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Cluster cyanide-bridged heterometallic coordination polymers: synthesis and crystal structures of compounds $[\{Cu_2(dien)_2(CN)\}_2\{Mo_4Te_4(CN)_{12}\}] \cdot 14.5H_2O$ and $(H_3O)_3K[\{Mn(H_2O)_2\}_2\{Mn(H_2O)_2(NO_3)\}_4\{W_4Te_4(CN)_{12}\}_2] \cdot 8H_2O$

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The reactions of anionic molybdenum and tungsten cyanide cuboidal clusters with Cu^{II} and Mn^{II} salts afforded two new cyanide-bridged heterometallic coordination polymers with the composition $[\{Cu_2(dien)_2(CN)\}_2\{Mo_4Te_4(CN)_{12}\}] \cdot 14.5H_2O$ (**1**) and $(H_3O)_3K[\{Mn(H_2O)_2\}_2\{Mn(H_2O)_2(NO_3)\}_4\{W_4Te_4(CN)_{12}\}_2] \cdot 8H_2O$ (**2**). The structures of these compounds were established by X-ray diffraction analysis. Compound **1** has a layered structure, in which the cuboidal cluster fragments $\{Mo_4Te_4(CN)_{12}\}^{6-}$ are linked to the copper atoms of the dinuclear fragments $\{(H_2O)(dien)Cu(\mu\text{-}CN)Cu(dien)(H_2O)\}$ through the bridging CN groups. Coordination polymer **2** has a framework structure, in which the cluster fragments $\{W_4Te_4(CN)_{12}\}^{6-}$ are linked to the manganese(II) aqua complexes of two types, *viz.*, the dinuclear fragment $\{Mn(\mu_2\text{-}H_2O)_2Mn\}$ and the tetranuclear cyclic fragment $\{(H_2O)_2Mn(\mu_2\text{-}NO_3)\}_4$, through the bridging CN groups.

Key words: clusters, molybdenum, tungsten, tellurium, coordination polymers.

Cyanide-bridged heterometallic complexes and coordination polymers, which were prepared from the mononuclear tetrahedral $[M(CN)_4]^{n-}$ and octahedral $[M(CN)_6]^{n-}$ complexes, are well known.[1—4] In these compounds, the bidentate bridging cyanide ligand is coordinated to one of the metal atoms through the carbon atom and to another metal atom through the nitrogen atom to form heterometallic cyanide-bridged complexes or coordination polymers. In recent years, studies have been initiated to synthesize coordination polymers containing transition metal cyanide cluster complexes. Tetranuclear molybdenum, tungsten, and rhenium chalcogenide cuboidal complexes and octahedral rhenium chalcogenide clusters are used as the above-mentioned clusters. Compound containing chains, networks, or three-dimensional frameworks of the M_n clusters ($n = 4$, M = Mo, W, Re; $n = 6$, M = Re), which are linked to the heterometal atoms M´ through the bridging cyanide ligands, *viz.*, ...M´—NC—M_n—CN—M´—NC..., have been synthesized and structurally characterized.[5—13] In our recent studies,[14—17] the molybdenum and tungsten cyanochalcogenide cuboidal complexes $[M_4Q_4(CN)_{12}]^{n-}$ (M = Mo, W; Q = S, Se, Te; $n = 6, 7, 8$) have been used for the preparation of the chain complex with the composition $[Cu(NH_3)_3][Cu(NH_3)_4][Cu(NH_3)_5][W_4Te_4(CN)_{12}] \cdot 5H_2O$,[18] 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, Er; $n = 6.5—7.5$),[19] and the unique framework polymers $[M(H_2O)_4]_3[W_4Q_4(CN)_{12}] \cdot nH_2O$ (M = Co, Q = Te;[20] M = Mn, Q = S [21]), which contain large cavities occupied by water molecules. Complexes with an island-type structure and composition $[Cu(en)_2]_2[Cu(en)_2(NH_3)][M_4Te_4(CN)_{12}] \cdot 5H_2O$ (M = Mo, W) have also been synthesized.[22]

In all the above-described compounds, the cyanide-bridged heterometallic coordination polymers consist of molybdenum or tungsten cuboidal clusters, which are linked to heterometal-containing mononuclear fragments. In the present study, we synthesized the previously unknown cyanide-bridged heterometallic coordination polymers, which are built of cuboidal clusters and polynuclear heterometal-containing complex fragments.

