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Crystal Structure of Potassium Dysprosium Octacyanotungstate(IV) Heptahydrate

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Abstract—The crystal structure of $KDyW(CN)_8 \cdot 7H_2O$ was determined by X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$, a = 7.6284(7) Å, b = 9.2435(9) Å, c = 14.4778(14) Å, α = 80.673(11)°, β = 87.561(11)°, γ = 77.603(11)°, V = 983.86(16) Å^3, Z = 2, ρ_{calcd} = 2.429 g/cm^3, R = 0.0249, w_R = 0.0502 for 3601 independent reflections. The coordination polyhedron of tungsten is a highly deformed tetragonal antiprism $[W(CN)_8]$, that of dysprosium is a tetragonal antiprism $[DyN_4(H_2O)_4]$. Some cyano groups are bridging being coordinated to tungsten and dysprosium by C and N atoms, respectively, and form a 3D structure via potassium atoms. The coordination polymer can be described as $\{[K(H_2O)][Dy(H_2O)_4][W(CN)_8]\}_n \cdot 2nH_2O$.

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Octacyanometallates $[M(CN)_8]^{n-}$ (M = Nb(IV), Mo(IV), W(IV), and W(V)) represent a large class of compounds that may form coordination polyhedra of various configurations (tetragonal antiprism, dodecahedron, bicapped trigonal prism) depending on the nature of outer-sphere cations [1–8]. Enhanced interest in octacyanometallates is due to not only their different crystal structures but also to peculiar magnetic properties [9, 10]. The lanthanide octacyanotungstates studied previously are $(H_3O)[Ce(H_2O)_4W(CN)_8] \cdot 2H_2O$ [6], $[Sm(H_2O)_5][W(CN)_8]$ [9], and $[Gd(DMF)_6][W(CN)_8]$ [10]. The purpose of this work is to study the crystal structure of potassium dysprosium octacyanotungstate(IV) heptahydrate (**I**).

EXPERIMENTAL

Synthesis of I was carried out at room temperature by mixing a 0.1 M aqueous solution of $K_4[W(CN)_8] \cdot 2H_2O$ acidified to pH ~ 3 with a stoichiometric amount of an aqueous solution of $DyCl_3$. After mixing, the solution was kept in a refrigerator in the dark to prevent hydrolysis. The yellow-orange crystals suitable for X-ray diffraction were obtained after several months.

X-Ray diffraction. The set of diffraction data was collected at 173 K on a Stoe IPDS diffractometer [11] (MoK_α radiation, λ = 0.71073 Å, graphite monochromator, φ scan mode 0°–200°, step $\Delta\varphi$ = 1.0°, 3 min exposure, 8.93 < d < 0.81 Å). The structure was solved by direct methods (SHELX-97) [12, 13]. The hydrogen atoms were located from the difference Fourier synthesis and refined in the isotropic approximation. The positions of other atoms were refined by the least-squares method (on F^2) in the full-matrix anisotropic approximation. The empirical absorption correction was applied using the DELrefABS in PLATON software [14], transmission factors T_{min}/T_{max} = 0.143/0.615. The asymmetric moiety of the structure (Fig. 1) is illustrated in PLATON [14] and the projection of the complex structure (Fig. 2) is depicted using ATOMS software [15]. The atom coordinates and other parameters of compound **I** are deposited with the Cambridge Crystallographic Data Collection (CCDC no. 664665).

The X-ray diffraction experiment details and crystallographic characteristics of **I** are presented in Table 1 and selected bond lengths and angles are in Table 2.

RESULTS AND DISCUSSION

The crystal structure of **I** is composed of two moieties, $[W(CN)_8]$ and $[DyN_4(H_2O)_4]$. The tungsten atom is surrounded by eight C atoms of the cyanide groups at the vertices of a highly distorted tetragonal antiprism (W–C, 2.133(5)–2.177(5) Å; C≡N, 1.143(5)–1.161(6) Å; WCN, 174.5(4)°–179.0(4)°). The dysprosium atom is surrounded by four N atoms of the cyano groups and four O atoms of water molecules (Dy–N, 2.413(4)–2.434(4) Å; Dy–O, 2.332(4)–2.468(4) Å). The coordination polyhedron of dysprosium can be described as a tetragonal antiprism.

