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Syntheses and crystal structures of heterometallic complexes $[\{Cu(en)_2\}_2\{Cu(en)_2(NH_3)\}\{M_4Te_4(CN)_{12}\}] \cdot 5H_2O$ (M = Mo, W)

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Evaporation of aqueous ammonia solutions of $K_7[Mo_4Te_4(CN)_{12}] \cdot 12H_2O$ or $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$, copper(II) chloride, and ethylenediamine afforded the isostructural heterometallic complexes $[\{Cu(en)_2\}_2\{Cu(en)_2(NH_3)\}\{M_4Te_4(CN)_{12}\}] \cdot 5H_2O$ (M = Mo or W), which were characterized by IR and ESR spectroscopy and X-ray diffraction analysis.

Key words: clusters, molybdenum, tungsten, tellurium, copper, X-ray diffraction analysis, IR spectroscopy, ESR spectroscopy.

The cyanide anion can serve as a bidentate-bridging ligand to form coordination bonds with two metal (M) atoms through the carbon and nitrogen atoms giving rise to heterometallic cyanide-bridged complexes or polymeric coordination compounds. Such compounds based on the mononuclear tetrahedral ($[M(CN)_4]^{n-}$) and octahedral ($[M(CN)_6]^{n-}$) complex anions are well known.[1—4] Coordination polymers based on transition metal cyanide clusters have been synthesized in recent years. Compounds containing chains (1D), networks (2D), and three-dimensional frameworks (3D), which consist of cluster anions (M_n) linked to each other by transition metal (M´) cations through the bridging cyanide ligands (...M′—NC—M_n—CN—M′—NC...), were prepared and structurally characterized. The octahedral $[Re_6Q_8(CN)_6]^{4-}$ [5—9] and tetrahedral $[Re_4Q_4(CN)_{12}]^{4-}$ [10,11] (Q = S, Se, or Te) rhenium clusters were used as building blocks in the synthesis of 1D, 2D, and 3D polymers consisting of $\{M_n\}$ clusters (n = 4 or 6), which are linked through heterometallic atoms (M′) *via* the cyanide ligands. In our recent studies, the cuboidal molybdenum and tungsten chalcogenide cyano complexes $[M_4Q_4(CN)_{12}]^{n-}$ (M = Mo or W; Q = S, Se, or Te; n = 6—8)[12—15] were used for the synthesis of the chain complex $[Cu(NH_3)_3][Cu(NH_3)_4][Cu(NH_3)_5][W_4Te_4(CN)_{12}] \cdot 5H_2O$,[16] the two-dimensional complexes $[Ln(DMF)(H_2O)_4][Ln(DMF)_2(H_2O)_4][M_4Te_4(CN)_{12}] \cdot DMF \cdot nH_2O$ (Ln = Ga, Ho, Sm, or Er; n = 6.5—7.5),[17] and the unique framework polymers $[M(H_2O)_4]_3[W_4Q_4(CN)_{12}] \cdot nH_2O$ (M = Co, Q = Te;[18] or M = Mn, Q = S[19]), which contain large cavities occupied by H_2O molecules.

In all the above-mentioned cases, heterometallic aqua or amino complexes were used. In the present study, we synthesized for the first time complexes containing the cuboidal $[M_4Te_4(CN)_{12}]^{6-}$ (M = Mo or W) fragment and the cationic $[Cu(en)_2]^{2+}$ and $[Cu(en)_2(NH_3)]^{2+}$ complexes coordinated to the cluster through the N atom of the CN ligand. Up to now, only cuboidal rhenium complexes with ethylenediamine and diethylenetriamine ligands coordinated to the Cu atoms have been described.[20,21]

Results and Discussion

The isostructural complexes with composition $[\{Cu(en)_2\}_2\{Cu(en)_2(NH_3)\}\{M_4Te_4(CN)_{12}\}] \cdot 5H_2O$ (M = Mo (**1**) or W (**2**)) were prepared by concentrating aqueous ammonia solutions of the molybdenum or tungsten telluride cluster complexes, *viz.*, $K_7[Mo_4Te_4(CN)_{12}] \cdot 12H_2O$ or $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$, copper(II) chloride, and ethylenediamine. Copper chloride and ethylenediamine were added to a solution in a ratio of 1 : 2. Under the synthesis conditions, the starting paramagnetic anion $[Mo_4Te_4(CN)_{12}]^{7-}$ is oxidized with atmospheric oxygen to give the diamagnetic $[Mo_4Te_4(CN)_{12}]^{6-}$ anion. Black needle-like crystals of compounds **1** and **2** were prepared in 60 and 75% yields, respectively. These compounds are stable in air and insoluble in water.