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Results and Discussion

The complex with the composition $[\{Cu_2(C_4N_3H_{13})_2(CN)\}_2\{Mo_4Te_4(CN)_{12}\}] \cdot 14.5H_2O$ (**1**) was prepared by slow evaporation in air of an aqueous-ammonium solution containing the cluster molybdenum telluride complex $K_7[Mo_4Te_4(CN)_{12}] \cdot 12H_2O$, copper(II) chloride, and diethylenetriamine (the $CuCl_2$: diethylenetriamine concentration ratio in the solution was 1 : 1.2). Under the synthesis conditions, the starting paramagnetic complex $[Mo_4Te_4(CN)_{12}]^{7-}$ was oxidized with atmospheric oxygen to form the diamagnetic $[Mo_4Te_4(CN)_{12}]^{6-}$ complex. Crystals of complex **1** slowly precipitated from the reaction mixture during 10 days (38% yield). Further evaporation of the mother liquor afforded a poorly separable mixture containing unidentifiable products. The complex with the composition $(H_3O)_3K[\{Mn(H_2O)_2\}_2\{Mn(H_2O)_2(NO_3)\}_4\{W_4Te_4(CN)_{12}\}_2] \cdot 8H_2O$ (**2**) was prepared in good yield by slow evaporation in air of a solution, which contained the cluster tungsten telluride complex $K_6[W_4Te_4(CN)_{12}] \cdot 6H_2O$ and manganese(II) nitrate in an acetate buffer (pH ~5). The maximum yield of complex **2** (78%) was achieved in the presence of a small excess of the manganese salt. To prepare crystalline samples of compounds **1** and **2**, the synthesis should be carried out in a dilute solution (see the Experimental section). The use of higher concentrations of the starting reagents leads to the rapid (in a matter of hours) formation of X-ray amorphous precipitates. Compounds **1** and **2** are insoluble in water and lose crystallization water upon storage in air over a long period.

The structures of compounds **1** and **2** were established by X-ray diffraction analysis. Complex **1** is a coordination polymer with a layered structure, in which the cuboidal cluster fragments $\{Mo_4Te_4(CN)_{12}\}$ are linked to the copper(II) diethylenetriamine complexes through the bridging CN groups (Fig. 1). The center of the cluster anion occupies the crystallographic 2*d* position (0, 1/2, 3/4) with the symmetry $\bar{4}$ (S_4). The Mo—Mo (aver., 2.962 Å) and Mo—Te (aver., 2.673 Å) distances agree well with the data obtained in our earlier studies[12—14] for other molybdenum telluride cuboidal complexes. The coordination environment of the copper(II) atom is formed by three nitrogen atoms of the ethylenediamine ligand (N(1), N(2), and N(3); aver., 2.018 Å), the nitrogen atom of the CN ligand of the cluster anion (N(13), 2.316(6) Å), the bridging CN ligand coordinated to the adjacent copper atom (C(21) and N(21), 1.980(6) Å), and the water molecule (O(1W), 2.803(8) Å). Elongation of the copper—ligand distances for the ligands located in the apical positions compared to the bond lengths for the ligands in the equatorial positions agrees well with the stereochemistry of octahedral copper(II) complexes characterized by the Jahn—Teller effect, which is manifested in distortion of the coordination octahedron of the copper atom. Therefore, the copper atoms are in a distorted octahedral environment, and the coordination number of copper is 4+2 (see Fig. 1). The structure of compound **1** can be described as a two-layer packing of polymer layers, which alternate along the *c* axis and are separated by one-half translation. The mutual arrangement and the orientation of the layers with respect to each other obey the symmetry $\bar{4}$ (S_4). The polymer layer can be described as a square network consisting of the cluster anions, which are linked to each other through the dinuclear $\{(H_2O)(dien)Cu(\mu\text{-}CN)Cu(dien)(H_2O)\}$ fragments (Fig. 2). Since the center of the dinuclear fragment, *viz.*, the midpoint of the bond of the CN ligand, lies on a twofold rotation axis, two possible orientations of the bridging CN group become equally possible, and the nitrogen and carbon atoms (N(21) and C(21)) occupy the positions with equal probability. In this case, the carbon and nitrogen atoms are indistinguishable and the description of the structures refers to the maximum crystal symmetry.

