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Stabilization of the tungstyl ion configuration: the W(V) diphosphate $KWOP_2O_7$

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A new W(V) diphosphate $KWOP_2O_7$ isotypic to the Mo(V) compound has been synthesized. It crystallizes in the space group $P12_1/n1$ with $a = 5.0629(3)$, $b = 11.770(2)$, $c = 11.551(1)$, $\beta = 91.039(6)$. This mixed framework of corner-sharing P_2O_7 groups and WO_6 octahedra forms large tunnels where the K^+ ions are located. This study evidences for the first time the ability of W(V) to form tungstyl ions in a phosphate matrix, the W(V) octahedra being characterized by an abnormally short W–O bond of 1.687 Å, similarly to Mo(V).

Introduction

The pentavalent states of molybdenum and tungsten display different crystal chemistries, in spite of the similarity of their d^1 electronic configurations. For instance, in both systems one observes oxygen bronzes, involving mixed valence Mo(V)–Mo(VI) and W(V)–W(VI) respectively, but the crystallographic nature of these bronzes is different (see for a review ref. 1 and 2). More specifically, the greatest difference concerns the existence of isolated Mo(V) and W(V) within the phosphate matrix. Numerous Mo(V) phosphates have been synthesized in recent years (see for a review ref. 3 and for examples ref. 4–6). In all these phosphates the MoO_6 octahedron exhibits systematically one free apex and is characterized by a pecular geometry: it forms an abnormally short Mo–O bond, called molybdenyl, with the free oxygen. In contrast to molybdenum phosphates, very few W(V) phosphates are actually known, in spite of the existence of a large family of phosphate tungsten bronzes.[7] To our knowledge, only two W(V) phosphates have been synthesized to date. Both characterized by the formula WPO_5, they correspond to a monophosphate $WOPO_4$[8] and a diphosphate $W_2O_3P_2O_7$[9] respectively. Remarkably, in these structures, the W(V) octahedra do not exhibit any free apex, and their geometry is regular, with six almost equal W–O distances, in contrast to Mo(V) phosphates.

In order to understand this different behavior of W(V) with respect to Mo(V), we have attempted to synthesize W(V) phosphates isotypic to Mo(V) phosphates, with an opened framework, *i.e.* involving WO_6 octahedra with one free apex. Our investigation is based on the idea that such phosphates might be metastable and then should require particular synthesis conditions, using flux agents or mineralizers. For this reason we have explored the W–P–O system, using PbO and KBr as flux agents. We describe herein the crystal growth and structure of the first tungstyl phosphate, $KWOP_2O_7$, which is isotypic to the diphosphate $KMoOP_2O_7$.[10]

Experimental

Crystal growth

Single crystals of the W(V) phosphate were grown from a mixture of nominal composition "$PbW_8P_8O_{40}$" with 5% KBr as flux agent. First $PbCO_3$, $H(NH_4)_2PO_4$ and WO_3 were mixed in an agate mortar with the molar ratio 1 : 8 : 6.33 and heated at 400 °C in air in a platinum crucible to decompose the ammonium phosphate and carbonate. In a second step the resulting mixture was then added to the required amount of metallic tungsten (1.66 mol) and to 5% (by weight) of KBr and sealed in an evacuated silica ampoule. The latter was heated at 620 °C for 7 h, then cooled over 5 h to 580 °C, maintained at this temperature for 10 h then slowly cooled at 3.5 °C h^{-1} to 330 °C and finally quenched at room temperature. The resulting products are well formed green crystals of the new W(V) diphosphate and well formed golden crystals of $W_2O_3P_2O_7$ as well as an unknown black sintered powder. The EDS analysis of the green crystals agrees with the formulation "KWP_2".

Attempts to obtain the pure phase $KWOP_2O_7$ using only KBr as a mineralizer failed. Clearly, PbO seems to play a crucial role in the stabilization of this phase, though no lead trace was detected by EDS analysis of the crystals.

X-Ray structure determination

A green crystal with dimensions $0.195 \times 0.018 \times 0.027$ mm^3 was selected for the structure determination. Its quality was tested by the X-ray film technique. The cell parameters (Table 1) were determined with a least squares method using 25 reflections with $18° < \theta < 22°$. The data were recorded at room temperature on an ENRAF-NONIUS CAD4 diffractometer using the $MoK\bar{\alpha}$ radiation ($\lambda = 0.71093$ Å) isolated by a graphite monochromator. Intensities were checked by monitoring

Table 1 Summary of crystal data, intensity measurement and structure refinement parameters for $KWOP_2O_7$

