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Synthesis and Structure of $(C_{18}H_{36}N_2O_6Na)_2Na_2[Nb_6Cl_{12}(OCH_3)_6]\cdot 15CH_3OH$

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By the reaction of $Nb_6Cl_{14}\cdot 6CH_3OH$ with sodium methoxide in methanol at 254 K, the triclinic cluster compound $Na_4[Nb_6Cl_{12}(OCH_3)_6]\cdot n CH_3OH$ **1** with a = 1125.2(11), b = 1156.9(11), c = 1294.9(13) pm, α = 89.66(8)°, β = 71.46(8)°, γ = 68.19(8)° and $V = 1471.7 \times 10^6$ pm^3 has been prepared. Reacting **1** with 222-cryptand yields triclinic crystals $(cryptNa)_2Na_2[Nb_6Cl_{12}(OCH_3)_6]\cdot 15CH_3OH$ **2** with space group $P\bar{1}$(No. 2), a = 1325.6(4), b = 1669.2(6), c = 2442.1(9) pm, α = 81.70(3)°, β = 77.09(3)°, γ = 77.95(3)°; $V = 5123.8(31) \times 10^6$ pm^3, Z = 2, Dc = 1.617 g/cm^3.

The structure of **2** is built from $(C_{18}H_{36}N_2O_6Na)^+$ and $[Na_2(CH_3OH)_8]^{2+}$ cations and $[Nb_6Cl_{12}(OCH_3)_6]^{4-}$ anions. The Nb-Nb and Nb-Cl^i distances in the range of 295.2 to 298.0 pm and 246.6 to 249.8 pm, respectively, being longer than expected for $[Nb_6Cl_{12}]^{2+}$ units, are not fully understood.

INTRODUCTION

Potentiometric titration of the $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ cluster in methanol/water solution with aqueous sodium hydroxide and back titration with perchloric acid indicate high reversibility of the reaction.[1] From alkaline methanol/water solution, the isolation of a hydroxo cluster like (as *e.g.*) $[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot 4H_2O$ is possible.[2] In contrast, similar reactions in pure methanolic solution are completely irreversible. Decomposition of the

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cluster can be prevented by performing the reaction at a low temperature. Preparation of two new chloro methoxo niobium clusters at low temperature is described in the following.

EXPERIMENTAL DETAILS

Preparation

The reaction was performed under an atmosphere of argon freed from traces of oxygen by passing through silica gel, coated with Cr^{2+}.[3] Methanol was dried by distilling from magnesium methanolate under argon. Sodium was handled by the Schlenk-technique. As the resulting cluster compound is only stable below 263 K, the flask was cooled to 233–263 K by a mixture of ice and methanol. $Nb_6Cl_{14}{\cdot}6CH_3OH$[4] was dried by leaving it in vacuum at room temperature for 2 hrs. In a 100 ml flask, 5 ml methanol were condensed onto 289 mg (0.232 mmol) $Nb_6Cl_{14}{\cdot}6CH_3OH$. Within 1/2 h, a cooled solution of 150 mg (6.52 mmol) sodium in 5 ml methanol was added to the stirred yellow-green suspension leading to a clear solution of unchanged colour. After 12 h stirring, the solution was concentrated to ~ 3 ml. After 48 hrs at 254 K, the product had completely crystallized from the nearly discoloured mother liquor. The crystals of $Na_4[Nb_6Cl_{12}(OCH_3)_6]{\cdot}nCH_3OH$ (**1**) were very small. An attempt to get larger ones *via* recrystallization was unsuccessful. The compound formed olive-coloured platelets smaller than 0.1 mm in diameter, which did not show any damage when kept under dry kerosene at room temperature for 1 h. The inertness of the solution of **1** against air is in marked contrast to the tantalum analogue. Solutions of $[Ta_6Cl_{12}(OCH_3)_6]^{4-}$ are readily oxidized in air, changing colour from a characteristic emerald-green to reddish-brown.[5] Unfortunately, crystals of **1** were unsuitable for a full structure analysis. Only the unit cell dimensions could be determined. The compound is triclinic: a = 1125.2(11), b = 1156.9(11), c = 1294.9(13) pm, α = 89.66(8)°, β = 71.46(8)°, γ = 68.19(8)° and $V = 1471.7 \times 10^6$ pm^3.