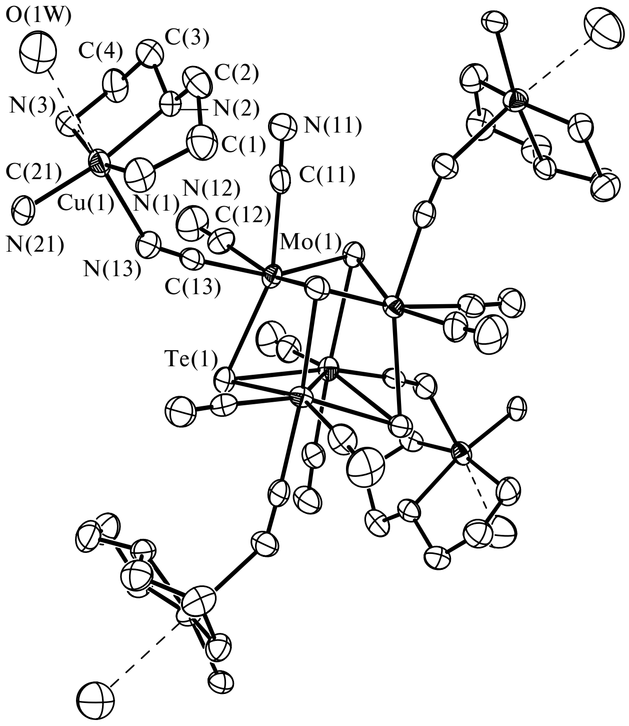

Fig. 1. Fragment of the structure of compound **1** (thermal ellipsoids are drawn at the 50% probability level).

Compound **2** is a coordination polymer with a framework structure, in which the cuboidal cluster fragments $\{W_4Te_4(CN)_{12}\}$ are linked to the manganese(II) aqua complexes through the bridging CN groups. The center of the cluster anion occupies the crystallographic 4*g* position (x, $x + 1/2$, 0; $-x$, $-x + 1/2$, 0; $-x + 1/2$, x, 0;