The $[W(CN)_8]^{4-}$ anion is connected to the dysprosium cations by four bridging cyano ligands. The structure is composed of double layers of the –Dy–N≡C–W–C≡N– chains extended in two dimensions. The solva-

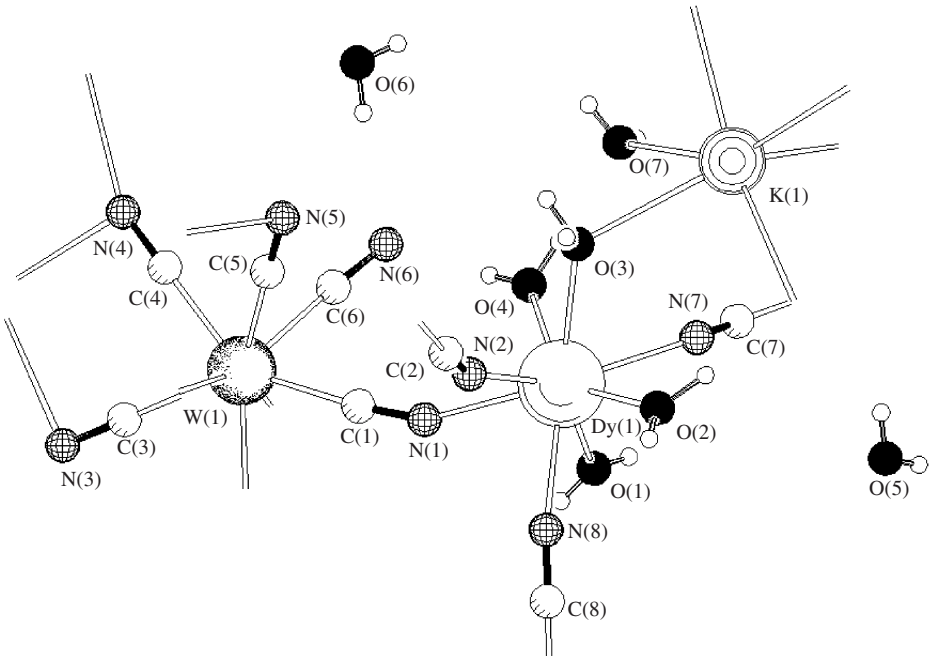

Fig. 1. Asymmetric part of the cell of the structure $\{[K(H_2O)][Dy(H_2O)_4][W(CN)_8]\}_n \cdot 2nH_2O$.

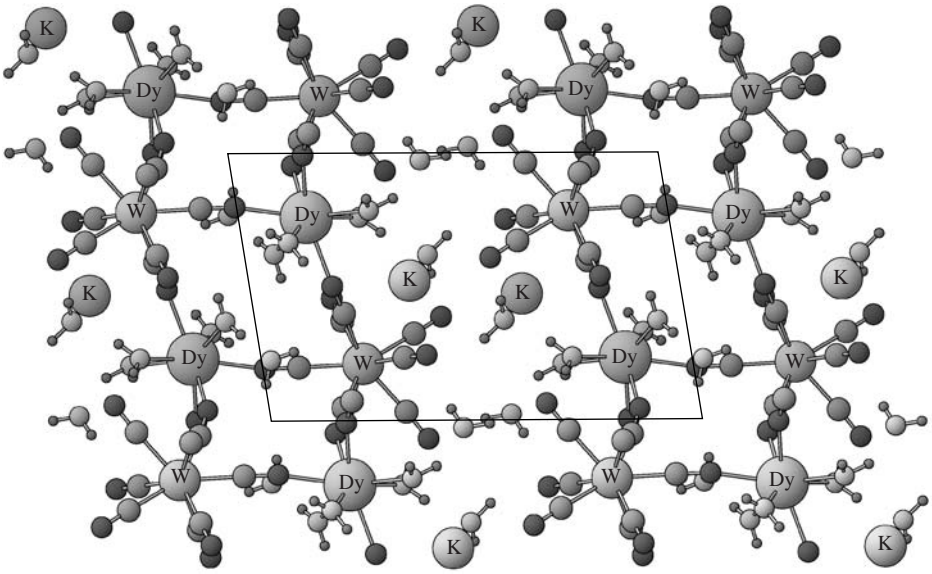

Fig. 2. Projection of the structure $\{[K(H_2O)][Dy(H_2O)_4][W(CN)_8]\}_n \cdot 2nH_2O$ along the *x* axis.

tion water molecules, O(5) and O(6), and potassium cations are arranged between the layers. The potassium atom is surrounded by five nitrogen atoms of C≡N groups and two oxygen atoms of water molecules to form a distorted monocapped trigonal prism. The coordination polymer formed in the 3D structure of **I** can be described as $\{[K(H_2O)][Dy(H_2O)_4][W(CN)_8]\}_n \cdot 2nH_2O$.