The IR spectra of complexes **1** and **2** are virtually identical and have bands of the ethylenediamine ligands

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and the uncoordinated water molecules. The complexes contain two types of CN ligands, *viz.*, ligands coordinated to the Cu atom and those, which are not involved in this coordination. For the CN ligands of the former type, the CN stretching band is shifted to a high-frequency region (2100 cm^{-1}), whereas the wavenumber for the latter band is somewhat smaller (2090 cm^{-1}). The mixed $\nu(MC)/\delta(MCN)$ vibrations are observed at 460 cm^{-1} in the spectra of both complexes **1** and **2** as low-intensity bands.

According to the X-ray diffraction data (Fig. 1), compounds **1** and **2** are isostructural and have island structures. Each metal atom in the cuboidal clusters M_4Te_4 (M = Mo or W) is in an octahedral environment and is coordinated by three μ_3-bridging Te atoms and three C atoms of the CN ligands. The M—M distances in the cuboidal clusters vary over wide ranges: 2.8203(4)—3.0670(4) Å, d_{av} = 2.965 Å (for **1**) and 2.8494(3)—3.0387(3) Å, d_{av} = 2.968 Å (for **2**). The M—Te distances vary over narrow ranges: 2.6594(4)—2.6966(4) Å, d_{av} = 2.678 Å (for **1**) and 2.6719(4)—2.7023(4) Å, d_{av} = 2.689 Å (for **2**). The above M—M and M—Te bond lengths are in good agreement with those observed in other cuboidal molybdenum and tungsten telluride complexes studied by us earlier.[12,13]

In complexes **1** and **2**, each Cu atom is coordinated by two ethylenediamine ligands. The Cu atoms and the N atoms of the chelating ligands coordinated to Cu are in a single plane (deviations from the plane are at most 0.13 Å for Cu(1) and 0.06 Å for Cu(1A)). The Cu—N distances are typical of copper(ɪɪ) complexes with ethylenediamine (average values are 2.014 Å for **1** and 2.015 Å for **2**). The coordination number of the Cu(1) and Cu(2) atoms is 4 + 1. In addition to the ethylenediamine ligands, each Cu atom is coordinated by one N atom of the bridging CN group serving as a bridging ligand between the Mo or W atom and the Cu atom. The Cu(1)—N(13) and Cu(2)—N(23) distances (2.325(3) and 2.311(3) Å for **1**; 2.336(4) and 2.312(4) Å for **2**, respectively) are substantially longer (by ~0.3 Å). The Cu(1A) atom has a coordination number of 4 + 1 + 1 and is coordinated by one N atom of the CN ligand of the cluster core, one N(1N) atom of the ammonia molecule, and four N atoms of two ethylenediamine molecules. The Cu(1A)—N(21) distance is 2.699(3) Å in **1** and 2.705(5) Å in **2**, which corresponds to a weak Cu—N chemical bond. An elongation of the Cu—N bonds involving the atoms at the fifth and sixth vertices of a strongly elongated octahedron is attributed to the Jahn—Teller effect resulting in distortion of the octahedral environment about the Cu atom.

