Chemistry of Metals and Alloys

Chem. Met. Alloys 3 (2010) 49-52
Ivan Franko National University of Lviv
www.chemetal-journal.org

Refinement of the crystal structure of potassium octacyanomolybdate(IV) dihydrate

Iryna TYPILO[1], Olha SEREDA[2], Helen STOECKLI-EVANS[2], Roman GLADYSHEVSKII[3], Dariya SEMENYSHYN[1]*

[1] *Institute of Chemistry and Chemical Engineering, National University "Lvivska Polytechnika", Bandera St. 12, UA-79013 Lviv, Ukraine*
[2] *Swiss Center for Electronics and Microtechnology, Rue Jaquet-Droz 1, CH-2002 Neuchâtel, Switzerland*
[3] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, UA-79005 Lviv, Ukraine*
* *Corresponding author. Tel.: +380-32-2582768; e-mail: semenyshyn@polynet.lviv.ua*

Received May 5, 2010; accepted June 29, 2010; available on-line November 5, 2010

X-ray diffraction on single crystal was used to refine the crystal structure of $K_4[Mo(CN)_8]\cdot 2H_2O$. For the first time the positions of all hydrogen atoms in the complex were localized, the crystal structure being determined at temperature 173 K. The compound crystallizes in the orthorhombic system, space group *Pnma*, cell parameters a = 16.6959(10), b = 11.6090(6) and c = 8.6796(6) Å, V = 1682.30(18) Å^3, Z = 4, D_X = 1.961 g·cm^{-3}, number of independent reflections 2365, reliability factors R = 0.0329, wR = 0.0590. The coordination polyhedron of the molybdenum atoms is a dodecahedron $[Mo(CN)_8]$. The potassium atoms have three different deformed polyhedra: trigonal bipyramid $[K1N_4OH_2]$, tetragonal pyramid $[K2N_5]$ and trigonal prism with one additional atom $[K3N_5(OH_2)_2]$. All cyanogroups in the complex are terminal.

Potassium octacyanomolybdate(IV) / Crystal structure / X-ray diffraction

Introduction

The crystal structure of $K_4[Mo(CN)_8]\cdot 2H_2O$ was established by Hoard and Nordsieck in 1939 [1]. This was the first study of the crystal structure of eight-coordination complexes, which revealed that the polyhedron $[Mo(CN)_8]$ has the form of a dodecahedron. Furtheron, the crystal structure of potassium octacyanomolybdate(IV) dihydrate was rerefined in [2] (a = 16.64(1), b = 11.660(7), c = 8.710(5) Å, V = 1689.9 Å^3), but the positions of the hydrogen atoms were not yet localized. The structure was studied at room temperature.

In order to determine the positions of the hydrogen atoms, we carried out the determination of the crystal structure of $K_4[Mo(CN)_8]\cdot 2H_2O$ on single-crystal diffraction data at 173 K.

Experimental

Synthesis

The potassium octacyanomolybdate(IV) dihydrate was prepared by the method described in [3]. Powdered $K_4[Mo(CN)_8]\cdot 2H_2O$ was dissolved in water, the solution was kept in dark for three months and well shaped yellow crystals suitable for X-ray diffraction studies were obtained. The size of the crystal used in the investigation was 0.10×0.17×0.20 mm.

X-ray diffraction

The intensity data were collected at 173 K on a diffractometer STOE IPDS II [4] with Mo $K\alpha$ radiation (graphite monochromator, φ-scan, 2θ range 2.29-59.53º). The structure was solved by direct methods and refined using the program SHELX-97 [5]. Hydrogen atoms of the water molecules were localized by difference Fourier synthesis and refined with fixed U_{iso}(H) = 1.5U_{eq}(O). All non-hydrogen atoms were refined anisotropically, using the full-matrix least-squares method on F^2. The empirical correction on absorption was made using DELrefABS in PLATON [6] (transmission factors T_{min}/T_{max} = 0.6382/0.8336).