Reacting **1** with 222-cryptand, single crystals of **2** were isolated which turned out to be $(cryptNa)_2Na_2[Nb_6Cl_{12}(OCH_3)_6]{\cdot}15CH_3OH$ instead of the desired phase $(cryptNa)_4[Nb_6Cl_{12}(OCH_3)_6]{\cdot}nCH_3OH$. The reaction was performed by first preparing a solution of **1** from 281 mg (0.226 mmol) $Nb_6Cl_{14}{\cdot}6CH_3OH$ and 139 mg (6.04 mmol) sodium in 7.5 ml methanol. A cooled solution of 357 mg (0.946 mmol) 222-cryptand in 5 ml methanol was slowly added, followed by 2.5 ml methanol. The clear solution was concentrated to ~ 5 ml below 263 K without any deposit forming. After keeping the solution at 254 K for 3 days, the product had crystallized and after 7 days the solution was nearly colourless.

The compound formed nearly rectangular brown platelets that could not be handled under kerosene at room temperature. If transferred to the kerosene together with some mother liquor, they decomposed. Within 10 minutes, needles of a less intense colour were formed. A suitable platelet of **2** was selected under cooled kerosene, fixed onto a X-ray capillary with grease and immediately cooled in a nitrogen stream on the diffractometer.

TABLE I

Details of crystal data, data collection and refinement for **2**

Formula, formula weight	: $Na_4Nb_6Cl_{12}O_{33}N_4C_{57}H_{150}$, 2494.6 g/mol
Unit-cell dimensions	: a = 1325.6(4) pm, b = 1669.2(6) pm,
	: c = 2442.1(9) pm, α = 81.70(3)°,
	: β = 77.09(3)°, γ = 77.95(3)°
Space group	: $P\bar{1}$ (No. 2)
Volume, formula units per cell	: 5123.8(31) × 10^6 pm^3, Z = 2
Density (X-ray)	: 1.617 g/cm^3
Crystal size	: ~ 0.2 × 0.1 × 0.05 mm^3
μ(Mo Kα), λ	: 1.049 mm^{-1}, 71.073 pm
Diffractometer system	: Stoe-IPDS, graphite monochromator
Distance, data collection range	: 75 mm, 8.3° < 2θ < 45°
Measurement	: 0 < ϕ < 200°, ϕ-oscillation, $\Delta\phi$ = 0.8°
Exposure time	: 30 min/image
Temperature	: 173 K
Number of reflections	: 25896 measured
Independant reflections	: 12526, R_{int} = 0.066, 12026 with $F_o^2 > -\sigma(F_o^2)$
Absorption correction	: empirical, ABSCOR
Structure solution	: Patterson
Refinement on F^2	: least squares, full matrix, 1066 parameters
F_{000}	: 2556
Weighting scheme	: $[exp(\sin\theta/\lambda)^2]/[\sigma^2(F_o^2) + (0.1192 \cdot P)^2 + 16.8 \cdot P]$,
	$P = (Max(F_o^2, 0) + 2 \cdot F_c^2)/3$
Extinction	: not significant
$\omega R2$	: 0.227 for all 12526 reflections
$R1$(aniso)	: 0.114 for all 12526 reflections
$R1$(aniso)	: 0.073 for $F_o > 4\sigma(F_o)$
Goodness of fit	: 1.135
Difference-Fourier peaks	: 1.34 bis −1.30 × 10^6 e$^-$/pm^3

Structure Solution and Refinement

Diffraction data were collected on a STOE imageplate system IPDS at 173 K. The positions of Nb and Cl atoms were derived *via* Patterson methods,[6] all other atoms were located in successive Difference-Fourier maps. After isotropic refinement of all non-hydrogen atoms, an empirical absorption correction was applied, using the ABSCOR program.[7] The following anisotropic refinement[8] (1066 free parameters) revealed the composition (cryptNa)$_2$Na$_2$[Nb$_6$Cl$_{12}$(OCH$_3$)$_6$]·15CH$_3$OH. Crystal data and details of structure refinement are summarized in Table I.

Hydrogen atoms of the methyl groups were placed at a fixed distance d(C-H) = 98 pm and ideal tetrahedral angles of 109.5°, hydrogen atoms of the methylene groups at d(C-H) = 99 pm. Their displacement factors were fixed at a value 1.2 times that of the corresponding C atoms. Hydrogen atoms of the hydroxyl groups could not be localized. Final atomic parameters and selected distances are summarized in Tables II and III.*

* Further details of the crystal structure investigation are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-404536, the names of the authors and the journal citation.

