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$Cs_5[Na\{W_4N_{10}\}]$: The First Framework Nitridotungstate(VI)

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Abstract. $Cs_5[Na\{W_4N_{10}\}]$ was prepared from a mixture of $NaNH_2$, $CsNH_2$ and tungsten powder (molar ratio 1 : 10 : 4) at 700 °C in autoclaves. After the reaction is finished the nitride is embedded in an alkali metal matrix. Dark red crystals were isolated by washing out the alkali metal with liquid ammonia at room temperature. The structure of $Cs_5[Na\{W_4N_{10}\}]$ was solved by X-ray single crystal data: $I4_1$ (No. 80), Z = 4, a = 13.926(3) Å, c = 8.723(3) Å, $Z(F_o^2) \geq 3\sigma(F_o^2) = 1535$, Z(Variables) = 63, $R/R_w = 0.040/0.052$.

The compound is highly sensitive against moisture giving oxotungstates and ammonia. It contains a framework of tetrahedra ${}^{3}_{\infty}[WNN_{3/2}{}^{1.5-}]$. Sodium shares four terminal nitrogen ligands. Including sodium a distorted, β-cristobalite type arrangement ${}^{3}_{\infty}[Na\{W_4N_{10}\}^{5-}]$ results. It contains caesium in all interstices formed by twelve nitrogen ligands in so-called *Friauf* polyhedra.

Keywords: Penta caesium sodium nitrido tetra tungstate(VI); synthesis; crystal structure

$Cs_5[Na\{W_4N_{10}\}]$: Das erste Nitridowolframat(VI) mit Gerüststruktur

Inhaltsübersicht. $Cs_5[Na\{W_4N_{10}\}]$ wurde aus einem Gemenge von $NaNH_2$, $CsNH_2$ und Wolframpulver (Molverhältnis 1 : 10 : 4) bei 700 °C in Autoklaven dargestellt. Nach beendeter Reaktion ist das Nitrid in einer Alkalimetallmatrix eingebettet. Dunkelrote Kristalle werden durch Auswaschen des Alkalimetalls mit flüssigem Ammoniak bei Raumteperatur isoliert. Die Struktur von $Cs_5[Na\{W_4N_{10}\}]$ wurde über Röntgeneinkristalldaten bestimmt: $I4_1$ (Nr. 80), Z = 4, a = 13,926(3) Å, c = 8,723(3) Å, $Z(F_o^2) \geq 3\sigma(F_o^2) = 1535$, Z(Variable) = 63, $R/R_w = 0{,}040/0{,}052$.

An feuchter Luft hydrolysiert die Verbindung schnell zu Oxowolframat und Ammoniak. Sie enthält ein Tetraedergerüst ${}^{3}_{\infty}[WNN_{3/2}{}^{1,5-}]$. Natrium ist von vier terminalen Stickstoffliganden umgeben. Einschließlich des Natriums ergibt sich eine Anordnung vom β-Cristobalittyp ${}^{3}_{\infty}[Na\{W_4N_{10}\}^{5-}]$. Dieses enthält Caesium in allen Lücken, sogenannten *Friauf*-Polyedern, die durch zwölf Stickstoffliganden gebildet werden.

Introduction

In all hitherto known alkali metal nitridotungstates(VI) the transition metal is co-ordinated tetrahedrally by nitrogen. With small alkali metal cations as in $Li_6[WN_4]$ [1] isolated nitrido-tungstate ions $[WN_4]^{6-}$ occur in the structure. In the sodium rich compounds $Na_3[WN_3]$ [2], $Na_2K[WN_3]$, $Na_{11}Rb[(WN_3)_4]$ [3] and $Na_5A[(WN_3)_2]$ (A = Rb, Cs) [4] infinite chains of corner sharing tetrahedra ${}^{1}_{\infty}[WN_2N_{2/2}{}^{3-}]$ were found. The anionic partial structures of the nitrido-metalate ions are closely related to that known from silicates. Now we thought about realising a higher degree of condensation in nitridotungstates. Increasing amounts of the heavier alkali metals should favour the condensation. With $Cs_5[Na\{W_4N_{10}\}]$ we prepared the first nitrido tecto tungstate(VI).

Preparation

Alkali metal nitridotungstates(VI) have been prepared by the reaction of mixtures of alkali metal amides with tungsten powder in autoclaves for salt melts (inconel 625, no. 2.4856) and excess amounts of alkali metal amides. At temperatures above 600 °C the amides decompose even in the autoclaves to alkali metal, nitrogen and hydrogen. The hydrogen leaves the autoclave through a nickel membrane while the nitrogen pressure rises up to about 1 Kbar. After the reaction is carried out the nitride is embedded in an alkali metal matrix. The alkali metal is washed out with liquid ammonia at room-temperature in a H-tube with stop cocks (Young, London) in order to isolate the nitrides.