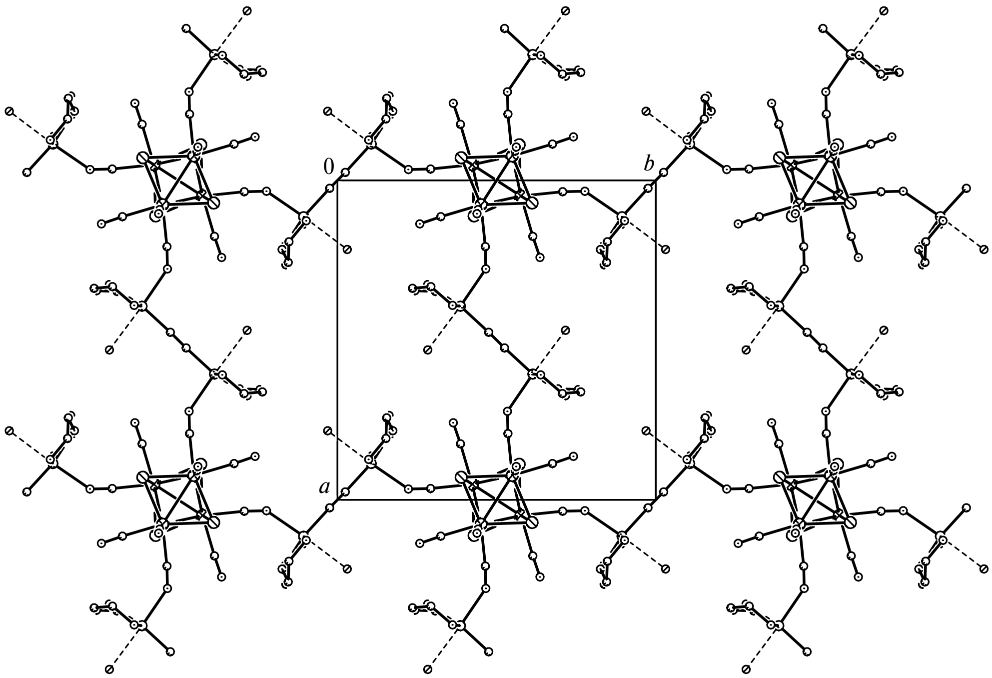

Fig. 2. Packing of the polymer layers in the crystal of compound **1** (projection onto the *ab* plane). The Cu(1)—O(1W) bonds are indicated by dashed lines.

$x + 1/2, -x, 0; x = 0.268$) with the symmetry *m*2*m* (C_{2v}). The W—W (aver., 2.972 Å) and W—Te (aver., 2.689 Å) distances agree well with the data obtained in our earlier studies[12—14] for other tungsten telluride cuboidal complexes. The crystal structure of complex **2** contains two crystallographically independent manganese atoms, Mn(1) and Mn(2). The coordination number of both manganese atoms is six. The coordination environment of

