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New coordination cyano-bridged polymers based on tetranuclear rhenium chalcocyanide clusters and copper(II) ammonia complexes

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The reactions of aqueous solutions of the tetranuclear chalcocyanide cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$, where Q = S, Se, or Te, with an ammonia solution of copper(II) chloride at room temperature afforded a series of polymeric cyano-bridged compounds $[\{Cu(NH_3)_3\}_2\{Re_4Q_4(CN)_{12}\}] \cdot nH_2O$ (Q = S (**1**), Se (**2**)) and $[\{Cu(NH_3)_3\}_{1.7}\{Cu(NH_3)_4\}_{0.3}Re_4Te_4(CN)_{12}]$ (**3**) having chain structures. The structures of the compounds were established by X-ray diffraction analysis. Compounds **1** and **2** are isostructural and have ordered structures. In structurally similar compound **3**, the copper atoms are disordered over two positions in such a way that the structure contains the bridging $\{Cu(NH_3)_3\}$ fragments along with the terminal $\{Cu(NH_3)_4\}$ fragments.

Key words: tetranuclear chalcocyanide clusters, rhenium, copper, crystal structure, X-ray diffraction analysis.

The formation of metal chalcogenide clusters is typical of the rhenium chemistry as well as of the chemistry of other early transition metals.[1—7] Recently, chalcocyanide complexes have attracted increasing attention. Although the first tetranuclear chalcocyanide cluster complexes of rhenium $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se) were prepared[8] as early as 1977, the chemistry of these compounds was long poorly known. Recently, we have developed[9,10] a new highly efficient procedure for the synthesis of such rhenium chalcocyanide complexes by the reactions of the $Re_4Q_4(TeCl_2)_4Cl_8$ compounds (Q = S, Se, Te) with an aqueous solution of KCN. As a result, the chalcocyanide anions $[Re_4Q_4(CN)_{12}]^{4-}$ became readily available, which opened a way to extensive studies of their chemical properties. One of the most interesting lines of investigation into the chemistry of chalcocyanide anions deals with their reactions with metal cations. Our first studies[10—12] have demonstrated that the behavior of the ammonia complexes of transition metals in such reactions differs substantially from that of aqua complexes.

Results and Discussion

The reactions of aqueous solutions of the $K_4Re_4Q_4(CN)_{12}$ complexes with an ammonia solution of $CuCl_2$ afforded three new complexes, *viz.*, $[\{Cu(NH_3)_3\}_2\{Re_4Q_4(CN)_{12}\}] \cdot nH_2O$, where Q is S (**1**) or Se (**2**), and $[\{Cu(NH_3)_3\}_{1.7}\{Cu(NH_3)_4\}_{0.3}Re_4Te_4(CN)_{12}]$ (**3**). The complexes crystallized as dark-red crystals. Their structures were established by X-ray diffraction analysis.

According to the results of X-ray diffraction analysis, complexes **1** and **2** are isostructural and are structurally similar to complex **3**. The main structural fragments of compounds **1—3** are shown in Figs. 1 and 2. In the cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$, the rhenium atoms form the Re_4 tetrahedron with the Re—Re distances in the ranges of 2.7533(7)—2.765(1) (**1**), 2.7953(6)—2.8037(6) (**2**), and 2.8645(8)—2.891(1) Å (**3**). The chalcogen atoms Q are μ_3-coordinated at the faces of the Re_4 tetrahedron. The Re—(μ_3-Q) distances are in the ranges of 2.381(2)—2.405(3) (**1**), 2.458(1)—2.473(1) (**2**), and