$Cs_5[Na\{W_4N_{10}\}]$ was initially observed in products of the reaction of a mixture of $NaNH_2$, KNH_2 and $CsNH_2$ (from Na, 99.9% Merck, Darmstadt, K, 98% Fluka, Neu-Ulm, Cs, Merck, Darmstadt, destillated over calcium and NH_3, 99.999% Air Liquide, Düsseldorf under conditions previously given in [2]) with tungsten powder (99.999%, Johnson Matthey, Karlsruhe) in a molar ratio of 2 : 3 : 3 : 1 at 650 °C. But the main product was $Na_2K[WN_3]$ [3]. $Cs_5[Na\{W_4N_{10}\}]$ was prepared as the main product from a mixture of $NaNH_2$, $CsNH_2$ and tungsten powder (1 : 10 : 4) at 700 °C within 4 days. The Guinier diagram still shows reflections of other, not yet identified products.

$Cs_5[Na\{W_4N_{10}\}]$ forms small dark red crystals with nearly octahedral habit. Like all other known compounds of this class it is very sensitive against moist air, giving oxometalates(VI) and ammonia. For X-ray investigations crystals were sealed in glass capillaries (Fa. Müller, Berlin).

X-ray investigations

$Cs_5[Na\{W_4N_{10}\}]$ crystallises with a tetragonal unit cell as elucidated by precession photographs (MoKα). Intensity data was collected on a four circle diffractometer CAD4 DT (Enraf Nonius, Delft, NL) with AgKα radiation. The observed reflection conditions led to the space group $I4_1/a$ (No. 88). Structure calculations (SDP system of programs, Enraf-Nonius, Delft, NL) in this space group result for some nitrogen atoms in split positions. Symmetry reduction led to the translation equivalent subgroups I2/a (C2/c, No. 15), $I\bar{4}$ (No. 82) and $I4_1$ (No. 80). Only the calculations in the space group $I4_1$ revealed independent positions for each atom. Table 1 gives technical and crystallographic data concerning the structure determination. Table 2 and 3 contain positional parameters, isotropic and anisotropic thermal displacement parameters. The data set did not allow to distinguish between the enantiomeres.

Table 1 Technical and crystallographic data concerning the structure determination on $Cs_5[Na\{W_4N_{10}\}]$

Crystall size [mm³]	0.075×0.1×0.125 dark red octahedra
Cell parameter a [Å]	13.926(3)
c [Å]	8.723(3)
Volume [Å³]	1691.5(8)
D_x [g cm⁻³]	6.138
Z	4
Spacegroup	$I\,4_1$ (No. 80)
Radiation	Ag Kα
$1/\mu_{(AgK\alpha)}$ [mm]	0.049
Absorption correction	empirical (ψ-scan)
Minium transmission	68%
Scan mode	$\Omega/2\theta$
Monochromator	graphite
$\theta_{min, max}$ [deg]	3, 27
h, k, l	±22, +22, −14 − +4
Independent reflections	2736
$F_o^2 \geq 3\sigma F_o^2$	1535
Variables	63
R_{int}	0.028
$R/R_{w(w=1)}/R_{(all\ reflections)}$	0.040/0.052/0.076
Largest peak in final electron difference map [Å⁻³]	2.2

Table 2 Atomic coordinates and isotropic thermal displacement parameters B [Å²] for $Cs_5[Na\{W_4N_{10}\}]$

size	atom	x	y	z	B [Å²]
8b	W(1)	0.20887(8)	0.10399(8)	0.279	0.87(1)
8b	W(2)	0.39518(8)	0.70656(7)	0.2505(1)	0.83(1)
8b	Cs(1)	0.0994(2)	0.3237(2)	0.0558(4)	2.64(5)
8b	Cs(2)	0.0988(2)	0.8110(1)	0.2328(3)	1.62(3)
4a	Cs(3)	1/2	0	0.2527(5)	1.38(4)
4a	Na(1)	0	0	0.000(3)	1.2(2)
8b	N(1)	0.102(2)	0.093(2)	0.157(4)	2.1(5)
8b	N(2)	0.133(2)	0.537(2)	0.132(4)	2.2(5)
8b	N(3)	0.299(2)	0.180(2)	0.172(4)	2.0(5)
8b	N(4)	0.315(2)	0.633(2)	0.125(4)	2.1(5)
8b	N(5)	0.480(2)	0.771(2)	0.121(4)	2.2(5)

Table 3 Anisotropic thermal displacement parameters U_{ij} [10³ Å²] for $Cs_5[Na\{W_4N_{10}\}]$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	13.2(3)	6.7(3)	13.3(4)	−0.8(4)	5.5(4)	1.3(4)
W(2)	9.3(3)	9.0(3)	13.2(4)	−2.0(4)	−0.7(4)	1.7(4)
Cs(1)	31(1)	26.7(9)	43(2)	1(1)	4(1)	11(1)
Cs(2)	23.5(8)	18.5(7)	19.5(9)	0.8(7)	−5(1)	−0.5(8)
Cs(3)	18.8(9)	26(1)	8(1)	−2(2)	0	0

