Synthesis and structure of the framework coordination polymer based on the cluster anion $[Nb_4OTe_4(CN)_{12}]^{6-}$ and Mn^{II} aqua complexes

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Dark-brown plate crystals of the $[Mn_7(H_2O)_{26}\{Nb_4OTe_4(CN)_{12}\}_2](OH)_2 \cdot 11H_2O$ compound (**1**) were prepared by the reaction of an aqueous ammonia solution of the $K_6[Nb_4OTe_4(CN)_{12}] \cdot K_2CO_3 \cdot KOH \cdot 8H_2O$ complex with a glycerol solution of manganese(II) nitrate. The structure of complex **1** was established by X-ray diffraction. Compound **1** has a polymer structure containing four types of manganese atoms. The nitrogen atoms of eight cyano groups of the tetranuclear niobium cluster are coordinated to the manganese atoms to form a {2,3,8}-connected three-dimensional network.

Key words: niobium, manganese, cluster complexes, coordination polymer, crystal structure, topological analysis, X-ray diffraction analysis.

Cyano-bridged heterometallic complexes and coordination polymers generated from mononuclear tetrahedral ($[M(CN)_4]^{n-}$) and octahedral ($[M(CN)_6]^{n-}$) complexes are well known.[1—4] Studies on the synthesis of coordination polymers containing transition metal cyanide cluster complexes have been initiated in recent years. Tetranuclear and octahedral molybdenum, tungsten, and rhenium chalcogenide complexes are used as such clusters. Heterometallic compounds containing chains, networks, and three-dimensional frameworks of clusters M_n (M = Mo, W, or Re; n = 4 or 6), which are linked to heterometal atoms M′ *via* the bridging cyanide ligands, ...M′—NC—M_n—CN—M′—NC..., were synthesized and structurally characterized.[5—18] The octahedral clusters $[M_6X_8(CN)_6]^{n-}$ (X = S, Se, or Te) contain six CN groups directed toward the vertices of the octahedron. This imposes restrictions on the geometry and topology of heterometallic coordination polymers. In particular, octahedral cyanide clusters are coordinated by at most six heterometal atoms, *i.e.*, serve as six-connected nodes. The use of tetrahedral cluster anions, such as $[Re_4X_4(CN)_{12}]^{4-}$ and $[M_4X_4(CN)_{12}]^{6-}$ (M = Mo or W), opens new possibilities for the design of coordination polymers. In these polymers, twelve cyano groups occupy vertices of a truncated tetrahedron. An increase in the number of coordination modes of heterometal atoms compared to octahedral anions leads to potentially wider diversity of structures and compositions of the resulting compounds.[19,20]

The present study is a continuation of our on-going research into synthesis methods, structures, and reactivity of cyanide chalcogenide-bridged cuboidal cluster compounds of early transition metals. We synthesized the first heterometallic coordination polymer based on the tetranuclear niobium tellurocyanide cluster $[Nb_4(\mu_4\text{-}O)(\mu_3\text{-}Te)_4(CN)_{12}]^{6-}$ (see Refs 21 and 22) and studied its structure.

Results and Discussion

The compound $[Mn_7(H_2O)_{26}\{Nb_4OTe_4(CN)_{12}\}_2](OH)_2 \cdot 11H_2O$ (**1**) was synthesized in 30% yield by carefully layering an aqueous ammonia solution of $K_6[Nb_4OTe_4(CN)_{12}] \cdot K_2CO_3 \cdot KOH \cdot 8H_2O$ over a glycerol solution of manganese(II) nitrate. In air, dark plate crystals rapidly lose water of crystallization. The cyano groups in complex **1** are easily identified in IR spectra based on ν(CN) stretching vibrations of the bridging and terminal cyano groups (two bands at 2134 and 2100 cm^{-1} for the coordination polymer and one band at 2095 cm^{-1} for the starting complex) and mixed ν(MC)/δ(MCN) vibrations at 410 and 470 cm^{-1} in the spectra of the starting complex and compound **1**, respectively.

