General and Inorganic Chemistry

Synthesis and structure of the polymeric cluster compound $[Mn(H_2O)_4]_3[W_4S_4(CN)_{12}] \cdot nH_2O$ containing very large cavities

V. P. Fedin,[a]* I. V. Kalinina,[a] A. V. Virovets,[a] and D. Fenske[b]

[a]*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
3 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 4489. E-mail: cluster@che.nsk.su
[b]*Institüt für Anorganishe Chemie, Universität Karlsruhe,*
Engesserstraße Geb. 30.45, Karlsruhe 76128, Germany.
Fax: +49 (072 1) 66 1921. E-mail: dieter.fenske@chemie.uni-karlsruhe.de

The compound $[Mn(H_2O)_4]_3[W_4S_4(CN)_{12}] \cdot nH_2O$ (**1**) was prepared by the reaction of an aqueous solution of $MnSO_4$ with a glycerol solution of $KCs_5[W_4S_4(CN)_{12}] \cdot 4H_2O$. Complex **1** was characterized by X-ray diffraction analysis and IR spectroscopy. According to the X-ray diffraction data, the three-dimensional polymeric framework of **1** comprises only 24.2% of the unit-cell volume. The volume of the cavities per formula unit is 1664 Å^3. The cavities are occupied by highly disordered water molecules.

Key words: tungsten, cluster complexes, sulfide complexes, synthesis, X-ray diffraction analysis.

The directed construction of solid compounds from molecular building blocks present in solutions is a new line of chemical investigations. In particular, the use of large (for example, cluster) building blocks allows one to prepare new crystalline polymeric compounds containing nanosized channels and cavities. These structures are of great interest for the design of a new generation of catalysts, sensors, and materials suitable for separation of large molecules and ionic exchange.[1—8]

In the present study, we synthesized the coordination polymer $[Mn(H_2O)_4]_3[W_4S_4(CN)_{12}]$ starting from the $[W_4(\mu_3\text{-}S)_4(CN)_{12}]^{6-}$ and $[Mn(H_2O)_4]^{2+}$ building fragments and established its crystal structure by X-ray diffraction analysis.

Results and Discussion

It is known that the cyanide anion can act as a bidentate-bridging ligand to form coordination bonds with two metal atoms through the C and N atoms, thus giving rise to polymeric coordination compounds. Such inorganic compounds based on the mononuclear tetrahedral $[M(CN)_4]^{n-}$ and octahedral $[M(CN)_6]^{n-}$ complex anions have been described in the literature.[9—12] Recently, salts of the cluster anions $[Re_6Q_8(CN)_6]^{4-}$ (where Q = S, Se, or Te) with transition metal cations have been prepared.[13—16] Among these compounds are those containing chains, networks, or three-dimensional frameworks, which consist of cluster anions linked to each other by transition metal cations through the bridg-

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ing cyanide ligands: ...M′—NC—{M$_n$}—CN—M′—NC..., where {M$_n$} is the Re_6Q_8 cluster core. Certain of these structures contain large cavities filled with water molecules, as, for example, $(H_5O_2)_2Zn_3[Re_6Se_8(CN)_6]_2 \cdot 18H_2O$, where the size of the hexagonal cavities reaches 11×11×5 Å.[17] Large cavities were also found in the compounds $M_4[Re_6Q_8(CN)_6]_3 \cdot nH_2O$ (where M = Ga or Fe)[18] and $[Cd_2(H_2O)_4][Re_6S_8(CN)_6] \cdot 14H_2O$,[19] which are structural analogs of Prussian blue, the volume of the cavities in the cadmium complex being 345 Å^3.

Previously, we have used the anionic cluster tungsten cyanide complex $[W_4(\mu_3\text{-Te})_4(CN)_{12}]^{6-}$ for the synthesis of a cobalt(II) compound, which possesses a very loose framework involving water molecules of solvation. According to the X-ray diffraction data at 160 K, the composition of the compound is $[Co(H_2O)_4]_3[W_4Te_4(CN)_{12}] \cdot 15.38\ H_2O$ (**2**).[20] Crystals of complex **2** were prepared by slow diffusion of the cobalt(II) salt and the cluster anion into a silicate gel. When removed from the gel and kept in air, the crystals very rapidly lost water and the compound became X-ray amorphous due to which investigations of the crystals by any methods, except for low-temperature X-ray diffraction analysis, present difficulties. In the present study, we synthesized the isostructural compound $[Mn(H_2O)_4]_3[W_4S_4(CN)_{12}] \cdot nH_2O$ (**1**).

