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Crystal structure of $Cs_8[W_2(CN)_{16}]\cdot3H_2O$

Dariya SEMENYSHYN[1]*, Iryna TYPILO[1], Marek DASZKIEWICZ[2], Lubomir GULAY[3]

[1] *Institute of Chemistry and Chemical Engineering, National University "Lvivska Polytechnika", Bandera St. 12, UA-79013 Lviv, Ukraine*
[2] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland*
[3] *Department of Ecology and Protection of Environment, Eastern European National University, Voli Ave. 13, 43009 Lutsk, Ukraine*
* *Corresponding author. Tel.:* +380-676759235*; e-mail: semenyshyn@polynet.lviv.ua*

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The $Cs_8[W_2(CN)_{16}]\cdot3H_2O$ compound crystallizes in the monoclinic system (space group $P2_1/c$ with cell parameters a = 22.7973(6), b = 9.3261(1), c = 18.4881(4) Å, β = 95.400(2)°, Z = 4, $R1$ = 0.0463). The W atoms occupy two crystallographically independent sites and the coordination polyhedra of the tungsten atoms are distorted trigonal prisms $[W(1)(CN)_8]$ and $[W(2)(CN)_8]$ with two additional atoms. The Cs atoms occupy eight sites and exhibit various coordination polyhedra: distorted tetragonal antiprisms, distorted pentagonal bipyramids, trigonal prisms with one addition atom, trigonal prisms with two additional atoms, and a 9-vertex polyhedron of irregular shape.

Cesium octacyanotungstate(IV) / Crystal structure / X-ray single crystal diffraction

1. Introduction

In recent years there has been strong interest in the study of octacyanide complexes of *s*–*d* elements due to their interesting physical properties. They may indeed have good sorption, magnetic, optical and other properties.

The earliest reported cyanide tungsten(IV,V) complexes were $K_3[W(CN)_8]$ [1,2] and $K_4[W(CN)_8]\cdot2H_2O$ [1,3]. Small soluble salts $Ag_4[R]$, $Mn_2[R]$, $Tl_4[R]$, $Cd_2[R]\cdot H_2O$, $Zn_2[R]\cdot4H_2O$, where $R = [W(CN)_8]^{4-}$ [4,5] were selectively obtained using reaction deposition. Readily soluble salts such as: $Na_4[R]\cdot H_2O$, $Rb_4[R]\cdot3H_2O$, $Sr_2[R]\cdot H_2O$, $Cd_2[R]\cdot8H_2O$, $Mg_2[R]\cdot6H_2O$, $Rb_4[R]\cdot H_2O$, and $Li_4[R]\cdot H_2O$ [4,5] were obtained by exchange reaction of $Ag_4[W(CN)_8]$ and metal chlorides. The complex acids $H_4[W(CN)_8]\cdot H_2O$ [1,5], $H_4[W(CN)_8]\cdot2H_2O$, $H_3[W(CN)_8]\cdot H_2O$ [6], $H_4[W(CN)_8]\cdot6H_2O$ [6,7] should also be mentioned. The complexes $Cs_3[W(CN)_8]\cdot2H_2O$ [8], $K_3[W(CN)_8]\cdot H_2O$, $Na_3[W(CN)_8]\cdot4H_2O$, $[n\text{-}Bu_4N]_3[W(CN)_8]$ [9] and $K_4[M(CN)_8]$, $K_4[M(CN)_6]$, $K_3[M(CN)_6]$, $K_3[M(CN)_8]$, (M = Mo, W), $K_2[W(CN)_5H_2O]$ [10] have also been investigated.

One of the first crystal structures to be investigated was that of $K_4[W(CN)_8]\cdot2H_2O$ [11], which is isomorphic with $K_4[Mo(CN)_8]\cdot2H_2O$ [12]. The coordination polyhedron $[W(CN)_8]^{4-}$ in this compound has the shape of a dodecahedron. Antiprismatic tetragonal configuration (symmetry D_{4d}) of the $[W(CN)_8]^{4-}$ ion was established by X-ray diffraction for $H_4[W(CN)_8]\cdot6H_2O$ [7,13]. In the compounds $H_4[W(CN)_8]\cdot H_2O$, $H_4[W(CN)_8]\cdot4HCl\cdot12H_2O$ [14], $Kat_m[W(CN)_8]\cdot nH_2O$, where Kat = H^+, Na^+, Ca^{2+} [4,5], and $Na_3[W(CN)_8]\cdot4H_2O$ [4,5], the complex anions have antiprismatic configuration. Saramaha and Dovgej [15] described the synthesis and crystal structure of the compound $Na_3H_3O[W(CN)_8]\cdot2H_2O$, in which the anion $[W(CN)_8]^{4-}$ has dodecahedral shape. The crystal structure of the complex $Rb_4[W(CN)_8]\cdot2H_2O$ [16] is isostructural with $K_4[W(CN)_8]\cdot2H_2O$.