The compound $K_4[Mo(CN)_8]\cdot 2H_2O$ crystallizes in the orthorhombic system, space group *Pnma*, with the cell parameters a = 16.6959(10), b = 11.6090(6) and c = 8.6796(6) Å, V = 1682.30(18) Å^3, Z = 4, D_X = 1.961 g cm^{-3}. The number of measured reflections was 19081, the number of independent reflections 2365 (R_{int} = 0.0704), the number of reflections with $I > 2\sigma(I)$ 1870, the number of refined

Table 1 Atomic coordinates and equivalent (isotropic) displacement parameters for $K_4[Mo(CN)_8]\cdot 2H_2O$.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq}/U_{iso}, Å^2
K1	8*d*	0.14835(4)	0.04756(6)	0.18788(7)	0.0228(2)
K2	4*c*	0.36535(6)	¼	0.02500(9)	0.0217(3)
K3	4*c*	0.46252(5)	¼	0.52249(9)	0.0171(3)
Mo	4*c*	0.13750(2)	¼	0.59643(3)	0.0075(1)
C1	8*d*	0.0391(2)	0.1388(2)	0.6648(3)	0.014(1)
C2	8*d*	0.1731(2)	0.0725(3)	0.5689(3)	0.015(1)
C3	4*c*	0.0619(2)	¼	0.3937(4)	0.015(1)
C4	4*c*	0.1418(2)	¼	0.8446(4)	0.015(1)
C5	4*c*	0.2168(2)	¼	0.3978(4)	0.014(1)
C6	4*c*	0.2602(2)	¼	0.6753(4)	0.018(1)
N1	8*d*	0.0123(1)	0.5809(2)	0.2893(3)	0.022(1)
N2	8*d*	0.3068(2)	0.0216(2)	0.0500(3)	0.025(1)
N3	4*c*	0.0210(2)	¼	0.2866(4)	0.022(1)
N4	4*c*	0.2614(8)	¼	0.2957(4)	0.021(1)
N5	4*c*	0.3260(2)	¼	0.7133(4)	0.032(1)
N6	4*c*	0.6401(2)	¼	0.5221(3)	0.020(1)
O	8*d*	0.3888(1)	0.0593(2)	0.4090(3)	0.027(1)
H1	8*d*	0.349(2)	0.080(4)	0.367(4)	0.040
H2	8*d*	0.412(2)	0.017(3)	0.347(4)	0.040

