The New Niobium Cluster Azides $(NH_4)_4[Nb_6Cl_{12}(N_3)_6](H_2O)_2$ and $Na_{1.15(3)}La_{0.85(3)}[Nb_6Cl_{12}(N_3)_6](H_2O)_{13(1)}$. Syntheses and Crystal Structure Determination

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In memoriam Joachim Strähle

The cluster compounds $(NH_4)_4[Nb_6Cl_{12}(N_3)_6](H_2O)_2$ (**1**) and $Na_{1.15(3)}La_{0.85(3)}[Nb_6Cl_{12}(N_3)_6]$-$(H_2O)_{13(1)}$ (**2**) have been synthesized by the reaction of an aqueous solution of Nb_6Cl_{14} with an excess of NaN_3 and the respective chloride salts. **1** crystallizes isotypically to the other alkali metal cluster azides in the space group $P\bar{1}$ (no. 2) with the lattice parameters $a = 908.97(8)$, $b = 932.78(8)$, $c = 1045.78(9)$ pm; and $\alpha = 95.94(1)$, $\beta = 101.68(1)$ and $\gamma = 102.41(1)°$, while **2** is found to be nearly isostructural to the alkaline earth metal cluster azides crystallizing in the space group $Fd\bar{3}m$ (no. 227) with the lattice parameter $a = 1996.9(1)$ pm. The stoichiometry of **2** was confirmed by EDX analyses which also led to a reconsideration of the water content of alkaline earth metal cluster azide compounds. The title compounds and results obtained from the reevaluation of the alkaline earth metal cluster azides are compared.

Key words: Azide, Cluster, Niobium, Alkaline Earth Metal, Rare Earth Metal

Introduction

Niobium cluster compounds such as Nb_6Cl_{14} [1] can be dissolved in water or similar polar solvents yielding deep olive-green solutions containing solvated $[Nb_6Cl_{12}]^{2+}$ ions [2]. This property makes this cluster ion an easy-to-use building block for reactions with water-soluble salts in aequeous solutions. Frequently used salts are ionic azide compounds which form $[Nb_6Cl_{12}(N_3)_6]^{4-}$ ions with the azides being attached to the terminal sites of the cluster. This reaction is accompanied by a color change of the solution to a deep olive-brown. So far only the alkali metals K^+ [3], Rb^+ and Cs^+ [4] and the alkaline earth metals Ca^{2+}, Sr^{2+} and Ba^{2+} [5] have been found to form well-crystallizing compounds. We report here the syntheses and the structure determination of $(NH_4)_4[Nb_6Cl_{12}(N_3)_6](H_2O)_2$ and of $Na_{1.15(3)}La_{0.85(3)}[Nb_6Cl_{12}(N_3)_6](H_2O)_{13(1)}$.

Experimental Section

Synthesis

Nb_6Cl_{14} was used as starting material. This compound was synthesized by reacting Nb_3Cl_8 with Nb foil at 840 °C [6]. In a typical reaction, 0.15 mmol (160 mg) fine-powdered Nb_6Cl_{14} was dissolved under stirring in approximately 10 mL H_2O at 70 °C, and 1 mmol (65 mg) NaN_3 was added. The color of the solution changed from deep olive-green to deep olive-brown. To such a solution either 0.6 mmol (31.5 mg) NH_4Cl or 0.6 mmol (223 mg) $LaCl_3 \cdot 7\ H_2O$ were added. Then, the water was evaporated at r. t. After 7 d either elongated plates of **1** or octahedra of **2** started to form. EDX analyses were performed (Tescan 5130MM / Oxford Instruments) on crystals of **2** which were used for X-ray crystallography. The analyses showed the expected elements with an approximate stoichiometry of $Na_{1.1(2)}La_{1.0(1)}[Nb_{6.0(3)}Cl_{12.9(5)}N_{19(3)}](O)_{11(1)}$ agreeing quite well with the formula $Na_{1.15(3)}La_{0.85(3)}[Nb_6Cl_{12}$-$(N_3)_6](O)_{13(1)}$ obtained by X-ray single-crystal structure determination. Crystals of **1** and **2** appear black, but if illuminated with intense light both compounds exhibit a dark brownish color. Both compounds are only moderately sensitive to pressure and heat, but if ground in a mortar, **1** and **2** decompose producing loud cracks and puffs of smoke.