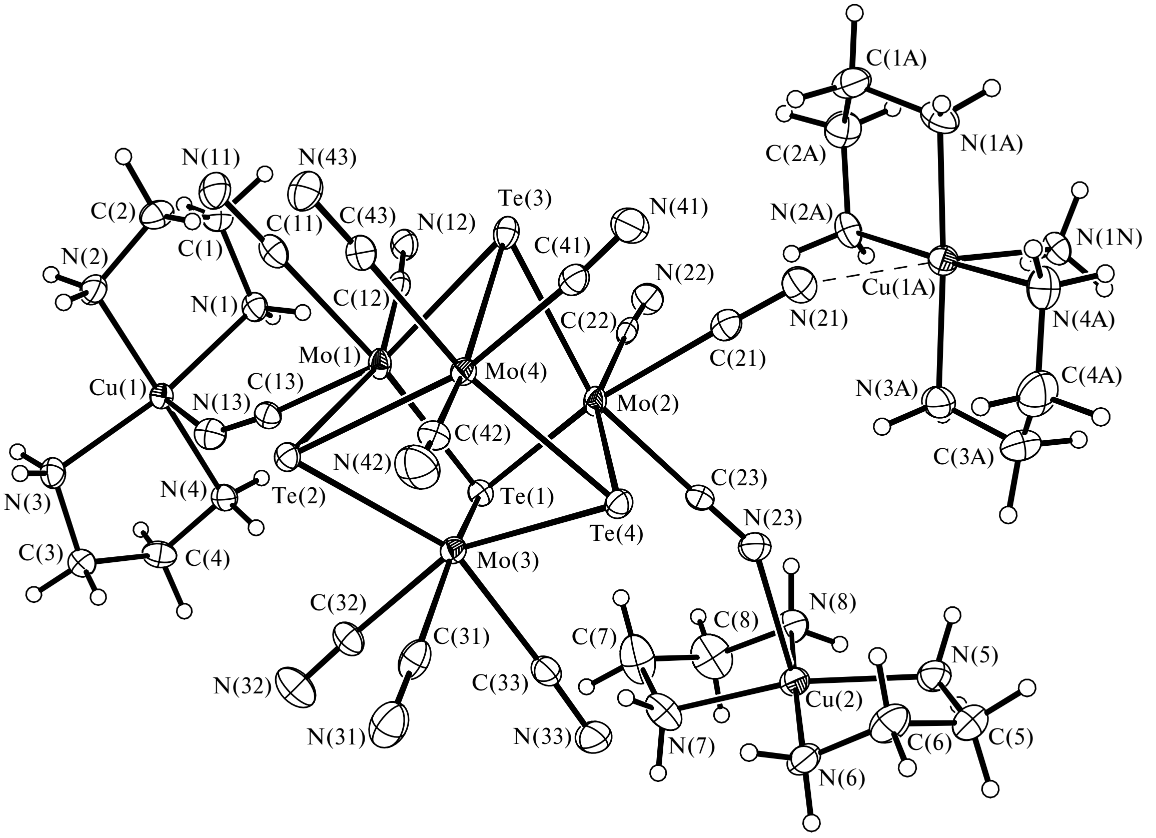

Fig. 1. Structure of the $[\{Cu(en)_2\}_2\{Cu(en)_2(NH_3)\}\{Mo_4Te_4(CN)_{12}\}]$ complex (**1**) (thermal ellipsoids were drawn at the 50% probability level).