In the crystalline state, compound **1** exists as a coordination polymer, in which the tetranuclear cluster fragments $[Nb_4(\mu_4\text{-}O)(\mu_3\text{-}Te)_4(CN)_{12}]$ and the mononuclear fragments $[Mn(H_2O)_n]$ (n = 3 or 4) are linked *via* the bridging cyano groups (Figs 1 and 2). The bond lengths in the cluster fragment are similar to those published earlier.[21] In the cluster complex, the Nb(1) atom is linked to three manganese atoms (Mn(1), Mn(2), and Mn(4)) *via* the bridging cyano groups. The Nb(2) atom is linked

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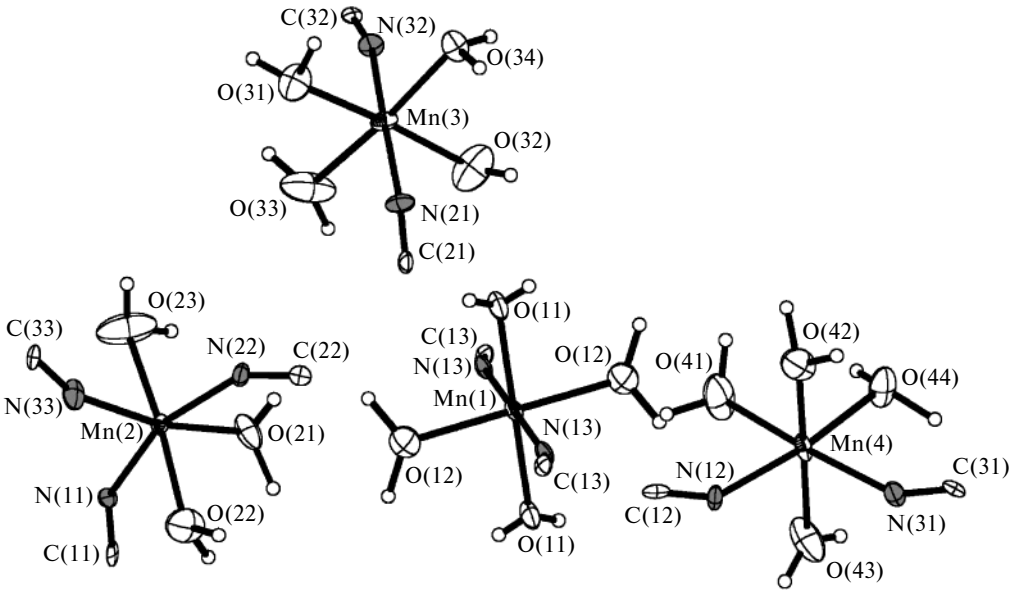

Fig. 1. Coordination environment of the manganese atoms in compound **1** represented by anisotropic displacement ellipsoids drawn at the 50% probability level.

to the Mn(2) and Mn(4) atoms, and the Nb(3) atom is linked to the Mn(2), Mn(3), and Mn(4) atoms. Therefore, each niobium cluster is coordinated to eight manganese atoms *via* eight of twelve CN groups. In turn, the manganese(II) atoms are coordinated by the oxygen atoms of the water molecules and the nitrogen atoms of the cyano groups, thus linking the cluster complexes to each other to form a positively charged framework (Fig. 3) with a total Mn : cluster ratio of 7 : 2. The compound was synthesized in the presence of ammonia, and the charge of the polymeric framework is most likely compensated by OH^- anions. However, we failed to distinguish these anions among the solvate water molecules occupying the cavities.

Let us consider the structure of compound **1** in terms of the framework topology. For this purpose, the structure is approximated by a graph, in which the cluster anion and the complex manganese cations serve as nodes, and the bridging CN groups serve as edges. Earlier, this approach has been widely used for the topological analysis of various frameworks.[23—29] The cluster anion contains 12 cyano groups and, consequently, can theoretically be coordinated by 12 transition metal atoms, *i.e.*, can serve as a 12-connected node. Besides, an octahedral coordination by six nitrogen atoms of cyano groups would be expected for the Mn^{II} cation. Therefore, in the limiting