It appears that the crystal structures of octacyanotungstate(IV) complexes of alkali metal cations have been determined only for a few compounds. With the aim to study the effect of the nature of the outer *s*-cation on the structures of octacyanotungstates(IV) of alkali metals, we synthesized and investigated the crystal structure of a new compound, the cesium octacyanotungstate(IV) sesquihydrate $Cs_8[W_2(CN)_{16}]\cdot3H_2O$.

2. Experimental

Synthesis

Octacyanotungstate(IV) acid required for the synthesis of the complex was obtained by passing a solution of

$K_4[W(CN)_8]\cdot 2H_2O$ through a cation exchanger KU-2 in H^+-form. A $Cs_8[W_2(CN)_{16}]\cdot 3H_2O$ powder sample was prepared by mixing aqueous solutions of $H_4[W(CN)_8]$ and cesium carbonate. The resulting solution was submitted to slow crystallization at room temperature in a dark place. A few weeks later crystals suitable for X-ray diffraction studies had formed. The yield of isolated product was 65 %. The composition of the single crystal used for the structure determination was confirmed by EDX analysis (EDAX PV9800 microanalyzer).

X-ray diffraction

X-ray diffraction data were collected on a KUMA Diffraction KM-4 four-circle diffractometer equipped with a CCD camera, using graphite-monochromatized Mo $K\alpha$ radiation (λ = 0.71073 Å). The raw data were treated with the CrysAlis Data Reduction program [17], taking into account an absorption correction. The intensities of the reflections were corrected for Lorentz and polarization factors. The crystal structure was solved by the Patterson method and refined by the full-matrix least-squares method using SHELXL-97 [18].

3. Results and discussion

Details of the structure investigation of $Cs_8[W_2(CN)_{16}]\cdot 3H_2O$ are given in Table 1, whereas the atomic coordinates and equivalent (isotropic) displacement parameters are listed in Table 2. The displacement parameters of the C and N atoms were refined in isotropic approximation. Selected bond lengths and angles are listed in Table 3.

The content of one unit cell of $Cs_8[W_2(CN)_{16}]\cdot 3H_2O$ and the coordination polyhedra of the W atoms are shown in Fig. 1. The structure of $Cs_8[W_2(CN)_{16}]\cdot 3H_2O$ consists of individual $[W(CN)_8]^{4-}$ ions, which are located between the cesium cations and water molecules. The tungsten atoms in the structure occupy two distinct sites. Each tungsten atom is surrounded by eight cyano groups in the form of a trigonal prism with two additional atoms (Fig. 1). The shortest W1–C and W2–C distances are in the ranges 2.14(2)-2.171(17) and 2.112(17)-2.174(16) Å, respectively. The bond lengths of C≡N at the W1 and W2 atoms have values within 1.140(19)-1.178(18) and 1.12(3)-1.177(18) Å, respectively. The W–CN angles vary from 172.9(19) to 178.4(18)° for W1 and from 175.1(19) to 179.1(19)° for W2.

Table 1 Experimental details of the structure refinement for $Cs_8[W_2(CN)_{16}]\cdot 3H_2O$.

