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Synthesis and crystal structure of the potassium imido nitrido polytungstate(VI) $K_{14}W_6N_{16}NH$

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Abstract

Dark-red, transparent crystals of potassium imido nitrido polytungstate(VI) ($K_{14}W_6N_{16}NH$) were obtained by the reaction of tungsten powder with an excess of KNH_2 in autoclaves at 600 °C for 6 days. The structure of this compound was determined from X-ray single-crystal data: space group, *Pbcm*; $Z=4$, $a=9.738(3)$ Å, $b=12.527(4)$ Å, $c=24.04(1)$ Å; $R/R_w=0.044/0.053$, with $N(F_o^2)\geqslant 3\sigma(F_o^2)=1784$, $N_{var}=134$. $K_{14}W_6N_{16}NH$ contains corner-sharing nitrogen tetrahedra around tungsten — $[WN_2N_{2/2}]$ — which are linked together in six-membered rings in boat form. These rings are connected to each other in para-positions via imide groups — NH^{2-} — to waved ropes which run along the *b* axis.

1. Introduction

Several attempts have been made to prepare ternary nitrides of group VI transition metals with heavy alkali metals, using metal oxides and alkali metal amides as starting materials. In contrast to group V transition metals [1], this synthesis in the case of group VI metals leads to quaternary oxonitrides [2, 3].

Therefore, we chose the metal powder of Mo and W as the starting material to exclude oxygen. Reactions in sodium amide melts produced two new nitrogen compounds, *i.e.* Na_3MoN_3 and Na_3WN_3 [4]. Here, we present the results we obtained by applying this synthesis to the appropriate reaction of tungsten powder and KNH_2.

2. Experimental details

KNH_2 was obtained by the reaction of potassium metal (J.T. Baker, Chem. Co., Phillipsburg, "purified") with NH_3 (Messer-Griesheim, 99.999%) in an autoclave [5].

The high oxidation sensitivity of ternary nitrides of the group VI transition metals requires handling in a glove box under an argon atmosphere [5], and a special treatment of the tungsten powder (Ventron, 99.98%). It was heated in flowing H_2 to 950 °C [6], in order to remove traces of oxygen. By the reaction of this reduced tungsten powder with an excess of KNH_2 (molar ratio, 1:6) at 600 °C for 6 days in autoclaves (to prevent early decomposition of KNH_2 to potassium, N_2 and H_2), we obtained crystals of the imido nitrido polytungstate (VI) up to several millimetres in size, which were embedded in the potassium metal formed by the thermal decomposition of the amide. (We believe the high N_2 pressure in the autoclave caused by the decomposition of the amide probably favours the formation of the ternary nitrogen compound.)

At temperatures below 600 °C, no reaction takes place. The product is highly insoluble in liquid ammonia but reacts within seconds in moist air to form K_2WO_4. Therefore, we cleaned the product by washing with liquid ammonia at room temperature to remove the potassium metal.

Guinier powder diagrams recorded with Cu Kα_1 radiation using silicon [7] as an internal calibration standard show that other not yet identified products are present, but $K_{14}W_6N_{16}NH$ is the main product. Some of the crystals clearly show twinning (see Fig. 1). Thus, suitable single crystals were chosen by making precession photographs (Mo Kα). The interpretation of the diffraction patterns gave *Pbcm* as the space group.

Intensity data for $K_{14}W_6N_{16}NH$ were collected on a modified Hilger & Watts Y290 diffractometer [8]. The structure was determined by interpretation of a Patterson map. Subsequent calculations were carried out using the SHELXTL software package [9]. The refinement of the anisotropic thermal displacement parameters was successful only for the cations. The highest peak in

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Fig. 1. Scanning electron microscopy image of crystals of $K_{14}W_6N_{16}NH$.

TABLE 1. Data characterizing X-ray structure determination on $K_{14}W_6N_{16}NH$

a (Å)	9.738(3)
b (Å)	12.527(4)
c (Å)	24.04(1)
Volume (Å^3)	2932.5
ρ_x (g cm^{-3})	4.282
Z	4
Space group	*Pbcm* (no. 57)
Radiation	Mo Kα_1
Monochromator	graphite
Crystal dimension (mm)	0.50×0.26×0.15
$1/\mu$ (mm) Transmission	0.037
Measuring range (deg.)	$2 \leqslant \theta \leqslant 30$
h, k, l	0+11, ±18, ±34
Absorption correction	DIFABS
F_o (asymm. unit)	4234
$F_o^2 \geqslant 3\sigma(F_o^2)$	1784
$N_{var.}$	134
R_{int}.	0.058 (after DIFABS)
R_u/R_w ($w=1$)	0.044/0.053
Residual electron density (e/Å^{-3})	2.1

the Fourier difference map which is assigned to an anion has to be interpreted (see below) as a divalent anion (NH^{2-}) with respect to the entire negative charge of the polyanion.