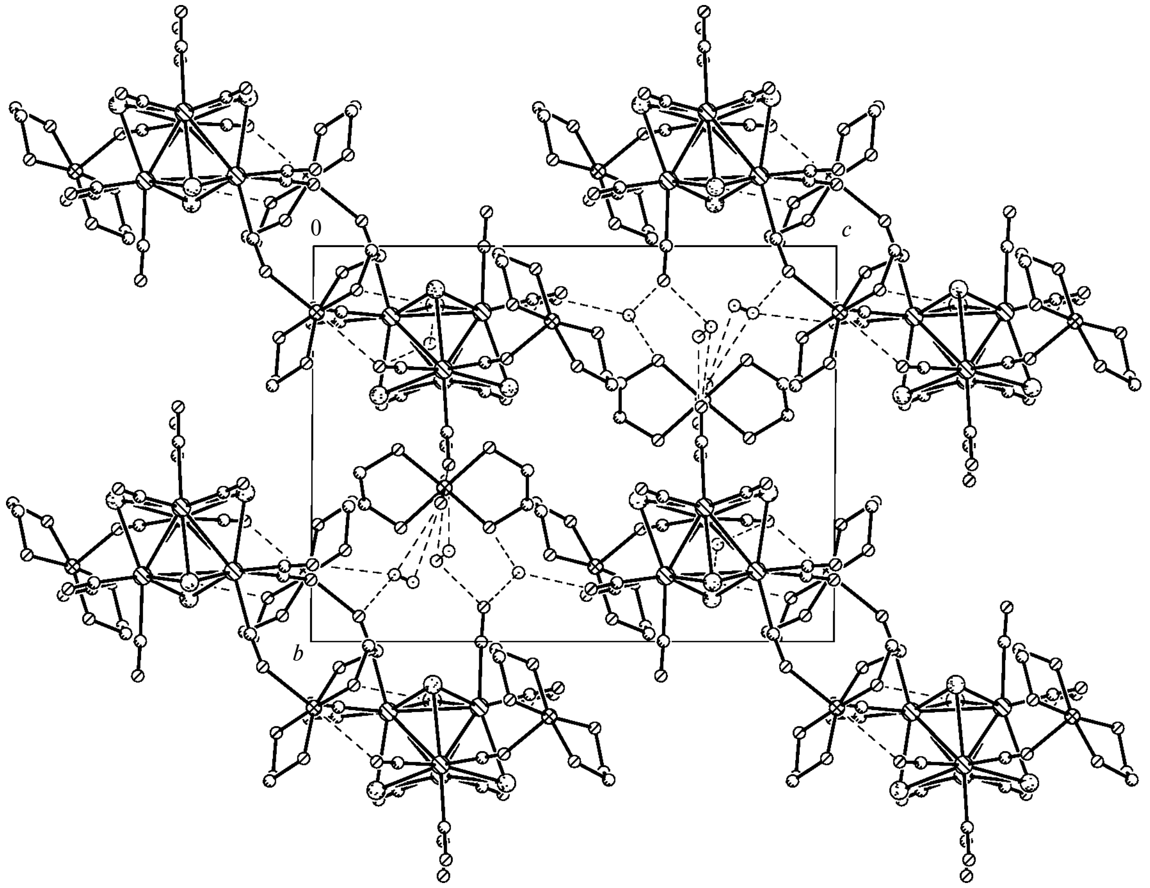

Fig. 2. Molecular packing in the crystals of **1** and **2** (projection onto the *bc* plane). Hydrogen bonds and Cu...N contacts are indicated by dashed lines.

The packing in the crystals of **1** and **2** is shown in Fig. 2. All structural units occupy general positions. The cluster anions are located on the body diagonal $\pm(b + c - a)$ in the vicinity of the (004) and $(00\bar{4})$ planes. The complexes related to each other by an inversion center are linked in pairs by short contacts (3.20 Å) between the copper atom (Cu(1)) of one complex and the nitrogen atom (N(22)) of the CN ligand of another complex. In the crystal structures, there are extensive hydrogen bond networks involving the water molecules of crystallization, on the one hand, and the terminal CN ligands (—C≡N...H—OH) and the NH_2 groups of ethylenediamine (H_2O...H—NH=), on the other hand.

Compounds **1** and **2** are paramagnetic. At 20 °C, the measured magnetic susceptibility is 1.90 μ_B per Cu atom of the complexes. The ESR spectra of powders of complexes **1** and **2** remain unchanged as the temperature increases from 77 to 300 K. The 9.5-GHz ESR spectra of complexes **1** and **2** are identical and consist of a single broad unsymmetrical line with a more extended wing in the lower-field region. The ESR spectra recorded at 35.5 GHz made it possible to resolve the anisotropy of the *g* factor. At this frequency, the ESR spectra of both compounds are also identical and characteristic of a paramagnetic center with the electron spin $S = 1/2$ and the anisotropic *g* factor (Fig. 3). The observed ESR spectrum with the *g* factors >2.0024 is attributed to the presence of ions with the more than half-filled d shell. In compounds **1** and **2**, these are the Cu^{II} ions. Complexes **1** and **2** each have three Cu^{II} ions in a planar environment. One of these ions is additionally coordinated by the N atom at

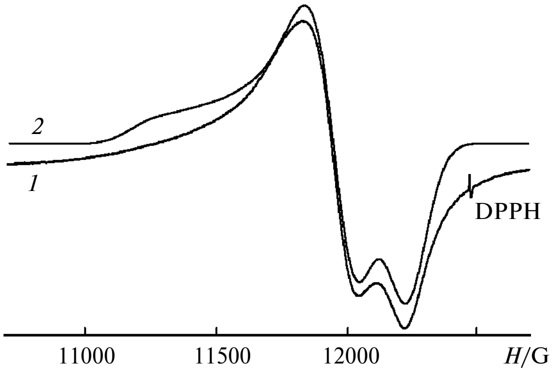

Fig. 3. Experimental (*1*) and calculated (*2*) 35.5-GHz ESR spectra of complex **1** at 300 K.