Discussion

In $Cs_5[Na\{W_4N_{10}\}]$ each tungsten atom is connected to one terminal and three bridging nitrogen atoms. This leads to a three-dimensional framework $^3_\infty[WNN_{3/2}{}^{1.5-}]$. Following the nomenclature for three-dimensional nets of Wells [5] the resulting network has to be assigned as the uniform net (10,3)d. It can be described by spiral chains

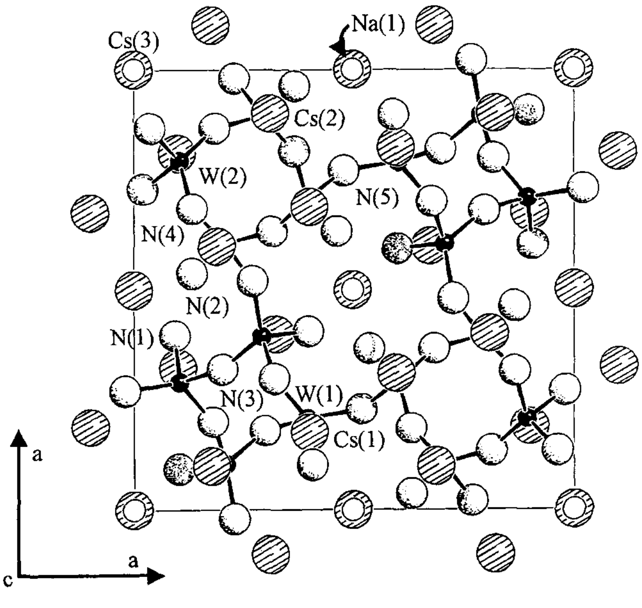

Fig. 1 Projection of the unit cell of $Cs_5[Na\{W_4N_{10}\}]$ parallel to the c-axis

Table 4 Selected distances [Å] and angles [deg] in $\mathrm{Cs_5[Na\{W_4N_{10}\}]}$

W(1)—N(1)	1.83(3)	W(2)—N(2)	1.80(3)
N(3)	1.88(3)	N(5)	1.86(3)
N(3)	1.89(3)	N(4)	1.87(3)
N(5)	1.93(3)	N(4)	1.90(3)

∅ W—N$_{\mathrm{terminal}}$	1.82
∅ W—N$_{\mathrm{bridging}}$	1.89

∢N(1)—W(1)—N(3)	105(1)	∢N(2)—W(2)—N(5)	109(1)
∢N(1)—W(1)—N(3)	107(1)	∢N(2)—W(2)—N(4)	112(1)
∢N(1)—W(1)—N(5)	107(1)	∢N(2)—W(2)—N(4)	101(2)
∢N(5)—W(1)—N(3)	113(1)	∢N(5)—W(2)—N(4)	96(1)
∢N(5)—W(1)—N(3)	128(1)	∢N(5)—W(2)—N(4)	107(1)
∢N(3)—W(1)—N(3)	94(1)	∢N(4)—W(2)—N(4)	130(1)

∢W(1)—N(3)—W(1)	158(2)
∢W(2)—N(4)—W(2)	157(2)
∢W(1)—N(5)—W(2)	153(2)

∢W(1)—N(1)—Na(1)	151(2)
∢W(1)—N(2)—Na(1)	155(2)

Cs(1)—N(2)	3.09(3)	Cs(2)—N(1)	3.18(3)
N(1)	3.24(4)	N(5)	3.21(3)
N(3)	3.31(3)	N(2)	3.27(4)
N(1)	3.33(3)	N(4)	3.61(3)
N(3)	3.58(3)	N(4)	3.71(4)
N(4)	3.60(3)	N(5)	3.74(4)
N(2)	3.60(3)	N(2)	3.94(3)
N(3)	3.63(4)	N(4)	3.94(3)
N(3)	3.80(3)	N(1)	3.98(3)
N(2)	3.83(3)	N(4)	4.01(3)
N(5)	3.97(3)	N(3)	4.22(3)
N(5)	4.20(4)	N(1)	4.23(3)

Cs(3)—N(4) 2×	3.35(3)	Na(1)—N(2) 2×	2.18(4)
N(5) 2×	3.40(3)	N(1) 2×	2.37(4)
N(1) 2×	3.58(4)		
N(3) 2×	3.82(3)		
N(2) 2×	3.83(4)		
N(5) 2×	3.92(3)		