TABLE II

Fractional atomic coordinates and equivalent isotropic displacement parameters/pm^2 of **2**

atom	x/a	y/b	z/c	U_{eq}
Nb1	0.3886(1)	0.2400(1)	0.1856(1)	407(3)
Nb2	0.2045(1)	0.3728(1)	0.1767(1)	406(3)
Nb3	0.1852(1)	0.1989(1)	0.1771(1)	406(3)
Nb4	0.2637(1)	0.1550(1)	0.2839(1)	415(3)
Nb5	0.2809(1)	0.3297(1)	0.2850(1)	413(3)
Nb6	0.0786(1)	0.2886(1)	0.2761(1)	405(3)
Cl1	0.3814(2)	0.3620(2)	0.1150(1)	446(7)
Cl2	0.3589(2)	0.1591(2)	0.1154(1)	454(7)
Cl3	0.4514(2)	0.1082(2)	0.2390(1)	464(7)
Cl4	0.4709(2)	0.3144(2)	0.2399(1)	457(7)
Cl5	0.1460(2)	0.3135(2)	0.1038(1)	468(7)
Cl6	0.0172(2)	0.4212(2)	0.2223(1)	466(7)
Cl7	0.2142(2)	0.0607(2)	0.2291(1)	475(7)
Cl8	–0.0043(2)	0.2134(2)	0.2225(1)	477(7)
Cl9	0.3216(2)	0.2125(2)	0.3575(1)	494(7)
Cl10	0.0871(2)	0.1662(2)	0.3475(1)	455(7)
Cl11	0.2533(2)	0.4671(2)	0.2317(1)	456(7)
Cl12	0.1072(2)	0.3692(2)	0.3473(1)	459(7)
O1	0.5551(5)	0.2184(5)	0.1428(3)	424(18)
O2	0.1727(6)	0.4821(5)	0.1243(3)	527(20)
O3	0.1293(6)	0.1376(5)	0.1183(3)	506(20)
O4	0.2953(6)	0.0435(5)	0.3384(3)	475(19)
O5	0.3365(6)	0.3923(5)	0.3387(3)	551(21)
O6	–0.0860(6)	0.3119(5)	0.3187(3)	479(19)
C1	0.6002(9)	0.1705(9)	0.0973(5)	591(34)
C2	0.2055(10)	0.5015(9)	0.0653(5)	632(37)
C3	0.0927(11)	0.0626(9)	0.1330(5)	643(36)
C4	0.3608(9)	–0.0295(7)	0.3215(5)	491(29)
C5	0.2911(10)	0.4658(8)	0.3646(5)	546(31)
C6	–0.1360(10)	0.3740(9)	0.3559(5)	592(34)
Na1	0.0431(3)	0.2312(3)	0.6143(2)	519(11)
N1	–0.0558(8)	0.1133(6)	0.6796(4)	562(27)
N2	0.1435(8)	0.3504(7)	0.5483(4)	575(27)
O7	0.1538(6)	0.1444(5)	0.6786(3)	557(21)
O8	0.2246(6)	0.1743(5)	0.5634(3)	546(21)
O9	–0.0429(7)	0.2944(6)	0.5346(3)	600(23)
O10	0.0122(6)	0.1292(5)	0.5556(3)	554(21)
O11	–0.1234(7)	0.2943(5)	0.6719(4)	601(22)
O12	0.0644(6)	0.3383(5)	0.6709(3)	553(21)
C7	0.0189(10)	0.0582(8)	0.7117(6)	604(34)
C8	0.0925(10)	0.1059(9)	0.7272(5)	610(35)

TABLE II

(continued)