Crystallographic studies

Suitable single crystals of **1** and **2** were selected under a microscope. Liquid and adhering material were removed

Table 1. Details of the X-ray single-crystal structure determination on $(NH_4)_4[(Nb_6Cl_{12})(N_3)_6](H_2O)_2$ (**1**) and $Na_{1.15(3)}La_{0.85(3)}[Nb_6Cl_{12}(N_3)_6](H_2O)_{13(1)}$ (**2**).

Compound	$(NH_4)_4[(Nb_6Cl_{12})(N_3)_6](H_2O)_2$	$Na_{1.15(3)}La_{0.85(3)}[Nb_6Cl_{12}(N_3)_6](H_2O)_{13(1)}$
Crystal color	dark olive-brown	dark olive-brown
Crystal shape	elongated plate	truncated octahedron
Crystal size, mm^3	$0.12 \times 0.28 \times 0.75$	$0.10 \times 0.14 \times 0.18$
Space group (no.), Z	$P\bar{1}$ (2), 2	$Fd\bar{3}m$ (227), 8
a, pm	908.97(8)	1996.89(14)
b, pm	932.78(8)	1996.89(14)
c, pm	1045.78(9)	1996.89(14)
α, deg	95.94(1)	90
β, deg	101.68(1)	90
γ, deg	102.41(1)	90
Cell volume, Å^3	838.0	7962.7
Calculated density, $g\,cm^{-3}$	2.66	2.68
$F(000)$, e	640	6106
Diffractometer	Stoe IPDS-II	
Radiation, monochromator; λ, pm	MoK_α, graphite; 71.073	
hkl ranges; $2\theta_{max}$, deg	± 13, $-11 \rightarrow 13$, ± 15; 63.86	$-25 \rightarrow 21$, ± 25, ± 24; 53.29
Data correction	Lp, numerical correction (X-SHAPE [8])	
μ, mm^{-1}	3.0	3.5
Transmission: min. / max.	0.267 / 0.871	0.566 / 0.689
Reflections measured / unique	19561 / 5660	13742 / 447
R_{int}	0.0616	0.0929
Unique reflections with $F_o \geq 4\sigma(F_o)$	4827	388
Refined parameters	201	45
$R1^a/wR2^b$/GoF^c (all refl.)	0.0388 /0.0869 / 1.075	0.0636, 0.0883, 1.328
Factors x / y (weighting scheme)	0.0492 / 0	0.0402 / 10.30
Max. shift/esd, last refinement cycle	< 0.0005	< 0.001
Extinction coefficient	0.0084(7)	–
$\Delta\rho_{fin}$ (max, min), e Å^{-3}	1.15 (207 pm to Nb1) -1.10 (77 pm to Nb2)	0.48 (110 pm to O22) -0.63 (69 pm to Nb)
CSD number	421012	421011

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (xP)^2 + yP]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$; [c] GoF $= [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

by rolling the crystals in grease. The cleaned crystals were enclosed in thin-walled glass capillaries. Preliminary examination and subsequent data collection were performed on an IPDS-II diffractometer with graphite-monochromatized MoK_α radiation (λ = 71.073 pm). The orientation matrix and the respective lattice parameters were obtained by using the Stoe IPDS software which was also used to integrate the data [7]. A numerical absorption correction was applied using XSHAPE [8]. The initial Nb and Cl or Na/La, Nb and Cl positions, respectively, were obtained by using Direct Methods in SHELXS-97 [9]. The O and N positions were apparent from the areas of highest electron density on the difference Fourier map resulting from the first refinement cycle by full-matrix least-squares techniques with the use of SHELXL-97 [10].