N(1)— W(1)	1.83(3)	N(2)—W(2)	1.80(3)
Na(1)	2.37(4)	Na(1)	2.18(4)
Cs(2)	3.18(3)	Cs(1)	3.09(3)
Cs(1)	3.24(4)	Cs(2)	3.27(4)
Cs(1)	3.33(3)	Cs(1)	3.60(3)
Cs(3)	3.58(4)	Cs(3)	3.83(4)
Cs(2)	3.98(3)	Cs(1)	3.83(3)
Cs(2)	4.23(3)	Cs(2)	3.94(3)

N(3)— W(1)	1.88(3)	N(4)—W(2)	1.87(3)
W(2)	1.89(3)	W(2)	1.90(3)
Cs(1)	3.31(3)	Cs(3)	3.35(3)
Cs(1)	3.58(3)	Cs(1)	3.60(3)
Cs(1)	3.63(4)	Cs(2)	3.61(3)
Cs(1)	3.80(3)	Cs(2)	3.71(3)
Cs(3)	3.82(3)	Cs(2)	3.94(3)
Cs(2)	4.22(3)	Cs(2)	4.01(3)

Table 4 (Continued)

N(5)— W(2)	1.86(3)		
W(1)	1.93(3)		
Cs(2)	3.21(3)	W—W	≥3.685(2)
Cs(3)	3.40(3)	W—Cs	≥3.738(3)
Cs(2)	3.74(4)	W—Na	≥3.89(1)
Cs(3)	3.92(3)	Cs—Cs	≥3.677(3)
Cs(1)	3.97(3)	Cs—Na	≥3.29(1)
Cs(1)	4.20(4)	N—N	≥2.76(5)

with a periodicity of four running parallel the c-axis. These chains are connected via nitrogen atoms giving a three-dimensional framework. The nitridotungstate anionic partial structure is also known from the synthetic silicate $\mathrm{K_2Ce[Si_6O_{15}]}$ [6]. Figure 1 shows a projection of the unit cell of $\mathrm{Cs_5[Na\{W_4N_{10}\}]}$ parallel to the c-axis.

Bridging nitrogen atoms are co-ordinated by two tungsten and six caesium atoms. Distances are given in Table 4. In contrast to bridging nitrogen atoms the co-ordination sphere of the terminal nitrogen atoms has close contacts to sodium atoms. Sodium is tetrahedrally surrounded only by four terminal nitrogen atoms. This can be seen as if sodium atoms overtake the function of tungsten atoms. A three-dimensional nitrido sodio tungstate(VI) framework $^3_\infty[\mathrm{Na\{W_4N_{10}\}^{5-}}]$ results. Examples of similar frameworks with alkali metals are known e.g. from litho silicates $\mathrm{Li_5Rb\{Li[SiO_4]\}_2}$ [7], $\mathrm{CsKNaLi_9\{Li[SiO_4]\}_4}$, $\mathrm{CsKNa_2Li_8\{Li[SiO_4]\}_4}$, $\mathrm{RbNa_3Li_8 \cdot Li_8\{SiO_4]\}_4}$ and $\mathrm{RbNaLi_4\{Li[SiO_4]\}_2}$ [8]. This special view of the function of the sodium atoms in the title compound is motivated by unusually short distances between sodium and nitrogen of $\bar{d}(\mathrm{Na—N}) = 2.28$ Å (Table 4).

The resulting framework of $^3_\infty[\mathrm{Na\{W_4N_{10}\}^{5-}}]$ shows the motif of a distorted β-cristobalite type structure. Caesium atoms fill up all the interstices in this framework. Twelve nitrogen ligands form *Friauf* polyhedra around Cs (Figure 2). This type of structure is known

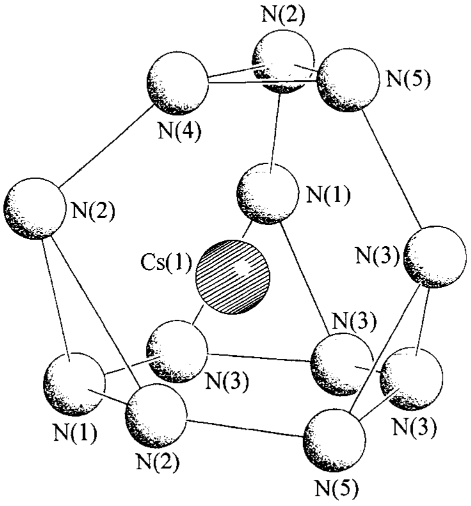

Fig. 2 *Friauf* polyhedra out of nitrogen around a caesium atom in $\mathrm{Cs_5[Na\{W_4N_{10}\}]}$. For distances see Table 4.

from the caesium nitridometalates(V) of niobium and tantalum, Cs[MN_2] (M = Nb, Ta) [9, 10], too. These compounds realise cubic filled up β-cristobalite type structures while the respective potassium and rubidium compounds [10] show slight orthorhombic distortions.

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