Experimental details, and the positional and thermal parameters are summarized in Tables 1–3.

TABLE 2. Atomic coordinates and isotropic thermal displacement parameters (Å^2) for $K_{14}W_6N_{16}NH$ (standard deviation)

Atom	Position	x	y	z	B
W(1)	4d	0.3890(1)	0.4925(1)	1/4	0.65(3)
W(2)	4d	0.0819(2)	0.6804(1)	1/4	0.73(3)
W(3)	8e	0.0828(1)	0.16015(8)	0.10879(5)	0.71(2)
W(4)	8e	0.3820(1)	0.35770(8)	0.10894(5)	0.70(2)
K(1)	4d	0.261(1)	0.2209(8)	1/4	2.5(3)
K(2)	4d	0.575(1)	0.2626(8)	1/4	5.7(6)
K(3)	8e	0.7196(7)	0.1399(6)	0.3718(3)	2.0(2)
K(4)	8e	0.0814(7)	0.1047(5)	0.5302(3)	1.6(1)
K(5)	8e	0.2475(7)	0.6314(6)	0.5218(3)	1.9(2)
K(6)	8e	0.4179(7)	0.1093(6)	0.4564(3)	2.2(2)
K(7)	8e	0.0448(8)	0.0814(7)	0.6716(3)	2.2(2)
K(8)	8e	0.6951(8)	0.0421(7)	0.6684(3)	2.6(2)
N(NH)	4d	0.239(4)	0.592(3)	1/4	1.1(6)
N(1)	4d	0.458(4)	0.068(3)	1/4	1.5(6)
N(2)	4d	0.144(4)	0.818(3)	1/4	1.6(6)
N(3)	8e	0.233(2)	0.257(2)	0.399(1)	1.1(4)
N(4)	8e	0.021(2)	0.155(2)	0.315(1)	1.6(4)
N(5)	8e	0.543(3)	0.297(2)	0.407(1)	1.9(5)
N(6)	8e	0.134(2)	0.027(2)	0.416(1)	1.4(4)
N(7)	8e	0.347(2)	0.469(2)	0.437(1)	1.5(4)
N(8)	8e	0.055(3)	0.707(2)	0.434(1)	1.9(5)
N(9)	8e	0.385(3)	0.405(2)	0.314(1)	1.7(4)

TABLE 3. Anisotropic thermal displacement parameters $U_{ij} \times 10^3$ Å^2 of tungsten and potassium in $K_{14}W_6N_{16}NH$ (standard deviation)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	7.7(7)	8.6(7)	8.4(7)	0.8(6)	0	0
W(2)	8.6(7)	10.9(7)	8.1(7)	2.8(5)	0	0
W(3)	9.7(5)	9.4(5)	7.8(5)	−0.6(4)	0.9(4)	0.2(4)
W(4)	9.8(5)	8.5(4)	8.1(5)	−1.1(4)	0.4(4)	−1.4(4)
K(1)	14(5)	16(5)	66(9)	1(4)	0	0
K(2)	14(5)	6(5)	198(21)	0(4)	0	0
K(3)	25(3)	23(3)	27(3)	−4(3)	8(3)	−14(3)
K(4)	21(3)	24(3)	16(3)	−4(3)	−5(3)	−5(3)
K(5)	30(4)	16(3)	25(3)	−5(3)	−3(3)	4(3)
K(6)	21(3)	24(4)	39(4)	3(3)	7(3)	18(3)
K(7)	29(4)	26(4)	30(4)	−5(3)	6(3)	−1(3)
K(8)	27(4)	46(5)	24(4)	7(3)	9(3)	3(4)

3. Discussion

The anionic partial structure in $K_{14}W_6N_{16}NH$ consists of corner-sharing nitrogen tetrahedra around tungsten – $[WN_2N_{2/2}]$ – which are connected to highly condensed units similar to those in Na_3MoN_3 and Na_3WN_3 [4]. In $K_{14}W_6N_{16}NH$, the $[WN_2N_{2/2}]$ tetrahedra build six-membered rings which approximately exhibit a boat configuration (see Fig. 2). These rings are linked together in para-position by NH groups and the configurations of the individual rings cause peculiar waved ropes which run one-dimensionally along the b axis (see Fig. 3). The polyanions are connected three-dimensionally via potassium ions.