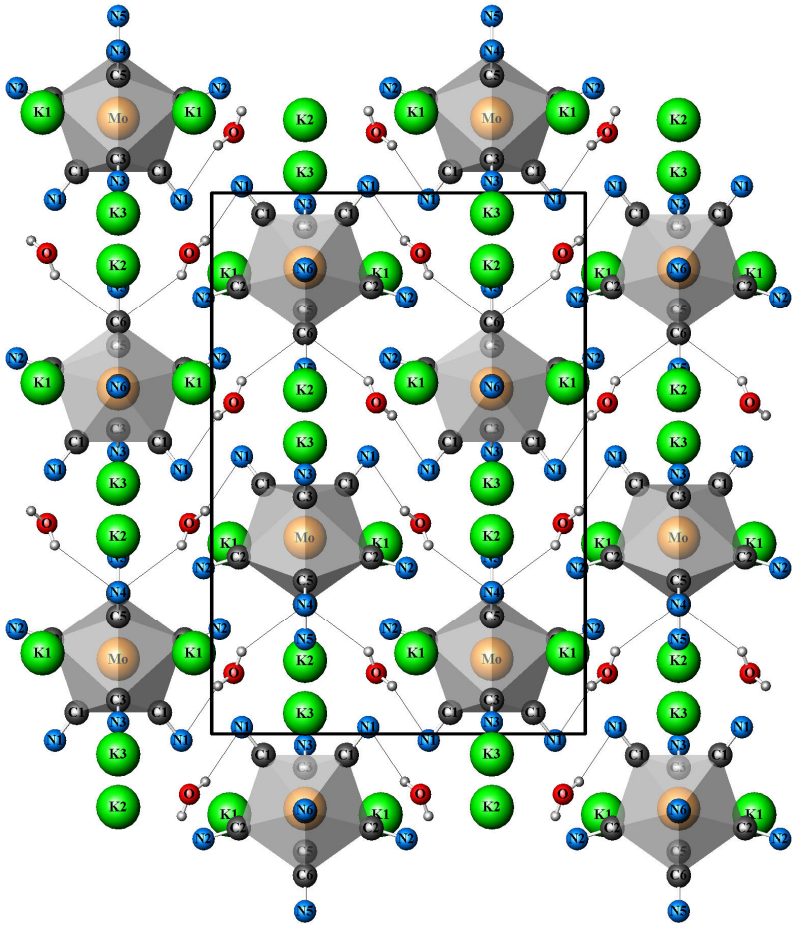

Fig. 1 Projection of the structure of $K_4[Mo(CN)_8]\cdot 2H_2O$ along [001].

parameters 127, reliability factors R = 0.0329, wR = 0.0590, S = 1.005, residual electron density $\Delta\rho_{min}/\Delta\rho_{max}$ = -0.986/0.937 e Å^{-3}.

A projection of the structure of $K_4[Mo(CN)_8]\cdot 2H_2O$ along the crystallographic direction [001] is presented in Fig. 1. The atomic

Table 2 Selected interatomic distances and angles for $K_4[Mo(CN)_8]\cdot 2H_2O$.

Atoms	δ, Å	Atoms	ω, °
K1–O	2.790(3)	C1–Mo–C1	72.91(9)
K1–N1	2.857(2)	C1–Mo–C2	70.81(9)
K1–N2	2.919(3)	C1–Mo–C2	143.72(9)
K1–N6	2.977(2)	C1–Mo–C3	77.35(10)
K1–N4	3.156(3)	C1–Mo–C4	75.65(10)
K2–N5	2.784(4)	C1–Mo–C5	132.64(9)
K2–2N2	2.834(2)	C1–Mo–C6	129.12(9)
K2–N4	2.921(4)	C2–Mo–C2	145.45(10)
K2–N3	3.070(4)	C2–Mo–C3	94.05(7)
K3–2O	2.718(2)	C2–Mo–C4	95.83(7)
K3–N5	2.818(3)	C2–Mo–C5	75.19(7)
K3–N3	2.855(4)	C2–Mo–C6	76.92(7)
K3–N6	2.965(3)	C3–Mo–C4	146.26(13)
K3–2N1	3.065(3)	C3–Mo–C5	73.18(13)
Mo–C4	2.155(3)	C3–Mo–C6	144.13(13)
Mo–2C2	2.158(3)	C4–Mo–C5	140.57(13)
Mo–C6	2.160(3)	C4–Mo–C6	69.61(13)
Mo–C3	2.166(3)	C5–Mo–C6	70.96(13)
Mo–2C1	2.173(2)		
Mo–C5	2.174(3)		
C1–N1	1.160(3)		
C2–N2	1.155(4)		
C3–N3	1.153(5)		
C4–N6	1.157(4)		
C5–N4	1.158(5)		
C6–N5	1.147(5)		

Table 3 Hydrogen bonds for $K_4[Mo(CN)_8]\cdot 2H_2O$.

