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$Na_5Rb[(WN_3)_2]$ and $Na_5Cs[(WN_3)_2]$, two new sodium nitrido tungstates(VI) with the heavier alkali metals rubidium and cesium

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Abstract

Alkali metal amides react above 600°C with tungsten powder in autoclaves to form nitrido tungstates(VI). Autoclaves are used for this type of reaction in order to avoid rapid decomposition of amides at relatively low temperatures to metal, nitrogen and hydrogen.

Starting with an excess of the corresponding mixtures of amides the compounds $Na_5Rb[(WN_3)_2]$ and $Na_5Cs[(WN_3)_2]$ were obtained. After the reaction is carried out the nitrido metallates(VI) are embedded in the alkali metal. Orange-brown (Rb) and orange (Cs) crystals were isolated by extracting the metals with liquid ammonia at room temperature.

The structures of the two compounds were determined by X-ray single crystal methods.

Space group $P2_1/c$ (No. 14), $Z = 8$.

$Na_5Rb[(WN_3)_2]$: $a = 9.355(2)$ Å, $b = 10.277(3)$ Å, $c = 19.165(3)$ Å, $\beta = 90.12(2)°$.

$Na_5Cs[(WN_3)_2]$: $a = 9.403(3)$ Å, $b = 10.236(2)$ Å, $c = 19.501(4)$ Å, $\beta = 90.01(2)°$.

The isotypic compounds contain infinite chains of corner sharing tetrahedra $^1_\infty[WN_2N^{3-}_{2/2}]$. These chains are linked together three dimensionally by sodium and the heavier alkali metal within each compound in a somewhat differing way.

Keywords: Sodium rubidium nitrido tungstate; Sodium cesium nitrido tungstate; Preparation; Crystal structure

1. Introduction

Some nitrido metallates of molybdenum and tungsten with alkali and alkaline earth metals have been known for a few years [1–9]. Recently we reported about the preparation and the crystal structures of $Na_3[MN_3]$ (M = Mo, W) [4,5], $K_{14}[W_6N_{16}NH]$ [6], $Na_2K[WN_3]$ and $Na_{11}Rb[(WN_3)_4]$ [10]. Their partial structures of nitrido metallate anions can be described as closely related to those of silicates. No further nitrido tungstates with the heavier alkali metals were known up to now. Here we deal with the preparation and the structures of the new compounds containing Rb and Cs, $Na_5Rb[(WN_3)_2]$ and $Na_5Cs[(WN_3)_2]$.

2. Preparation

Previous investigations revealed that molybdenum or tungsten powders react with excess alkali metal amides and mixtures of them to give ternary and quaternary nitrido metallates(VI) [4–6,10]. Tungsten powder (99.999%, Johnson Matthey, Karlsruhe) was added to mixtures of $NaNH_2$ and $RbNH_2$ or $CsNH_2$ (Na 99.9% from Merck, Darmstadt, Rb 99.8% from Johnson Matthey, Karlsruhe, Cs from Merck, Darmstadt, distilled over calcium with NH_3, 99.999% from Air Liquide, Düsseldorf under conditions previously given in Ref. [5]) in autoclaves for salt melts (Inconel 625, no. 2.4856) [6] and heated to 600°C for 5 days.

With the aim to synthesize, if possible, a neat cesium compound, the starting molar ratio chosen for $NaNH_2$:$CsNH_2$:W was 3:3:1. This allows the formation of a compound of composition $A_3[WN_3]$ for both alkali metals and ensures the formation of enough alkali metal by thermal decomposition of the residual amides serving as a matrix for the crystallization of the nitride. In the case of the rubidium compound we obtained $Na_{11}Rb[(WN_3)_4]$ [10] by using the same excess of both alkali metal amides. So we reduced the amount of sodium amide to a molar ratio of 5:7:2

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Fig. 1. Scanning electron microscopy image of a crystal conglomerate of $Na_5Cs[(WN_3)_2]$.

