New Types of Complexes Based on Re_4 Chalcocyanide Clusters − Syntheses and Crystal Structures of $[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}]\cdot 3.4H_2O$ and $[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]\cdot 4H_2O$

Yuri V. Mironov,[a] Oliver Oeckler,[b] Arndt Simon,*[b] and Vladimir E. Fedorov[a]

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Two new tetrahedral rhenium chalcocyanide cluster compounds $[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}]\cdot 3.4H_2O$ (**1**) and $[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]\cdot 4H_2O$ (**2**), exhibiting molecular (**1**) and chain-like polymeric structures (**2**), have been synthesized by treatment of the salt-like cluster compound $K_4Re_4Te_4(CN)_{12}\cdot 5H_2O$ with solutions of nickel acetate and cadmium sulfate, respectively, in aqueous ammonia. Both compounds have been characterized by single-crystal X-ray diffraction analysis. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ [a = 19.572(3), b = 14.849(2), c = 23.576(3) Å, β = 145.97(1)°, Z = 4, V = 3834.4(9) Å^3], while compound **2** crystallizes in the triclinic space group $P\bar{1}$ [a = 12.726(2), b = 13.408(2), c = 13.918(2) Å, α = 111.31(2), β = 116.77(2), γ = 90.17(2)°, Z = 2, V = 1935.3(5) Å^3].

Introduction

The chemistry of transition metal chalcocyanide cluster compounds, existing as either discrete or interconnected clusters, has been extensively developed in recent years.[1−14] One of the most interesting features of CN ligands is their ability to form cyano-bridged complexes with transition metals. In the past few years, many such complexes incorporating cluster chalcocyanide anions have been obtained, most of them based on the cluster anions $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se) with an octahedral core.[9−14] In these polymeric compounds, all or some of the CN^- ligands may be bridging, thus allowing the formation of structures of different dimensionalities, i.e. 1D, 2D, or 3D. In recent publications,[6,15] we have reported the syntheses of the layered compound $[Cu_4(\mu_3\text{-}OH)_4][Re_4Te_4(CN)_{12}]$, obtained at pH ≈ 7, and three 3D-polymeric compounds $Mn_2[Re_4Se_4(CN)_{12}]\cdot 6H_2O$, $Cd_2[Re_4Te_4(CN)_{12}]\cdot 6H_2O$, and $Cu_2[Re_4Te_4(CN)_{12}]\cdot 4H_2O$, obtained at pH ≈ 1−5. We have now extended our studies to aqueous ammonia. Our findings demonstrate the significant dependence of the nature of the product on the reaction conditions used. In the present work, we have prepared one molecular complex $[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}]\cdot 3.4H_2O$ (**1**) and one chain-like complex $[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]\cdot 4H_2O$ (**2**). Compound **1** contains only terminal $[Ni(NH_3)_5]^{2+}$ cations, while compound **2** contains both bridging $[Cd(NH_3)_3]^{2+}$ and terminal $[Cd(NH_3)_5]^{2+}$ cations.

[a] Institute of Inorganic Chemistry of the Russian Academy of Sciences,
pr. Lavrentyeva 3, 630090 Novosibirsk, Russia
[b] Max-Planck-Institut für Festkörperforschung,
Heisenbergstraße 1, 70569 Stuttgart, Germany

Results

The treatment of $K_4Re_4Te_4(CN)_{12}$ with transition metal salts in aqueous solution leads to the formation of cyano-bridged cluster complexes, in which the transition metal atom may be coordinated by one, two, or three N atoms of CN ligands of the cluster anion $[Re_4Te_4(CN)_{12}]^{4-}$. In our earlier investigations in this area, it became clear that the preparation of single crystals of such complexes requires a very slow diffusion of the starting components. Mixing of aqueous solutions usually results only in powders, the structures of which are often different from those of the compounds obtained by slow diffusion. In the studied reactions, the transition metal adducts are aquo complexes $[M(H_2O)_6]^{n+}$. The M−(OH_2) bonds in these complexes are weaker than M−(NC) bonds and hence ligand exchange occurs.

We now extend our investigations in this area to complexes of the transition metals with ammonia. In the adduct complexes $[M(NH_3)_6]^{n+}$, the metal−ligand bonds are stronger than those in aquo complexes. Thermodynamic as well as kinetic factors may affect both the compositions of the products and the rates of their formation. Indeed, we have obtained some new types of Re_4 cluster complexes with transition metals starting from ammine complexes. Here we present two new cluster compounds with transition metals, namely $[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}]\cdot 3.4H_2O$ (**1**) and $[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]\cdot 4H_2O$ (**2**). Both compounds were prepared under similar conditions by treating an aqueous solution of $K_4Re_4Te_4(CN)_{12}$ with the ammine complexes of the corresponding transition metals.