Crystals of coordination polymer **1** were prepared by superposition of an aqueous solution of $MnSO_4$ on a solution of $KCs_5[W_4S_4(CN)_{12}] \cdot 4H_2O$ in glycerol. Their behavior in air is similar to that of the crystals of complex **2**. Thus, these crystals are stable in the mother liquor for several months. However, they lost water during several minutes and became X-ray amorphous on storage in air as a result of which it is difficult to obtain reliable analytical data for complex **1**, in particular, to determine the amount of water of solvation.

The cyano groups in complex **1** were identified in the IR spectra based on the ν(CN) stretching vibrations at 2130 cm^{-1} and the mixed ν(MC)/δ(MCN) vibrations at 420 cm^{-1}. These vibration bands are somewhat shifted to the high-frequency region compared to those observed in the spectrum of the initial complex $KCs_5[W_4S_4(CN)_{12}] \cdot 4H_2O$ (2125 cm^{-1} (ν(CN)) and 410 cm^{-1} (ν(MC)/δ(MCN)).[21]

The Mn atoms in **1**, like the Co atoms in **2**, are in a distorted octahedral coordination formed by two N atoms of the cyano groups in the *trans* positions and four O atoms of the H_2O molecules (Fig. 1). The Mn—N bonds (2.241(19) Å) are slightly longer than those in the $\{[Mn(PrOH)_2(H_2O)]_2[Re_6S_8(CN)_6]\} \cdot 2PrOH$ polymer (2.16—2.19 Å) studied recently.[22] The Mn positions are statistically occupied by 50%. The coordinated H_2O molecules are disordered over two positions with equal occupancies. The cubane clusters together with the Mn atoms make up a polymeric framework in which the W_4S_4 fragments form the cubic primitive packing. The W_4S_4 fragments are linked to each other *via* edges by pairs of Mn atoms through the CN groups (Fig. 2), the Mn—N—C—W fragments being virtually linear. Based on the occupancies of the Mn positions, there are three Mn atoms per cluster fragment and the framework as a whole is electroneutral.

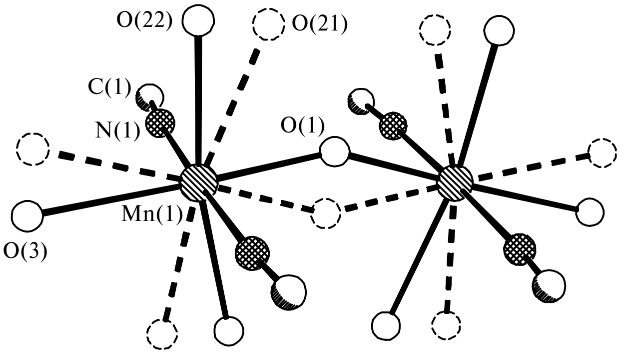

Fig. 1. Coordination environment about the Mn atoms in the crystal of **1**. The positions of the disordered O atoms are indicated by dashed lines.