For **1**, a split position for the O position was found. The two resulting O positions were restrained to each other to add up to a site occupation factor of 100 %. For **2**, Na and La were refined on the Wyckoff position 16c and were also restrained to each other to add up to a site occupation factor of 100 %. The N1 position was refined on the Wyckoff position 48f with full occupation, but the positions N2 and N3 (both on 96g) were restrained to a site occupation factor of 50 %. The equivalent isotropic displacement parameters for the nitrogen atoms of the azide group differ considerably in size, the U_{eq} of the N1 atom bound directly to the Nb being only about half the size of that of N2 and only 1/8 of U_{eq} of N3. Both the 50 % site occupation and the significant size differences of the equivalent displacement parameters of the N atoms can be understood by a precession of the fairly rigid triatomic azide with N1 bound terminally to the Nb cluster and therefore basically 'fixed' to its position without rotation. The site occupation factors for O1, O21, O22 and O3 have been freely refined and showed only partial occupation which makes sense because of the proximity of symmetry-equivalent positions (see Fig. 2). Removing the O1, O21, O22 and O3 positions from the refinement resulted in significant residual electron densities on the difference Fourier map on these very positions. Unfortunately, the O21, O22 and O3 positions could be refined only isotropically since the anisotropic refinement resulted in ill-defined displacement parameters. This and the quite large displacement parame-

Table 2. Atomic coordinates and equivalent isotropic[a] displacement parameters (pm^2) of $(NH_4)_4[(Nb_6Cl_{12})(N_3)_6](H_2O)_2$ (**1**) and $Na_{1.15(3)}La_{0.85(3)}[Nb_6Cl_{12}(N_3)_6](H_2O)_{13(1)}$ (**2**).

Atom	Wyckoff site	Occupancy	x/a	y/b	z/c	U_{eq} (pm^2)
Nb1	2*i*	1	−0.12355(3)	0.16237(3)	−0.00625(3)	188(1)
Nb2	2*i*	1	0.17501(3)	0.13770(3)	0.14969(3)	183(1)
Nb3	2*i*	1	−0.11017(1)	−008787(3)	0.13928(3)	184(1)
Cl1	2*i*	1	−0.27411(9)	0.08908(9)	0.15788(9)	291(2)
Cl2	2*i*	1	0.34838(9)	−0.03074(9)	0.18504(9)	284(2)
Cl3	2*i*	1	0.01724(10)	−0.29394(10)	0.17291(9)	288(2)
Cl4	2*i*	1	0.05903(9)	0.35247(8)	0.16820(8)	276(2)
Cl5	2*i*	1	0.07305(10)	0.05952(10)	0.34020(10)	312(2)
Cl6	2*i*	1	−0.33574(9)	−0.26467(9)	−0.01099(8)	276(2)
$(NH_4)1$	2*i*	1	−0.3207(5)	0.4672(5)	0.2330(4)	453(9)
$(NH_4)2$	2*i*	1	0.3488(6)	0.2279(5)	0.4714(6)	617(12)
N11	2*i*	1	−0.2570(4)	0.3401(4)	−0.0101(3)	323(6)
N12	2*i*	1	−0.3335(4)	0.3619(4)	−0.1151(4)	382(7)
N13	2*i*	1	−0.4064(5)	0.3843(5)	−0.2149(4)	466(9)
N21	2*i*	1	0.3704(4)	0.2875(4)	0.3139(3)	309(6)
N22	2*i*	1	0.3395(4)	0.3634(4)	0.3981(3)	339(6)
N23	2*i*	1	0.3131(6)	0.4366(5)	0.4804(4)	562(11)
N31	2*i*	1	−0.2244(4)	−0.1912(4)	0.2913(3)	352(7)
N32	2*i*	1	−0.2934(4)	−0.1338(4)	0.3543(3)	342(7)
N33	2*i*	1	−0.3643(5)	−0.0800(6)	0.4199(4)	510(10)
O1	2*i*	0.681(17)	0.0918(7)	−0.3746(9)	0.5660(7)	597(24)
O2	2*i*	0.319(17)	0.0370(16)	−0.3081(15)	0.5029(16)	571(53)
Na/La	16*c*	0.575(5)/0.425(5)	0	0	0	494(10)
Nb	48*f*	1	0.52130(4)	1/8	1/8	235(3)
Cl	96*g*	1	0.50292(6)	$x - 1/4$	0.12575(8)	326(4)
N1	48*f*	1	0.4080(4)	1/8	1/8	377(20)
N2	96*g*	1/2	0.3700(9)	0.0983(6)	0.1517(6)	764(52)
N3	96*g*	1/2	0.3287(20)	0.0694(15)	0.1806(15)	2328(239)
O1	32*e*	0.92(7)	0.4582(8)	$1/2 - x$	$x - 1/4$	2155(242)
O21	192*i*	0.18(2)	0.071(2)	0.100(2)	0.032(2)	1431(283)
O22	96*g*	0.10(3)	0.004(7)	0.134(8)	x	1688(620)
O3	96*h*	0.30(3)	0.3357(15)	$x - 1/4$	1/4	1154(183)

