[{Cu(en)$_2$}$_2$Re$_4$Te$_4$(CN)$_{12}$]·5H$_2$O and [{Cu(en)$_2$}$_2$Re$_6$Te$_8$(CN)$_6$]·5H$_2$O: Bonding of a Transition-Metal Complex to a Rhenium Chalcocyanide Cluster

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The use of a cyano group of a transition-metal cluster complex to bond to another transition-metal complex has been realized in the syntheses of [{Cu(en)$_2$}$_2$Re$_4$Te$_4$(CN)$_{12}$]·5H$_2$O (**1**) and [{Cu(en)$_2$}$_2$Re$_6$Te$_8$(CN)$_6$]·5H$_2$O (**2**), (en = ethylenediamine). These compounds have been synthesized by the reaction of an aqueous solution of K$_4$[Re$_4$Te$_4$(CN)$_{12}$]·5H$_2$O (for **1**) or K$_4$[Re$_6$Te$_8$(CN)$_6$] (for **2**) with an ammonia solution of Cu(en)$_2$Cl$_2$. In each compound, two Cu(en)$_2$ groups are bonded to the Re cluster through Cu−N(cyanide) bonds. In compound **1**, which contains a tetrahedral cluster core, the Cu(en)$_2$ groups are necessarily bonded to cis cyano groups; in compound **2**, which has an octahedral cluster core, they are bonded to trans cyano groups. Compound **1** crystallizes in the monoclinic space group $C2/c$ with four formulas in unit cell of dimensions $a = 18.9077(10)$, $b = 15.4841(8)$, $c = 14.4483(8)$ Å, $\beta = 95.124(1)°$, and $V = 4213.1(4)$ Å^3 ($T = 153$ K); compound **2** crystallizes in the triclinic space group $P\bar{1}$ with one formula in a unit cell of dimensions $a = 9.4906(3)$, $b = 10.6529(4)$, $c = 12.6252(5)$ Å, $\alpha = 113.599(1)°$, $\beta = 103.404(1)°$, $\gamma = 92.659(1)°$, and $V = 1123.87(7)$ Å^3 ($T = 153$ K).

Introduction

The chemistry of chalcocyanide transition-metal cluster compounds has been developed extensively in recent years.[1−20] Even though the chemistry of mononuclear cyanobridged complexes is well developed,[21,22] the first cluster compounds to involve cyano bridges were obtained only a few years ago.[5−7] In these, the chalcocyanide transition-metal clusters are bridged by M(H$_2$O)$_n$ or M(OH)$_n$ species, where M = transition metal, but recently the first examples involving M(NH$_3$)$_n$ species were obtained.[23] In an attempt to bridge such clusters with the use of transition-metal complexes, we have extended these studies to Cu(en)$_2$ species. No extended structures were formed, but rather the molecular compounds [{Cu(en)$_2$}$_2$Re$_4$Te$_4$(CN)$_{12}$]·5H$_2$O (**1**) and [{Cu(en)$_2$}$_2$Re$_6$Te$_8$(CN)$_6$]·5H$_2$O (**2**) were obtained. These are described here.

Experimental Section

Materials and Syntheses. All reagents were used as purchased. K$_4$[Re$_4$Te$_4$(CN)$_{12}$]·5H$_2$O was synthesized through the reaction of Re$_4$Te$_4$(TeCl$_2$)$_4$Cl$_8$ with KCN (Fisher, 99.9%) in water.[10] Re$_4$Te$_4$(TeCl$_2$)$_4$Cl$_8$ was synthesized through the reaction of ReCl$_5$ (Strem, 99.9%) with elemental Te (Aldrich, 99.8%) in the ratio 1:2.2 at 350 °C.[24] K$_4$[Re$_6$Te$_8$(CN)$_6$] was synthesized through the reaction of Re$_6$Te$_{15}$[25] with KCN

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at 650 °C.[3] Microanalyses for C, H, and N were performed by Oneida Research Services, Whitesboro, NY.