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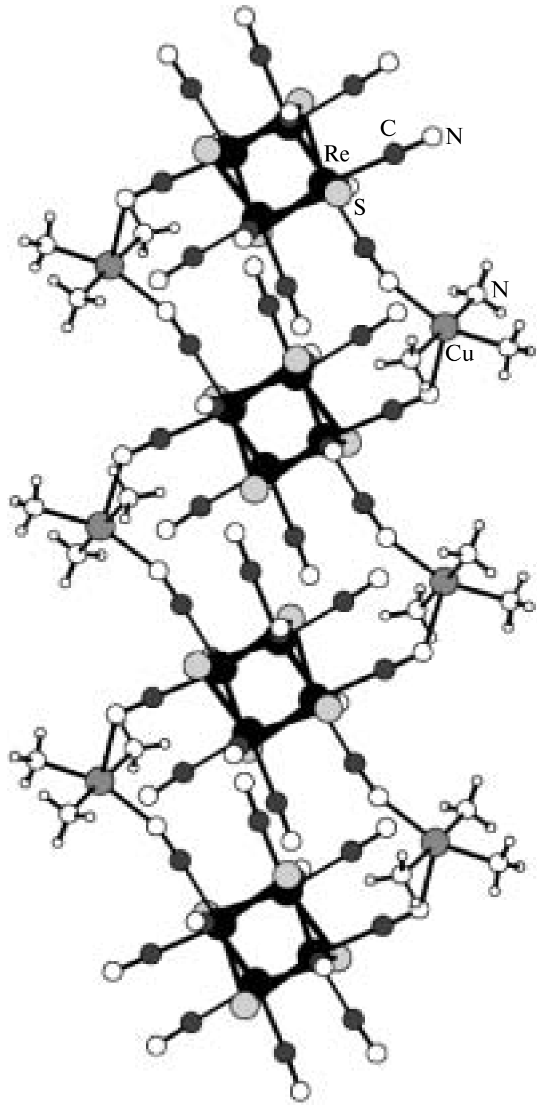

Fig. 1. Fragment of the structure of complex **1**.

2.6321(7)—2.652(2) Å (**3**). The Re—Re and Re—(μ_3-Q) distances increase in the series $\{Re_4S_4\}^{8+} < \{Re_4Se_4\}^{8+} < \{Re_4Te_4\}^{8+}$ and are in good agreement with the data for the related compounds.[7] Each rhenium atom is additionally coordinated by three terminal CN^- ligands. The Re—C distances are virtually independent of the nature of the chalcogen atom in the cluster core and are in the ranges of 2.086(11)—2.121(12) (**1**), 2.111(6)—2.122(6) (**2**), and 2.081(8)—2.118(8) Å (**3**). In compounds **1** and **2**, the $[Re_4Q_4(CN)_{12}]^{4-}$ clusters anions are linked to each other by the bridging cyano ligands through the $[Cu(NH_3)_3]^{2+}$ cations to form infinite chains (see Fig. 1).

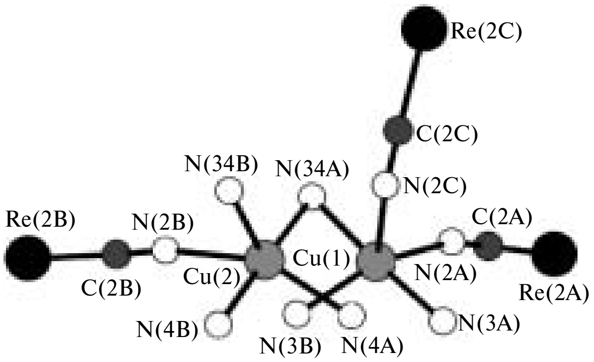

Fig. 2. Disorder of the copper atom over two positions in the structure of complex **3**.

In complexes **1** and **2**, the coordination polyhedra of the copper ions are the distorted square pyramids $[Cu(NH_3)_3(CN)_2]$. The Cu—N (NH_3) distances are in the ranges of 1.990(9)—2.004(9) Å (**1**) and 1.986(5)—2.003(6) Å (**2**). The Cu—N (CN) distances are 2.041(9) and 2.392(10) Å (**1**) and 2.035(5) and 2.410(6) Å (**2**). This coordination mode is also characteristic of the copper compounds involving cluster rhenium chalcocyanide complexes studied earlier.[11,13]

