Chemistry of Metals and Alloys

Chem. Met. Alloys 2 (2009) 25-29
Ivan Franko National University of Lviv
www.chemetal-journal.org

Crystal structure of the complex $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$

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

[1] *Institute of Chemistry and Chemical Engineering, National University "Lvivska Polytechnika", Bandera St. 12, UA-79013 Lviv, Ukraine*
[2] *Institut de Microtechnique, Université de Neuchâtel, Rue Emile-Argand 11, C.P. 158, CH-2009 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 January 26, 2009; accepted June 30; available on-line November 16, 2009

The complex $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$ was prepared by hydrolysis of $K_4[W(CN)_8]\cdot 2H_2O$ and its crystal structure solved by direct methods. Crystal data: $C_{10}H_8K_4N_{10}O_7W_2$, M_r = 904.34, triclinic system, space group $P\bar{1}$, cell parameters a = 8.7910(8), b = 8.8424(8), c = 9.4743(9) Å, α = 82.316(11), β = 64.843(10), γ = 64.945(10)°, V = 602.92(10) Å^3, Z = 1, D_X = 2.491 g cm^{-3}, R = 0.0236 and wR = 0.0584 for 2175 independent reflections. The coordination polyhedra of the tungsten(VI) atoms are pentagonal bipyramids $W(CN)_5O_2$, which are linked into pairs by sharing one of the oxygen atoms and twisted by 36° with respect to each other. The hydrogen bonds interconnect the pairs of pentagonal bipyramids into infinite complex chains. The coordination polyhedra of the two independent potassium atoms are trigonal prisms with one capped face (by a NC unit), but have different composition, $K(1)(NC)_4O(OH_2)_2$ and $K(2)(NC)_5(OH_2)_2$. The formula of this coordination compound can be written as $K_4[OW(CN)_5OW(CN)_5O]\cdot 4H_2O$.

Tungsten(VI) complex / Crystal structure / Coordination cyanide

Introduction

The last years there has been increasing interest in the synthesis and crystal structure determinations of complexes containing $[M(CN)_8]^{3-/4-}$ anions (M = Mo, W) because of their interesting magnetic properties [1-4]. There exist only a few reports on investigations of cyanide complexes of tungsten and molybdenum that contain oxygen atoms. The synthesis and IR spectroscopy studies of molybdenum(IV) complexes $K_4[MoO_2(CN)_4]\cdot 6H_2O$, $K_4[MoO_2(CN)_4]$, $K_3[MoO(OH)(CN)_4]$, $K_2[Mo(OH)_2(CN)_4]$, $Cd(H_2O)_6[Mo(OH)_2(CN)_4]$, $Mo(OH)_2(CN)_2\cdot H_2O$, $K_6[Mo^{4+}{}_2Mo^{6+}(CN)_8O_6]\cdot 2H_2O$ are described in [5]. The authors of [6] report on photolysis of $Na_4[W(CN)_8]$ that led to the formation of the complex $Na_4[WO_2(CN)_4]\cdot 12H_2O$. The crystal structure of the complex $Na_3[MoO(OH)(CN)_4]\cdot 4H_2O$ belongs to space group $P2_1/m$ [7] and crystallographic data for $Rb_3[WO_2(CN)_3H_2O]\cdot 3H_2O$ are the following: monoclinic system, space group $P2_1$, cell parameters a = 12.047(3), b = 7.980(2), c = 7.815(2) Å, γ = 108.05(2)° [8]. Here we present the crystal structure of a novel complex, $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$.

Experimental

Synthesis

The complex $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$ was prepared by hydrolysis of $K_4[W(CN)_8]\cdot 2H_2O$. A solution of $K_4[W(CN)_8]\cdot 2H_2O$ was stored in dark at room temperature. Orange, well-shaped crystals, suitable for single-crystal diffraction, were formed after several months.

X-ray diffraction

The single crystal of $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$ selected for the diffraction experiment was approximately 0.50×0.25×0.20 mm large. Intensity data were collected at 173 K on a STOE IPDS device [9] using graphite-monochromated Mo Kα radiation (image plate distance 70 mm, ϕ oscillation scans 0-200°, step $\Delta\phi$ = 1.0°, exposure time 3 min, θ range 2.38-25.83°). The structure was solved by direct methods using programs from SHELX-97 [10,11]. The non-hydrogen atoms were refined anisotropically from weighted full-matrix least-squares on F^2; hydrogen atoms were located from Fourier difference maps. An empirical absorption correction was applied using the

Table 1 Experimental details of the structure refinement for $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$.