The structures of both complexes were solved by single-crystal X-ray analysis. Both compounds contain the $[Re_4Te_4(CN)_{12}]^{4-}$ cluster anion, the structure of which is similar to that found in other complexes containing this anion. It contains an $[Re_4Te_4]$ cubane-like core formed from an almost regular tetrahedron of Re atoms in oxidation

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state IV with all triangular faces symmetrically capped by μ_3-Te ligands. The Re−Re bond lengths are in the ranges 2.8540(6)−2.8767(7) Å (**1**) and 2.8676(14)−2.8775(11) Å (**2**), the Re−Te bond lengths are in the ranges 2.6230(8)−2.6469(8) Å (**1**) and 2.6224(14)−2.6454(14) Å (**2**), and the Re−C distances are 2.09(1)−2.13(1) Å (**1**) and 2.03(2)−2.08(2) Å (**2**), respectively.

In the molecular structure of compound **1**, two $[Ni(NH_3)_5]^{2+}$ cations are coordinated to the N atoms of CN ligands of the $[Re_4Te_4(CN)_{12}]^{4-}$ anion (Figure 1). Each Ni atom is coordinated by the five N atoms of the NH_3 ligands with Ni−N distances ranging from 2.081(9) to 2.150(9) Å, and by one N atom from a CN ligand of the cluster with Ni−N distances of 2.067(8) and 2.097(8) Å. Interestingly, both cations are coordinated to the same Re atom. This is the first example of a chalcocyanide complex with a transition metal that exhibits a discrete molecular structure.

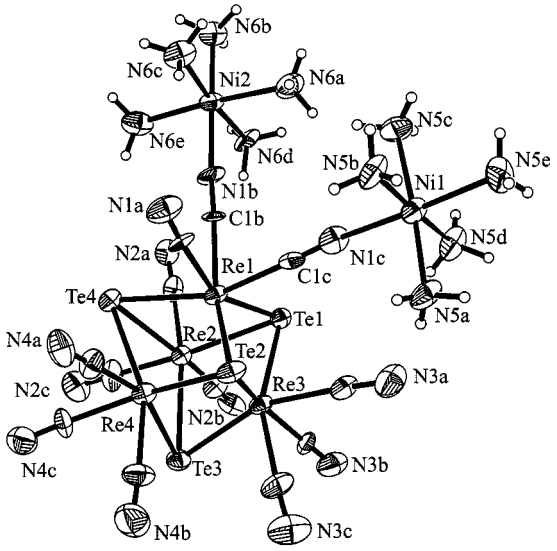

Figure 1. Crystal structure of $[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}]\cdot 3.4H_2O$; thermal ellipsoids are drawn at a 75% probability level