Chemical formula	KWP_2O_8
Molecular weight	412.89
Crystal system	Monoclinic
Space group	$P12_1/n1$
Cell dimensions	$a = 5.0629(3)$ Å $b = 11.770(2)$ Å $c = 11.551(1)$ Å $\beta = 91.039(6)°$
Volume/Å^3	688.2(1)
Z	4
Density/Mg m^{-3}	3.985
$\mu(MoK\bar{\alpha})/mm^{-1}$	17.86
Temperature of data collection/°C	21
Unique reflections with $I > 3\sigma(I)$	2648
No. of variables	110
Agreement factors	$R = 0.0357$, $R_W = 0.0356$
Weighting scheme	$w = 1/\sigma^2$

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Table 2 Atomic coordinates and thermal factors of $KWOP_2O_7$

	x	y	z	$U_{(eq)}$/Å^2
W(1)	0.26183(5)	0.11761(2)	0.16749(2)	0.00593(5)
P(1)	0.7520(4)	0.4345(2)	0.3671(2)	0.0067(4)
P(2)	0.7664(4)	0.3054(2)	0.1511(2)	0.0070(4)
K(1)	0.7734(4)	0.1295(2)	0.4494(2)	0.0239(5)
O(1)	0.312(1)	0.1291(6)	0.3118(5)	0.020(2)
O(2)	0.052(1)	0.2616(5)	0.1455(5)	0.014(1)
O(3)	0.573(1)	0.2112(5)	0.1179(5)	0.012(1)
O(4)	−0.071(1)	0.0248(5)	0.1817(4)	0.011(1)
O(5)	0.460(1)	−0.0284(5)	0.1434(5)	0.014(1)
O(6)	0.187(1)	0.1080(5)	−0.0144(4)	0.014(1)
O(7)	0.719(1)	0.3234(4)	0.2883(5)	0.011(1)
O(8)	0.730(1)	0.4116(5)	0.0863(5)	0.017(2)

Atomic displacement parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	0.00244(8)	0.00772(9)	0.00762(9)	−0.0007(1)	0.00013(5)	−0.0016(1)
P(1)	0.0049(7)	0.0071(7)	0.0080(7)	0.0007(6)	0.0004(6)	−0.0005(6)
P(2)	0.0045(7)	0.0061(7)	0.0103(9)	−0.0002(6)	0.0010(6)	−0.0020(6)
K(1)	0.0250(9)	0.0173(9)	0.0289(9)	0.0018(7)	−0.0096(7)	−0.0031(8)
O(1)	0.016(2)	0.031(4)	0.013(2)	−0.002(3)	−0.001(2)	−0.004(3)
O(2)	0.003(2)	0.012(2)	0.027(3)	0.002(2)	0.001(2)	−0.001(2)
O(3)	0.005(2)	0.014(2)	0.017(2)	−0.005(2)	0.003(2)	−0.003(2)
O(4)	0.006(2)	0.013(2)	0.013(2)	−0.004(2)	−0.001(2)	0.000(2)
O(5)	0.008(2)	0.010(2)	0.025(3)	0.001(2)	−0.000(2)	0.001(2)
O(6)	0.012(2)	0.019(3)	0.010(2)	−0.000(2)	0.001(2)	0.001(2)
O(7)	0.013(2)	0.006(2)	0.015(2)	−0.002(2)	0.003(2)	−0.000(2)
O(8)	0.020(3)	0.010(2)	0.022(3)	0.001(2)	0.002(2)	0.005(2)

$U_{eq} = \frac{1}{3}\sum_i U_{ii}$.

three standard reflections every hour. No significant deviations in intensity measurements were observed. The data were corrected for the Lorentz polarization and absorption effects. The systematic absences $h+l=2n+1$ for $h0l$ and $k=2n+1$ for $0k0$ are characteristic of $P12_1/n1$ (no. 14). One observes also in the whole space a systematic weakening of the reflections $h+l=2n+1$ with $k=2n$.

The structure was solved using the heavy atom method. The full-matrix least squares refinements were performed on F using a SPARC station with the Xtal 3.4 system[11] leading to $R=0.0356$ and $R_w=0.0356$ and to the atomic parameters listed in Table 2.

CCDC reference number 1145/269. See http://www.rsc.org/suppdata/jm/b0/b007592m/ for crystallographic files in .cif format.

Results and discussion

The atomic coordinates of this new phase clearly show that it is isotypic to $KMoOP_2O_7$.[10] The $[MoP_2O_8]_\infty$ framework is built up from single WO_6 octahedra sharing corners with P_2O_7 groups and delimiting large tunnels running along ***a*** where the potassium cations are located (Fig. 1). Thus, each WO_6 octahedron is isolated: it shares five apices with five P_2O_7 groups, its sixth apex O(1) being free and directed toward the center of the tunnel. Reciprocally, each P_2O_7 group shares five apices with different MoO_6 octahedra and exhibits also one free apex O(8), also pointing toward the center of the tunnel.