Crystal color	yellow
Crystal size, mm	0.50×0.25×0.20
Empirical formula	$C_{10}H_8K_4N_{10}O_3W_2$
M_r	904.34
System	triclinic
Space group	$P\bar{1}$
a, Å	8.7910(8)
b, Å	8.8424(8)
c, Å	9.4743(9)
α, º	82.316(11)
β, º	64.843(10)
γ, º	64.945(10)
V, Å^3	602.92(10)
Z	1
D_X, g cm^{-3}	2.491
μ, mm^{-1}	10.274
Radiation	Mo Kα
λ, Å	0.71073
Range θ, º	2.38-25.83
Number of measured reflections	4761
Number of independent reflections	2175
Number of reflections with $I > 2\sigma(I)$	2069
R_{int}	0.0451
Number of refined parameters	151
R, *wR*, *S*	0.0236, 0.0584, 1.121
R, *wR* ($I > 2\sigma(I)$)	0.0221, 0.0580
ρ_{min}/ρ_{max}, e Å^{-3}	-1.411/0.948
T, K	173(2)

Table 2 Atomic coordinates and equivalent/isotropic displacement parameters for $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$.

Atom	Wyckoff position	*x*	*y*	*z*	U_{eq}, Å^2
K(1)	2*i*	0.32902(16)	0.41507(16)	0.21352(13)	0.0307(3)
K(2)	2*i*	0.56862(17)	0.26959(17)	0.59955(14)	0.0367(4)
W	2*i*	0.09248(2)	0.11461(2)	0.08357(2)	0.0158(1)
C(1)	2*i*	0.0444(6)	0.3019(6)	0.9137(5)	0.0220(14)
C(2)	2*i*	0.2834(6)	0.8641(6)	0.1016(5)	0.0191(14)
C(3)	2*i*	0.3391(6)	0.0382(6)	0.8659(5)	0.0230(12)
C(4)	2*i*	0.8079(6)	0.3002(6)	01952(5)	0.0218(14)
C(5)	2*i*	0.9560(6)	0.0209(6)	0.3053(5)	0.0221(14)
N(1)	2*i*	0.0209(6)	0.3914(5)	0.8189(5)	0.0297(12)
N(2)	2*i*	0.1174(6)	0.0304(6)	0.5814(5)	0.0292(14)
N(3)	2*i*	0.3802(6)	0.7279(6)	0.1073(5)	0.0271(12)
N(4)	2*i*	0.5324(6)	0.0031(6)	0.2483(5)	0.0326(14)
N(5)	2*i*	0.6597(6)	0.3942(6)	0.2581(5)	0.0298(12)
O(1)	2*i*	0.1316(5)	0.6394(5)	0.4826(4)	0.0352(12)
O(2)	2*i*	0.1732(5)	0.2134(4)	0.1637(4)	0.0245(11)
O(3)	2*i*	0.3214(5)	0.2633(5)	0.4959(4)	0.0364(12)
O(4)	1*a*	0	0	0	0.0195(14)
H(1A)	2*i*	0.0316	0.7255	0.4905	0.053
H(1B)	2*i*	0.1023	0.5936	0.5711	0.053
H(3A)	2*i*	0.2376	0.2574	0.5859	0.054
H(3B)	2*i*	0.3633	0.1605	0.4575	0.054