the fifth site. Two other Cu^{II} ions are additionally coordinated by two N atoms at the fifths and sixths sites. The presence of four approximately equal Cu—N distances about the copper ion gives rise to an axial environment resulting in the equality of the principal values of the g tensor, g_{xx} and g_{yy} ($g_{xx} = g_{yy} = g_{\perp}$). The observed spectrum is a superposition of two spectra with different values of $g_{\perp}$ for the five- and six-coordinate copper ions. Due to a superposition of the ESR spectra and the influence of the dipole-dipole and exchange interactions, the components of the spectra with g_{zz} and A_{zz} for the five- and six-coordinate copper ions are unresolvable in the spectra recorded both at 9.5 and 35.5 GHz and appear as an extended line wing at low field. The simulation of the experimental ESR spectrum showed that it is a superposition of two spectra described by the spin-Hamiltonian

$$H = g_{zz}\beta H_zS_z + g_{xx}\beta H_xS_x + g_{yy}\beta H_yS_y + A_{zz}S_zI_z + \\ + A_{xx}S_xI_x + A_{yy}S_yI_y$$

with the parameters $g_{xx} = g_{yy} = 2.0594$, $A_{xx} = A_{yy} \cong 0$ for the six-coordinate Cu ion and $g_{xx} = g_{yy} = 2.094$, $A_{xx} = A_{yy} \cong 0$ for two five-coordinate Cu ions; β is the Bohr magneton; H_i, S_i, and I_i are the projections of the magnetic field and the electronic and nuclear magnetic moments, respectively.

The line wing in the low-field region of the spectrum remains unresolved on going from 9.5 to 35.5 GHz, which is, presumably, attributed to averaging of the components g_{zz} and A_{zz} because of superposition of three spectra and broadening of the spectral lines due to dipole-dipole and exchange interactions between the Cu ions. Figure 3 (curve *2*) presents the calculated ESR spectrum taking into consideration a superposition of three spectra for arbitrary values of g_{zz} (2.180) and A_{zz} (180—200 G), at which the calculated spectral pattern is in the best agreement with the experimental pattern. Unfortunately, the available computer programs do not allow one to take into account the influence of exchange interactions on the shapes of the ESR spectral lines. The observed g factors and the principal values of the A tensor correspond to square-planar copper(II) complexes.

To summarize, the reactions of the cluster molybdenum and tungsten cyanide complexes with Cu^{II} in the presence of ethylenediamine afforded the cyanide-bridged heterometallic complexes $[\{Cu(en)_2\}_2\{Cu(en)_2(NH_3)\}\{M_4Te_4(CN)_{12}\}] \cdot 5H_2O$, which have an island structure and contain two five-coordinate Cu atoms (coordination number is 4 + 1) and one six-coordinate Cu atom (coordination number is 4 + 1 + 1). The results of ESR spectroscopy for powders

Table 1. Principal crystallographic characteristics and details of X-ray diffraction study of compounds **1** and **2**

Parameter	1	2
Molecular formula	$C_{24}H_{61}Cu_3Mo_4N_{25}O_5Te_4$	$C_{24}H_{61}Cu_3N_{25}O_5Te_4W_4$
Molecular weight	1864.76	2216.40
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	12.0810(1)	12.0570(1)
b/Å	13.1490(1)	13.1420(1)
c/Å	17.3040(2)	17.3270(2)
α/deg	90.0140(5)	90.0120(4)
β/deg	92.8620(4)	92.7340(5)
γ/deg	97.7900(7)	97.7980(5)
V/Å^3	2719.96(4)	2716.97(4)
Z	2	2
d_{calc}/g cm^{-3}	2.277	2.709
F(000)	1766	2022
μ(Mo-K$_\alpha$)/mm^{-1}	4.202	11.744
Crystal dimensions/mm	0.22×0.23×0.51	0.23×0.25×0.53
θ Scan range/deg	1.95—30.03	2.35—32.33
Ranges of h, k, l indices	$-17 \le h \le 16$, $-18 \le k \le 18$, $-24 \le l \le 24$	$-18 \le h \le 17$, $-19 \le k \le 19$, $-24 \le l \le 25$
Number of measured reflections	30752	33873
Number of independent reflections	15868 (R_{int} = 0.0329)	17927 (R_{int} = 0.0363)
Number of reflections with $F > 4\sigma(F)$	12755	15799
Number of parameters in refinement	586	586
R factors based on reflections with $F > 4\sigma(F)$	$R_1 = 0.0318$, $wR_2 = 0.0584$	$R_1 = 0.0361$, $wR_2 = 0.0841$
R factors based on all reflections	$R_1 = 0.0487$, $wR_2 = 0.618$	$R_1 = 0.0447$, $wR_2 = 0.0871$
GOOF on F^2	1.025	1.078
Residual electron density (min/max)/e Å^{-3}	−0.932/1.065	−3.562/2.270