Parameters and their values	
Crystal color	yellow
Empirical formula	$C_{16}\,H_6\,N_{16}\,O_3\,Cs_8\,W_2$
M_r	1901.35
System	monoclinic
Space group	$P2_1/c$
Cell parameters (Å)	a = 22.7973(6), b = 9.32614(18), c = 18.4881(4) β = 95.400(2)°
V (Å^3)	3913.34(16)
Formula units per cell, Z	4
Density, D_x (g cm^{-3})	3.227
μ (mm^{-1})	13.251
F(000)	3304
Radiation	Mo $K\alpha$
λ (Å)	0.71073
Range θ (°)	$2.97 < \theta < 26.02$
Index ranges	$-10 \le h \le 10$, $-11 \le k \le 11$, $-22 \le l \le 22$
Number of measured reflections	24859
Number of independent reflections	4119
Number of reflections with $I > 2\sigma(I)$	2918
R_{int}	0.0663
Number of refined parameters	231
Goodness of fit on F^2	1.166
R [$I > 2\,\sigma(I)$]	$R1$ = 0.0463, $wR2$ = 0.0754
R (all data)	$R1$ = 0.0849, $wR2$ = 0.0894
$\Delta\rho_{min}/\Delta\rho_{max}$ (e Å^{-3})	-0.952/1.451

Table 2 Atomic coordinates and equivalent/isotropic displacement parameters for $Cs_8[W_2(CN)_{16}]\cdot 3H_2O$.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq}/U_{iso} (Å^2)
W1	4*e*	0.14339(5)	0.70792(7)	0.60056(3)	0.0261(4)
W2	4*e*	0.38277(5)	0.23409(7)	0.34641(3)	0.0248(4)
Cs1	4*e*	0.48034(7)	0.33079(11)	0.17332(6)	0.0360(6)
Cs2	4*e*	0.24615(7)	0.81959(12)	0.43387(6)	0.0431(6)
Cs3	4*e*	0.34465(8)	0.72890(12)	0.24609(7)	0.0488(6)
Cs4	4*e*	0.41862(7)	0.62898(13)	0.53278(6)	0.0460(6)
Cs5	4*e*	0.18735(7)	0.40027(12)	0.26902(6)	0.0490(6)
Cs6	4*e*	0.27680(8)	0.30686(12)	0.56227(7)	0.0549(6)
Cs7	4*e*	0.06348(8)	0.28734(14)	0.04657(7)	0.0606(7)
Cs8	4*e*	0.08315(8)	0.98404(14)	0.29969(7)	0.0680(7)
O1	4*e*	0.0267(9)	0.6817(18)	0.3157(9)	0.119(7)
O2	4*e*	0.3417(8)	-0.0314(15)	0.5525(8)	0.096(6)
O3	4*e*	0.0909(10)	0.290(2)	0.3711(10)	0.151(8)
N1	4*e*	0.3940(8)	-0.1039(15)	0.4064(7)	0.044(4)
N2	4*e*	0.3904(8)	0.0308(14)	0.2003(7)	0.042(4)
N3	4*e*	0.4227(8)	0.2653(15)	0.5212(8)	0.055(5)
N4	4*e*	0.3021(8)	0.4988(16)	0.4046(7)	0.050(5)
N5	4*e*	0.3304(8)	0.4071(14)	0.1971(7)	0.042(4)
N6	4*e*	0.4572(8)	0.5409(16)	0.3523(7)	0.053(5)
N7	4*e*	0.1542(8)	0.4972(15)	0.4585(7)	0.047(5)
N8	4*e*	0.0746(8)	0.8861(15)	0.4623(7)	0.048(5)
N9	4*e*	0.2019(8)	1.0270(16)	0.5859(7)	0.051(5)
N10	4*e*	0.2463(10)	0.1110(18)	0.3462(8)	0.066(6)
N11	4*e*	0.0584(9)	0.9342(18)	0.6758(9)	0.065(5)
N12	4*e*	0.0145(11)	0.553(2)	0.5968(9)	0.077(7)
N13	4*e*	0.2017(8)	0.7520(13)	0.7711(7)	0.036(4)
N15	4*e*	0.1620(7)	0.3758(14)	0.6666(7)	0.038(4)
N14	4*e*	0.5238(10)	0.1721(14)	0.3391(7)	0.034(5)
N16	4*e*	0.2854(10)	0.6508(14)	0.5889(7)	0.034(5)
C1	4*e*	0.3907(9)	0.0148(17)	0.3861(8)	0.032(5)
C2	4*e*	0.3870(9)	0.0993(16)	0.2515(8)	0.030(5)
C3	4*e*	0.4061(10)	0.2513(17)	0.4594(9)	0.040(5)
C4	4*e*	0.3280(10)	0.4022(18)	0.3847(8)	0.032(5)
C5	4*e*	0.3484(9)	0.3453(17)	0.2501(8)	0.033(5)
C6	4*e*	0.4315(9)	0.4345(17)	0.3488(8)	0.029(5)
C7	4*e*	0.1482(10)	0.5718(19)	0.5061(9)	0.046(6)
C8	4*e*	0.0968(10)	0.8172(17)	0.5087(9)	0.035(5)
C9	4*e*	0.1853(9)	0.9124(17)	0.5921(8)	0.031(5)
C10	4*e*	0.2942(12)	0.1491(19)	0.3449(9)	0.039(6)
C11	4*e*	0.0849(12)	0.849(2)	0.6496(10)	0.061(7)
C12	4*e*	0.0586(13)	0.606(2)	0.5970(10)	0.051(6)
C13	4*e*	0.1794(9)	0.7377(16)	0.7114(8)	0.030(5)
C14	4*e*	0.4735(15)	0.1889(18)	0.3418(8)	0.035(6)
C15	4*e*	0.1554(10)	0.4930(18)	0.6446(8)	0.036(5)
C16	4*e*	0.2364(14)	0.6684(16)	0.5947(8)	0.026(5)