[a] U_{eq} is defined as a third of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (pm) und angles (deg) in compounds containing $[Nb_6Cl_{12}^{i}(N_3)_6^{a}]^{4-}$ anions.

Compound	$\bar{d}$ (Nb–Nb)	$\bar{d}$ (Nb–X)	$\bar{d}$ (Nb–N1)	$\bar{d}$ (N1–N2)	$\bar{d}$ (N2–N3)	∡ (N1–N2–N3)	Ref.
$A_4[Nb_6Cl_{12}(N_3)_6](H_2O)_2$ (A = K, Rb, Cs)	293.2	246.5	226.3	119.2	116.5	177.7	[3, 4]
$(NH_4)_4[Nb_6Cl_{12}(N_3)_6](H_2O)_2$	293.2	246.7	226.8	119.5	116.6	178.5	
$Ca_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{12}$	292.73(6)	246.38(7)	226.9(4)	111(1)	114(3)	180(2)	
$Sr_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{12}$	292.74(9)	246.6(1)	226.5(8)	107(2)	113(5)	175(3)	
$Na_{1.15(3)}La_{0.85(3)}[Nb_6Cl_{12}(N_3)_6](H_2O)_{13(1)}$	292.9(1)	246.5(1)	226.2(9)	107(2)	116(3)	180(5)	

ters of these positions is not uncommon for crystal structures with disordered solvent molecules being distributed over a large volume. Positions for H atoms could not be refined for both of the title compounds. In further cycles the refinements converged and resulted in stable models for the crystal structures of **1** and **2**. Crystallographic details are described in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are shown in Table 2. Tables 3 and 4 display selected bond lengths of **1** and **2** and of related compounds for comparison.

Taking into account the results for **2**, the crystal structure refinement of the corresponding Ca^{2+} and Sr^{2+} cluster azide compounds [5] was redone. This led to a nearly identical stoichiometry as for **2**, but resulted in a slightly different coordination of the cationic site by oxygen atoms (crystal water molecules).

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49(0)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-421012 for **1** and CSD-421011 for **2**. On quoting the depository numbers CSD-4122557 for $Ca_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{12}$ and CSD-4122558 for $Sr_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{12}$, the corrected data can be ob-

Table 4. Selected bond lengths (pm) and coordination of the cation M by nitrogen and oxygen.