of these complexes agree well with the X-ray diffraction data.

Experimental

The reagents of analytical grade were used. The starting $K_6[W_4Te_4(CN)_{12}]\cdot5H_2O$ and $K_7[Mo_4Te_4(CN)_{12}]\cdot12H_2O$ complexes were prepared according to known procedures[13,14] from a mixture of polymeric tungsten ditelluride WTe_2 or the triangular molybdenum telluride complex $Mo_3Te_7I_4$ and KCN. The IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer in KBr pellets. All syntheses were carried out in concentrated aqueous ammonia solutions in air. Magnetic measurements were carried out at 20 °C by the Faraday method. The ESR spectra were recorded on an E-109 (Varian) spectrometer at a frequency of 35.5 and 9.5 GHz at 77 and 300 K. Diphenylpicrylhydrazyl (DPPH) was used as the external reference for the *g* factor.

Bisdiethylenediaminecopper(II)amminediethylenediamine-copper(II)dodecacyanotetra-μ_3-tellurotetramolybdate(Mo—Mo) pentahydrate, $[\{Cu(en)_2\}_2\{Cu(en)_2(NH_3)\}\{Mo_4Te_4(CN)_{12}\}]\cdot5H_2O$ (1). An aqueous ammonia solution (10 mL) of $K_7[Mo_4Te_4(CN)_{12}]\cdot12H_2O$ (50 mg, 0.03 mmol) was added to an aqueous ammonia solution (5 mL) of $CuCl_2\cdot2H_2O$ (17 mg, 0.10 mmol) and ethylenediamine (12 mg, 0.20 mmol). Black crystals of complex **1** precipitated after 3 days. The crystals were filtered off and dried in air for one day. The yield was 30 mg (60%). Found (%): C, 12.50; H, 2.01; N, 15.43. $C_{24}H_{61}Cu_3Mo_4N_{25}O_5Te_4$. Calculated (%): C, 12.86; H, 2.21; N, 15.80. IR, ν/cm^{-1}: 3300 (br), 3240 (br), 2100 (s), 2090 (sh),