The crystal of **I** has hydrogen bonds between the coordinated and uncoordinated water molecules and terminal C≡N groups of the cyanotungstate anion (Table 3). The oxygen atoms of the uncoordinated water molecules form hydrogen bonds with the hydrogen atoms of coordinated water molecules.

A comparison of the crystal data of **I** and $(H_3O)[Ce(H_2O)_4W(CN)_8] \cdot 2H_2O$ (**II**) [6] shows that these crystals corresponding to the same space group have different lattice parameters and different coordination polyhedra of lanthanide and tungsten atoms. The

Table 1. Crystal data and X-ray experiment details for $KDyW(CN)_8 \cdot 7H_2O$

Parameter	Value
Empirical formula	$C_8H_{14}DyKN_8O_7W$
M	719.72
System	Triclinic
Space group	$P\bar{1}$
Unit cell parameters:	
a, Å	7.6284(7)
b, Å	9.2435(9)
c, Å	14.4778(14)
α, deg	80.673(11)
β, deg	87.561(11)
γ, deg	77.603(11)
V, Å^3	983.86(16)
Z	2
ρ_{calcd}, g/cm^3	2.429
μ_{Mo}, mm^{-1}	9.866
Crystal size, mm	$0.48 \times 0.48 \times 0.35$
θ, deg	2.28–26.00
The number of measured reflections	7866
The number of independent reflections	3601
The number of reflections with $I > 2\sigma(I)$	3112
R_{int}	0.0326
The number of refined parameters	277
R-factors (for all reflections)	$R = 0.0249$, $wR = 0.0502$
R-factors ($I > 2\sigma(I)$)	$R = 0.0205$, $wR = 0.0491$
S	0.974
ρ_{min}/ρ_{max}, e Å^{-3}	–1.121/1.152

Table 2. Selected interatomic distances and bond angles in the structure $KDyW(CN)_8 \cdot 7H_2O$

Bond	d, Å	Angle	ω, deg
W(1)–C(1)	2.133(5)	C(1)W(1)C(7)	94.52(17)
W(1)–C(2)	2.152(4)	C(1)W(1)C(2)	93.96(16)
W(1)–C(3)	2.177(5)	C(7)W(1)C(2)	147.04(15)
W(1)–C(4)	2.153(5)	C(1)W(1)C(4)	145.78(16)
W(1)–C(5)	2.168(4)	C(7)W(1)C(4)	95.50(17)
W(1)–C(6)	2.156(5)	C(2)W(1)C(4)	95.15(17)
W(1)–C(7)	2.146(4)	C(1)W(1)C(8)	70.76(17)
W(1)–C(8)	2.154(4)	C(7)W(1)C(8)	76.44(16)
Dy(1)–O(1)	2.401(3)	C(2)W(1)C(8)	76.47(16)
Dy(1)–O(2)	2.332(4)	C(4)W(1)C(8)	143.46(17)
Dy(1)–O(3)	2.426(3)	C(1)W(1)C(6)	74.56(17)
Dy(1)–O(4)	2.334(3)	C(7)W(1)C(6)	143.48(14)
Dy(1)–N(1)	2.413(4)	C(2)W(1)C(6)	69.39(15)
Dy(1)–N(2)	2.422(4)	C(4)W(1)C(6)	78.00(18)
Dy(1)–N(7)	2.468(4)	C(8)W(1)C(6)	128.66(17)
Dy(1)–N(8)	2.434(4)	C(1)W(1)C(5)	76.16(17)
K(1)–O(3)	2.825(3)	C(7)W(1)C(5)	71.82(15)
K(1)–O(7)	2.990(4)	C(2)W(1)C(5)	141.11(16)
K(1)–N(3)	3.088(5)	C(4)W(1)C(5)	76.11(16)
K(1)–N(4)	2.807(4)	C(8)W(1)C(5)	131.48(17)
K(1)–N(4)	3.001(5)	C(6)W(1)C(5)	71.73(15)
K(1)–N(5)	2.844(4)	C(1)W(1)C(3)	143.18(16)
K(1)–N(7)	3.283(4)	C(7)W(1)C(3)	76.87(16)
N(1)–C(1)	1.156(6)	C(2)W(1)C(3)	77.33(16)
N(2)–C(2)	1.143(5)	C(4)W(1)C(3)	71.04(16)
N(3)–C(3)	1.146(6)	C(8)W(1)C(3)	72.42(17)
N(4)–C(4)	1.153(7)	C(6)W(1)C(3)	131.66(17)
N(5)–C(5)	1.144(6)	C(5)W(1)C(3)	131.50(16)
N(6)–C(6)	1.161(6)		
N(7)–C(7)	1.158(6)		