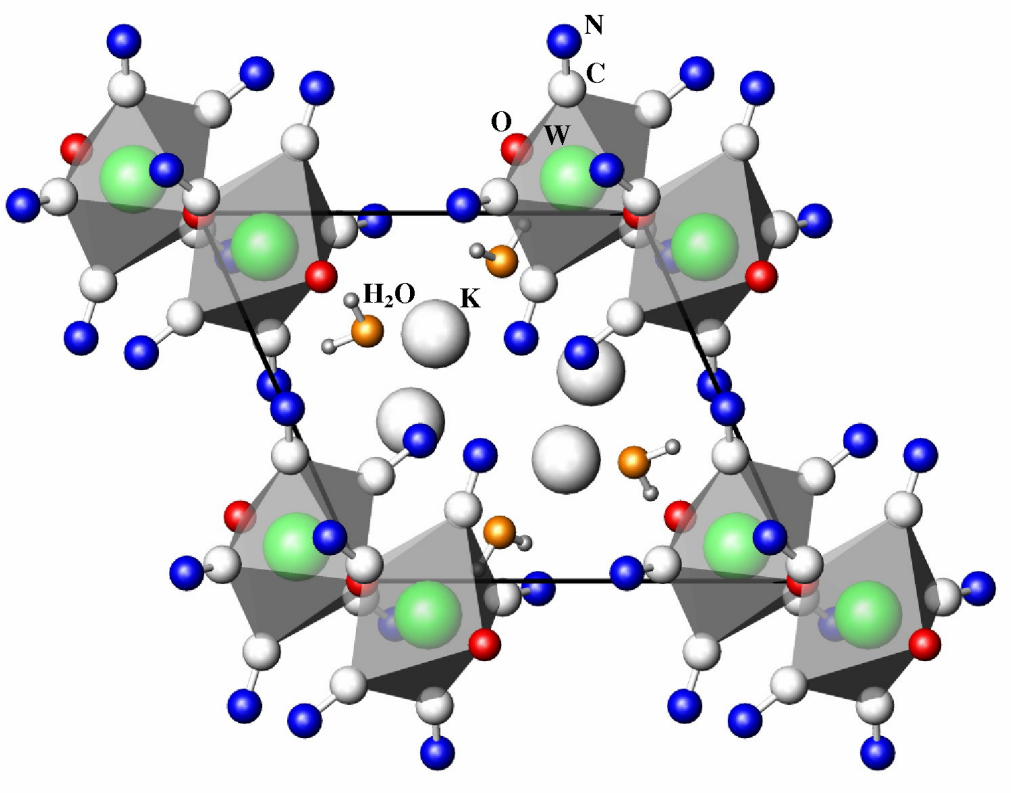
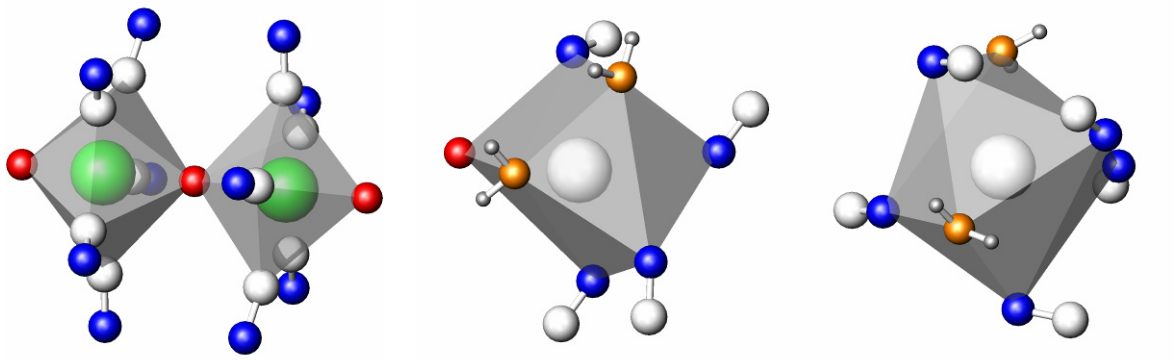


Fig. 1 Projection of the structure of $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$ along [001].



$W_2(CN)_{10}O_3$ $K(1)(NC)_4O(OH_2)_2$ $K(2)(NC)_5(OH_2)_2$

Fig. 2 Coordination polyhedra of the W and K atoms in $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$.

DELrefABS routine in PLATON [12]; transmission factors T_{min}/T_{max} = 0.086/0.120. A projection of the $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$ structure and the coordination polyhedra of the W and K atoms (drawn with ATOMS [13]) are presented in Figs. 1 and 2, respectively. Details of the structure investigation are given in Table 1, atomic coordinates and equivalent (isotropic for H atoms) displacement parameters in Table 2, and selected bond lengths and angles in Table 3.

Results and discussion

The X-ray diffraction study of the crystal structure of $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$ reveals that it consists of three structural units, $W_2(CN)_{10}O_3$, $K(1)(NC)_4O(OH_2)_2$ and $K(2)(NC)_5(OH_2)_2$. The coordination polyhedra of the tungsten(VI) atoms are pentagonal bipyramids $W(CN)_5O_2$, which are linked into pairs by common oxygen atoms and twisted by 36º with respect to each

Table 3 Selected bond distances and angles in $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$.