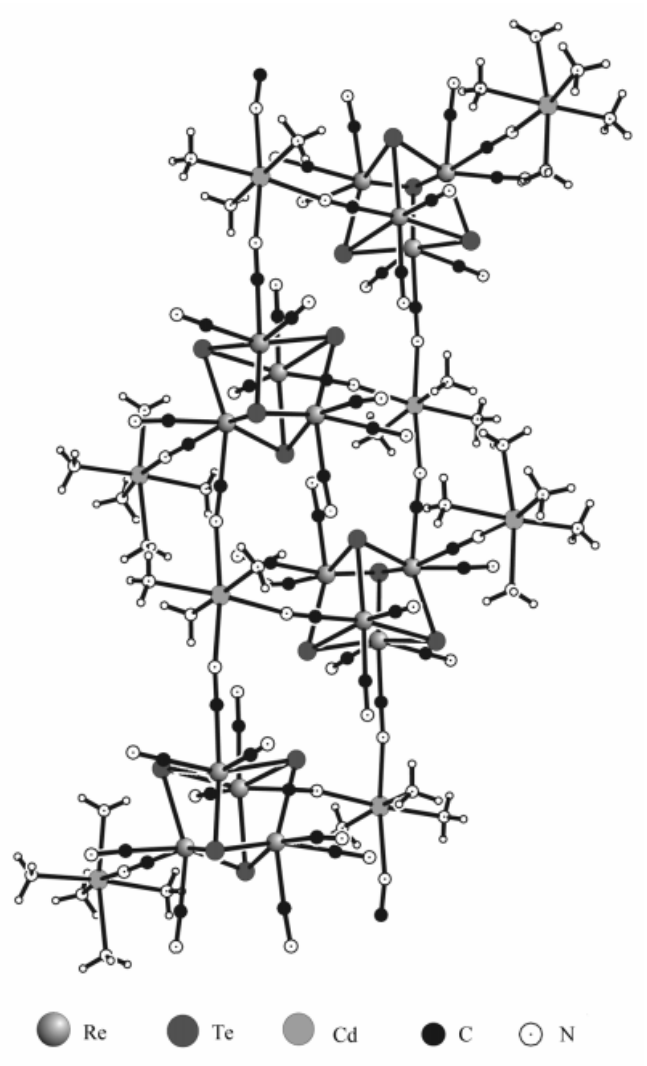

Figure 2. A fragment of the crystal structure of $[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]\cdot 4H_2O$

The second compound $[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]$ (**2**) contains two types of cations, namely terminal $[Cd(NH_3)_5]^{2+}$ and bridging $[Cd(NH_3)_3]^{2+}$ cations (Figure 2). The Cd atom of each $[Cd(NH_3)_5]^{2+}$ cation is coordinated by the five N atoms of the NH_3 ligands [Cd−N distances in the range 2.29(3)−2.47(4) Å] and one N atom of a CN ligand of the cluster. The Cd−N distance [2.43(3) Å] is similar to the Ni−N distance found in the Ni salt. The Cd atom of each bridging $[Cd(NH_3)_3]^{2+}$ cation is coordinated by the three N atoms of the NH_3 ligands with Cd−N distances ranging from 2.25(2) to 2.39(2) Å, and by three N atoms of CN ligands of different clusters with Cd−N distances in the range 2.36(2)−2.42(2) Å, thereby forming a chain-like structure. Each $[Re_4Te_4(CN)_{12}]^{4-}$ anion is coordinated by one terminal $[Cd(NH_3)_5]^{2+}$ group.

In the infrared spectra, two bands at 2169 and 2133 cm^{-1} (compound **1**), or at 2163 and 2133 cm^{-1} (compound **2**), can be assigned to the bridging and terminal CN groups, respectively. For both complexes, four additional bands are seen, due to coordinated ammonia molecules. Two of these, at 3345 and 1615 cm^{-1} (compound **1**) and 3340 and 1605 cm^{-1} (compound **2**), coincide with vibrations of water.

Comparison of the interaction of aqueous solutions of $[Re_4Te_4(CN)_{12}]^{4-}$ cluster anions with transition metal aquo $[M(OH_2)_6]^{2+}$ and ammine $[M(NH_3)_6]^{2+}$ complexes demonstrates that the formation of cyano-bridged complexes is dependent on the strength of the M−X (X = OH_2, NH_3, NC) bonds. In the case of aquo complexes, the weaker M−OH_2 bonds can be cleaved under formation of the thermodynamically more favourable M−NC bonds. As a result, polymeric complexes are formed, often with the maximum number of M−NC bonds. Starting from the ammine complexes $[M(NH_3)_6]^{2+}$, we observed the formation of the molecular complex **1** with only one substituted NH_3 ligand, and of the chain-like complex **2** with two types of cations, namely $[Cd(NH_3)_5]^{2+}$, from which one NH_3 molecule has been substituted, and $[Cd(NH_3)_3]^{2+}$, from which three NH_3 molecules have been substituted. This difference between these two compounds may have a kinetic origin. Under similar conditions, compound **1** is formed within 24 h, whereas

compound **2** only forms within 48 h. The compounds described herein may possibly represent the first and second steps in the formation of cyano-bridged polymeric complexes.

Experimental Section

General: All experimental manipulations were performed in air. $K_4Re_4Te_4(CN)_{12}\cdot 5H_2O$ was prepared by the reaction of $Re_4Te_4(TeCl_2)_4Cl_8$ with KCN.[5] All other reagents were used as received from commercial sources. − FT-IR: Bruker IFS-85. − Elemental analyses: Carlo Erba 1106.