Liebau [10] gave a structural classification concept for silicates. Applying this principle to $K_{14}W_6N_{16}NH$, this compound represents an imido nitrido monopoly tungstate (VI) with loop-branched single chains. Pellyite [11], *i.e.* $CaBa_2(Fe,Mg)_2Si_6O_{17}$, is an example of a structural correspondence in silicate chemistry.

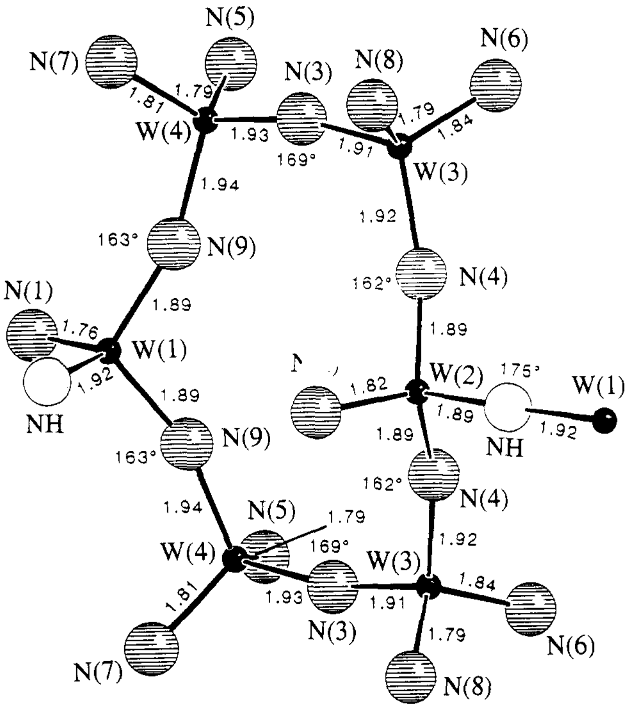

Fig. 2. Six-membered ring built of corner-sharing nitrogen tetrahedra around tungsten – $[WN_2N_{2/2}]$ – in $K_{14}W_6N_{16}NH$.

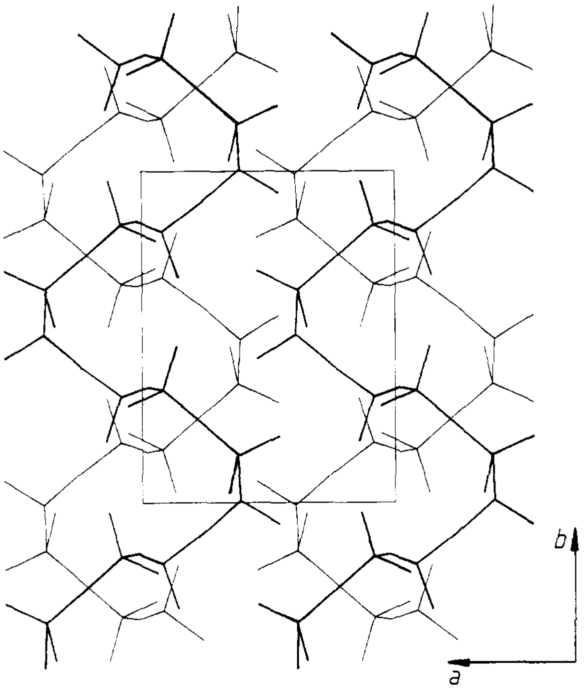

Fig. 4. Arrangement of the six-membered ring chains in one unit cell of $K_{14}W_6N_{16}NH$ (chains of different height in direction [001] are marked by the width of scratch).