Table 2. Selected bond lengths (*d*) in compound **1**

Bond	*d*/Å	Bond	*d*/Å
Mo(1)—Mo(2)	3.0670(4)	C(31)—N(31)	1.154(5)
Mo(1)—Mo(3)	3.0142(4)	C(32)—N(32)	1.154(4)
Mo(1)—Mo(4)	2.9445(4)	C(33)—N(33)	1.152(4)
Mo(1)—Te(1)	2.6785(3)	C(41)—N(41)	1.152(4)
Mo(1)—Te(2)	2.6600(3)	C(42)—N(42)	1.157(5)
Mo(1)—Te(3)	2.6594(4)	C(43)—N(43)	1.155(4)
Mo(1)—C(11)	2.160(3)	Cu(1)—N(1)	2.027(3)
Mo(1)—C(12)	2.159(3)	Cu(1)—N(2)	2.006(3)
Mo(1)—C(13)	2.153(3)	Cu(1)—N(3)	2.017(3)
Mo(2)—Mo(3)	2.9552(4)	Cu(1)—N(4)	2.004(3)
Mo(2)—Mo(4)	2.9879(4)	N(1)—C(1)	1.486(4)
Mo(2)—Te(1)	2.6698(4)	C(1)—C(2)	1.515(5)
Mo(2)—Te(3)	2.6702(3)	C(2)—N(2)	1.476(4)
Mo(2)—Te(4)	2.6684(4)	N(3)—C(3)	1.482(4)
Mo(2)—C(21)	2.164(4)	C(3)—C(4)	1.518(5)
Mo(2)—C(22)	2.167(3)	C(4)—N(4)	1.479(4)
Mo(2)—C(23)	2.165(3)	Cu(2)—N(5)	2.024(3)
Mo(3)—Mo(4)	2.8203(4)	Cu(2)—N(6)	2.003(3)
Mo(3)—Te(1)	2.6917(4)	Cu(2)—N(7)	2.014(3)
Mo(3)—Te(2)	2.6716(3)	Cu(2)—N(8)	2.008(3)
Mo(3)—Te(4)	2.6908(4)	N(5)—C(5)	1.483(5)
Mo(3)—C(31)	2.158(4)	C(5)—C(6)	1.524(5)
Mo(3)—C(32)	2.162(4)	C(6)—N(6)	1.479(5)
Mo(3)—C(33)	2.159(3)	N(7)—C(7)	1.464(5)
Mo(4)—Te(2)	2.6943(3)	C(7)—C(8)	1.482(6)
Mo(4)—Te(3)	2.6966(4)	C(8)—N(8)	1.475(5)
Mo(4)—Te(4)	2.6844(3)	Cu(1A)—N(1A)	2.030(3)
Mo(4)—C(41)	2.168(4)	Cu(1A)—N(2A)	2.008(3)
Mo(4)—C(42)	2.173(4)	Cu(1A)—N(3A)	2.022(3)
Mo(4)—C(43)	2.172(3)	Cu(1A)—N(4A)	2.002(3)
C(11)—N(11)	1.161(4)	Cu(1A)—N(1N)	2.430(3)
C(12)—N(12)	1.157(4)	N(1A)—C(1A)	1.460(5)
C(13)—N(13)	1.159(4)	C(1A)—C(2A)	1.510(5)
N(13)—Cu(1)	2.325(3)	C(2A)—N(2A)	1.474(5)
C(21)—N(21)	1.151(4)	N(3A)—C(3A)	1.475(5)
C(22)—N(22)	1.163(4)	C(3A)—C(4A)	1.510(6)
C(23)—N(23)	1.156(4)	C(4A)—N(4A)	1.473(5)
N(23)—Cu(2)	2.311(3)	Cu(1A)*—N(21)	2.699(3)

* The coordinates of the atoms are generated from those of the basis atoms by the symmetry operation $2 - x$, $1 - y$, $-z$.