atom	x/a	y/b	z/c	U_{eq}
C9	0.2400(10)	0.0909(9)	0.6491(6)	649(37)
C10	0.2932(10)	0.1420(9)	0.6002(6)	635(36)
C11	0.2682(12)	0.2284(9)	0.5151(6)	681(38)
C12	0.2553(10)	0.3148(9)	0.5301(6)	646(36)
C13	0.0906(11)	0.3797(9)	0.5010(6)	676(38)
C14	–0.0239(11)	0.3758(9)	0.5159(6)	671(39)
C15	–0.0281(12)	0.2424(8)	0.4910(5)	611(36)
C16	–0.0558(12)	0.1626(9)	0.5170(6)	733(42)
C17	–0.0076(10)	0.0520(8)	0.5888(5)	585(33)
C18	–0.0888(10)	0.0678(8)	0.6414(5)	544(31)
C19	–0.1480(10)	0.1558(9)	0.7184(6)	659(37)
C20	–0.1940(10)	0.2362(9)	0.6883(6)	699(39)
C21	–0.1082(11)	0.3316(9)	0.7173(5)	629(36)
C22	–0.0343(10)	0.3894(8)	0.6945(6)	594(33)
C23	0.1458(10)	0.3836(8)	0.6429(5)	599(34)
C24	0.1310(11)	0.4179(9)	0.5840(5)	669(38)
Na2	0.4479(4)	0.2779(3)	0.8383(2)	530(12)
N3	0.3551(7)	0.2126(7)	0.7681(4)	543(26)
N4	0.5416(8)	0.3371(7)	0.9065(4)	556(26)
O13	0.5373(6)	0.2966(5)	0.7400(3)	488(19)
O14	0.4698(7)	0.4226(5)	0.8083(3)	564(21)
O15	0.3433(7)	0.2762(6)	0.9329(3)	642(24)
O16	0.2604(7)	0.3462(6)	0.8405(4)	736(27)
O17	0.4480(7)	0.1270(5)	0.8624(4)	614(23)
O18	0.6272(7)	0.1922(5)	0.8436(3)	604(23)
C25	0.4085(10)	0.2369(9)	0.7104(5)	613(34)
C26	0.5231(10)	0.2388(9)	0.7086(5)	640(36)
C27	0.5253(11)	0.3800(9)	0.7135(5)	602(34)
C28	0.5469(10)	0.4306(8)	0.7530(5)	556(32)
C29	0.4849(11)	0.4648(8)	0.8480(6)	643(36)
C30	0.5663(10)	0.4174(9)	0.8809(6)	627(36)
C31	0.4649(10)	0.3477(9)	0.9604(5)	614(35)
C32	0.3985(12)	0.2789(10)	0.9761(5)	716(40)
C33	0.2462(10)	0.3313(12)	0.9392(6)	910(58)
C34	0.1908(12)	0.3229(13)	0.8932(7)	962(58)
C35	0.2231(10)	0.3358(10)	0.7913(6)	703(42)
C36	0.2406(10)	0.2494(8)	0.7787(5)	562(32)
C37	0.3708(10)	0.1232(8)	0.7815(5)	576(33)
C38	0.3660(12)	0.0977(10)	0.8439)6)	718(40)
C39	0.5489(11)	0.0748(9)	0.8518(6)	708(39)
C40	0.6248(11)	0.1125(8)	0.8737(6)	690(39)
C41	0.6913(11)	0.2384(10)	0.8626(6)	693(39)
C42	0.6368(10)	0.2793(9)	0.9145(5)	623(36)

TABLE II

(continued)

atom	x/a	y/b	z/c	U_{eq}
Na3	0.6532(3)	0.2490(3)	0.2982(2)	578(13)
Na4	0.8102(4)	0.2972(3)	0.1586(2)	601(13)
O43	0.7003(6)	0.1938(5)	0.2071(3)	488(19)
C43	0.7552(11)	0.1109(9)	0.2090(6)	669(37)
O44	0.7669(6)	0.3461(5)	0.2500(3)	485(19)
C44	0.7175(11)	0.4325(8)	0.2469(6)	688(38)
O45	0.7899(6)	0.2038(6)	0.3457(4)	712(28)
C45	0.8030(12)	0.1510(11)	0.3944(7)	893(52)
O46	0.5808(8)	0.1259(8)	0.3359(5)	950(37)
C46	0.5454(11)	0.0868(10)	0.3892(7)	806(45)
O47	0.5288(6)	0.3407(6)	0.3568(3)	677(25)
C47	0.5228(11)	0.3232(10)	0.4145(5)	722(41)
O48	0.6626(6)	0.3395(5)	0.1145(3)	561(21)
C48	0.6641(10)	0.3798(9)	0.0594(5)	616(35)
O49	0.9374(6)	0.2210(6)	0.0967(4)	680(26)
C49	0.9445(15)	0.2232(15)	0.0387(7)	1198(79)
O50	0.8909(9)	0.4091(9)	0.1178(5)	1046(41)
C50	0.9145(22)	0.4570(19)	0.0796(16)	2294(210)
O60	0.1481(12)	0.6309(9)	0.1566(6)	1226(46)
C60	0.0703(10)	0.6806(10)	0.1307(7)	827(49)
O61	0.2075(9)	0.1249(8)	0.0097(4)	870(32)
C61	0.3088(13)	0.0683(12)	0.0019(6)	910(51)
O62	0.1096(10)	0.1364(11)	–0.0793(5)	1146(44)
C62	0.0884(29)	0.0581(25)	–0.0817(14)	2357(203)
O63	0.2295(7)	–0.0121(5)	0.4403(3)	583(22)
C63	0.2413(13)	0.0421(9)	0.4775(6)	758(42)
O64	0.3321(8)	–0.1622(7)	0.4601(4)	866(32)
C64	0.4356(11)	–0.1498(10)	0.4565(6)	769(43)
O65	0.3723(10)	–0.3207(9)	0.4400(6)	1210(46)
C65	0.3040(15)	–0.3708(13)	0.4639(8)	1051(59)
O66	0.5812(9)	–0.3808(9)	0.4046(5)	941(34)
C66	0.5900(13)	–0.4684(14)	0.4140(10)	1135(67)

Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor

TABLE III

Selected bond lengths/pm in **2**

Nb1-Nb2	295.9(2)	Nb1-Nb3	297.3(2)	Nb1-Nb4	295.7(2)
Nb1-Nb5	296.3(2)	Nb2-Nb3	296.5(2)	Nb2-Nb5	298.0(2)
Nb2-Nb6	297.3(2)	Nb3-Nb4	296.0(2)	Nb3-Nb6	295.2(2)
Nb4-Nb5	297.5(2)	Nb4-Nb6	297.1(2)	Nb5-Nb6	296.2(2)
Nb1-Cl1	247.1(3)	Nb1-Cl2	247.2(3)	Nb1-Cl3	247.6(3)
Nb1-Cl4	248.6(3)	Nb2-Cl1	247.5(3)	Nb2-Cl5	248.8(3)
Nb2-Cl6	249.8(3)	Nb2-Cl11	247.4(3)	Nb3-Cl2	247.3(3)
Nb3-Cl5	248.0(3)	Nb3-Cl7	246.6(3)	Nb3-Cl8	248.5(3)
Nb4-Cl3	249.4(3)	Nb4-Cl7	247.7(3)	Nb4-Cl9	248.3(3)
Nb4-Cl10	249.1(3)	Nb5-Cl4	248.9(3)	Nb5-Cl9	249.8(3)
Nb5-Cl11	246.7(3)	Nb5-Cl12	247.8(3)	Nb6-Cl6	248.5(3)
Nb6-Cl8	248.8(3)	Nb6-Cl10	248.8(3)	Nb6-Cl12	248.2(3)
Nb1-O1	220.0(7)	Nb2-O2	209.5(8)	Nb3-O3	220.7(8)
Nb4-O4	215.0(8)	Nb5-O5	122.3(8)	Nb6-O6	217.7(7)
O1-C1	141.2(13)	O2-C2	141.8(13)	O3-C3	141(2)
O4-C4	139.8(13)	O5-C5	142(2)	O6-C6	143.4(14)
Na1-N1	271.5(11)	Na1-N2	274.8(11)	Na1-O7	249.1(9)
Na1-O8	250.7(9)	Na1-O9	246.9(9)	Na1-O10	252.6(10)
Na1-O11	245.5(10	Na1-O12	250.7(10)		
N1-C7	148(2)	N1-C18	147(2)	N1-C19	149(2)
N2-C12	147(2)	N2-C13	146(2)	N2-C24	148(2)
O7-C8	143(2)	O7-C9	142(2)	O8-C10	140(2)
O8-C11	147(2)	O9-C14	143(2)	O9-C15	142(2)
O10-C16	143(3)	O10-C17	146(2)	O11-C20	144(2)
O11-C21	142(2)	O12-C22	145(2)	O12-C23	144(2)
C7-C8	152(2)	C9-C10	149(2)	C11-C12	150(2)
C13-C14	149(2)	C15-C16	147(2)	C17-C18	150(2)
C19-C20	151(2)	C21-C22	148(2)	C23-C24	151(2)
Na2-N3	277.0(11)	Na2-N4	268.5(11)	Na2-O13	243.4(8)
Na2-O14	249.4(10)	Na2-O15	241.5(9)	Na2-O16	250.1(10)
Na2-O17	250.3(10)	Na2-O18	252.5(9)		
N3-C25	147(2)	N3-C36	149(2)	N3-C37	146(2)
N4-C30	146(2)	N4-C31	148(2)	N4-C42	145(2)
O13-C26	141(2)	O13-C27	144(2)	O14-C28	143(2)
O14-C29	144(2)	O15-C32	142(2)	O15-C33	141(2)
O16-C34	146(2)	O16-C35	144(2)	O17-C38	146(2)
O17-C39	143(2)	O18-C40	143(2)	O18-C41	144(2)
C25-C26	151(2)	C27-C28	148(2)	C29-C30	151(2)
C31-C32	154(2)	C33-C34	151(2)	C35-C36	148(2)
C37-C38	151(2)	C39-C40	151(2)	C41-C42	149(2)
Na3-Cl4	300.9(5)	Na3-O43	243.4(9)	Na3-O44	244.1(9)
Na3-O45	230.5(9)	Na3-O46	242.2(12)	Na3-O47	237.4(10)
Na4-C18	317.6(5)	Na4-O43	248.9(9)	Na4-O44	239.4(9)
Na4-O48	233.3(9)	Na4-O49	229.5(10)	Na4-O50	233.2(14)
Na3-Na4	365.2(7)				

TABLE III

(continued)