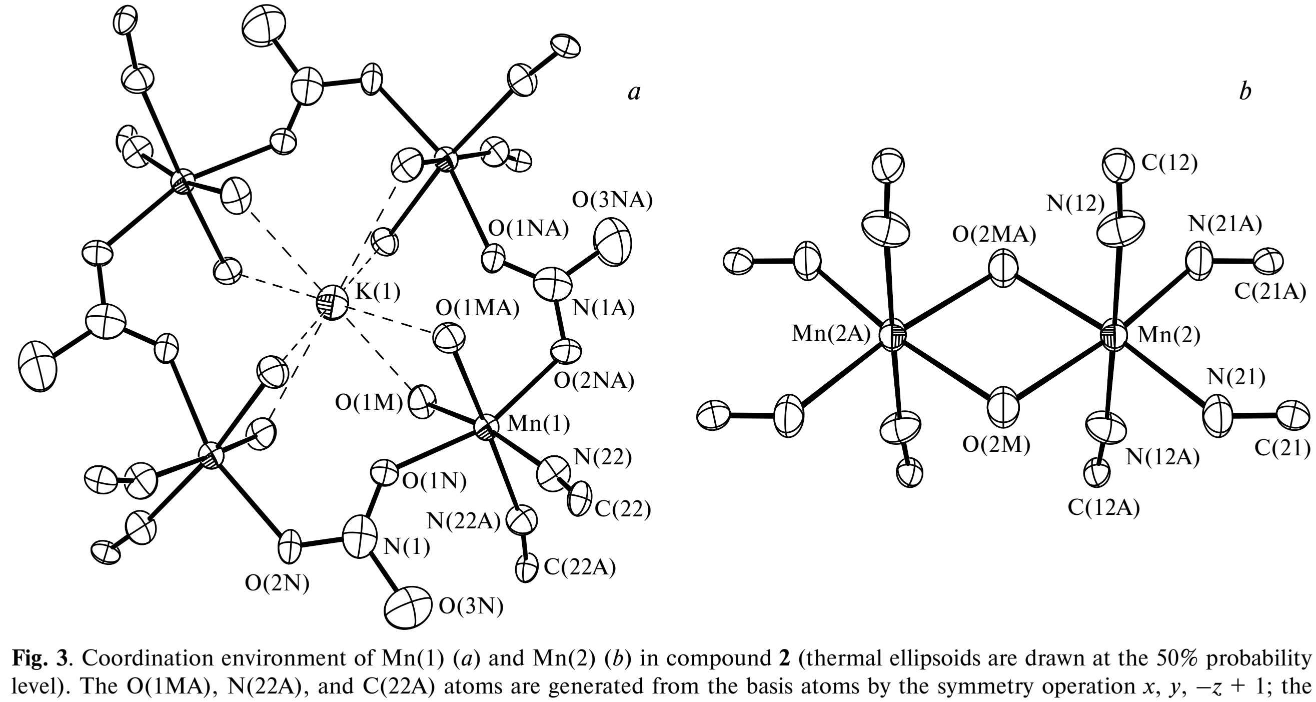

Fig. 3. Coordination environment of Mn(1) (*a*) and Mn(2) (*b*) in compound **2** (thermal ellipsoids are drawn at the 50% probability level). The O(1MA), N(22A), and C(22A) atoms are generated from the basis atoms by the symmetry operation $x, y, -z + 1$; the N(1A), O(1NA), O(2NA), and O(3NA) atoms are generated by the symmetry operation $y - 1, -x + 1, -z + 1$; the N(12A) and C(12A) atoms are generated by the symmetry operation $-x + 1/2, y - 1/2, -z$; and the O(2MA), N(21A), and C(21A) atoms are generated by the symmetry operation $x, y, -z$.

the Mn(1) atom is formed by two water molecules (O(1M) and O(1MA)), two oxygen atoms of two bridging NO_3^- ligands (O(1N) and O(2NA)), and two nitrogen atoms of the CN groups of two cluster anions (N(22) and N(22A)). The nearly planar 16-membered ring $\{(H_2O)_2Mn(\mu_2\text{-}NO_3)\}_4$ containing four Mn(1) atoms is formed through the bridging NO_3^- ligands. The aqua ligands and the bridging CN groups are located along the inner and outer rims of the ring, respectively. The K^+ cation occupies the center of the cyclic fragment in the 2*b* position (0, 0, 1/2; 1/2, 1/2, 1/2) with the symmetry 4/*m* (C_{4h}). The K^+ cation forms bonds with the water molecules coordinated to the manganese(II) atom (Fig. 3, *a*). The coordination environment of the Mn(2) atom involves two bridging water molecules (O(2M) and O(2MA)) and four nitrogen atoms of the CN groups of three cluster anions (N(12), N(12A), N(21), and N(21A)). The Mn(2) atoms form dimers (Mn...Mn, 3.566(3) Å) through the bridging water molecules (see Fig. 3, *b*). The center of the dimer occupies the crystallographic 2*d* position (0, 1/2, 0; 1/2, 0, 0) with the symmetry *mmm* (D_{2h}). The projection of the unit cell onto the *ab* plane is shown in Fig. 4. The cuboidal cluster fragments and the $\{Mn(\mu_2\text{-}H_2O)_2Mn\}$ dimers are located in a single plane and form layers, which alternate along the *c* axis and are separated by one-half translation. The layers are linked to each other through coordination of the CN groups of the cluster complexes to the Mn(1) atoms, which are located between the layers. In the $\{Mn(\mu_2\text{-}H_2O)_2Mn\}$ dimer, the Mn(2) atoms link four tungsten clusters in the layer through the bridging CN ligands. The Mn(1) atoms in the 16-membered ring $\{(H_2O)_2Mn(\mu_2\text{-}NO_3)\}_4$ link four cuboidal clusters from the adjacent layers (see Fig. 4).

Compounds **1** and **2** are paramagnetic. At 20 °C, the measured magnetic susceptibilities are 1.78 and 5.92 μ_B per Cu^{II} and Mn^{II} atom for complexes **1** and **2**, respectively. These values are in good agreement with the theoretical effective magnetic moments for the Cu^{II} and Mn^{II} atoms and are indicative of the absence of exchange interactions between the paramagnetic centers in these coordination polymers.

To summarize, we synthesized two new cyanide-bridged heterometallic coordination polymers by the reactions of anionic molybdenum and tungsten cyanide