[{Cu(en)$_2$}$_2$Re$_4$Te$_4$(CN)$_{12}$]·5H$_2$O (1). A solution of 0.010 g (0.039 mmol) of $Cu(en)_2Cl_2$ in 3 mL of aqueous ammonia was added to a solution of 0.010 g (0.0057 mmol) of $K_4Re_4Te_4(CN)_{12}\cdot 5H_2O$ in 2 mL of water. The resultant solution was kept in an open vessel at room temperature for two weeks, during which time black crystals formed. These were filtered off and dried on filter paper. Yield: 0.011 g (91%). Anal. Calcd for $C_{20}H_{42}Cu_2N_{20}O_5Re_4Te_4$: C, 11.86; H, 2.09; N, 13.84%. Found: C, 11.90; H, 1.82; N, 14.06%. IR (cm^{-1}): 2132 s (ν_{CN}).

Synthesis of [{Cu(en)$_2$}$_2$Re$_6$Te$_8$(CN)$_6$]·5H$_2$O (2). A solution of 0.010 g (0.039 mmol) of $Cu(en)_2Cl_2$ in 3 mL of aqueous ammonia was added to a solution of 0.010 g (0.0041 mmol) of $K_4[Re_6Te_8(CN)_6]$ in 2 mL of water. The resultant solution was kept in an open vessel at room temperature for two weeks, during which time black crystals formed. These were filtered off and dried on filter paper. Yield: 0.010 g (90%). Anal. Calcd for $C_{14}H_{42}Cu_2N_{14}O_5Re_6Te_8$: C, 6.11; H, 1.54; N, 7.13%. Found: C, 6.55; H, 1.36; N, 7.15%. IR (cm^{-1}): 2072 s, 2102 m, 2139 w (ν_{CN}).

Crystallography. Single-crystal X-ray diffraction data were collected at 153 K on a Bruker Smart-1000 CCD diffractometer with the program SMART.[26] Graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) was used. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 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 setting 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,[26] and face-indexed absorption corrections were performed numerically with the use of the program XPREP.[27] The program SADABS[26] was then employed to make incident beam and decay correction.

Both structures were solved by means of the direct methods program SHELXS, of the SHELXT-PC[27]suite of programs, and refined by full-matrix least-squares techniques.[27] The final refinements included anisotropic displacement parameters for the non-hydrogen atoms. For compound **1**, the positions and isotropic displacement parameters for the hydrogen atoms were refined. For compound **2**, the positions of the hydrogen atoms on the en groups were idealized. Additional experimental details are given in Table 1 and in Supporting Information.

Magnetic Measurements. Magnetic measurements were carried out with a SQUID magnetometer (MPMS5, Quantum Design). The samples, 24.8 mg of (**1**) and 22.6 mg of (**2**), containing single crystals were loaded into gelatin capsules. The magnetic susceptibility measurements on these compounds were made at 200 G over the temperature range 5−300 K with a zero-field cooling procedure. Data were corrected for the diamagnetic contributions of the atomic cores.[28]

Results and Discussion

Syntheses. The molecular compound $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (**1**) has been synthesized by the reaction of an aqueous solution of the tetrahedral tellurocyanide cluster $K_4[Re_4Te_4(CN)_6]\cdot 5H_2O$ with an ammonia solution of $Cu(en)_2Cl_2$. In a similar manner, the molecular compound $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]\cdot 5H_2O$ (**2**) has been synthesized with the use of the octahedral tellurocyanide cluster $K_4[Re_6Te_8(CN)_6]$. Both compounds **1** and **2** are synthesized in a facile manner in excellent yields by this procedure. Clearly, this approach is a general one and depends only on having an open or exchangeable coordination site at the transition metal.