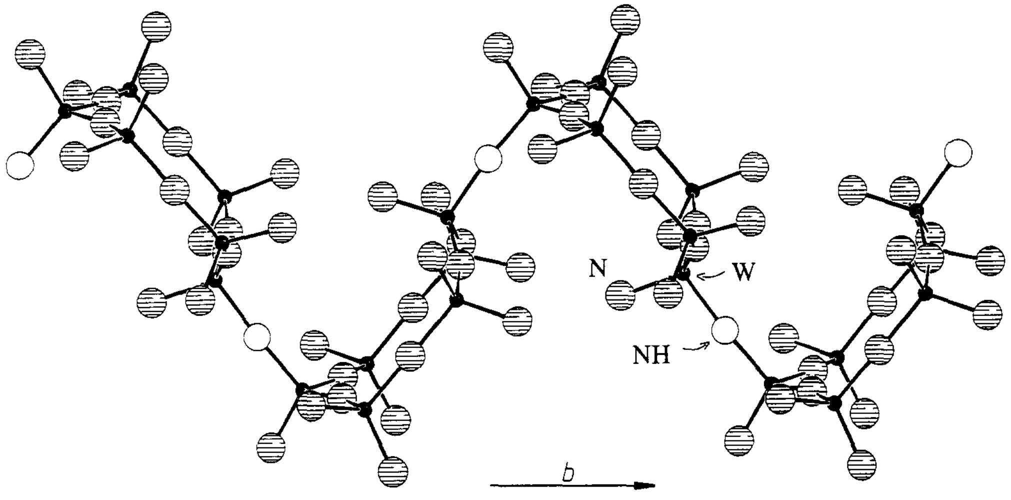

Fig. 3. Waved rope of $[WN_2N_{2/2}]$ tetrahedra in $K_{14}W_6N_{16}NH$.

The arrangement of the polyanion ropes in one unit cell is shown in Fig. 4. Four polyanion chains run through the unit cell in two different planes. In this way, layers of wrinkled polyanion ropes occur, which are stacked together along the *c* axis. In Fig. 5, a projection of the structure shows that the anion planes are linked to each other via layers of K^+, which explains reasonably the easy cleavage perpendicular to the direction [001].

The average distance W–N of 1.87 Å is in the same range as that in Na_3MoN_3 and Na_3WN_3 [4]. The shorter distances to the N terminal (on average, 0.1 Å) indicate π-interactions. The bond lengths and angles are summarized in Table 4.

The highest peak in the Fourier difference map which can be assigned to an anion has to be considered as a two-valent particle with respect to the entire negative charge of the polyanion. This two-valent anion is located in the bridging position between two six-membered rings. First, we considered oxygen in this position; however, the occurrence of such amounts of oxygen in this compound is not very probable, because

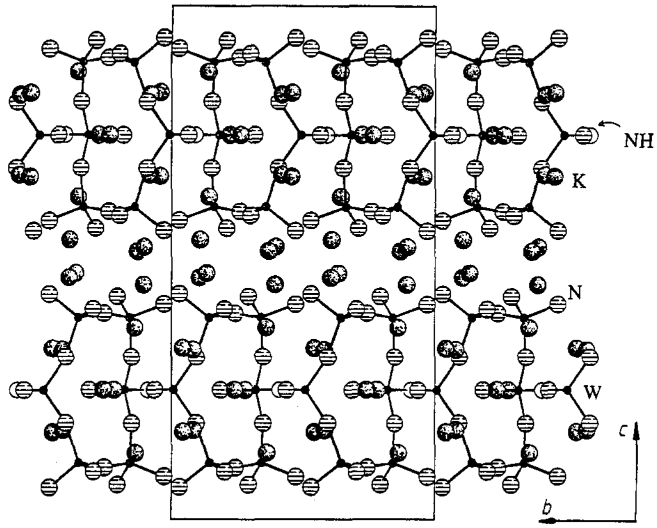

Fig. 5. Projection in direction [100] of the structure of $K_{14}W_6N_{16}NH$.