Table 1
Technical and crystallographic data concerning the structure determinations of $Na_5Rb[(WN_3)_2]$ and $Na_5Cs[(WN_3)_2]$

	$Na_5Rb[(WN_3)_2]$		$Na_5Cs[(WN_3)_2]$	
Crystal size (mm^3)	$0.1 \times 0.125 \times 0.175$		$0.1 \times 0.1 \times 0.45$	
	yellow-brown needle		orange transparent crystal	
Diffractometer	Guinier		Guinier	
Unit cell parameters (Å)				
a	9.355(2)	9.333(3)	9.403(3)	9.408(1)
b	10.277(3)	10.266(4)	10.236(2)	10.225(2)
c	19.165(5)	19.116(9)	19.501(4)	19.499(4)
β (deg)	90.12(2)	90.10(5)	90.01(2)	90.02(2)
Volume ($Å^3$)	1842.5	1831.5	1877.0	1874.3
D_x	4.70		4.95	
Z	8		8	
Space group	$P2_1/c$ (No. 14)		$P2_1/c$ (No. 14)	
Radiation	Ag Kα		Ag Kα	
$1/\mu$ (Ag Kα) (mm)	0.061		0.065	
Absorption correction	empirical (ψ-scan)		empirical (ψ-scan)	
Scan mode	$\Omega/2\Theta$		$\Omega/2\Theta$	
Monochromator	graphite		graphite	
$\Theta_{min,max}$ (deg)	3;25		3;27	
h, k, l	+14, +15, −28 to +16		±15, −16 to +8, +31	
F_o asym. unit	6553		8305	
$F_0 \geq 4\sigma F_o$	4042		6021	
Variables	254		194	
$R_{int}(F^2)$	0.040		0.054	
$R/R_{(all\ data)}$	0.041/0.079		0.066/0.094	
Largest peak in final electron density difference map ($Å^{-3}$)	8.7		21.9	
Twin ratio	0.0170(5)		0.374(2)	

($NaNH_2$:$RbNH_2$:W) to enhance the formation of the rubidium-rich compound $Na_5Rb[(WN_3)_2]$.

With rising temperatures the alkali amides decompose to the corresponding alkali metals, nitrogen and hydrogen. The hydrogen leaves the autoclaves through a nickel membrane while the nitrogen pressure rises up to about 1 kbar. After the reaction is carried out the excess alkali metal is washed out at room temperature with liquid ammonia in an H-tube with stopcocks (Young, London) in order to isolate the nitrides.

$Na_5Rb[(WN_3)_2]$ forms orange-brown needles which can easily be split into smaller ones, as was found for crystals of $Na_{11}Rb[(WN_3)_4]$ [10]. $Na_5Cs[(WN_3)_2]$ forms orange crystals with the shape shown in Fig. 1. Both compounds react vigorously with moist air giving alkali metal oxo tungstates(VI) and ammonia.

3. X-ray investigations

Precession photographs (Mo Kα) and Guinier patterns (Cu Kα_1) of both compounds fit with an orthorhombic unit cell. Only on precession photographs of $Na_5Rb[(WN_3)_2]$ was a slight deviation of intensities from orthorhombic symmetry observed. Intensity data was collected on a four circle diffractometer CAD 4 DT (Enraf Nonius, Delft, NL) with Ag Kα radiation. The reflection conditions observed for both compounds correspond to no possible orthorhombic space group. A slight but reproducible difference of one of the cell angles of $Na_5Rb[(WN_3)_2]$ from 90° with 90.1° and the large difference between the internal consistency R-values of measured intensities $R_{INT} = 0.040$ (monoclinic) instead of 0.270 (orthorhombic) led to a monoclinic unit cell and to the space group $P2_1/c$ (No. 14). The structure of $Na_5Rb[(WN_3)_2]$ was refined with the program system SHELXL-93 [11]. Analogous calculations for an isotypic structure of $Na_5Cs[(WN_3)_2]$ end with a reliability value of $R = 0.212$. The small difference in the internal R-values for the monoclinic ($R_{INT} = 0.054$) in comparison with the orthorhombic setting ($R_{INT} = 0.095$) hints to twins caused by merohedry. The structure was solved as a pseudo-merohedral twin to a final reliability value of $R = 0.066$. Table 1 gives technical and crystallographic data concerning the structure determinations. Tables 2–5 contain positional parameters, isotropic and anisotropic thermal parameters for both compounds.