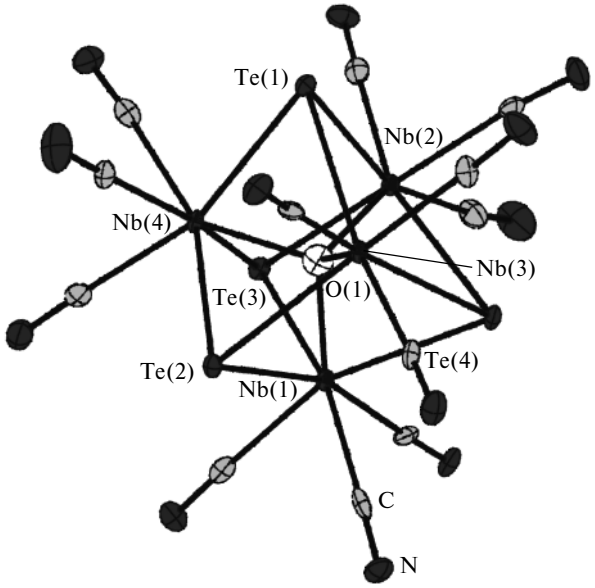

Fig. 2. Structure of the tetranuclear cluster fragment in the crystal structure of **1** represented by anisotropic displacement ellipsoids drawn at the 50% probability level.

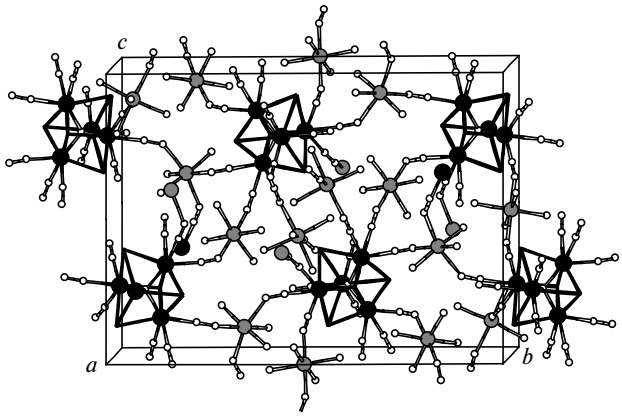

Fig. 3. Fragment of the crystal packing in the crystal structure of **1** (solvate water molecules and hydrogen atoms are omitted).

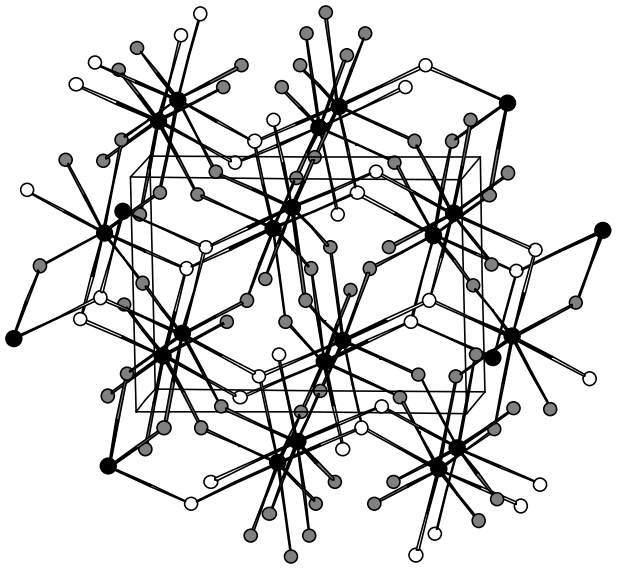

Fig. 4. Schematic representation of the coordination polymer framework in the crystal structure of **1** (niobium clusters are indicated by solid circles; manganese atoms linking three clusters, by empty circles; manganese atoms linking two clusters, by shaded circles).