$[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}]\cdot 3.4H_2O$ (1): A solution of $Ni(CH_3COO)_2$ (20 mg) in concentrated aqueous ammonia (3 mL) was mixed with a solution of $K_4Re_4Te_4(CN)_{12}\cdot 5H_2O$ (10 mg) in water (2 mL). At ambient temperature, the resulting solution was transferred to a crystallizing dish, which was then covered by a watch glass. After 24 h, black crystals had formed, which were collected by filtration and dried on filter paper. Yield: 10 mg (95%). − $C_{12}H_{30}N_{22}Ni_2Re_4Te_4\cdot 3H_2O$ (1909.19): calcd. C 7.55, H 1.90, N 16.14; found C 7.22, H 1.41, N 15.54; the solvent content probably varies to a certain extent. − IR (KBr): $\tilde{\nu}$ = 3345 (m), 2169 (w), 2133 (s), 1615 (m), 1219 (m), 667 cm^{-1} (m). − μ_{eff} = 2.96 μ_B (298 K), 2.80 μ_B (78 K).

$[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]\cdot 4H_2O$ (2): A solution of $CdSO_4\cdot 8H_2O$ (20 mg) in concentrated aqueous ammonia (3 mL) was mixed with a solution of $K_4Re_4Te_4(CN)_{12}\cdot 5H_2O$ (10 mg) in water (2 mL). At ambient temperature, the resulting solution was transferred to a crystallizing dish, which was then covered by a watch glass. After 2 days, black crystals of **2** had formed, which were collected by filtration and dried on filter paper. Yield: 10 mg (91%). − $C_{12}H_{32}Cd_2N_{20}O_4Re_4Te_4$ (2000.58): calcd. C 7.20, H 1.61, N 14.00; found C 7.26, H 0.88, N 13.65. − IR (KBr): $\tilde{\nu}$ = 3340 (w), 2163 (m), 2133 (s), 1605 (m), 1204 (m), 612 cm^{-1} (m).

X-ray Structural Analyses: Stoe IPDS diffractometer, graphite monochromator, Mo-K_α radiation (λ = 0.71073 Å); the SHELX-97 program package[16] was used for structure solution by direct methods and for refinement by full-matrix least-squares techniques.[17]

$[Ni(NH_3)_5]_2[Re_4Te_4(CN)_{12}]\cdot 3.4H_2O$ (1): M_r = 1918, monoclinic, space group $P2_1/c$, a = 19.572(3), b = 14.849(2), c = 23.576(3) Å, β = 145.97(1)°, V = 3834.4(9) $Å^3$, Z = 4, $D_{calcd.}$ = 3.32 $g\cdot cm^{-3}$, μ = 16.58 mm^{-1}, T = 93(2) K. Crystal size 0.18 × 0.07 × 0.01 mm; $2\theta_{max}$ = 53° ($-25 \le h \le 25$, $-17 \le k \le 17$, $-30 \le l \le 30$), 8390 symmetry-independent reflections from 52895 collected reflections (R_{int} = 0.078); max./min. transmission: 0.83/0.28; 439 parameters refined; $R1$ = 0.0333, $wR2$ = 0.0655 [$I > 2\sigma(I)$]; $R1$ = 0.0624, $wR2$ = 0.0737 (all reflections), GoF = 0.932; $\Delta\rho_{max}$ = 1.84 $e\cdot Å^{-3}$, $\Delta\rho_{min}$ = −1.57 $e\cdot Å^{-3}$.

$[Cd(NH_3)_5][Cd(NH_3)_3][Re_4Te_4(CN)_{12}]\cdot 4H_2O$ (2): M_r = 2000.58, triclinic, space group $P\bar{1}$, a = 12.726(2), b = 13.408(2), c = 13.918(2) Å, α = 111.31(2), β = 116.77(2), γ = 90.17(2)°, V = 1935.3(5) $Å^3$, Z = 2, $D_{calcd.}$ = 3.433 $g\cdot cm^{-3}$, μ = 16.543 mm^{-1}, T = 293(2) K. Crystal size 0.20 × 0.15 × 0.11 mm; $2\theta_{max}$ = 50° ($-15 \le h \le 15$, $-15 \le k \le 15$, $-16 \le l \le 16$), 5626 symmetry-independent reflections from 18453 collected reflections (R_{int} = 0.089); max./min. transmission: 0.288, 0.937; 423 parameters refined; $R1$ = 0.0634, $wR2$ = 0.1677 [$I > 2\sigma(I)$]; $R1$ = 0.0742, $wR2$ = 0.1753 (all reflections), GoF = 1.052; $\Delta\rho_{max}$ = 3.57 $e\cdot Å^{-3}$, $\Delta\rho_{min}$ = −2.12 $e\cdot Å^{-3}$.

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[17] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data (depository numbers CCDC-158006 for **1**, -158005 for **2**) may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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