The formation of twins by pseudo-merohedry in the case of the cesium compound may be favoured by the

Table 2
Atomic coordinates and isotropic thermal displacement parameters B for $Na_5Rb[(WN_3)_2]$, all atoms on site 4e

Atom	x	y	z	B (Å^2)
W(1)	0.07978(4)	0.23368(4)	0.28850(2)	0.419(7)
W(2)	0.17110(4)	0.23879(4)	0.09384(2)	0.415(7)
W(3)	0.57771(4)	0.25423(4)	0.08735(2)	0.436(7)
W(4)	0.67276(5)	0.23767(4)	0.28319(2)	0.438(7)
Rb(1)	0.1302(1)	0.7671(1)	0.04027(6)	1.40(2)
Rb(2)	0.3845(1)	0.2297(2)	0.41930(6)	1.65(2)
Na(1)	0.1084(8)	0.5097(6)	0.6820(3)	1.7(1)
Na(2)	0.12218(6)	0.8277(6)	0.3412(3)	1.21(8)
Na(3)	0.1259(7)	0.5020(5)	0.1809(4)	1.9(1)
Na(4)	0.1262(6)	0.0190(5)	0.4477(3)	1.09(8)
Na(5)	0.1310(6)	0.4892(5)	0.4407(3)	1.10(8)
Na(6)	0.3720(7)	0.0055(6)	0.2971(4)	2.1(1)
Na(7)	0.3788(6)	0.3307(6)	0.2161(3)	1.39(9)
Na(8)	0.3768(7)	0.4966(5)	0.0638(3)	1.39(9)
Na(9)	0.3816(6)	0.0023(5)	0.0630(3)	1.02(8)
Na(10)	0.6340(7)	0.0090(5)	0.1722(3)	1.28(9)
N(1)	0.074(1)	0.375(1)	0.0542(6)	1.6(2)
N(2)	0.110(1)	0.082(1)	0.0610(6)	1.7(2)
N(3)	0.122(1)	0.7532(9)	0.2058(5)	1.3(1)
N(4)	0.130(1)	0.074(1)	0.3220(5)	1.4(2)
N(5)	0.131(1)	0.251(1)	0.1923(5)	1.6(2)
N(6)	0.168(1)	0.366(1)	0.3345(6)	2.0(2)
N(7)	0.374(1)	0.260(1)	0.0814(5)	1.3(1)
N(8)	0.579(1)	0.369(1)	0.3271(6)	1.8(2)
N(9)	0.617(1)	0.078(1)	0.3153(6)	1.8(2)
N(10)	0.630(1)	0.258(1)	0.1856(5)	1.7(2)
N(11)	0.640(1)	0.105(1)	0.0484(5)	1.5(2)
N(12)	0.654(1)	0.396(1)	0.0437(7)	2.2(2)

Table 3
Atomic coordinates and isotropic thermal displacement parameters B for $Na_5Cs[(WN_3)_2]$, all atoms on site 4e

Atom	x	y	z	B (Å^2)
W(1)	0.07914(6)	0.23871(5)	0.28631(3)	0.387(8)
W(2)	0.17312(6)	0.24412(5)	0.09503(3)	0.401(8)
W(3)	0.57797(7)	0.25525(4)	0.08906(3)	0.442(9)
W(4)	0.67396(6)	0.24229(5)	0.28129(4)	0.425(8)
Cs(1)	0.1271(1)	0.7606(1)	0.04259(6)	1.15(2)
Cs(2)	0.3832(1)	0.2337(1)	0.41997(6)	1.25(2)
Na(1)	0.114(1)	0.5060(8)	0.6816(6)	2.4(2)
Na(2)	0.1204(9)	0.8316(7)	0.3409(4)	1.3(1)
Na(3)	0.1245(9)	0.5059(7)	0.1827(6)	1.6(2)
Na(4)	0.125(1)	0.0206(7)	0.4468(4)	1.2(1)
Na(5)	0.130(1)	0.4923(7)	0.4389(5)	1.4(1)
Na(6)	0.371(1)	0.0113(7)	0.2964(6)	2.2(2)
Na(7)	0.3790(8)	0.3347(7)	0.2155(5)	1.6(1)
Na(8)	0.375(1)	0.4971(6)	0.0640(4)	1.2(1)
Na(9)	0.3813(9)	0.0058(7)	0.0628(5)	1.1(1)
Na(10)	0.632(1)	0.0124(6)	0.1734(5)	1.3(1)
N(1)	0.082(1)	0.386(1)	0.0584(8)	1.1(2)
N(2)	0.107(1)	0.090(1)	0.0590(7)	0.6(2)
N(3)	0.123(1)	0.7538(8)	0.2104(6)	0.6(1)
N(4)	0.135(2)	0.081(1)	0.3221(7)	0.7(2)
N(5)	0.136(2)	0.249(1)	0.1917(9)	1.4(2)
N(6)	0.161(2)	0.374(1)	0.3312(8)	1.1(2)
N(7)	0.380(1)	0.264(1)	0.0836(7)	0.6(2)
N(8)	0.588(2)	0.380(1)	0.3238(8)	1.1(2)
N(9)	0.618(2)	0.083(1)	0.3149(8)	1.2(2)
N(10)	0.628(2)	0.258(1)	0.1852(8)	1.1(2)
N(11)	0.638(2)	0.104(1)	0.0498(8)	1.0(2)
N(12)	0.651(2)	0.397(2)	0.045(1)	1.7(3)