The cesium atoms occupy eight crystallographic positions and have different coordination polyhedra: $Cs(1)N_7$ – a pentagonal bipyramid, $Cs(2)N_7O$ – a deformed tetragonal antiprism, $Cs(3)N_7$ – a slightly deformed trigonal prism with one additional atom, $Cs(4)N_8O$ – a 9-vertex polyhedron of undefined shape, $Cs(5)N_7O$ – a slightly deformed trigonal prism with two additional atoms, $Cs(6)N_7O$ – a trigonal prism with two additional atoms, $Cs(7)N_6O_2$ – a deformed trigonal prism with two additional atoms, $Cs(8)N_4O_3$ – a deformed trigonal prism with one additional atom. The coordination polyhedra of the cesium atoms in the structure of $Cs_8[W_2(CN)_{16}]\cdot 3H_2O$ are shown in Fig. 2.

Table 3 Selected bond lengths and angles for $Cs_8[W_2(CN)_{16}]\cdot3H_2O$.

Atoms	δ (Å)	Atoms	δ (Å)	Atoms	ω (°)
W1–C11	2.14(2)	C1–N1	1.169(18)	W1–C7N7	176.0(2)
W1–C9	2.145(18)	C2–N2	1.151(17)	W1–C8N8	174.0(16)
W1–C12	2.15(3)	C3–N3	1.177(19	W1–C9N9	172.9(19)
W1–C13	2.153(16)	C4–N4	1.16(2)	W1–C11N11	173.0(2)
W1–C16	2.16(3)	C5–N5	1.178(18)	W1–C12N12	178.4(18)
W1–C8	2.170(17)	C6–N6	1.151(19)	W1–C13N13	176.9(18)
W1–C7	2.170(18)	C7–N7	1.140(19)	W1–C15N15	178.2(14)
W1–C15	2.171(17)	C8–N8	1.152(19)	W1–C16N16	177.1(14)
W2–C3	2.112(17)	C9–N9	1.144(19)	W2–C1N1	178.6(18)
W2–C14	2.12(3)	C10–N10	1.13(2)	W2–C2N2	177.9(17)
W2–C5	2.144(16)	C11–N11	1.142(18)	W2–C3N3	175.3(19)
W2–C4	2.164(19)	C12–N12	1.12(3)	W2–C4N4	175.1(19)
W2–C10	2.17(3)	C13–N13	1.177(18)	W2–C5N5	179.1(14)
W2–C2	2.168(15)	C14–N14	1.16(3)	W2–C6N6	177.9(15)
W2–C6	2.173(18)	C15–N15	1.171(17)	W2–C10N10	176.0(18)
W2–C1	2.174(16)	C16–N16	1.14(3)	W2–C14N14	176.3(16)