The remarkable feature of this structure concerns the geometry of the W(v) octahedron (Table 3), which is very similar to that observed for the Mo(v) octahedron in $KMoOP_2O_7$. One indeed observes for the first time for W(v) an abnormally short W–O bond of 1.687 Å corresponding to the free apex O(1), similar to that observed for Mo(v) in the corresponding diphosphate (1.675 Å). In contrast, a very long W–O bond (2.131 Å) is opposite this abnormally short bond, like in the Mo(v) phosphate (2.144 Å), whereas the four intermediate W–O distances are almost equal (2.012 to

Table 3 Selected bond lengths in $KWOP_2O_7$

W1–O1	1.687(5)	K1–O8^{v}	2.598(6)
W1–O2	2.013(5)	K1–O1	2.802(6)
W1–O3	2.013(5)	K1–O8^{iii}	2.818(6)
W1–O4	2.019(5)	K1–O2^{iii}	2.850(6)
W1–O5	2.012(5)	K1–O7	2.954(6)
W1–O6	2.131(5)	K1–O3^{iii}	3.082(6)
P1–O4^{i}	1.506(6)	K1–O6^{iii}	3.150(7)
P1–O5^{ii}	1.528(5)	K1–O1^{iv}	3.180(6)
P1–O6^{iii}	1.499(5)	K1–O8	3.236(6)
P1–O7	1.601(5)	K1–K1	3.978(3)
P2–O2^{iv}	1.538(5)		
P2–O3	1.523(6)		
P2–O7	1.622(6)		
P2–O8	1.467(6)		

Symmetry codes: i: $1/2-x$, $1/2+y$, $1/2-z$; ii: $3/2-x$, $1/2+y$, $1/2-z$; iii: $1/2+x$, $1/2-y$, $1/2+z$; iv: $1+x$, y, z; v: $3/2-x$, $y-1/2$, $1/2-z$.

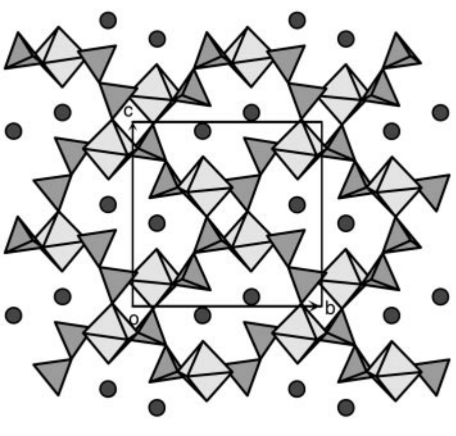

Fig. 1 Projection of the structure of $KWOP_2O_7$ along the ***a*** axis. The light gray octahedra correspond to WO_6 and the gray tetrahedra correspond to PO_4.

2.019 Å) similarly to the Mo(v) phase (2.008 to 2.016 Å). This behavior of W(v) is dramatically different from that of the two W(v) phosphates (WO)PO_4[8] and $(W_2O_3)P_2O_7$,[9] whose WO_6 octahedra are practically regular with W–O distances ranging from 1.837 to 2.004 Å, and from 1.849 to 2.049 Å, respectively.

As expected the geometry of the diphosphate groups is similar to that found in the molybdenum compound: they exhibit a staggered configuration, the longest P–O bond (1.601 to 1.622 Å) corresponding to the bridging oxygen O(7) and the shortest one (1.467 Å) corresponding to the free apex O(8).

Like in $K(MoO)P_2O_7$, the K^+ ions located in the tunnels are surrounded by nine oxygen atoms at distances ranging from 2.598 to 3.236 Å. Note that the shortest bonds, K–O(8) and K–O(1), correspond to the free apices of the P_2O_7 groups and WO_6 octahedron respectively. It is also worth pointing out that the large size of the tunnels suggests a possible mobility of the potassium cations along ***a***. The anisotropic thermal factors of K^+, U_{11} and U_{33}, which are twice as large as U_{22} (Table 2), strongly support this hypothesis.

In conclusion, a new W(v) phosphate, involving isolated WO_6 octahedra, has been synthesized, which is isotopic to the Mo(v) diphosphate $KMoOP_2O_7$. This study evidences for the first time the ability of pentavalent tungsten to exhibit a tungstyl configuration similar to that of molybdenyl. Based on the very rich crystal chemistry of Mo(v) phosphates, these results open the route to the synthesis of a large series of W(v) phosphates, bearing in mind that adequate mineralizers or flux agents will be necessary to stabilize such an exceptional configuration of W(v) octahedra.

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