Table 1. Crystal Data and Structure Refinement for $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (**1**) and $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]\cdot 5H_2O$ (**2**)

compound	$[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]\cdot 5H_2O$	$[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]\cdot 5H_2O$
chemical formula	$C_{20}H_{42}Cu_2N_{20}O_5Re_4Te_4$	$C_{14}H_{42}Cu_2N_{14}O_5Re_6Te_8$
fw	2025.02	2751.7
a (Å)	18.9077(10)	9.4906(3)
b (Å)	15.4841(8)	10.6529(4)
c (Å)	14.4483(8)	12.6252(5)
α (deg)	90	113.599(1)
β (deg)	95.124(1)	103.404(1)
γ (deg)	90	92.659(1)
V (Å^3)	4213.1(4)	1123.87(7)
$\rho_{calcd.}$ (g/cm^3)	3.193	4.066
space group	$C2/c$	$P\bar{1}$
Z	4	1
μ (cm^{-1})	152.11	221.44
T (K)	153	153
$R(F)^a$	0.0198	0.0301
$R_w(F^2)^b$	0.0471	0.0762

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

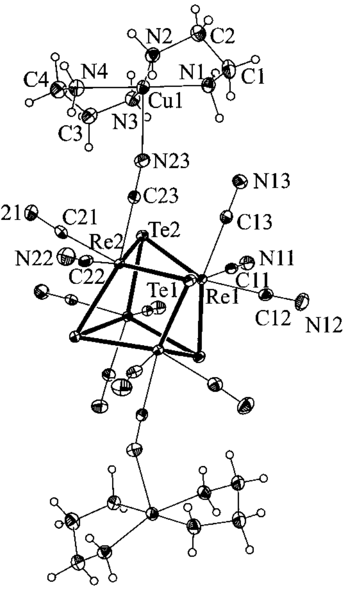

Figure 1. View of the $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]$ molecule in (**1**). Displacement ellipsoids are drawn at the 50% probability level.

Structures. The compounds $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (**1**) and $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]\cdot 5H_2O$ (**2**) have been characterized by single-crystal X-ray diffraction methods. The structure of the $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]$ molecule is shown in Figure 1 , and selected bond distances and angles are tabulated in Table 2. In the molecule, which has crystallographic 2 symmetry, the tetrahedral cluster $[Re_4Te_4(CN)_{12}]$ is coordinated by two $[Cu(en_2)]$ groups. The $[Re_4Te_4(CN)_{12}]$ part of the structure is similar to that in the starting material and related compounds. It contains a Re_4Te_4 cubane-like cluster core formed from a nearly regular Re_4 tetrahedron, with Re−Re and Re−μ_3−Te distances in the ranges 2.8469(2)−2.8859(3) Å and 2.6257(3)−2.6406(3) Å, respectively (Table 2). Each Re atom is further ligated by three terminal cyano ligands. One CN group in two of the four $Re(CN)_3$ moieties is further coordinated to a $[Cu(en)_2]$ group by a Cu−N bond, leading to a square-pyramidal arrangement about the Cu atom.

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Table 2. Selected Bond Lengths [Å] and Angles [deg] for $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (**1**)[a]

Re(1)−Re(2)	2.8469(2)	N(23)−Cu(1)	2.298(3)
Re(1)−Re(2)#1	2.8633(2)	Cu(1)−N(1)	2.005(4)
Re(1)−Re(1)#1	2.8801(3)	Cu(1)−N(2)	2.015(4)
Re(2)−Re(2)#1	2.8859(3)	Cu(1)−N(4)	2.021(4)
Re(1)−Te(2)#1	2.6257(3)	Cu(1)−N(3)	2.028(4)
Re(2)−Te(2)	2.6290(3)	N(3)−C(3)	1.471(6)
Re(2)−Te(1)	2.6314(3)	N(2)−C(2)	1.479(5)
Re(1)−Te(2)	2.6321(3)	N(1)−C(1)	1.480(6)
Re(2)−Te(1)#1	2.6362(3)	N(4)−C(4)	1.481(5)
Re(1)−Te(1)	2.6406(3)	C(1)−C(2)	1.503(6)
Re(1)−C(11)	2.091(4)	C(3)−C(4)	1.528(6)
Re(1)−C(13)	2.097(4)	C(23)−N(23)−Cu(1)	153.1(3)
Re(2)−C(23)	2.099(4)	N(1)−Cu(1)−N(2)	85.08(15)
Re(2)−C(22)	2.108(4)	N(1)−Cu(1)−N(4)	178.87(16)
Re(1)−C(12)	2.111(4)	N(2)−Cu(1)−N(4)	94.78(15)
Re(2)−C(21)	2.113(4)	N(1)−Cu(1)−N(3)	95.40(15)
C(22)−N(22)	1.138(5)	N(2)−Cu(1)−N(3)	162.90(16)
C(23)−N(23)	1.145(5)	N(4)−Cu(1)−N(3)	84.40(15)
C(21)−N(21)	1.149(6)	N(1)−Cu(1)−N(23)	93.77(14)
C(12)−N(12)	1.154(6)	N(2)−Cu(1)−N(23)	98.41(14)
C(11)−N(11)	1.161(6)	N(4)−Cu(1)−N(23)	87.36(15)
C(13)−N(13)	1.163(5)	N(3)−Cu(1)−N(23)	98.61(14)