Table 4
Anisotropic thermal displacement parameters U_{ij} (10^3 Å^2) for $Na_5Rb[(WN_3)_2]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	3.0(2)	5.8(2)	7.1(2)	−0.4(1)	−0.5(1)	−0.3(1)
W(2)	2.8(2)	6.0(2)	7.0(2)	0.1(1)	−0.6(1)	0.1(1)
W(3)	2.7(2)	6.9(2)	7.0(2)	−0.3(1)	−1.0(1)	0.0(1)
W(4)	2.9(2)	6.2(2)	7.6(2)	0.0(1)	−0.9(1)	0.8(1)
Rb(1)	17.2(6)	20.3(5)	15.8(5)	−1.1(5)	2.3(4)	−0.6(4)
Rb(2)	17.7(6)	30.3(6)	14.5(5)	−0.6(5)	−0.5(4)	4.4(5)
Na(1)	40(4)	12(2)	14(3)	2(2)	0(2)	−2(2)
Na(2)	8(2)	21(3)	17(3)	0(2)	0(2)	−3(2)
Na(3)	11(3)	10(2)	52(4)	1(2)	6(3)	−6(2)
Na(4)	9(3)	16(2)	15(3)	−3(2)	2(2)	−4(2)
Na(5)	10(3)	19(2)	12(3)	0(2)	−2(2)	−3(2)
Na(6)	8(3)	13(2)	60(5)	0(2)	−2(3)	−14(3)
Na(7)	8(2)	20(3)	26(3)	2(2)	−3(2)	−4(2)
Na(8)	25(3)	11(2)	17(3)	3(2)	0(2)	2(2)
Na(9)	10(3)	13(2)	15(3)	1(2)	−5(2)	−3(2)
Na(10)	16(3)	8(2)	25(3)	−3(2)	−5(2)	−3(2)
N(1)	17(5)	21(5)	24(5)	7(4)	−3(4)	3(4)
N(2)	16(5)	21(4)	28(6)	−2(4)	−3(4)	5(4)
N(3)	3(3)	16(4)	29(5)	5(3)	−5(3)	−8(3)
N(4)	19(5)	16(4)	19(5)	5(4)	−5(4)	8(3)
N(5)	26(5)	22(5)	15(4)	4(4)	−2(4)	5(4)
N(6)	21(6)	31(6)	23(6)	0(4)	−14(4)	−6(4)
N(7)	2(3)	26(5)	21(4)	−5(3)	3(3)	2(4)
N(8)	22(6)	20(5)	27(6)	8(4)	−4(4)	−4(4)
N(9)	18(5)	18(5)	33(6)	0(4)	4(4)	14(4)
N(10)	27(5)	21(5)	19(4)	−2(4)	−10(4)	−7(4)
N(11)	19(5)	27(5)	13(5)	3(4)	0(4)	−10(4)
N(12)	22(6)	27(6)	36(7)	0(5)	−5(5)	8(5)

Table 5
Anisotropic thermal displacement parameters U_{ij} (10^3 Å^2) for $Na_5Cs[(WN_3)_2]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	4.7(2)	4.0(2)	6.0(2)	0.1(2)	0.1(2)	0.4(2)
W(2)	5.1(2)	4.6(2)	5.6(2)	0.3(2)	−0.2(2)	0.4(2)
W(3)	5.8(2)	5.8(2)	5.9(2)	0.1(2)	−0.9(2)	−0.3(2)
W(4)	4.4(2)	5.3(2)	6.4(2)	0.5(2)	−0.7(2)	0.7(2)
Cs(1)	16.6(5)	17.1(4)	10.0(4)	−1.0(4)	0.5(4)	−0.6(3)
Cs(2)	14.9(4)	20.0(4)	12.6(4)	−0.5(4)	−1.1(4)	2.1(4)
Na(1)	51(7)	14(3)	23(5)	5(4)	7(5)	2(3)
Na(2)	7(3)	22(3)	21(4)	5(3)	4(3)	2(3)
Na(3)	5(3)	13(3)	45(6)	−7(3)	11(4)	−7(3)
Na(4)	17(4)	18(3)	11(3)	−3(3)	6(3)	−3(3)
Na(5)	12(4)	16(3)	26(5)	−2(3)	1(3)	−4(3)
Na(6)	9(3)	14(3)	60(7)	0(3)	10(5)	−13(4)
Na(7)	9(3)	20(3)	31(5)	1(2)	−5(4)	−4(3)
Na(8)	23(4)	5(2)	17(4)	3(3)	0(3)	2(2)
Na(9)	10(3)	10(3)	23(4)	−1(3)	1(3)	−5(2)
Na(10)	16(3)	5(2)	27(4)	5(2)	−4(4)	1(2)