TABLE 4. Some relevant bond lengths (Å) and angles (deg.) in $K_{14}W_6N_{16}NH$

W(1)–N(1)		1.76(4)	W(3)–N(8)		1.79(3)
N(9)	2×	1.89(3)	N(6)		1.84(2)
N(NH)		1.92(3)	N(3)		1.91(2)
K	$\geqslant$	3.40(1)	N(4)		1.92(3)
W	$\geqslant$	3.789(1)	K	$\geqslant$	3.412(7)
			W	$\geqslant$	3.763(1)
W(2)–N(2)		1.82(4)	W(4)–N(5)		1.79(1)
N(NH)		1.89(3)	N(7)		1.81(1)
N(4)	2×	1.89(2)	N(3)		1.93(2)
K	$\geqslant$	3.38(1)	N(9)		1.94(3)
W	$\geqslant$	3.763(1)	K	$\geqslant$	3.504(7)
			W	$\geqslant$	3.789(1)
K(1)–N(1)		2.71(4)	K(5)–N(6)		2.72(3)
N(4)	2×	2.94(3)	N(5)		2.81(3)
N(9)	2×	3.03(3)	N(8)		2.96(3)
K	$\geqslant$	3.09(1)	N(8)		2.97(3)
W	$\geqslant$	3.38(1)	N(7)		3.04(3)
N(3)	2×	3.61(2)	K	$\geqslant$	3.15(1)
K(2)–N(1)		2.69(4)	K(6)–N(7)		2.82(3)
N(NH)		2.80(4)	N(5)		2.91(3)
N(2)		2.83(4)	N(7)		2.92(3)
N(9)	2×	3.00(3)	N(3)		2.93(2)
K	$\geqslant$	3.09(1)	N(6)		3.11(3)
W	$\geqslant$	3.40(1)	K	$\geqslant$	3.48(1)
N(5)	2×	3.81(3)	W	$\geqslant$	3.504(7)
N(1)		3.83(4)	N(5)		3.70(3)
K(3)–N(7)		2.74(3)	K(7)–N(2)		2.92(3)
N(5)		2.75(3)	N(4)		3.04(3)
N(8)		2.78(3)	N(6)		3.05(3)
N(NH)		3.01(1)	N(3)		3.21(2)
N(4)		3.24(3)	N(4)		3.33(3)
N(9)		3.41(3)	N(9)		3.34(3)
W	$\geqslant$	3.545(7)	K	$\geqslant$	3.43(1)
K	$\geqslant$	3.60(1)	N(NH)		3.45(3)
N(2)		3.91(3)	W	$\geqslant$	3.492(8)
N(1)		3.99(3)	N(8)		3.80(3)
			N(7)		3.99(3)
K(4)–N(8)		2.85(3)	K(8)–N(6)		2.76(3)
N(3)		2.85(2)	N(1)		2.82(3)
N(7)		2.86(3)	N(2)		3.07(3)
N(6)		2.96(3)	N(5)		3.09(3)
N(8)		2.96(3)	N(9)		3.12(1)
N(6)		2.97(3)	K	$\geqslant$	3.35(1)
K	$\geqslant$	3.23(1)	W	$\geqslant$	3.593(8)
W	$\geqslant$	3.412(7)	N(4)		3.72(3)
N(3)		3.98(2)			
N(1)–W(1)–N(9)		109(1)	N(5)–W(4)–N(7)		111(1)
N(1)–W(1)–N(9)		109(1)	N(5)–W(4)–N(3)		111(1)
N(1)–W(1)–N(NH)		107(2)	N(5)–W(4)–N(9)		109(1)
N(9)–W(1)–N(9)		109(1)	N(7)–W(4)–N(3)		108(1)
N(9)–W(1)–N(NH)	2×	111.1(9)	N(7)–W(4)–N(9)		111(1)
			N(3)–W(4)–N(9)		108(1)
N(2)–W(2)–N(NH)		106(2)			
N(2)–W(2)–N(4)	2×	110(1)	W(2)–N(NH)–W(1)		175(2)
N(NH)–W(2)–N(4)	2×	109.3(9)	W(3)–N(3)–W(4)		169(1)
N(4)–W(2)–N(4)		112(1)	W(2)–N(4)–W(3)		162(2)
N(8)–W(3)–N(6)		108(1)	W(1)–N(9)–W(4)		163(2)
N(8)–W(3)–N(3)		109(1)			
N(8)–W(3)–N(4)		109(1)			
N(6)–W(3)–N(3)		110(1)			
N(6)–W(3)–N(4)		111(1)			
N(3)–W(3)–N(1)		111(1)			

$K_{14}W_6N_{16}NH$ is the main product of the reaction. It is possible that the decomposition of the amide is not yet complete at 600 °C, and an NH^{2-} group is located in the bridging position. Even so, the angle W–NH–W of 175° is somewhat unexpected for bridging imide groups.

4. Concluding remarks

Powders of molybdenum and tungsten react in melts of $NaNH_2$ and KNH_2 to give ternary nitrido metallates. To reach temperatures of about 600 °C, autoclaves are used as containers. They prevent early decomposition of the amides used. The amides decompose to alkali metals, nitrogen and hydrogen. While hydrogen diffuses through the material from which the autoclaves are manufactured, the N_2 partial pressure rises. Therefore, the formation of ternary nitrides is favoured. After the reaction is carried out, the ternary nitrides are embedded in the corresponding solid alkali metal. The product is washed with liquid ammonia. In the nitrides, the transition metals have the oxidation state +6. The compounds are diamagnetic substances and are deep red and yellow (Na_3WN_3) in colour. They react vigorously with moisture giving the corresponding oxometallates.

Ternary nitrides with sodium – Na_3MoN_3 and Na_3WN_3 [4] – contain in their structures one-dimensional infinite chains of corner-sharing $[MN_2N_{2/2}]$ tetrahedra. The degree of condensation in polyanions increases from sodium to potassium compounds. Some examples of ternary transition metal nitrides of group six with $[MN_4]$-units have been published [12, 13]. The only further compound with a dianion is $LiBa[Mo_2N_7]$

[14]. The tendency for an increasing degree of condensation going from sodium to potassium compounds is also observed by us for oxonitrido metallates [2, 3], alkali metal nitrido tantalates [1] and niobates [15, 16].

Acknowledgments

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