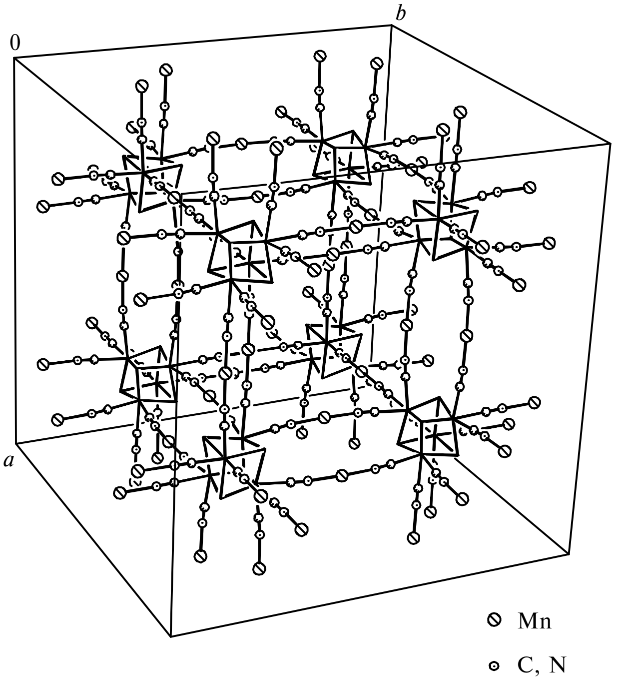

Fig. 2. Structure of the polymeric framework in the crystal of **1**. The O atoms are omitted. The distorted W_4S_4 cube is shown by solid lines; the Mn atom are represented by circles with one dash; the C and N atoms are represented by small circles. The C atoms in the C—N—Mn—N—C fragments are bound to the W atoms.

The calculated packing coefficient indicates that the framework comprises only 24.2% of the unit-cell volume, which is somewhat smaller than the corresponding value for complex **2** (27.3%). Therefore, there is a cavity of size 1664 Å^3 per formula unit (for compound **2**, this parameter is 1520 Å^3). Judging from the difference electron density synthesis, this cavity in the crystal of **1** is occupied by highly disordered water molecules. Attempts to reliably locate these molecules failed. Taking into account the revealed water molecules of solvation, the formula of the compound may be written as $[Mn(H_2O)_4]_3[W_4S_4(CN)_{12}] \cdot 5.41\ H_2O$, and the packing coefficient calculated for this formula is only 27.1%. Most likely the actual number of water molecules of solvation in the crystal structure of **1** should be much larger. Assuming that the overall free volume of the unit cell (except for the framework) is occupied by solvate water molecules that form an ice-like structure and taking into account that the average volume per water molecule in ices 1h[23] and 1c[24] is 32.3 Å^3, the calculated limiting value of the hydration number for **1** is ~51.5. This value is an order of magnitude larger than that determined from the X-ray diffraction data.

The cluster fragment occupies the position with the ideal point symmetry T_d. The bond lengths in this fragment are similar to those found in the salts $KCs_5[W_4S_4(CN)_{12}] \cdot 4H_2O$,[21] $K_6[W_4S_4(CN)_{12}] \cdot 2CH_3OH \cdot 2H_2O$,[25] and $(NH_4)_6[W_4S_4(CN)_{12}] \cdot 6H_2O$.[26]

Localization of water molecules of solvation presented serious difficulties. The refinement of the oxygen positions demonstrated that none of them is completely occupied. The refinement of the occupancies was alternated with the refinement of the thermal parameters until the convergence was attained. As a result, only three oxygen positions were revealed. The final difference electron density synthesis contained a number of peaks. Based on analysis of their environment, these peaks can be theoretically interpreted as oxygen atoms of the solvate water molecules. However, all attempts to make allowance for these atoms failed because the refinement by the least-squares method did not converged. We have met with analogous difficulties in the solution of the crystal structure of compound **2**. This may be due to the high symmetry of the structure, which imparts high disorder to the hydration shell.

We attempted to solve the structure of **1** in the lower-symmetry space group *Fm*3. However, the disorder persisted. In the case of compound **2**, analogous attempts have also been unsuccessful.

Experimental

The reagents of analytical grade were used. The starting complex $KCs_5[W_4S_4(CN)_{12}] \cdot 4H_2O$ was prepared from a mixture of the cluster tungsten thiobromide complex $W_3S_7Br_4$ and KCN according to a procedure reported previously.[21] The tungsten complex was synthesized by heating stoichiometric amounts of tungsten, sulfur, and bromine.[27] The IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer in KBr pellets.

Synthesis of manganese(II) dodecacyanotetra-μ_3-thiotetratungstanate(W—W) hydrate $[Mn(H_2O)_4]_3[W_4S_4(CN)_{12}] \cdot nH_2O$. An aqueous solution of $MnSO_4$ (5 mL, $6.6 \cdot 10^{-2}$ mol L^{-1}) was superposed on a solution of $KCs_5[W_4S_4(CN)_{12}] \cdot 4H_2O$ in glycerol (5 mL, $3.0 \cdot 10^{-3}$ mol L^{-1}) in 10-mm glass tubes. Brown cubic crystals of $[Mn(H_2O)_4]_3[W_4S_4(CN)_{12}] \cdot nH_2O$, which precipitated at the interface in seven days, were filtered off on a porous filter and rapidly washed with cold water. The results of the synthesis were well reproducible. The yield was 0.060—0.085 g (~10—14%). Since the resulting crystal hydrate was air-unstable in the absence of the mother liquor, we failed to obtain reliable data from chemical analysis. IR, cm^{-1}: 2130 ν(CN), 420 ν(WC)/δ(WCN).