pseudo symmetry as given by the monoclinic angle $\beta = 90.0°$. In the case of the rubidium compound the twin ratio was refined to 0.0170(5). No twinning occurs in this case. This may be correlated with a slightly greater deviation from orthorhombic lattice symmetry with $\beta = 90.1°$. High peaks in final electron density difference maps (Table 1) for the cesium compound are located near the tungsten atoms. They may be explained by large twin domains which can cause problems with extinction correction.

4. Discussion of results

The new isotypic compounds $Na_5A[(WN_3)_2]$ (A = Rb, Cs) contain corner sharing nitrogen tetrahedra around tungsten, as was found in all other hitherto known nitrido tungstates(VI) of the heavier alkali metals Na–Cs. They form one-dimensional infinite chains $^1_\infty[WN_2N^{3-}_{2/2}]$ as shown in Fig. 2. In each chain all tungsten atoms and the bridging nitrogen atoms lie nearly in one plane (Fig. 3). Within these planes the chains are connected by rubidium or cesium to layers. Mainly in this direction (*c*-axis, Fig. 4) the unit cell parameter expands from the rubidium to the cesium compound (see Table 1). The sodium atoms are located mainly between these layers.

The chain conformation is already known from some silicates, for example in batisite, $Na_2BaTi_2[(SiO_3)_4]O_2$ [12], or in the oxo metallates with the same composition as for the nitrides $Na_5Cs[(FeO_3)_2]$ [13] and $Na_5Cs[(GaO_3)_2]$ [13,14]. However, these are not isotypic with $Na_5A[(WN_3)_2]$ (A = Rb, Cs). Following the nomenclature of Liebau [15] for silicate structures this chain conformation has to be assigned as an unbranched 'vierer' single chain, i.e. four tetrahedra units repeated along the chain.

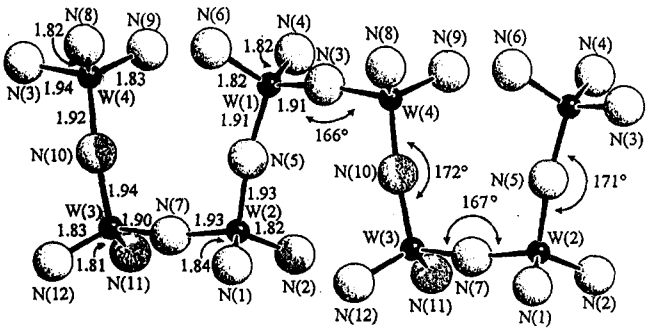

Fig. 2. Fragment of a $^1_\infty[WN_2N^{3-}_{2/2}]$-chain in the structure of $Na_5Rb[(WN_3)_2]$, distances (Å) and angles (deg). For distances and angles of the compound $Na_5Cs[(WN_3)_2]$ see Table 6.

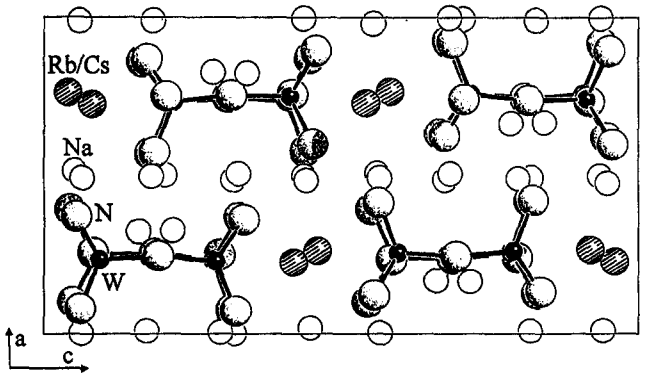

Fig. 3. View down the *b*-axis in the crystal structures of $Na_5Rb[(WN_3)_2]$ and $Na_5Cs[(WN_3)_2]$.