[a] Symmetry transformation used to generate equivalent atoms, #1: $-x + 1, y, -z + 3/2$.

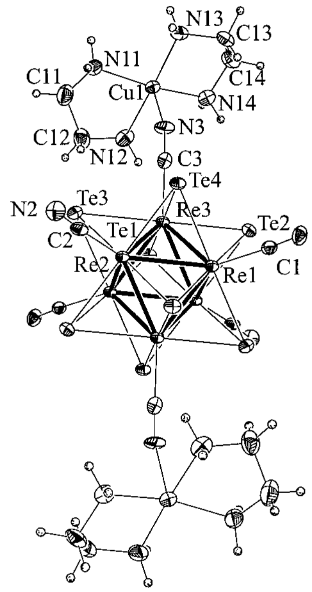

Figure 2. View of the $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]$ molecule in (**2**). Displacement ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]\cdot 5H_2O$ (**2**)[a]

Re(1)−Re(3)	2.6738(3)	N(3)−Cu(1)	2.228(5)
Re(3)−Te(1)	2.6756(4)	Cu(1)−N(14)	2.011(6)
Re(2)−Re(3)	2.6774(3)	Cu(1)−N(11)	2.012(6)
Re(1)−Re(2)	2.6782(3)	Cu(1)−N(13)	2.025(4)
Re(2)−Re(3)#1	2.6813(4)	Cu(1)−N(12)	2.037(4)
Re(1)−Re(2)#1	2.6873(3)	N(14)−C(14)	1.479(7)
Re(1)−Re(3)#1	2.6877(3)	N(12)−C(12)	1.481(8)
Re(3)−Te(4)	2.6856(4)	N(11)−C(11)	1.489(9)
Re(1)−Te(3)#1	2.6870(5)	N(13)−C(13)	1.493(9)
Re(2)−Te(3)	2.6934(4)	C(11)−C(12)	1.496(12)
Re(1)−Te(2)	2.6954(4)	C(13)−C(14)	1.506(9)
Re(1)−Te(1)#1	2.6955(4)	C(3)−N(3)−Cu(1)	151.8(5)
Re(1)−Te(4)	2.6972(5)	N(14)−Cu(1)−N(11)	162.8(2)
Re(3)−Te(2)	2.6982(5)	N(14)−Cu(1)−N(13)	85.9(2)
Re(2)−Te(2)#1	2.7010(4)	N(11)−Cu(1)−N(13)	93.7(2)
Re(3)−Te(3)	2.7046(5)	N(14)−Cu(1)−N(12)	94.8(2)
Re(2)−Te(1)#1	2.7078(4)	N(11)−Cu(1)−N(12)	84.5(2)
Re(2)−Te(4)	2.7086(4)	N(13)−Cu(1)−N(12)	176.1(2)
Re(3)−C(3)	2.093(6)	N(14)−Cu(1)−N(3)	96.5(2)
Re(2)−C(2)	2.095(7)	N(11)−Cu(1)−N(3)	100.7(2)
Re(1)−C(1)	2.104(6)	N(13)−Cu(1)−N(3)	97.01(19)
C(3)−N(3)	1.131(8)	N(12)−Cu(1)−N(3)	86.74(19)
C(2)−N(2)	1.140(8)		
C(1)−N(1)	1.147(8)		

[a] Symmetry transformation used to generate equivalent atoms, #1: $-x, -y + 1, -z -1$.