X-ray diffraction study. The structure of $[Mn(H_2O)_4]_3[W_4S_4(CN)_{12}] \cdot nH_2O$ was established by X-ray diffraction analysis. The X-ray data were collected according to a standard procedure on an automated four-circle STOE STADI4 diffractometer from a single crystal of dimensions

Table 1. Crystallographic characteristics and details of X-ray data collection for complex **1**

Parameter	**1**
Molecular formula	$C_{12}H_{34.83}Mn_3N_{12}O_{17.41}S_4W_4$
Molecular weight	1654.40
Space group	$Fm\bar{3}m$
System	Cubic
a/Å	25.993(14)
d_{calc}/g cm^{-3}	1.251
Z	8
μ(Mo-Kα)/mm^{-1}	5.765
θ/2θ scanning range	1.6—25.0
Number of measured reflections	1393
Number of independent reflections	834 (R_{int} = 0.1212)
Number of reflections with $F_{hkl} \geq 4\sigma(F)$	492
Weighting scheme, w^{-1}	$\sigma^2(F_o^2) + (0.0783P)^2 + 353.63P$, where $P = (F_o^2+2F_c^2)/3$
R_1; wR_2 for $F_{hkl} \geq 4\sigma(F)$	0.0551, 0.1515
R_1; wR_2 for all independent F_{hkl}	0.1149, 0.1856
GOOF for all independent F_{hkl}	1.161

Table 2. Bond lengths (d) and selected angles (ω) in the crystal structure of **1**

Bond	d/Å	Angle	ω/deg
W(1)—W(1)^a	2.843(2)	N(1)—C(1)—W(1)	179(2)
W(1)—S(1)	2.391(7)	C(1)—N(1)—Mn(1)	175(2)
W(1)—C(1)	2.18(2)	N(1)^b—Mn(1)—N(1)	177.3(12)
C(1)—N(1)	1.09(3)	N(1)—Mn(1)—O(21)	89.61(19)
N(1)—Mn(1)	2.241(19)	N(1)—Mn(1)—O(22)	90.15(8)
Mn(1)—O(1)	1.906(17)	N(1)—Mn(1)—O(3)	91.3(6)
Mn(1)—O(21)	2.32(5)	O(1)—Mn(1)—N(1)	88.7(6)
Mn(1)—O(22)	2.25(4)	O(1)—Mn(1)—O(21)^c	87(3)
Mn(1)—O(3)	2.27(4)	O(1)—Mn(1)—O(22)	83(2)
		O(1)—Mn(1)—O(3)	178(3)
		O(22)—Mn(1)—O(21)^c	170(4)
		O(22)—Mn(1)—O(22)^c	167(4)
		O(22)—Mn(1)—O(3)	95(3)
		O(3)—Mn(1)—O(21)^c	95(3)

^{a} $x, -y + 1/2, -z + 1/2$. ^{b} $x, -y + 1, z$. ^{c} $z, -y + 1, x$.

0.22×0.21×0.20 mm at −62 °C. The diffraction maxima were substantially broadened; however, they showed no splitting. The crystallographic characteristics are given in Table 1. Taking into account that the crystal could decompose in the course of X-ray data collection, we measured only reflections, which are present within the *F* lattice and are independent within the Laue class *m3*. A total of 1393 reflections were measured, which were averaged within the *m3m* class to obtain 834 independent reflections (R_{int} = 0.1212). The absorption correction was applied taking into account the crystal habitus. The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for all atoms, except for the O atoms, using the SHELX-97 program package.[28] The positions of the H atoms were not revealed. The principal bond lengths and angles are given in Table 2.

The packing coefficients were calculated using the KPACK program[29] with 600 test points per Å^3. The following radii were used (Å): C, 1.71; N, 1.55; O, 1.40; S, 1.80; Mn, 1.35; and W, 1.37.

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