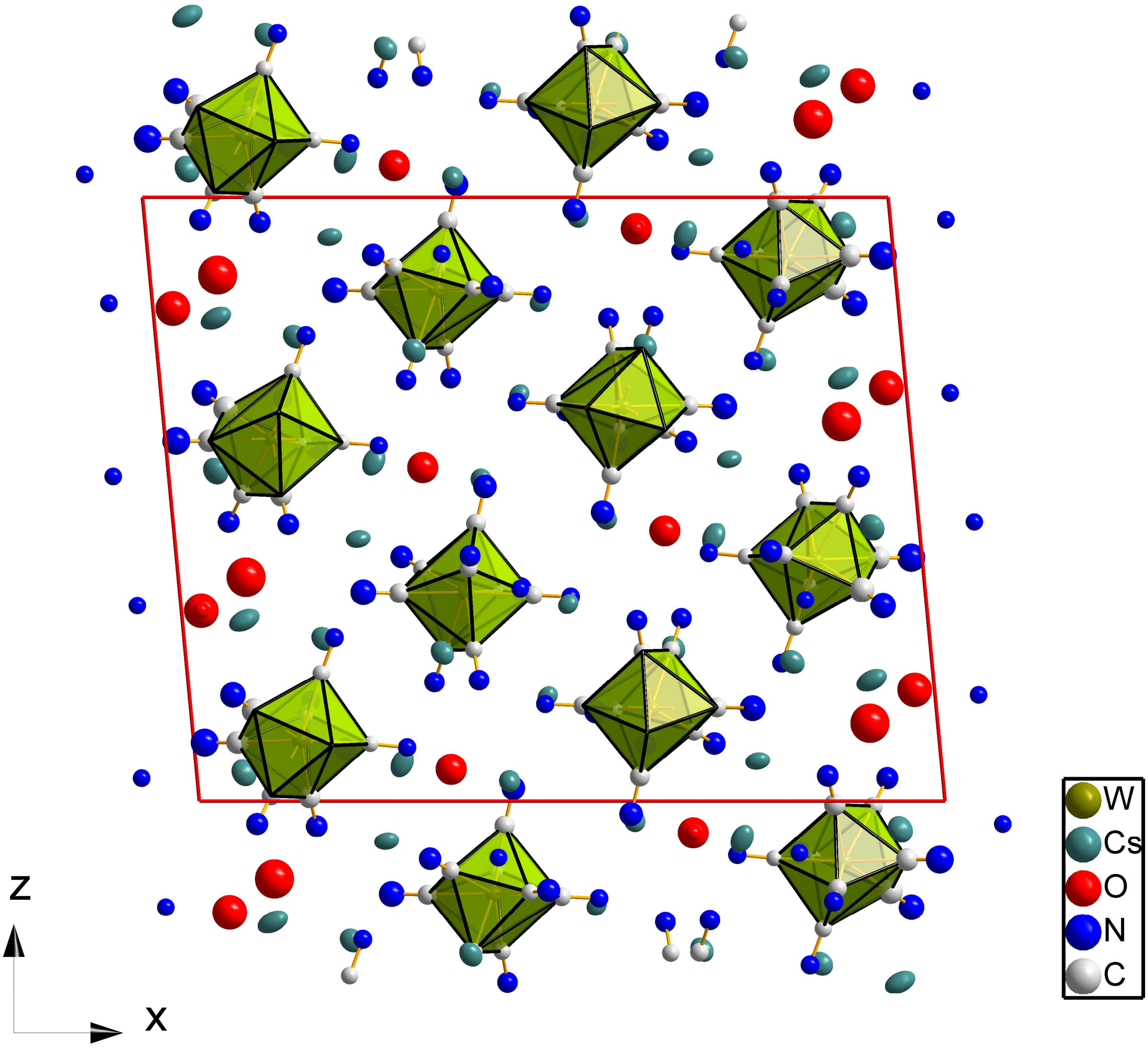

Fig. 1 Unit cell of $Cs_8[W_2(CN)_{16}]\cdot3H_2O$ and coordination polyhedra of the W atoms.