The structure of compound **3** is similar to that of compounds **1** and **2**; however, there are some differences. In contrast to the structures of compounds **1** and **2** in which all cations are ordered, the copper atoms in the structure of **3** are disordered over two positions denoted as Cu(1) and Cu(2) with the occupancies of 83% and 17%, respectively. The distance between the copper atoms located in these positions (2.300(7) Å) is too short compared to the Cu—Cu contacts in the known structures.[14,15] Hence, we concluded that the structure of compound **3** should be described as the structure containing disordered copper atoms. The disorder is confirmed by the statistical character of the coordination environment about the Cu(1) and Cu(2) positions. This environment is formed by the nitrogen atoms whose occupancies correspond to the occupancies of the copper atoms to which they are coordinated. The coordination numbers of both copper atoms, Cu(1) and Cu(2), are 5. The Cu(1) atom is coordinated by three N atoms of the ammonia molecules (Cu(1)—N (NH_3) distances are in the range of 2.014(8)—2.027(8) Å) and two N atoms of the CN ligands of the cluster anion (Cu(1)—N (CN) distances are 2.019(6) and 2.490(7) Å). The Cu(2) atom is coordinated by four N atoms of the ammonia molecules (Cu(2)—N (NH_3) distances are in the range of 1.98(5)—2.194(15) Å) and one N atom of the CN ligand of the cluster anion (Cu(2)—N (CN) distance is 2.261(10) Å). X-ray diffraction analysis of compound **3** was initially performed using a twin crystal and the structure of **3** was solved taking into account this factor. To test the validity of the results and settle the question about the disorder of the copper atoms, we additionally studied two other crystals of compound **3**, which appeared to be single crystals rather than twins. X-ray diffraction studies of these crystals were carried out independently on different diffractometers, including a low-temperature study. The solutions of their structures gave identical results to confirm that the copper atoms are disordered over two positions as described above (see Fig. 2). The low-temperature structural data demonstrated that the character of disorder of the copper atoms is static rather than dynamic. Since three independent structure solutions of compound **3** gave basically identical results, we used the most precise data for the description of its structure. Analysis of the disorder of the copper atoms in the structure of compound **3** led to the formula $[\{Cu(NH_3)_3\}_{1.7}\{Cu(NH_3)_4\}_{0.3}Re_4Te_4(CN)_{12}]$. In this case, the chains have a discrete structure consisting of the $\{Cu(NH_3)_3\}$ bridging fragments along with the $\{Cu(NH_3)_4\}$ terminal fragments.

Experimental

The $K_4Re_4Te_4(CN)_{12}$ complex was prepared from $Re_4Te_8Cl_{16}$ by the reaction with KCN in water.[9] The $K_4Re_4Se_4(CN)_{12}$ and $K_4Re_4S_4(CN)_{12}$ compounds were synthesized analogously starting from $Re_4Se_4Te_4Cl_{16}$ and $Re_4S_4Te_4Cl_{16}$, respectively. The starting cluster chalcogenides $Re_4Te_8Cl_{16}$, $Re_4Se_4Te_4Cl_{16}$, and $Re_4S_4Te_4Cl_{16}$ were prepared from $ReCl_5$ and Te or $ReCl_5$, S or Se, and Te.[16] Elemental analysis was carried out on a Carlo Erba 1106 instrument. The IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer in KBr pellets.

Dodecacyanotetra-μ$_3$-sulfidotetrarhenium(Re-Re)bis{triamminecopper(II)} hydrate, $[\{Cu(NH_3)_3\}_2Re_4S_4(CN)_{12}]\cdot1.3H_2O$ (1). A solution of $CuCl_2$ (0.025 g, 0.19 mmol) in a concentrated aqueous ammonia solution (2 mL) was added to a solution of $K_4Re_4S_4(CN)_{12}\cdot5H_2O$ (0.015 g, 0.01 mmol) in water (3 mL) and the reaction mixture was kept in an untightly closed tube. After 3 days, the dark-red crystals that precipitated were filtered off and dried on a paper filter. The yield was 0.013 g (86%). Found (%): C, 9.84; N, 17.20; H, 1.35; S, 8.71. $C_{12}H_{20.6}N_{18}O_{1.3}Cu_2Re_4S_4$. Calculated (%): C, 10.02; N, 17.53; H, 1.44; S, 8.92. IR, ν_{CN}/cm^{-1}: 2197 m, 2156 s; ν_{NH_3}/cm^{-1}: 3354 m, 3333 s, 3262 m, 1616 s, 1239 m, 708 m.