O43-C43	142(2)	O44-C44	145(2)	O45-C45	140(2)
O46-C46	140(2)	O47-C47	138(2)	O48-C48	142(2)
O49-C49	139(2)	O50-C50	117(3)		
O60-C60	139(2)	O61-C61	146(2)	O62-C62	140(3)
O63-C63	142(2)	O64-C64	141(2)	O65-C65	134(2)
O66-C66	143(2)				

RESULTS AND DISCUSSION

Compound **2** can be described as $(cryptNa)_2[Na_2(CH_3OH)_8][Nb_6Cl_{12}(OCH_3)_6]\cdot 7CH_3OH$. The structure contains the cluster anion $[Nb_6Cl_{12}(OCH_3)_6]^{4-}$, two cryptated sodium and two additional sodium cations, which are solvated by methanol molecules. The Nb_6Cl_{12} cluster is coordinated by methanolate ligands in X^a positions,[9] see Figure 1.

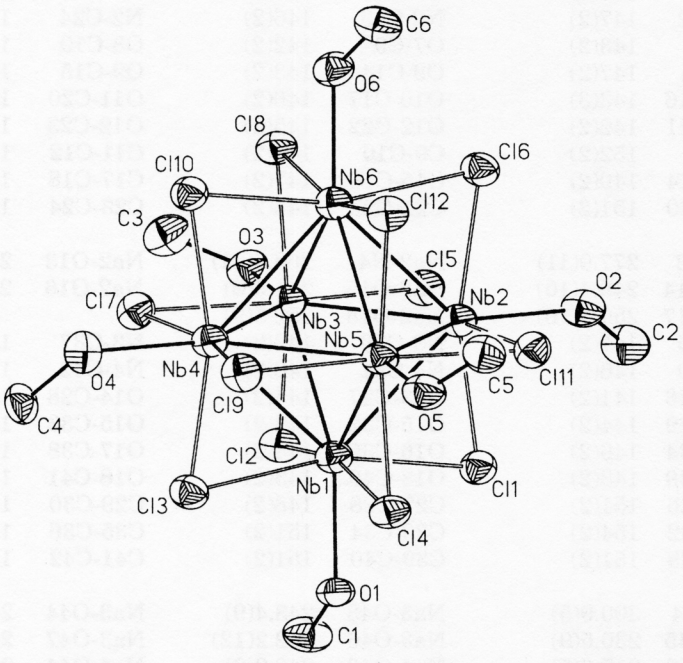

Figure 1. Structure of the $[Nb_6Cl_{12}(OCH_3)_6]^{4-}$ anion, ellipsoids drawn at a 40% probability level.

TABLE IV

Relevant O-O distances/pm for hydrogen bonding

O1-O48	266.8(12)	O1-O43	267.8(11)
O2-O60	264.8(18)	O3-O61	264.5(12)
O3-O49	275.7(11)	O4-O63	255.2(10)
O5-O47	263.0(12)	O6-O45	261.0(13)
O6-O44	276.8(11)	O61-O62	273.7(18)
O63-O64	262.3(13)	O64-O65	268.1(19)
O65-O66	272.9(16)		

The Nb_6 octahedron is slightly distorted. Three Nb atoms in meridonal arrangement exhibit larger-than-average distances to the centre of gravity. However, the degree of distortion is only small since the Nb-Nb distances lie in the range of 295.2 to 298.0 pm and Nb-Nb-Nb angles exhibit values from 59.61° to 60.42° and 89.68° to 90.56°, respectively. The distortion of the Nb_6 octahedron may be explained as due to different coordinations of the Nb atoms by methanolate groups. The latter belong to two categories, see Table IV and Figure 2, which differ in the number of closely approaching methanol molecules. Atoms O2, O4 and O5 can form hydrogen bonds to one,