Table 3. Selected bond lengths (*d*) in compound **2**

Bond	*d*/Å	Bond	*d*/Å
W(1)—W(2)	3.0387(3)	C(31)—N(31)	1.169(7)
W(1)—W(3)	3.0151(3)	C(32)—N(32)	1.168(7)
W(1)—W(4)	2.9597(3)	C(33)—N(33)	1.154(7)
W(1)—Te(1)	2.6899(4)	C(41)—N(41)	1.158(7)
W(1)—Te(2)	2.6740(4)	C(42)—N(42)	1.161(7)
W(1)—Te(3)	2.6719(4)	C(43)—N(43)	1.143(7)
W(1)—C(11)	2.161(5)	Cu(1)—N(1)	2.029(4)
W(1)—C(12)	2.156(5)	Cu(1)—N(2)	2.016(4)
W(1)—C(13)	2.146(5)	Cu(1)—N(3)	2.023(4)
W(2)—W(3)	2.9325(3)	Cu(1)—N(4)	2.010(4)
W(2)—W(4)	3.0053(3)	N(1)—C(1)	1.491(7)
W(2)—Te(1)	2.6842(4)	C(1)—C(2)	1.522(8)
W(2)—Te(3)	2.6851(4)	C(2)—N(2)	1.487(8)
W(2)—Te(4)	2.6856(4)	N(3)—C(3)	1.475(7)
W(2)—C(21)	2.151(5)	C(3)—C(4)	1.516(8)
W(2)—C(22)	2.150(5)	C(4)—N(4)	1.467(7)
W(2)—C(23)	2.159(5)	Cu(2)—N(5)	2.021(5)
W(3)—W(4)	2.8494(3)	Cu(2)—N(6)	1.998(5)
W(3)—Te(1)	2.7023(4)	Cu(2)—N(7)	2.008(5)
W(3)—Te(2)	2.6864(3)	Cu(2)—N(8)	2.014(5)
W(3)—Te(4)	2.6988(4)	N(5)—C(5)	1.488(8)
W(3)—C(31)	2.148(6)	C(5)—C(6)	1.518(9)
W(3)—C(32)	2.151(5)	C(6)—N(6)	1.477(8)
W(3)—C(33)	2.154(5)	N(7)—C(7)	1.471(9)
W(4)—Te(2)	2.6990(4)	C(7)—C(8)	1.486(10)
W(4)—Te(3)	2.7012(4)	C(8)—N(8)	1.446(9)
W(4)—Te(4)	2.6920(3)	Cu(1A)—N(1A)	2.029(5)
W(4)—C(41)	2.155(5)	Cu(1A)—N(2A)	2.012(5)
W(4)—C(42)	2.156(5)	Cu(1A)—N(3A)	2.018(5)
W(4)—C(43)	2.170(5)	Cu(1A)—N(4A)	2.005(5)
C(11)—N(11)	1.153(7)	Cu(1A)—N(1N)	2.418(4)
C(12)—N(12)	1.150(7)	N(1A)—C(1A)	1.473(8)
C(13)—N(13)	1.163(6)	C(1A)—C(2A)	1.513(9)
N(13)—Cu(1)	2.336(4)	C(2A)—N(2A)	1.484(8)
C(21)—N(21)	1.153(7)	N(3A)—C(3A)	1.481(8)
C(22)—N(22)	1.164(7)	C(3A)—C(4A)	1.506(11)
C(23)—N(23)	1.155(6)	C(4A)—N(4A)	1.480(8)
N(23)—Cu(2)	2.312(4)	Cu(1A)*—N(21)	2.705(5)

* The coordinates of the atoms are generated from those of the basis atoms by the symmetry operation $2 - x$, $1 - y$, $-z$.

1585 (s), 1445 (m), 1390 (w), 1370 (w), 1310 (m), 1275 (s), 1170 (m), 1090 (m), 1030 (s), 715 (s), 520 (s), 460 (m). The magnetic susceptibility is 1.90 μ_B per Cu atom.

Bisdiethylenediaminecopper(II)amminediethylenediaminecopper(II)dodecacyanotetra-μ_3-tellurotetratungstate(W—W) pentahydrate, $[\{Cu(en)_2\}_2\{Cu(en)_2(NH_3)\}\{W_4Te_4(CN)_{12}\}]\cdot5H_2O$ (2). An aqueous ammonia solution (10 mL) of $K_6[W_4Te_4(CN)_{12}]\cdot5H_2O$ (50 mg, 0.03 mmol) was added to an aqueous ammonia solution (5 mL) of $CuCl_2\cdot2H_2O$ (15 mg, 0.09 mmol) and ethylenediamine (11 mg, 0.18 mmol). Black crystals of complex **2** precipitated after 3 days. The crystals were filtered off and dried in air for one day. The yield was 41 mg (75%). Found (%): C, 10.82; H, 1.61; N, 13.33. $C_{24}H_{61}Cu_3N_{25}O_5Te_4W_4$. Calculated (%): C, 10.62; H, 1.83; N, 13.07. IR, ν/cm^{-1}: 3430 (br), 3310 (br), 3250 (br), 2100 (s), 2090 (sh), 1585 (s) 1450 (m), 1390 (m), 1360 (w), 1310 (m), 1290 (m), 1170 (m), 1100 (m), 1030 (s), 715 (s), 520 (s), 460 (m), 410 (w). The magnetic susceptibility is 1.90 μ_B per Cu atom.

Single-crystal X-ray diffraction study of complexes 1 and 2 was carried out at 150(2) K on a four-circle automated Nonius KappaCCD diffractometer equipped with a two-coordinate detector. The principal crystallographic characteristics and details of X-ray diffraction study are given in Table 1. The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms (except for the disordered water molecule of crystallization) using the SHELX-97 program package.[22] The selected bond lengths in complexes **1** and **2** are given in Tables 2 and 3, respectively. The complete tables of the bond lengths and bond angles as well as the atomic coordinates were deposited with the Cambridge Structural Database and can be obtained from the authors.

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