case, a combination of Mn^{II} and $[Nb_4OTe_4(CN)_{12}]^{6-}$ can give rise to a three-dimensional network (framework) with the connectivity (12, 6) (based on the classification proposed in the study[24]). The framework is electroneutral if there are three cations per anion. However, along with the nitrogen atoms of the cyano groups, some coordination sites in the environment of manganese atoms can be occupied by water molecules. In addition, not necessarily all cyano groups are involved in the coordination environment of manganese atoms in the anions. Hence, the number of theoretically possible clusters is very large, and it is very difficult to achieve the desired framework structure. One of the possible frameworks is observed in the structure of **1**. In this structure, there are four crystallographically different octahedrally coordinated manganese atoms (see Fig. 1), which can be divided into three types according to the structure of the first coordination sphere: *trans*-N_2O_4 (Mn(1) and Mn(3)), *cis*-N_2O_4 (Mn(4)), and *mer*-N_3O_3 (Mn(2)). It can easily be seen that the $[Mn(H_2O)_4]^{2+}$ groups serve as linear and angular two-connected nodes; the $[Mn(H_2O)_3]^{2+}$ groups, as three-connected nodes with T geometry; the cluster anion, as an eight-connected node. This gives rise to a network with the connectivity {2,3,8}, which is characterized by the stoichiometry $(2\text{-c})_5(3\text{-c})_2(8\text{-c})_2$ and is described by the Schlafly symbol $\{4;6^2\}2\{4^2;6^8;8^{14};10^4\}2\{4\}2\{6\}3$ (Fig. 4).

Earlier,[10,15,16] attempts have been made to use the tetrahedral cluster complexes $[M_4Q_4(CN)_{12}]^{n-}$ (M = Re; Q = S, Se, or Te; $n = 4$ and M = W; Q = S, Te; $n = 6$) for the preparation of framework coordination polymers. The compositions of the structurally characterized compounds and the framework topology are given in Table 1. It can easily be seen that in all complexes considered earlier, like in complex **1**, the transition metal atoms (Mn, Co, Cu, and Cd) serve as two- or three-connected nodes. Only six of twelve cyano groups are involved in coordination to the metal atoms in the cluster anions. Eight CN groups are involved in coordination only in the structure of **1**. The structures show wide diversity of the framework topology; however, the maximum connectivity of the cyano cluster unit (12) is still unachievable.

Experimental

Reagents were of analytical grade. The $K_6[Nb_4OTe_4(CN)_{12}] \cdot K_2CO_3 \cdot KOH \cdot 8H_2O$ compound was synthesized according to a known procedure.[21] Elemental analysis was carried out in the Laboratory of Microanalysis of the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The

Table 1. Framework coordination polymers based on tetrahedral cyano cluster anions and transition metal cations

Complex	Stoichiometry of the framework[a]	Schlafly symbol	N_{CN}[b]	Reference
$[Co(H_2O)_4]_3[W_4Te_4(CN)_{12}] \cdot 15.38H_2O$	$(2\text{-c})_3(6\text{-c})$	$\{8^{12};12^3\}\{8\}3$	6	15
$[Mn(H_2O)_4]_3[W_4S_4(CN)_{12}] \cdot 5.41H_2O$	$(2\text{-c})_3(6\text{-c})$	$\{8^{12};12^3\}\{8\}3$	6	16
$Cu_2[Re_4Te_4(CN)_{12}] \cdot 4H_2O$	(2-c)(4-c)(6-c)	$\{4^4;6^2\}\{4^4;6^7;8^4\}\{6\}$	6	10
$Mn_2[Re_4Se_4(CN)_{12}] \cdot 6H_2O$[c]	(2-c)(4-c)(6-c)	$\{4^4;6^2\}\{4^4;6^7;8^4\}\{6\}$	6	10
$Cd_2[Re_4Te_4(CN)_{12}] \cdot 6H_2O$[c]	(2-c)(4-c)(6-c)	$\{4^4;6^2\}\{4^4;6^7;8^4\}\{6\}$	6	10
1	$(2\text{-c})_5(3\text{-c})_2(8\text{-c})_2$	$\{4;6^2\}2\{4^2;6^8;8^{14};10^4\}2\{4\}2\{6\}3$	8	—[d]

[a] The connectivities of nodes (2-c is a two-connected node, *etc.*) are given in parentheses; the relative numbers of a particular type of nodes in the framework are given as subscripts.

[b] The number of cyano groups of the cluster anion involved in the framework formation.

[c] The compounds are isomorphous to the copper-containing analog; however, the Mn and Cd atoms are disordered over two crystallographically related positions. The topology is given for the framework corresponding to one mode of arrangement.