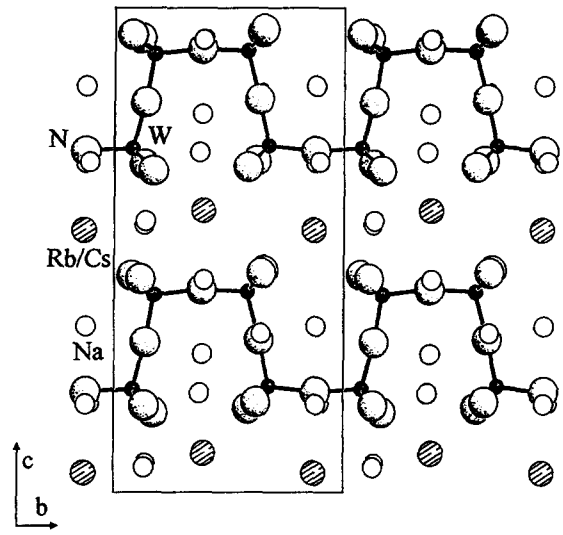

Fig. 4. View down the *a*-axis in the crystal structures of $Na_5Rb[(WN_3)_2]$ and $Na_5Cs[(WN_3)_2]$.

The mean distance of tungsten atoms to the terminal nitrogen atoms in both compounds with $\bar{d}(W\text{–}N_{terminal}) = 1.83$ Å is almost 0.1 Å shorter than the mean distance to the bridging ligands $\bar{d}(W\text{–}N_{bridging}) = 1.92$ Å. This is already known from the other alkali metal nitrido metallates(VI) of molybdenum and tungsten. Further information on distances and angles are given in Fig. 2 and Table 6.

Terminal nitrogen atoms prefer a coordination of 4 + 2 by alkali metal atoms. Bridging nitrogen atoms with a bonding angle of about $\sphericalangle(W\text{–}N_{bridging}\text{–}W) \approx 170°$ have pseudo-octahedral coordination by the two tungsten and four further alkali metal atoms.

The heavier alkali metal atoms Rb and Cs lie in strongly distorted trigonal prisms of nitrogen. Sodium prefers a tetrahedral or 4 + 1 coordination by nitrogen.

It is astonishing that these nitrido tungstates(VI) and further nitrido metallates with molybdenum or tungsten in their highest oxidation states are formed in the presence of normally strongly reducing alkali metals at temperatures above 600°C. Further investigations on nitrido molybdates and tungstates are in progress.

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Table 6
Selected distances (Å) and angles (deg) in the crystal structures of $Na_5Rb[(WN_3)_2]$/$Na_5Cs[(WN_3)_2]$