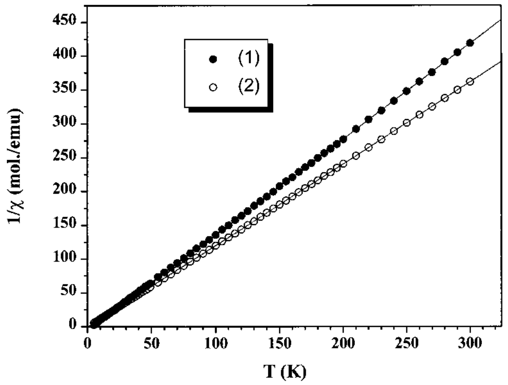

Figure 3. The temperature dependence of the inverse magnetic susceptibility for $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (**1**) and $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]\cdot 5H_2O$ (**2**).

The hydrogen bonds in compound **1** are all relatively weak. They include intramolecular N−H···N hydrogen bonds between some of the en NH groups and the CN groups, N−H···O bonds between some en NH groups and water molecules, O−H···N(CN) bonds, and O−H···O bonds.

The structure of the $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]$ molecule of compound **2** is shown in Figure 2 , and selected bond distances and angles are tabulated in Table 3. In the molecule, which has crystallographic $\bar{1}$ symmetry, the octahedral cluster $[Re_6Te_8(CN)_6]$ is coordinated by two trans $[Cu(en_2)]$ groups. The structure of the $[Re_6Te_8(CN)_6]$ unit is similar to that in the starting material and related compounds. It contains the octahedral Re_6 cluster core inscribed in a cube of μ_3−Te ligands; each Re atom in addition is ligated by a CN group. The Re−Re distances range from 2.6738(3) to 2.6877(3) Å and the Re−μ_3−Te distances from 2.6856(4) to 2.7086(4) Å. A CN group in each of two opposite vertices of the Re6 cluster is further coordinated to a $[Cu(en)_2]$ group by a Cu−N bond, leading to a square-pyramidal arrangement about the Cu atom, as in compound **1**. In neither compound **1** nor **2** is there a significant change in the geometry of the Re−C−N moiety upon bridging to the Cu atom. As for compound **1**, compound **2** has an extensive network of weak hydrogen bonds.

Magnetism. Figure 3 displays the temperature dependence of the inverse magnetic susceptibility for $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (**1**) and $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]\cdot 5H_2O$ (**2**). These compounds are paramagnetic down to 5 K. Over the temperature range 10−300 K, the magnetic susceptibility data are well described by the Curie−Weiss law, $\chi = \chi_o + C/(T-\theta_P)$. Least-squares fitting of these data leads to $\chi_o = 5.28\ 10^{-4}$ emu mol^{-1}, $C = 0.707(1)$ emu K mol^{-1}, and $\theta_P = 3.08(2)$ K for (**1**); and $\chi_o = 7.67\ 10^{-4}$ emu mol^{-1}, $C = 0.829(3)$ emu K mol^{-1}, and $\theta_P = 0.323(5)$ K for (**2**). The effective magnetic moments per Cu^{2+} obtained from the Curie constants C are 1.68(2) and 1.82(6) μ_B for (**1**) and (**2**), respectively. These values are in close agreement with the theoretical spin-only effective moment of 1.73 μ_B per Cu^{2+} calculated from the equation

$\mu_{eff} = g[S(S+1)]^{1/2}\ \mu_B$, where g is the gyromagnetic ratio and S is the sum of the spin quantum numbers of the individual unpaired electrons.[29] In compound **2**, there is no evidence for magnetic exchange coupling between the Cu(II) centers through the intervening Re_6 cluster.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]\cdot5H_2O$ (**1**) and $[\{Cu(en)_2\}_2Re_6Te_8(CN)_6]\cdot5H_2O$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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[29] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, Fifth ed.; John Wiley & Sons: New York, 1988.