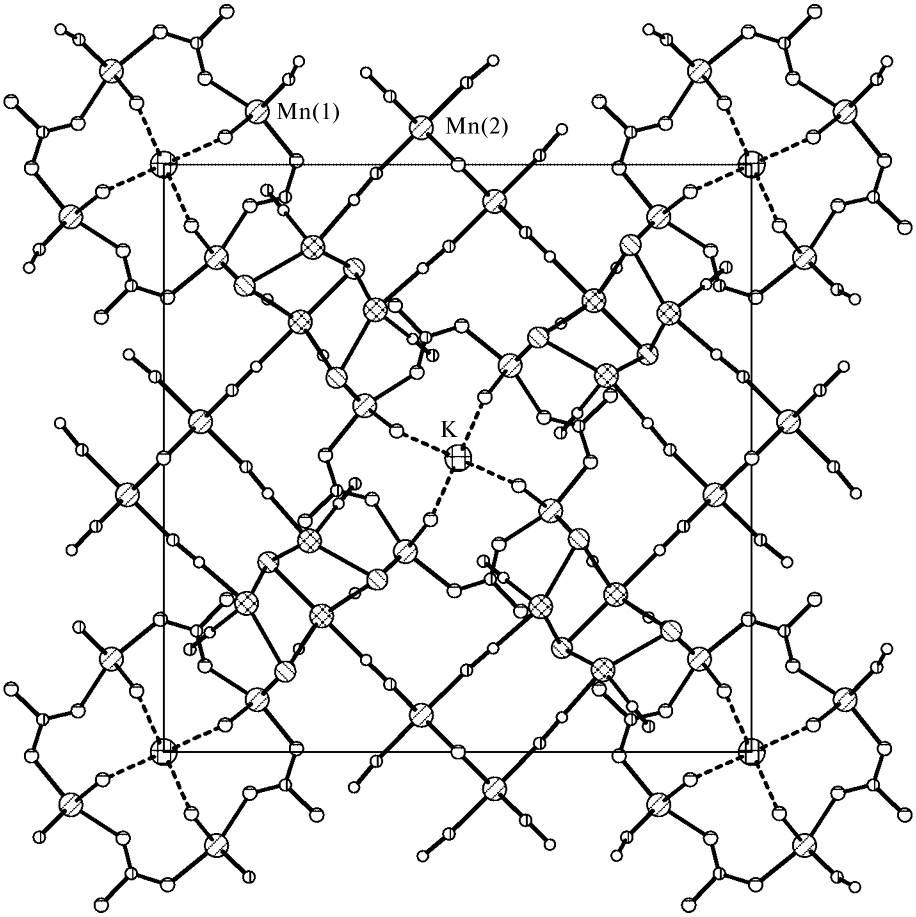

Fig. 4. Packing in the crystal structure of compound **2** (projection onto the *ab* plane). The K(1)...O(1M) contacts are indicated by dashed lines.

cuboidal clusters with Cu^{II} and Mn^{II} salts. The structures of these coordination polymers were established by X-ray diffraction analysis. For molybdenum and tungsten cuboidal complexes, heterometallic cyanide-bridged coordination polymers were prepared for the first time. In these coordination polymers, the heterometals (Cu^{II} and Mn^{II}) form polynuclear fragments, *viz.*, the dinuclear fragments ($\{(H_2O)(dien)Cu(\mu\text{-}CN)Cu(dien)(H_2O)\}$ for **1** and $\{Mn(\mu_2\text{-}H_2O)_2Mn\}$ for **2** and the tetranuclear cyclic fragment $\{(H_2O)_2Mn(\mu_2\text{-}NO_3)\}_4$ for **2**.

Experimental

All syntheses were carried out in air. The reagents of analytical grade were used. The starting cluster complexes $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$ and $K_7[Mo_4Te_4(CN)_{12}] \cdot 12H_2O$ were prepared from a mixture of polymeric tungsten ditelluride WTe_2 or the triangular molybdenum telluride complex $Mo_3Te_7I_4$, respectively, and KCN according to procedures described earlier.[13,14] Magnetic measurements were carried out by the Faraday method at 20 °C.