Atoms	δ, Å	Atoms	ω, °
W-C(3)	2.177(5)	C(1)-W-C(2)	141.78(17)
W-C(2)	2.179(5)	C(1)-W-C(3)	71.63(18)
W-C(5)	2.185(5)	C(1)-W-C(4)	72.69(18)
W-C(1)	2.187(5)	C(1)-W-C(5)	143.7(2)
W-C(4)	2.193(5)	C(2)-W-C(3)	70.92(17)
W-O(2)	1.733(4)	C(2)-W-C(4)	143.56(18)
W-O(4)	1.9428(3)	C(2)-W-C(5)	71.79(18)
C(3)-N(4)	1.139(7)	C(3)-W-C(4)	144.19(18)
C(4)-N(5)	1.140(7)	C(3)-W-C(5)	142.32(18)
C(1)-N(1)	1.142(6)	C(4)-W-C(5)	72.03(18)
C(5)-N(2)	1.142(7)	O(2)-W-C(1)	95.69(18)
C(2)-N(3)	1.154(7)	O(2)-W-C(2)	94.11(19)
K(1)-O(3)	2.815(4)	O(2)-W-C(3)	93.8(2)
K(1)-O(1)	2.850(4)	O(2)-W-C(4)	92.55(19)
K(1)-O(2)	2.850(5)	O(2)-W-C(5)	94.02(19)
K(1)-N(1)	2.948(6)	O(4)-W-C(1)	86.06(15)
K(1)-N(3)	2.965(5)	O(4)-W-C(2)	84.92(15)
K(1)-N(3)	3.009(5)	O(4)-W-C(3)	87.41(15)
K(1)-N(5)	3.038(6)	O(4)-W-C(4)	87.29(15)
K(2)-O(3)	2.761(5)	O(4)-W-C(5)	84.15(15)
K(2)-O(1)	2.843(5)	O(4)-W-O(2)	178.12(11)
K(2)-N(5)	2.899(5)		
K(2)-N(4)	2.911(5)		
K(2)-N(2)	2.930(5)		
K(2)-N(3)	3.001(5)		
K(2)-N(5)	3.148(5)		
O(1)-H(1B)	0.860		
O(1)-H(1A)	0.870		
O(3)-H(3A)	0.870		
O(3)-H(3B)	0.890		

Table 4 Hydrogen bonds for $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$.

D-H...A	D-H, Å	H…A, Å	D…A, Å	D-H...A, °
O(1)-H(1A)...N(2)	0.870	2.190	2.988(7)	152.0
O(3)-H(3A)...N(1)	0.870	2.260	3.024(6)	146.0
O(3)-H(3B)...N(4)	0.890	2.130	2.893(6)	143.0

other. The W atom is seven-fold coordinated by five carbon atoms from CN groups (C(1), C(2), C(3), C(4), C(5)) and two oxygen atoms (O(2), O(4)). The W-C distances range from 2.177(5) to 2.193(5) Å and the C≡N distances from 1.139(7) to 1.154(7) Å. The W-C-N bond angles range from 175.4(4) to 179.2(4)° and do thus not deviate much from 180°.

The water molecules (O(1), O(3)) and potassium atoms are located between the $W_2(CN)_{10}O_3$ units. K(1) is surrounded by four N atoms from CN groups (N(1), two N(3), N(5)), two O atoms from water molecules (O(1), O(3)), and one more oxygen atom (O(2)). K(2) is surrounded by five N atoms from CN groups (N(4), two N(5), N(2), N(3)) and two O atoms from water molecules (O(1), O(3)). The coordination polyhedra of both potassium sites are trigonal prisms with one face centered by a NC group, but they have different compositions, $K(1)(NC)_4O(OH_2)_2$ and $K(2)(NC)_5(OH_2)_2$. The formula of the compound can conveniently be written as $K_4[OW(CN)_5OW(CN)_5O]\cdot 4H_2O$.

Hydrogen bonding is observed in the structure of $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$ between the water molecules (H(1A), H(3A), H(3B)) and CN groups of the $W_2(CN)_{10}O_3$ units. The hydrogen atom H(1B) does not form hydrogen bonding. H-bond distances in $K_4[W_2(CN)_{10}O_3]\cdot 4H_2O$ are listed in Table 4. The hydrogen bonds interconnect the pairs of pentagonal bipyramids into infinite complex chains running along [10$\bar{1}$] (Fig. 3).