[d] The results of the present study.

IR spectra were recorded on a Bruker IFS-85 Fourier transform spectrometer in KBr pellets. The synthesis was performed in 12-mm glass tubes.

Bis(dodecacyanotetratelluridomonooxotetraniobium)hexacosaaquadihydroxoheptamanganese undecahydrate (1). An aqueous ammonia solution of $K_6[Nb_4OTe_4(CN)_{12}]\cdot K_2CO_3\cdot KOH\cdot 8H_2O$ (10 mL, 0.663 mmol) was carefully (without mixing) layered over a 0.01 *M* $Mn(NO_3)_2$ solution in glycerol (5 mL). After 5 days, dark plate crystals of the complex grew at the interface. The crystals were washed with ethanol and dried in air. The yield was 0.0085 g (30% based on $Mn(NO_3)_2$ consumed). Found (%): C, 8.01; H, 2.16; N, 9.50. $C_{24}H_{76}Mn_7N_{24}Nb_8O_{41}Te_8$. Calculated (%): C, 8.22; H, 2.19; N, 9.60. IR, ν/cm^{-1}: 3420 s (br.), 2134 s, 2100 sh, 1768, 1639 s, 1414 m, 1344, 1308 m, 1049 s, 824 s, 730 s, 588 s, 470 s, 394 m.

X-ray diffraction study. Crystallographic characteristics and the X-ray diffraction data statistics for complex **1** are given in Table 2. The X-ray diffraction data were collected at $T = 100$ K on an automated Bruker X8Apex CCD diffractometer equipped with an area detector using graphite-monochromated Mo-Kα radiation. A semiempirical correction for absorption was applied with the use of the SADABS program.[30] The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters (except for the oxygen atoms of the disordered solvate water molecules) using the SHELXTL program package.[31] The hydrogen atoms of the solvate water molecules and the hydroxo groups were not located. The hydrogen atoms of the coordinated water molecules were located in electron difference maps and refined with fixed $U_{iso} = 0.05$ Å^{-2}.

The topological analysis of frameworks was performed using the TOPOS 4.0 Professional program package[32] (http://topos.ssu.samara.ru). We employed the algorithm of simplification of crystal structures, which has been applied earlier to analysis of silicates, borates, carbonates, and nitrates.[27–29] After the calculation of the connectivity graph (AutoCN program), the cluster anion, the complex cations $[Mn(H_2O)_n]^{2+}$ ($n = 3$ and 4), and the bridging CN groups were isolated. Then the connectivity graph was simplified (ADS program) by contracting the anions and cations (together with the terminal aqua ligands and CN groups involved in these moieties) to a point, the centers of gravity being transformed into nodes and the bridging CN groups being transformed into edges of the simplified graph. The topological characteristics of the simplified graph, such as the node connectivities, the coordination sequences (number of nodes in the *n*th coordination sphere about a particular node), the Schlafly symbols, and the stoichiometry of the frameworks, were calculated with the use of the same program.

Table 2. Crystallographic characteristics and X-ray diffraction data statistics for complex **1**

Parameter	Characteristic
Molecular formula	$C_{24}H_{76}Mn_7N_{24}Nb_8O_{41}Te_8$
$F(000)$	3270
M	3505.75
Crystal system	Monoclinic
Space group	$P2_1/n$
Z	2
a/Å	11.8577(3)
b/Å	23.8689(7)
c/Å	17.4153(5)
β/deg	96.2720(10)
V/Å^3	4899.6(2)
d_{calc}/g cm^{-3}	2.376
μ/mm^{-1}	4.179
Crystal dimensions/mm	0.409×0.139×0.020
Color	Dark-brown
Diffractometer	«Bruker X8Apex CCD»
T/K	100
$2\theta_{max}$/deg	55
Number of measured/ independent/observed reflections	37533/10650/7384
R_{int}	0.0700
R_1, wR_2 for $F \geq 4\sigma(F)$	0.0470, 0.0894
R_1, wR_2 for all F	0.0876, 0.1052
GOOF	1.029
Δρ (min/max)/e Å^{-3}	2.289/−1.297

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