Synthesis of bis{cyanobis(diethylenetriamine)dicopper(II)}dodecacyanotetra-μ_3-telluridotetramolybdenum 14.5-hydrate (1). An aqueous-ammonium solution (10 mL) of $K_7[Mo_4Te_4(CN)_{12}] \cdot 12H_2O$ (34 mg, 0.020 mmol) was added to an aqueous-ammonium solution (5 mL) of $CuCl_2 \cdot 2H_2O$ (17 mg, 0.10 mmol) and diethylenetriamine (12 mg, 0.12 mmol) and the reaction mixture was kept in air at 20 °C. After 10 weeks, the volume of the starting solution decreased to 10 mL and dark crystals of **1** precipitated. The crystals were filtered off and dried in air for one day. The yield of crystal hydrate **1** containing 14.5 H_2O molecules was 17 mg (38%). Found (%): C, 16.52; H, 3.53; N, 16.89. $C_{30}H_{81}Cu_4Mo_4N_{26}O_{14.5}Te_4$. Calculated (%): C, 16.48; H, 3.73; N, 16.66. The magnetic susceptibility is 1.78 μ_B per copper atom.

Synthesis of bis{diaquamanganese(II)}tetrakis{nitratodiaquamanganese(II)}-bis(dodecacyanotetra-μ_3-telluridotetratungstate) trihydroxonium potassium octahydrate (2). The $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$ complex (50 mg, 0.03 mmol) was added to a solution (15 mL) of $Mn(NO_3)_2 \cdot 6H_2O$ (34 mg, 0.12 mmol) in an acetate buffer (0.2 *M* AcONa + 0.2 *M* AcOH) and the reaction mixture was kept in air at 20 °C. After two weeks, the volume of the starting solution decreased to 10 mL and dark crystals of **2** precipitated. The crystals were filtered off and dried in air for one day. The yield was 89 mg (72%). Found (%): C, 7.15; H, 0.98; N, 9.55. $C_{24}H_{49}KMn_6N_{28}O_{35}Te_8W_8$. Calculated (%): C, 6.95; H, 1.19; N, 9.45. The magnetic susceptibility is 5.92 μ_B per manganese atom.

X-ray diffraction study. The main crystallographic characteristics and details of X-ray diffraction studies of compounds **1**

Table 1. Main crystallographic characteristics and details of X-ray diffraction study

Parameter	1	2
Molecular formula	$C_{30}H_{81}Cu_4Mo_4N_{26}O_{14.5}Te_4$	$C_{24}H_{49}KMn_6N_{28}O_{35}Te_8W_8$
Molecular weight	2186.53	4150.25
Crystal system	Tetragonal	
Space group	$I\bar{4}$	*P*4/*mbm*
a/Å	16.383(3)	20.1507(14)
c/Å	12.566(5)	11.0821(14)
V/Å^3	3372.6(16)	4499.9(7)
Z	2	2
ρ_{calc}/g cm^{-3}	2.153	3.063
F(000)	2102	3692
μ(Mo-Kα)/mm^{-1}	3.720	13.656
Crystal dimensions/mm	0.20×0.11×0.08	0.13×0.09×0.06
θ Scan range/deg	2.49—28.54	2.86—28.04
Ranges of *h, k, l* indices	$-21 \le h \le 21$, $-22 \le k \le 21$, $-12 \le l \le 16$	$-26 \le h \le 19$, $-26 \le k \le 26$, $-14 \le l \le 13$
Number of measured reflections	13500	26529
Number of independent reflections	4286 (R_{int} = 0.0670)	2980 (R_{int} = 0.1011)
Number of reflections with $F > 4\sigma(F)$	3339	2334
Number of parameters in refinement	186	153
R indices based on reflections with $F > 4\sigma(F)$		
R_1	0.0366	0.0430
wR_2	0.0791	0.1049
R indices based on all reflections		
R_1	0.0649	0.0638
wR_2	0.0918	0.1159
Goodness-of-fit on F^2	1.048	1.063
Residual electron density (min/max, e/Å^{-3})	−0.654/0.710	−1.455/3.064