W(1)–N(6)	1.82(1)/1.80(2)	W(2)–N(2)	1.82(1)/1.84(1)
N(4)	1.824(9)/1.84(1)	N(1)	1.84(1)/1.83(2)
N(3)	1.901(9)/1.92(1)	N(5)	1.93(1)/1.92(2)
N(5)	1.91(1)/1.92(2)	N(7)	1.926(9)/1.97(1)
W(3)–N(11)	1.81(1)/1.82(1)	W(4)–N(8)	1.82(1)/1.82(2)
N(12)	1.83(1)/1.81(2)	N(9)	1.83(1)/1.84(2)
N(7)	1.909(9)/1.86(1)	N(10)	1.92(1)/1.93(2)
N(10)	1.94(1)/1.93(2)	N(3)	1.938(9)/1.91(1)
	Ø $W–N_{terminal}$ = 1.82/1.83		
	Ø $W–N_{bridging}$ = 1.92/1.92		
∢N(6)–W(1)–N(4)	112.7(5)/111.4(7)	∢N(2)–W(2)–N(1)	112.3(5)/112.0(6)
∢N(6)–W(1)–N(3)	110.1(5)/110.4(6)	∢N(2)–W(2)–N(5)	109.5(5)/109.7(6)
∢N(6)–W(1)–N(5)	106.5(5)/107.7(7)	∢N(2)–W(2)–N(7)	111.3(5)/112.1(5)
∢N(4)–W(1)–N(3)	109.3(5)/110.1(5)	∢N(1)–W(2)–N(5)	105.1(5)/106.2(7)
∢N(4)–W(1)–N(5)	110.9(5)/109.4(6)	∢N(1)–W(2)–N(7)	110.4(5)/109.7(6)
∢N(3)–W(1)–N(5)	107.3(5)/107.7(7)	∢N(5)–W(2)–N(7)	107.9(5)/106.8(7)
∢N(11)–W(3)–N(12)	111.1(6)/111.6(8)	∢N(8)–W(4)–N(9)	111.9(6)/113.4(7)
∢N(11)–W(3)–N(7)	109.0(5)/108.9(6)	∢N(8)–W(4)–N(10)	105.5(5)/106.2(7)
∢N(11)–W(3)–N(10)	109.8(5)/110.2(6)	∢N(8)–W(4)–N(3)	111.5(5)/110.8(6)
∢N(12)–W(3)–N(7)	109.9(5)/108.3(7)	∢N(9)–W(4)–N(10)	111.5(5)/110.9(6)
∢N(12)–W(3)–N(10)	109.2(5)/110.4(7)	∢N(9)–W(4)–N(3)	108.7(5)/110.8(6)
∢N(7)–W(3)–N(10)	107.7(5)/107.4(7)	∢N(10)–W(4)–N(3)	107.6(5)/107.3(7)
Rb(1)–N(1)	3.01(1)/3.16(2)	Rb(2)–N(8)	2.92(1)/3.08(2)
Cs(1)–N(11)	3.04(1)/3.17(1)	Cs(2)–N(6)	2.95(1)/3.07(2)
N(12)	3.08(1)/3.15(2)	N(7)	3.11(1)/3.19(1)
N(3)	3.18(1)/3.27(1)	N(9)	3.34(1)/3.38(2)
N(2)	3.27(1)/3.33(1)	N(4)	3.42(1)/3.40(1)
N(2)	3.35(1)/3.39(1)	N(12)	3.52(1)/3.53(2)
Na(1)–N(3)	2.48(1)/2.53(1)	Na(2)–N(10)	2.49(1)/2.53(2)
N(2)	2.51(1)/2.59(2)	N(4)	2.56(1)/2.58(1)
N(5)	2.69(1)/2.62(2)	N(5)	2.58(1)/2.63(2)
N(4)	2.82(1)/2.89(2)	N(3)	2.71(1)/2.67(1)
N(6)	2.90(1)/2.88(2)	N(1)	2.77(1)/2.79(2)
Na(3)–N(4)	2.51(1)/2.56(2)	Na(4)–N(1)	2.36(1)/2.39(2)
N(9)	2.53(1)/2.55(2)	N(1)	2.39(1)/2.41(2)
N(5)	2.59(1)/2.64(2)	N(12)	2.42(1)/2.46(2)
N(3)	2.63(1)/2.59(1)	N(4)	2.47(1)/2.51(2)
N(1)	2.80(1)/2.75(2)		
Na(5)–N(6)	2.42(1)/2.44(2)	Na(6)–N(4)	2.42(1)/2.39(2)
N(11)	2.46(1)/2.47(2)	N(9)	2.43(1)/2.46(2)
N(2)	2.43(1)/2.45(2)	N(10)	2.56(1)/2.62(2)
N(2)	2.45(1)/2.50(2)	N(8)	2.80(1)/2.73(2)
Na(7)–N(5)	2.50(1)/2.49(2)	Na(8)–N(12)	2.35(1)/2.42(2)
N(10)	2.53(1)/2.54(2)	N(7)	2.46(1)/2.42(1)
N(9)	2.61(1)/2.61(2)	N(9)	2.47(1)/2.52(2)
N(7)	2.68(1)/2.67(2)	N(12)	2.82(2)/2.81(2)
		N(1)	3.13(1)/2.98(2)
Na(9)–N(11)	2.41(1)/2.47(2)	Na(10)–N(6)	2.38(1)/2.40(2)
N(8)	2.53(1)/2.58(2)	N(8)	2.46(1)/2.50(2)
N(11)	2.66(1)/2.63(2)	N(10)	2.58(1)/2.52(1)
N(7)	2.67(1)/2.67(1)	N(11)	2.57(1)/2.59(2)
N(2)	2.67(1)/2.72(1)	N(9)	2.84(1)/2.86(2)
N(1)–W(2)	1.84(1)/1.83(2)	N(2)–W(1)	1.82(1)/1.84(1)
N(1)–Na(4)	2.36(1)/2.39(2)	N(1)–Na(5)	2.43(1)/2.45(2)
N(1)–Na(4)	2.39(1)/2.41(2)	Na(5)	2.45(1)/2.50(2)
Na(2)	2.77(1)/2.79(2)	Na(1)	2.51(1)/2.56(2)
Na(3)	2.80(1)/2.75(2)	Na(9)	2.67(1)/2.72(2)
Rb(1)/Cs(1)	3.01(1)/3.16(2)	Rb(1)/Cs(1)	3.27(1)/3.33(1)
Na(9)	3.13(1)/2.96(2)	Rb(1)/Cs(1)	3.35(1)/3.39(1)