Compound	$\bar{d}$ (M–N)	CN(M)	$\bar{d}$ (M–O)	CN(M)	Ref.
$Ca_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{12}$	246(3)	6 / 2	228(2) 239(1)	2 / 1 (O2) 6 / 3 (O3)	
$Sr_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{12}$	260(5)	6 / 2	227(5) 254(2)	2 / 1 (O2) 6 / 3 (O3)	
$Na_{1.15(3)}La_{0.85(3)}[Nb_6Cl_{12}(N_3)_6](H_2O)_{13(1)}$	251(2)	6 / 2	253(4) 267(17) 242(4)	12 / 6 (O21) 6 / 10 (O22) 6 / 3 (O3)	
β-NaN_3	250.7	6	–	–	[11]
$Ca(N_3)_2$	257.2	8	–	–	[12]
$Sr(N_3)_2$	269.8	8	–	–	[12]
$Cs_3La(N_3)_6$	268	9	–	–	[13]

tained which have replaced the previously deposited details of the crystal structure investigation.

Results and Discussion

Crystal structure

1 is isotypic to the other known alkali metal cluster azides $A_4[Nb_6Cl_{12}(N_3)_6](H_2O)_2$ (A = K, Rb, Cs) [3, 4] exhibiting bond lengths and coordination patterns typical for a 16 e^- $[Nb_6Cl_{12}(N_3)_6]^{4-}$ cluster compound (Table 3). The clusters form 2D sheets coordinated by NH_4^+ ions and water molecules filling the largest gaps of the structure (Fig. 1).

Except for its crystal water content and positions, the other title compound **2** is isostructural to the alkaline earth metal cluster azides $M_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{4-x}$ (M = Ca, Sr, Ba) reported earlier [5].

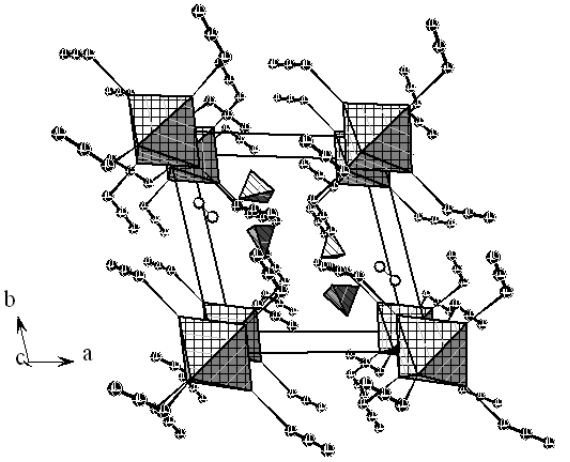

Fig. 1. View parallel to the b axis of **1**. Nb_6 units are displayed as hatched octahedra, Cl atoms are omitted for clarity. NH_4 cations are shown as grey hatched tetrahedra, N atoms are shown as black octands, and the disordered oxygen atoms are white and connected with lines not representing a bond.

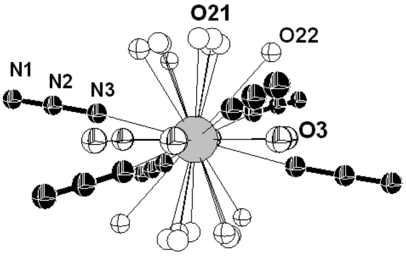

Fig. 2. The coordination of the Na/La position by disordered azide anions and water in **2**. The cation is shown as light-grey sphere, N atoms are displayed as black octands and O atoms representing water molecules are drawn as white circles.