Table 2. Selected bond lengths in complex **1**

Bond	*d*/Å	Bond	*d*/Å
Mo(1)—Mo(1)[a]	2.9546(12)	Cu(1)—N(2)	2.023(6)
Mo(1)—Mo(1)[b]	2.9743(13)	Cu(1)—N(3)	2.022(7)
Mo(1)—Te(1)	2.6792(9)	Cu(1)—X(21)[c]	1.980(6)
Mo(1)—Te(1)[a]	2.6737(12)	Cu(1)—N(13)	2.316(6)
Mo(1)—Te(1)[b]	2.6674(9)	Cu(1)—O(1W)	2.803(8)
Mo(1)—C(11)	2.160(8)	C(21)[c]—N(21)[c,d]	1.142(12)
Mo(1)—C(12)	2.156(8)	C(1)—N(1)	1.475(11)
Mo(1)—C(13)	2.165(7)	C(1)—C(2)	1.479(12)
C(11)—N(11)	1.148(10)	C(2)—N(2)	1.472(11)
C(12)—N(12)	1.164(11)	N(2)—C(3)	1.471(10)
C(13)—N(13)	1.150(9)	C(3)—C(4)	1.488(12)
Cu(1)—N(1)	2.010(7)	C(4)—N(3)	1.492(10)

[a] The coordinates of the atoms are generated from those of the basis atoms by the symmetry operation $y + 1/2$, $-x - 1/2$, $-z - 1/2$.

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

[c] The position is occupied by the C(21) and N(21) atoms with half weights.

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

and **2** are given in Table 1. X-ray diffraction data were collected on an automated Bruker Smart 1000 CCD diffractometer equipped with a two-coordinate detector (Mo-Kα radiation, graphite monochromator). The unit cell parameters of compounds **1** and **2** were refined using 853 and 965 reflections in angle ranges $2.49 \le \theta \le 23.53°$ and $2.91 \le \theta \le 26.98°$, respectively. The absorption corrections for compounds **1** and **2** were applied taking into account the crystal shape using the XPREP program incorporated in the SHELXTL program package[23] (face indices: $1\bar{1}0$, $\bar{1}10$, 110, $\bar{1}\bar{1}0$, 101, $\bar{2}0\bar{1}$, $01\bar{1}$, $\bar{1}\bar{2}2$, $0\bar{1}\bar{1}$, $\bar{1}01$ for **1**, and 100, $\bar{1}00$, 010, $0\bar{1}0$, 001, $00\bar{1}$ for **2**). The structures of complexes **1** and **2** were solved by direct methods and refined anisotropically (except for the hydrogen atoms and disordered water molecules) by the full-matrix least-squares method using the SHELX-97 program package.[24] The positions of the hydrogen atoms of the diethylenetriamine ligands were calculated geometrically and refined in the rigid-body approximation. The hydrogen atoms of the water molecules were not revealed. Selected bond lengths in compounds **1** and **2** are given in Tables 2 and 3, respectively. The atomic coordinates were deposited with the Cambridge Structural Database and can be obtained from the authors.

Table 3. Selected bond lengths in complex **2**

Bond	*d*/Å	Bond	*d*/Å
W(1)—W(1)[a]	3.0319(11)	C(21)—N(21)	1.161(19)
W(1)—W(2)	2.9783(7)	C(22)—N(22)	1.147(13)
W(1)—Te(1)	2.6828(11)	Mn(1)—N(22)	2.195(10)
W(1)—Te(2)	2.6824(9)	Mn(1)—O(1M)	2.263(8)
W(1)—C(11)	2.135(10)	Mn(1)—O(1N)	2.123(11)
W(1)—C(12)	2.156(14)	Mn(1)—O(2N)[b]	2.153(11)
W(2)—W(2)[c]	2.8870(12)	N(1)—O(1N)	1.239(19)
W(2)—Te(1)	2.6988(8)	N(1)—O(2N)	1.299(19)
W(2)—Te(2)[c]	2.6913(11)	N(1)—O(3N)	1.50(2)
W(2)—C(21)	2.149(14)	Mn(2)—N(12)	2.198(13)
W(2)—C(22)	2.149(10)	Mn(2)—N(21)	2.204(14)
C(11)—N(11)	1.186(15)	Mn(2)—O(2M)	2.288(10)
C(12)—N(12)	1.179(19)		

[a] The coordinates of the atoms are generated from those of the basis atoms by the symmetry operation $y - 1/2$, $x + 1/2$, $-z$.

[b] The coordinates of the atoms are generated from those of the basis atoms by the symmetry operation $y - 1$, $-x + 1$, $-z + 1$.

[c] The coordinates of the atoms are generated from those of the basis atoms by the symmetry operation x, y, $-z$.

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