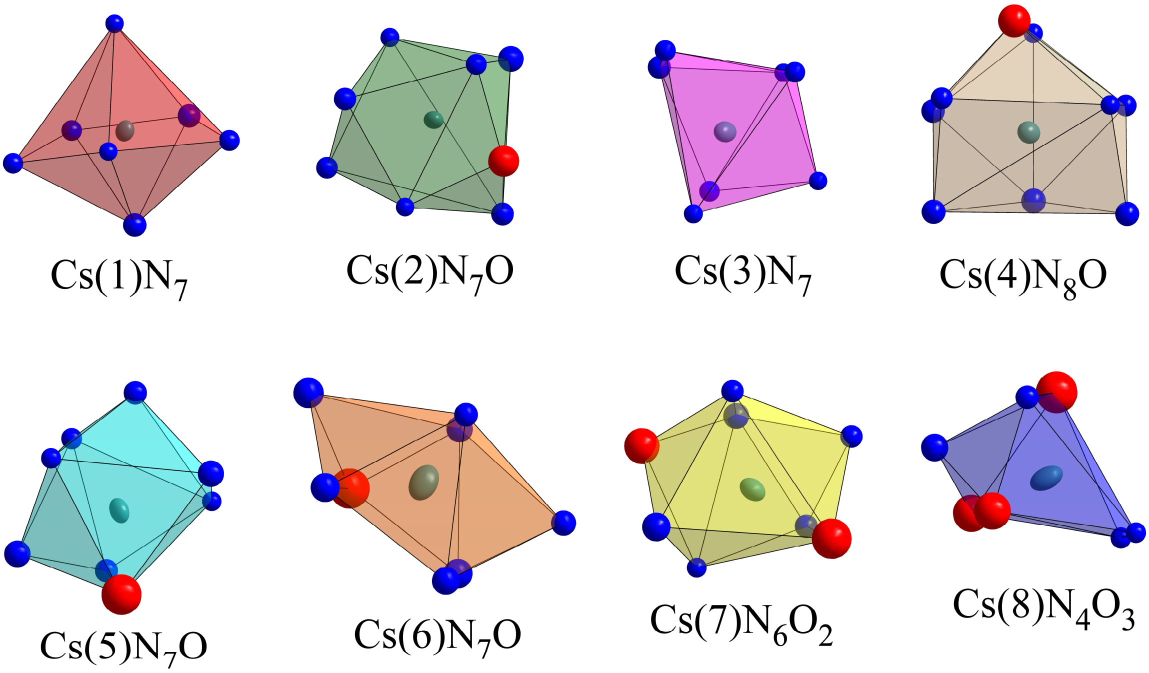

Fig. 2 Coordination polyhedra of the cesium atoms in $Cs_8[W_2(CN)_{16}]\cdot 3H_2O$.

Conclusions

The crystal structure of the $Cs_8[W_2(CN)_{16}]\cdot 3H_2O$ ($Cs_4[W(CN)_8]\cdot 1.5H_2O$) complex differs significantly from the structures of the complexes $K_4[W(CN)_8]\cdot 2H_2O$ [11], $Rb_4[W(CN)_8]\cdot 2H_2O$ [16], and $K_4[Mo(CN)_8]\cdot 2H_2O$ [12,19], which are isomorphous, and from the molybdenum complexes $(NH_4)_4[Mo(CN)_8]\cdot 0.5H_2O$ and $Rb_4[Mo(CN)_8]\cdot 3H_2O$ [20], which have different crystal structures. The size of the cesium cation ($r(Cs^+) = 1.65$ Å) differs significantly the sizes of the potassium, ammonium and rubidium cations ($r(K^+) = 1.33$, $r(NH_4^+) = 1.43$, $r(Rb^+) = 1.49$ Å). Therefore the tungsten compounds with cesium are not isostructural.

Besides, changing the number of water molecules in the complexes of molybdenum with ammonium $(NH_4)_4[Mo(CN)_8]\cdot 0.5H_2O$ and rubidium $Rb_4[Mo(CN)_8]\cdot 3H_2O$ leads to significant differences in the structures, which belong to different space groups. The molybdenum atoms in the $(NH_4)_4[Mo(CN)_8]\cdot 0.5H_2O$ compound occupy two distinct positions and have different coordination polyhedra: $[Mo1(CN)_8]^{4-}$ dodecahedra and $[Mo2(CN)_8]^{4-}$ tetragonal antiprisms. The coordination polyhedra of the molybdenum atoms in the structure of the $Rb_4[Mo(CN)_8]\cdot 3H_2O$ compound are exclusively dodecahedra. Already in 1985 [20] the authors emphasized the influence of the number of molecules of crystallization water on the crystal structures of alkaline metal octacyanotungstates(IV). The $Rb_4[W(CN)_8]\cdot 2H_2O$ [16] and $Rb_4[Mo(CN)_8]\cdot 3H_2O$ [20] complexes with different structures also contain different numbers of water molecules.

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