The formula of **2** found by X-ray methods agrees quite well with the results of the EDX analyses confirming the presence of Na next to La and 11(1) oxygen atoms (*viz.*: water molecules) per formula unit. The structural pattern of **2** can be derived from the cubic Laves phase $MgCu_2$, with $[Nb_6Cl_{12}(N_3)_6]$ clusters in the 8b position replacing Mg, and the Na/La cations in 16c taking the part of the Cu atoms. The azide anions coordinate the cations. The N3 nitrogen atoms of the azide anions surround the 16c cation site (shared by Na^+ and La^{3+}) forming a flat trigonal antiprism with an M–N distance of 251(2) pm being closer to the Na–N distance of 250.7 pm known from β-NaN_3 [11] than to the La–N distance of 268 pm reported for $Cs_3La(N_3)_6$ [13]. This makes sense because the coordination numbers are lower for β-NaN_3 and **2** (Table 4).

The same azide coordination was reported for the alkaline earth metal analogs, but for **2** we found additional electron densities in the difference Fourier map around the cation site which are most probably caused by crystal water molecules. This result at least explains the oxygen (water) content indicated by the EDX analyses. If oxygen is placed and refined on these positions, the cationic site is coordinated at three different posi-

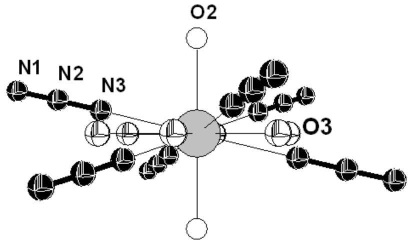

Fig. 3. The coordination of the *M* position by disordered azide anions and water in the reevaluated structures of $M_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{12}$ (M = Ca, Sr). The same color code as in Fig. 2 was used.

tions. O3 and O22 lie in six symmetry-equivalent positions which are occupied to approximately 1/3 and 1/10, while the O21 position has twelve symmetry equivalent positions occupied to a little less than 1/6 (Fig. 2). This model could only be refined with a partial occupation of the additional positions since full occupancy of the oxygen (water) positions would result in O–O distances below 100 pm.

These results gave reason to re-evaluate our earlier results concerning the alkaline earth metal cluster compounds. In fact, introducing the additional O positions (H_2O molecules) led to considerably lower *R* values (improvement for *wR*2 from 0.0833 to 0.0687 for the Ca^{2+} compound and from 0.1102 to 0.0821 for the Sr^{2+} compound) changing the formula from $M_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{4-x}$ to $M_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{12}$. The only difference between **2** and the alkaline earth metal compounds is found for the O21/O22 and the O2 positions. For the Ca^{2+} and the Sr^{2+} compounds the O2 site is in the center of the hexagon formed by O21 on the special position 32*e* resulting in only twelve molecules of water per formula unit and a smaller coordination number compared to **2** (Fig. 3 and Table 4). The different coordination patterns can be understood with respect to the different cations and their average coordination pattern. Ca^{2+} and Sr^{2+} usually exhibit smaller coordination numbers and distances towards water molecules as ligands in contrast to La^{3+}, as also found in the case of **2** where water molecules on the site O21 increase the coordination number and distance. Na^+ cations partially occupying the same cation site as La^{3+} cations would be expected to give a similar coordination pattern as for the related alkaline earth metal cations. This is the reason for the extra water molecules on the position O22. Since in the refinement the Na^+ and La^{3+} positions were coupled, no distinction between the respective coordination spheres can be made on the basis of our data.

Conclusion

The compounds $(NH_4)_4[Nb_6Cl_{12}(N_3)_6](H_2O)_2$ and $Na_{1.15(3)}La_{0.85(3)}[Nb_6Cl_{12}(N_3)_6](H_2O)_{13(1)}$ were synthesized and characterized by X-ray single-crystal structure determination and by EDX analyses. Based on these results, the intensity data of $A_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{4-x}$ (A = Ca, Sr, Ba) [5] were reevaluated, and the compositions were found to be $M_2[Nb_6Cl_{12}(N_3)_6](H_2O)_{12}$ (M = Ca, Sr). The changes introduced did not solve the refinement problems with the probably multiply disordered azide anion encountered in the compound $Ba_2[Nb_6Cl_{12}(N_3)_6](H_2O)_x$.

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