D–H...A	D–H, Å	H...A, Å	D...A, Å	D–H...A, °
O–H1...N4	0.80(3)	2.53(4)	3.224(3)	146(4)
O–H2...N1	0.83(3)	2.34(3)	3.140(3)	162(3)

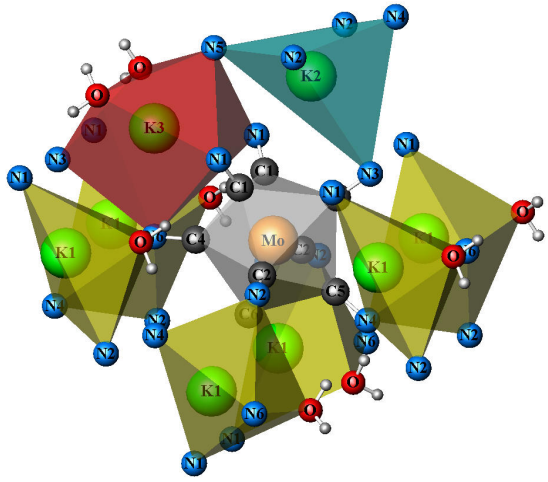

Fig. 2 Arrangement of the coordination polyhedra of the potassium atoms around the Mo-centered dodecahedra in the structure of $K_4[Mo(CN)_8]\cdot 2H_2O$.

coordinates and equivalent (isotropic) displacement parameters are given in Table 1. Selected interatomic distances and angles are listed in Table 2.

Results and discussion

In the structure of $K_4[Mo(CN)_8]\cdot 2H_2O$ the positions of the hydrogen atoms are localized for the first time. The structure of the complex is ionic and consists of anions $[Mo(CN)_8]^{4-}$, in which the Mo atoms occupy one Wyckoff position, and potassium cations, which are distributed among three positions. In the structure, each Mo atom is surrounded by eight cyanogroups forming a dodecahedron. The Mo–C distances vary from 2.155(3) to 2.174(3) Å and the length of the C≡N bonds is within the range 1.147(5)-1.160(3) Å. The values of the Mo–C≡N angles vary from 175.8(2) to 179.4(3)°. The potassium atoms have three different coordination polyhedra: trigonal bipyramid $[K1N_4(OH_2)]$ (the O atom at one of the vertexes of the bipyramid), tetragonal pyramid $[K2N_5]$ and trigonal

prism with one additional atom [$K3N_5(OH_2)_2$] (the O atoms form one of the basal triangles, the additional atom (N) centers the face of composition $N_2(OH_2)_2$). The arrangement of the coordination polyhedra of the molybdenum and potassium atoms in the structure of the complex is shown in Fig. 2. Thus, there are two water molecules around the site K3, one around the site K1 and none around the site K2. The crystallization water molecules are connected to the nitrogen atoms of the cyanogroups by hydrogen bonds. As can be seen from Table 3, the distances H1...N4 and H2...N1 are 2.53(4) and 2.34(3) Å, respectively, and thus smaller than 2.7 Å, which indicates the existence of strong hydrogen bonds in the studied compound. *Via* the hydrogen bonds the dodecahedra [$Mo(CN)_8$] form puckered layers perpendicular to [100] (see Fig. 1).

Conclusion

The crystal structure of potassium octacyanomolybdate(IV) dihydrate was determined at 173 K and the positions of the hydrogen atoms were established for the first time. The lattice parameters and the atomic coordinates (for non-hydrogen atoms) are only slightly different from those reported in the literature [2] for the complex studied at room temperature. The H...N distances indicate the existence of strong hydrogen bonds in $K_4[Mo(CN)_8]\cdot 2H_2O$.

References

[1] J.L. Hoard, H.H. Nordsieck, *J. Am. Chem. Soc.* 61 (1939) 2853-2857.
[2] J.L. Hoard, T.A. Hamor, M.D. Glick, *J. Am. Chem. Soc*. 90 (1968) 3177-3184.
[3] V.M. Litvinchuk, K.N. Mikhalevych, D.I. Zubritskaya, *Zh. Neorg. Khim*. 17(5) (1972) 1357-1360.
[4] *Stoe & Cie. X-Area V1.52, X-RED32 V1.48 & X-SHAPE Software*, Stoe & Cie GmbH, Darmstadt, 2009.
[5] G.M. Sheldrick, *Acta Crystallogr. A* 64 (2008) 112-122.
[6] A.L. Spek, *Acta Crystallogr. D* 65 (2009) 148-155.