Dodecacyanotetra-μ$_3$-selenidotetrarhenium(Re-Re)bis{triamminecopper(II)} hydrate, $[\{Cu(NH_3)_3\}_2Re_4Se_4(CN)_{12}]\cdot1.1H_2O$ (2). Compound **2** was prepared analogously from $K_4Re_4Se_4(CN)_{12}\cdot5H_2O$ (0.015 g, 0.009 mmol) and $CuCl_2$ (0.025 g, 0.19 mmol). The yield was 0.01 g (66.5%). Found (%): C, 8.94; N, 15.48; H, 1.20. $C_{12}H_{20.2}N_{18}O_{1.1}Cu_2Re_4Se_4$. Calculated (%): C, 8.89; N, 15.54; H, 1.26. IR, ν_{CN}/cm^{-1}: 2184 m, 2151 s; ν_{NH_3}/cm^{-1}: 3372 m, 3337 s, 3266 m, 1615 m, 1244 m, 708 m.

Dodecacyanotetra-μ$_3$-telluridotetrarhenium(Re-Re){triamminecopper(II)}{tetraamminecopper(II)}, $[\{Cu(NH_3)_3\}_{1.7}\{Cu(NH_3)_4\}_{0.3}Re_4Te_4(CN)_{12}]$ (3). Compound **3** was prepared analogously from $K_4Re_4Te_4(CN)_{12}\cdot5H_2O$ (0.015 g, 0.008 mmol) and $CuCl_2$ (0.025 g, 0.19 mmol). The yield was 0.014 g (94%). Found (%): C, 7.57; N, 14.19; H, 0.97.

Table 1. Crystallographic data for $[\{Cu(NH_3)_3\}_2Re_4S_4(CN)_{12}]\cdot1.3H_2O$ (**1**), $[\{Cu(NH_3)_3\}_2Re_4Se_4(CN)_{12}]\cdot1.1H_2O$ (**2**), and $[\{Cu(NH_3)_3\}_{1.7}\{Cu(NH_3)_4\}_{0.3}Re_4Te_4(CN)_{12}]$ (**3**)

Parameter	1	2	3
Empirical formula	$C_{12}H_{20.6}N_{18}O_{1.3}Cu_2Re_4S_4$	$C_{12}H_{20.2}N_{18}O_{1.1}Cu_2Re_4Se_4$	$C_{12}H_{18.9}Cu_2N_{18.3}Re_4Te_4$
Molecular weight	1438	1622	1801.8
Crystal dimensions/mm	0.08×0.1×0.6	0.40×0.14×0.04	0.09×0.09×0.13
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a/Å	20.779(4)	20.828(2)	21.183(6)
b/Å	13.568(3)	13.5980(10)	13.657(4)
c/Å	14.398(3)	14.5000(10)	14.918(4)
β/deg	129.64(3)	130.37(2)	131.40(2)
V/Å^3	3125.9(11)	3128.8(10)	3237.3(16)
Z	4	4	4
ρ_{calc}/mg cm^{-3}	3.074	3.456	3.618
μ/mm^{-1}	17.077	21.444	19.123
Ranges of reflection indices	$-18 \le h \le 24$, $-16 \le k \le 0$, $-17 \le l \le 0$	$-27 \le h \le 27$, $-17 \le k \le 17$, $-18 \le l \le 18$	$-28 \le h \le 29$, $-19 \le k \le 14$, $-19 \le l \le 20$
Transmission coefficients	0.581/0.760	0.0862/0.2183	1.15/1.95
Number of measured /independent reflections, R_{int}	2877/2757 0.0264	12806/3387 0.0413	13147/4720 0.0448
Number of parameters in refinement	195	195	210
R (*I* > 2σ)			
R_1	0.0326	0.0259	0.0298
wR_2	0.0720	0.0621	0.0515
R (all reflections)			
R_1	0.0469	0.0279	0.0468
wR_2	0.0769	0.0631	0.0538

$C_{12}H_{18.9}N_{18.3}Cu_2Re_4Te_4$. Calculated (%): C, 8.0; N, 14.23; H, 1.06. IR, ν_{CN}/cm^{-1}: 2158 w, 2130 s; ν_{NH_3}/cm^{-1}: 3340 m, 3318 m, 1602 m, 1233 m, 698 s.