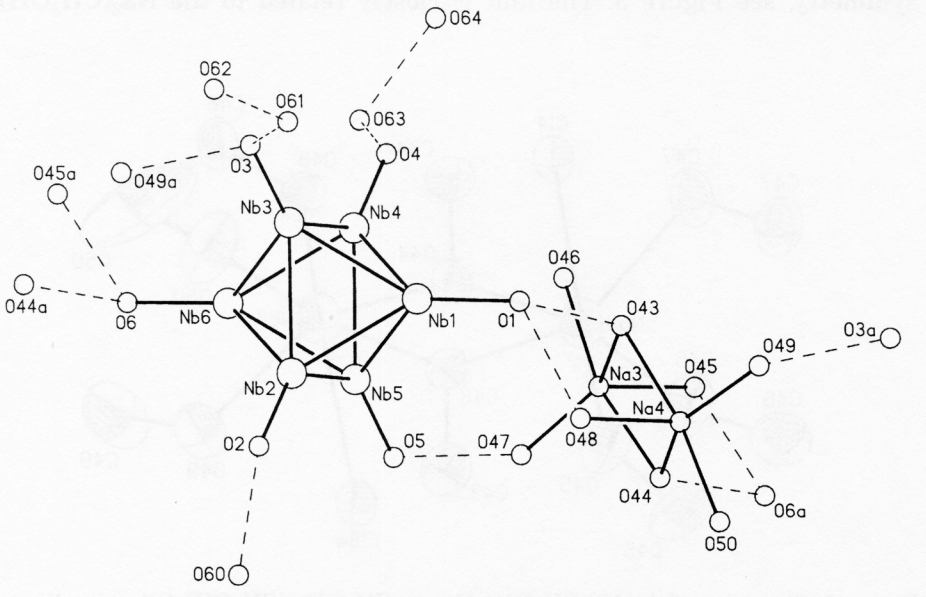

Figure 2. Closest O-O contacts in **2** as possible locations for hydrogen bridges.

atoms O1, O3 and O6 hydrogen bonds to two neighbouring methanol molecules, respectively. Hence, O atoms of the first category exhibit shorter Nb-O distances (209.5 to 215.0 pm) as well as O-O distances (255 to 265 pm) than atoms belonging to the second category (217.7 to 220.7 pm and 261 to 277 pm, respectively). In turn, those Nb atoms bonded to O atoms of the first category, Nb2, Nb4 and Nb5, have slightly larger distances to the centre (210.0 to 210.3 pm) than Nb1, Nb3 and Nb6 (209.0 to 209.5 pm). The above discussion, based on bond length-bond strength arguments, convincingly explains the differentiation of Nb-Nb and Nb-O distances. This explanation has to stay qualitative as long as the hydrogen atoms in the bridges cannot be localized.

The Nb-Cl^i distances range from 246.6 to 249.8 pm (248.2 pm on average). Clearly, the Nb-O bonds found are rather long if compared to other compounds, *e.g.* $Na_2[Ta_6Cl_{12}(OCH_3)_6]\cdot 12CH_3OH$[10] or $(cryptNa)_2[Ta_6Cl_{12}(OCH_3)_6]\cdot 6CH_3OH$,[11] and, on the other hand, they are shorter than expected for a neutral methanol molecule coordinating the cluster as *e.g.* in $[Ta_6Cl_{12}(CH_3OH)_6]Br_3$ or $[Ta_6Cl_{12}(CH_3OH)_6]Br_3\cdot 4H_2O$.[12]

The $(cryptNa)^+$ cations are twisted around their N-Na-N axes and exhibit nearly 3-fold symmetry. The coordination geometry and range of interatomic distances are as usual, each Na being surrounded by 2 N and 6 O atoms with distances 269 to 227 pm and 242 to 253 pm, respectively.

The atoms in the $Na_2(CH_3OH)_8Cl_2$ unit are crelated by near inversion symmetry, see Figure 3. The unit is closely related to the $Na_2(CH_3OH)_9^{2+}$

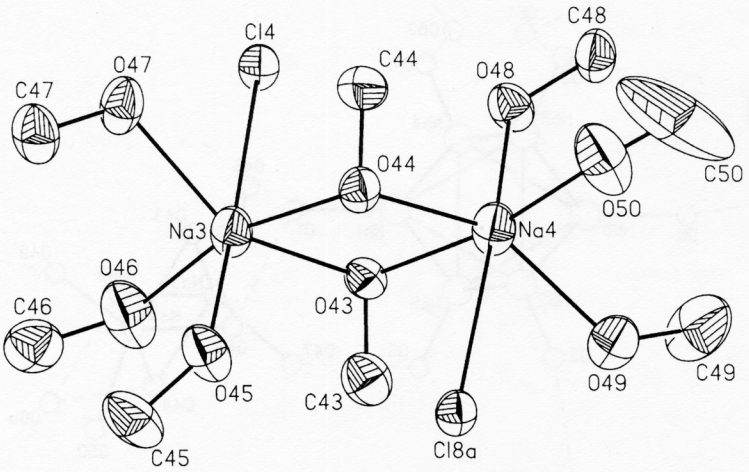

Figure 3. Structure of the $[Cl(CH_3OH)_3Na_2(\mu_2\text{-}CH_3OH)_2(CH_3OH)_3Cl]$ unit, ellipsoids drawn at a 40% probability level.

cation found in the structure of $Na_2[Ta_6Cl_{12}(OCH_3)_6]\cdot 12CH_3OH$.[10] The unit in **2** differs by replacement of one μ_2-bridging methanol molecule by two Cl atoms belonging to adjacent Nb_6Cl_{12} clusters. In both, Na atoms have (distorted) octahedral coordination with face-sharing of octahedra in the case of $Na_2(CH_3OH)_9^{2+}$ and edge-sharing for $Na_2(CH_3OH)_8Cl_2$. As expected, the Na-O distances for the μ_2-bridging methanol ligands are, on average, slightly longer than for the terminal methanol molecules, 244 and 234 pm, respectively.