Table 6 (*continued*)

N(3)–W(1)	1.909(9)/1.91(1)	N(4)–W(1)	1.824(9)/1.84(1)
W(4)	1.938(9)/1.92(1)	Na(6)	2.42(1)/2.39(2)
Na(1)	2.48(1)/2.53(1)	Na(3)	2.51(1)/2.56(2)
Na(3)	2.63(1)/2.59(2)	Na(4)	2.47(1)/2.51(2)
Na(2)	2.71(1)/2.67(1)	Na(2)	2.56(1)/2.58(2)
Rb(1)/Cs(1)	3.18(1)/3.27(1)	Na(1)	2.82(1)/2.89(2)
		Rb(2)/Cs(2)	3.42(1)/3.40(1)
N(5)–W(1)	1.91(1)/1.92(2)	N(6)–W(1)	1.82(1)/1.81(2)
W(2)	1.93(1)/1.92(2)	Na(10)	2.37(1)/2.40(2)
Na(7)	2.50(1)/2.49(2)	Na(5)	2.42(1)/2.44(2)
Na(3)	2.59(1)/2.64(2)	Na(1)	2.90(1)/2.88(2)
Na(2)	2.58(1)/2.63(2)	Rb(2)/Cs(2)	2.95(1)/3.07(2)
Na(1)	2.69(1)/2.62(2)	Na(7)	3.05(1)/3.11(2)
		Rb(1)/Cs(1)	3.80(1)/3.84(2)
N(7)–W(3)	1.909(9)/1.86(1)	N(8)–W(4)	1.82(1)/1.82(2)
W(2)	1.926(9)/1.97(1)	Na(10)	2.46(1)/2.48(2)
Na(8)	2.46(1)/2.42(1)	Na(9)	2.54(1)/2.58(2)
Na(7)	2.68(1)/2.67(2)	Na(6)	2.80(1)/2.73(2)
Na(9)	2.67(1)/2.67(1)	Na(7)	2.86(1)/2.92(2)
Rb(2)/Cs(2)	3.11(1)/3.19(1)	Rb(2)/Cs(2)	2.92(1)/3.04(2)
		Na(1)	3.20(1)/3.26(2)
N(9)– W(4)	1.83(1)/1.84(2)	N(10)–W(4)	1.92(1)/1.93(2)
Na(6)	2.43(1)/2.46(2)	W(3)	1.94(1)/1.93(2)
Na(8)	2.47(1)/2.52(2)	Na(2)	2.49(1)/2.53(2)
Na(3)	2.53(1)/2.55(2)	Na(7)	2.53(1)/2.54(2)
Na(7)	2.61(6)/2.61(2)	Na(10)	2.56(1)/2.52(1)
Na(10)	2.84(1)/2.86(2)	Na(6)	2.58(1)/2.52(2)
Rb(2)/Cs(2)	3.34(1)/3.38(2)		
N(11)–W(3)	1.81(1)/1.82(1)	N(12)–W(3)	1.83(1)/1.81(2)
Na(9)	2.41(1)/2.47(2)	Na(8)	2.35(1)/2.42(2)
Na(5)	2.46(1)/2.47(2)	Na(4)	2.42(1)/2.46(2)
Na(10)	2.57(1)/2.59(2)	Na(8)	2.82(2)/2.81(2)
Na(9)	2.66(1)/2.63(2)	Rb(1)/Cs(1)	3.08(1)/3.15(2)
Rb(1)/Cs(1)	3.04(1)/3.17(2)	Na(2)	3.14(2)/3.17(2)
∢W(1)–N(3)–W(4)	165.6(6)/169.4(6)		
∢W(1)–N(5)–W(2)	170.5(6)/173(1)		
∢W(2)–N(7)–N(7)	166.7(6)/167.1(8)		
∢W(3)–N(10)–W(4)	172.1(1)/174.3(8)		
W–Rb/Cs	≥3.678/3.773		
W–Na	≥3.045/3.024		
Rb/Cs–Na	≥3.148/3.238		
Na–Na	≥2.820/2.83		

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