X-ray diffraction study. The structures of complexes **1**—**3** were established by single-crystal X-ray diffraction analysis. X-ray diffraction studies were carried out on Siemens P4 (compound **1**), Stoe IPDS (compound **2**), and Bruker Smart-1000 CCD (compound **3**) diffractometers using Mo-Kα radiation (0.71073 Å) and a graphite monochromator. The intensities of the measured reflections were corrected for absorption using five azimuth scanning curves (**1**), based on the crystal habitus (**2**), and using the SADABS program[17] (**3**). The crystallographic data and principal parameters of the refinement are given in Table 1. The structures were solved by direct methods in the space group *C*2/*c* and refined by the full-matrix least-squares method using the SHELX-97,[18,19] SHELXT-PC,[20] and Stoe IPDS program packages.[21]

The positions of the hydrogen atoms of the ammonia molecules in compounds **1** and **2** were calculated geometrically and refined in the rigid-body approximation with isotropic thermal parameters equal to 150% of the equivalent thermal parameters of the corresponding nitrogen atoms. The atomic coordinates were deposited with the Cambridge Structural Database and can also be obtained from the authors.

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References

1. V. E. Fedorov, A. V. Mishchenko, and V. P. Fedin, *Usp. Khim.*, 1985, **54**, 694 [*Russ. Chem. Rev.*, 1985, **54** (Engl. Transl.)].
2. A. Perrin and M. Sergent, *New J. Chem.*, 1988, **12**, 337.
3. T. Saito, *Advances in Inorg. Chem.*, 1997, **44**, 45.
4. Yu. V. Mironov and V. E. Fedorov, *Zh. Strukt. Khim.,* 1999, **40**, 1183 [*J. Struct. Chem.*, 1999, **40** (Engl. Transl.)].
5. T. Saito, *J. Chem. Soc., Dalton Trans.*, 1999, 97.
6. J.-C. P. Gabriel, K. Boubekeur, S. Uriel, and P. Batail, *Chem. Rev.*, 2001, **101**, 2037.
7. Yu. V. Mironov and V. E. Fedorov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 529 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 569].
8. M. Laing, P. M. Kiernan, and W. P. Griffith, *J. Chem. Soc., Chem. Commun.*, 1977, 221.
9. Y. V. Mironov, T. E. Albrecht-Schmitt, and J. A. Ibers, *Z. Kristallogr., New Crystal Structures*, 1997, **212**, 308.
10. Y. V. Mironov, A. V. Virovets, W. S. Sheldrick, and V. E. Fedorov, *Polyhedron*, 2001, **20**, 969.
11. Y. V. Mironov, A. V. Virovets, S. B. Artemkina, and V. E. Fedorov, *Angew. Chem., Int. Ed.*, 1998, **37**, 2507.
12. Y. V. Mironov, O. Oeckler, A. Simon, and V. E. Fedorov, *Eur. J. Inorg. Chem.*, 2001, 2751.
13. Y. V. Mironov, V. E. Fedorov, I. Ijjaa, and J. A. Ibers, *Inorg. Chem.*, 2001, **40**, 6320.
14. V. M. Rao and H. Manohar, *Inorg. Chim. Acta*, 1979, **34**, L213.
15. V. M. Rao, D. N. Sathyanarayana, and H. Manohar, *J. Chem. Soc., Dalton Trans.*, 1983, 2167.
16. Y. V. Mironov, T. E. Albrecht-Schmitt, and J. A. Ibers, *Inorg. Chem.*, 1997, **36**, 944.
17. *SMART Version 5.054 Data Collection and SAINT-PLUS Version 6.0 Data Processing Software for SMART System*, Bruker Analytical X-Ray Instruments, Inc., Madison (WI), 1999.
18. G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1990.
19. G. M. Sheldrick, *SHELXL-97, Program for the Crystal Structure Refinement*, University of Göttingen, Göttingen (Germany), 1997.
20. G. M. Sheldrick, *SHELXTL DOS/Windows/NT, Version 5.10*; Bruker Analytical X-Ray Instruments, Inc., Madison (WI), 1997.
21. *Stoe IPDS Software*, Darmstadt, 1998.

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