The methanol molecules that are not coordinated to Na atoms are numbered 60 to 66. Table IV shows all short O-O approaches (below an obvious gap between 276.8 and 310.0 pm) for these molecules allowing for hydrogen bond formation.

Finally, a general problem of the structure determination of **2** should be addressed. We discussed the slight distortion of the Nb_6 octahedron in terms of the differences in the bonding of methanolate ligands in X^a positions. However, keeping in mind the rather large average value of the Nb-Nb distances, 296.6 pm, we could also face the problem of a (partially) oxidized cluster. $[Nb_6Cl_{12}Cl_6]^{4-}$ anions in the structures of several compounds exhibit Nb-Nb distances from 291 to 292 pm, as well as Nb-Cl^i distances ranging from 244 to 252 pm (245 pm on average), just to mention $K_4[Nb_6Cl_{12}Cl_6]$,[13] $KLu[Nb_6Cl_{12}Cl_6]$,[14] $CsLu[Nb_6Cl_{12}Cl_6]$,[15] and $KGd[Nb_6Cl_{12}Cl_6]$.[16]

$[Nb_6Cl_{12}Cl_6]^{3-}$ anions in $Lu[Nb_6Cl_{12}Cl_6]$,[14] and $(NMe_4)_3[Nb_6Cl_{12}Cl_6]$[17] are characterized by longer Nb-Nb distances (294 to 299 pm) and shorter Nb-Cl^i distances (243 pm on average). These differences are well understood, as the HOMO has Nb-Nb bonding and Nb-Cl antibonding character,[18] and releasing an electron from this orbital leads to a weakening of M-M bonding, simultaneously strengthening the Nb-Cl bonds. Indeed, the longest Nb-Nb (302 to 305 pm) and shortest Nb-Cl^i distances (243 pm on average) were found for the clusters in $(NMe_4)_2[Nb_6Cl_{12}Cl_6]$[19] and $(PyH)_2[Nb_6Cl_{12}Cl_6]$.[20] A comparison of the distances in the cluster in the structure of **2** with those in oxidized species is puzzling, as both Nb-Nb and Nb-Cl distances (and Nb-O distances) are rather long. Chemical evidence is also against the assumption of a partially oxidized cluster in **2**: A solution kept in contact with crystals of **2** for months (at 263 K) still has the characteristic olive-green colour of the reduced species. Clearly, an unambiguous determination of the hydrogen atom positions, *e.g.*, *via* neutron diffraction, would be necessary to give a decisive interpretation of the distance anomalies discussed.

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SAŽETAK

Priprava i strukture $(C_{18}H_{36}N_2O_6Na)_2Na_2[Nb_6Cl_{12}(OCH_3)_6]\cdot 15CH_3OH$

Ulrich Beck, Arndt Simon, Nevenka Brničević i Siniša Širac

Reakcijom $Nb_6Cl_{14}\cdot 6CH_3OH$ s natrijevim metoksidom u metanolu pri 254 K priređen je monoklinski kluster $Na_4[Nb_6Cl_{12}(OCH_3)_6]\cdot nCH_3OH$ **1** s a = 1125.2(11), b = 1156.9(11), c = 1294.9(13) pm, α = 89.66(8)°, β = 71.46(8)°, γ = 68.19(8)° i V = 1471.7 × 10^6 pm^3. Reakcijom **1** sa 222-kriptandom nastaje $(kriptNa)_2Na_2[Nb_6Cl_{12}(OCH_3)_6]\cdot 15CH_3OH$ **2**, prostorna grupa $P\bar{1}$ (Br. 2), a = 1325.6(4), b = 1669.2(6), c = 2442.1(9) pm, α = 81.70(3)°, β = 77.09(3)°, γ = 77.95(3)°; V = 5123.8(31) × 10^6 pm^3, Z = 2, D_c = 1.617 g/cm^3.

Struktura spoja **2** se sastoji od kationa $(C_{18}H_{36}N_2O_6Na)^+$ i $[Na_2(CH_3OH)_8]^{2+}$ i aniona $[Nb_6Cl_{12}(OCH_3)_6]^{4-}$. Nisu posve razumljivi razlozi udaljenosti Nb-Nb i Nb-Cl^i koje su u rasponu od 295.2 do 298.0 i od 246.6 do 249.8 pm, t.j. dulje nego što bi se očekivalo za jedinicu $[Nb_6Cl_{12}]^{2+}$.