3.03 Å in 2, and 3.03 Å in 3); O–H···N hydrogen bonds between CN groups and H₂O molecules (2.78 Å in 1 and 2.86 Å in 2); O–H···N bonds between NH₂ groups and H₂O molecules (2.94 Å in 1, 3.02 Å in 2); and O–H···O bonds between water molecules of crystallization (2.86 Å in 1).

Recently we have described similar ionic cluster compounds with common formula $[CuNH_3(trien)][Re_6Q_8(CN)_6]$ · nH_2O (Q = S, Se, Te) [18] in which all the Cu coordination sites were blocked by the polydentate trien ligand (trien = triethylenetetramine) and the ammonia molecule. These compounds comprise cation $[CuNH_3(trien)]^{2+}$, cluster anions, and water molecules of crystallization.

Note that similar reactions of chalcocyanide tetrahedral cluster anions with Cu^{2+} in the presence of dien result in the formation of both molecular [26] and polymeric [26-28] structures. For example, the structure of [{Cu(dien)}₃W₄Te₄(CN)₁₂]·9H₂O consists of infinite layers of cluster units connected to one another by {Cu(dien)} fragments [28]. An unusual example of bridged dien coordination to Cu atoms is found in the polymeric compounds [{Cu₂(dien)₃}Re₄S₄(CN)₁₂] and [K(H₂O)₂]₂[{Cu₃(dien)₄} {Re₄Q₄(CN)₁₂}·8H₂O (Q = Se, Te) [26]. In these compounds the cluster anions are connected to one another by oligomeric fragments {(dien)Cu–(µ-dien)–Cu(dien)}⁴⁺ and {(dien)Cu–(µ-dien)–Cu–(µ-dien)–Cu(dien)}⁶⁺, respectively.

In conclusion, the present research, which continues our investigations of the structural effects resulting from the addition of multidentate ligands to reactions involving M^{2+} cations with chalcocyanide cluster anions, demonstrates that the addition of dien to an $M^{2+}/[\text{Re}_6\text{Te}_8(\text{CN})_6]^{4-}$ system prevents the formation of coordination polymers involving the chalcocyanide octahedral cluster anions and leads to the formation of ionic compounds.

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