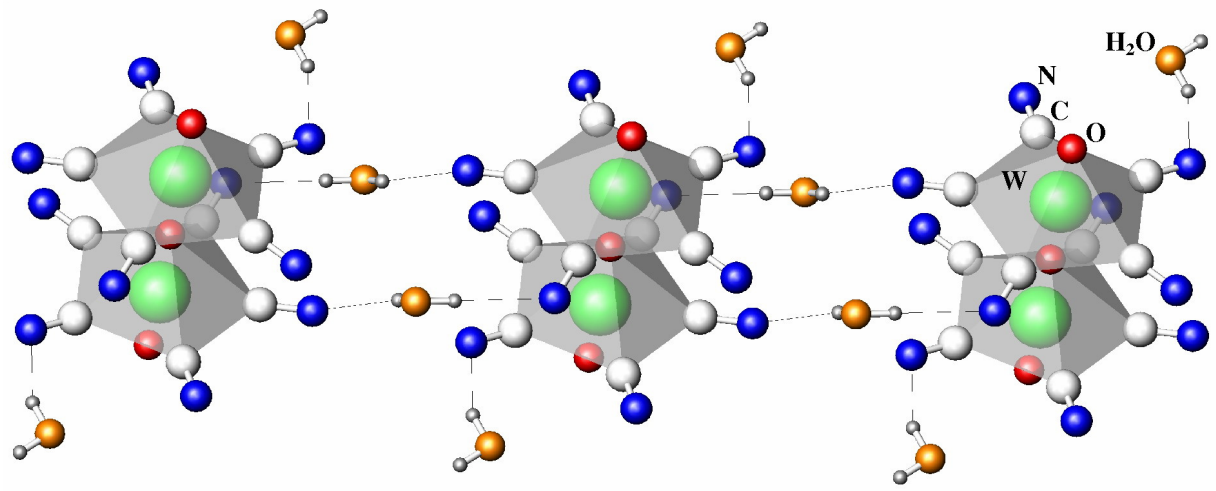


Fig. 3 Part of an infinite chain of $W_2(CN)_{10}O_3\cdot$units interconnected *via* hydrogen bonding.

Conclusions

The formula of this coordination compound can be written as $K_4[OW(CN)_5OW(CN)_5O]\cdot 4H_2O$. The structure is quite different from those of other tungsten-cyanide complexes and the first representative where the coordination polyhedra of the tungsten atoms form pairs.

References

[1] T. Hozumi, S. Ohkoshi, Y. Arimoto, H. Saino, Y. Mizobe, K. Hashimoto, *J. Phys. Chem. B* 107 (2003) 11571-11574.
[2] S. Ikeda, T. Hozumi, K. Hashimoto, S. Ohkoshi, *Dalton Trans.* (2005) 2120-2123.
[3] S. Kaneko, Y. Tsunobuchi, K. Nakabayashi, S. Ohkoshi, *Polyhedron* 28 (2009) 1893-1897.
[4] O.A. Sereda, H. Stoeckli-Evans, I.V. Typilo, D.I. Semenyshyn, R.E. Gladyshevskii, *Koord. Khim.* 35 (2009) 17-20.
[5] J. van de Poel, H.M. Neumann, *Inorg. Chem.* 7 (1968) 2086-2091.
[6] A. Samotus, M. Dudek, A. Kanas, *J. Inorg. Nucl. Chem.* 37(4) (1975) 943-948.
[7] K. Stadnicka, *Rocz. Chem.* 47(11) (1973) 2021-2034.
[8] B. Chernyak, R. Gladyshevskii, V. Kovbashyn, V. Yarovets, *Coll. Abstr. VI All-Union Conf. Chem. Technol. Mo W*, Nalchuk, 1988, p. 43.
[9] *Stoe IPDS Software*, Stoe & Cie GmbH, Darmstadt, Germany, 2000.
[10] G.M. Sheldrick, *Acta Crystallogr. A* 46 (1990) 467-473.
[11] G.M. Sheldrick, *SHELXS-97*, Universität Göttingen, Göttingen, Germany, 1999.
[12] A.L. Spek, *J. Appl. Crystallogr.* 36 (2003) 7-13.
[13] E. Dowty, *Atoms - A Computer Program for Displaying Atomic Structures*, Kingsport, TN, 1999.