coordination polyhedron of cerium in **II** is a nine-vertex polyhedron $[CeN_5(H_2O)_4]$ shaped like a trigonal prism with three centered side faces, while that of dysprosium in **I** is an eight-vertex polyhedron $[DyN_4(H_2O)_4]$ shaped like a tetragonal antiprism. The coordination polymer $\{[K(H_2O)][Dy(H_2O)_4][W(CN)_8]\}_n \cdot 2nH_2O$(I) has a 3D structure and forms infinite chains –Dy–N≡C–W–C≡N– in three dimensions, unlike **II**, which has a 2D structure.

Compound **I** also differs in the structure from tungsten(V) compounds, $[Sm(H_2O)_5][W(CN)_8]$ (**III**) [9] and $[Gd(DMF)_6][W(CN)_8]$ (**IV**) [10]. The crystals of **III** are tetragonal. The samarium ion in **III** is surrounded by four N atoms of the cyano groups and five O atoms of water molecules forming a monocapped tetragonal antiprism. The coordination polyhedron of tungsten in **III** is tetragonal antiprism. The 2D structure of **III** is represented by –Sm–N≡C–W–C≡N– layers combined

Table 3. Geometric parameters of hydrogen bonds for $KDyW(CN)_8 \cdot 7H_2O$

D–H···A	Distance, Å			The D–H···A angle, deg	The symmetry code for A atom
	D–H	H···A	D···A		
O(1)–H(1*A*)···O(5)	0.85(6)	1.96(6)	2.796(6)	171(5)	$1 - x, 1 - y, -z$
O(2)–H(2*A*)···O(5)	0.76(7)	2.12(7)	2.867(6)	165(6)	$2 - x, 1 - y, -z$
O(2)–H(2*B*)···N(3)	0.94(6)	1.84(6)	2.776(6)	178(7)	$1 + x, 1 + y, z$
O(3)–H(3*A*)···O(6)	1.00(6)	1.73(6)	2.660(6)	154(6)	
O(3)–H(3*B*)···N(6)	0.80(6)	2.13(6)	2.885(5)	157(5)	$1 + x, y, z$
O(4)–H(4*A*)···O(7)	0.90(6)	1.81(6)	2.699(5)	171(5)	
O(4)–H(4*B*)···N(6)	0.89(6)	2.08(6)	2.968(5)	175(6)	
O(5)–H(5*A*)···N(3)	0.82(7)	2.58(7)	3.263(6)	141(6)	$1 + x, 1 + y, z$
O6)–H(6*A*)···N(5)	0.79(8)	2.24(9)	3.025(6)	169(8)	
O(6)–H(6*B*)···N(6)	0.91(9)	2.11(9)	3.004(6)	170(7)	$1 - x, - y, 1 - z$
O(7)–H(7*A*)···N(5)	0.92(7)	2.21(7)	3.021(5)	147(5)	$1 - x, -y, 1 - z$
O(7)–H(7*B*)···N(4)	0.79(7)	2.35(7)	3.113(7)	165(7)	$x, 1 + y, z$

by hydrogen bonds. The monoclinic crystal of **IV** has a 1D structure. The coordination polyhedron of tungsten in **IV** is a tetragonal antiprism, that of gadolinium is a distorted tetragonal antiprism $[GdN_2O_6]$ (the oxygen atoms belong to DMF molecules).

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