Synthesis, Crystal Structure, and Electronic Structure of $In_2Li_2Nb_6Cl_{18}$

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The synthesis and the single-crystal X-ray structure analysis of a new niobium cluster compound are reported in this paper. $In_2Li_2Nb_6Cl_{18}$ was obtained by solid state reactions of stoichiometric amounts of $NbCl_5$, niobium metal, LiCl, and $InCl_3$ at 820°C. The structure was refined in the space group $P\bar{1}$ ($Z = 1$) with $a = 922.0$ (2) pm, $b = 927.2$ (3) pm, $c = 926.7$ (2) pm, $\alpha = 119.28$ (2)°, $\beta = 96.51$ (2)°, $\gamma = 105.14$ (3)°, $R = 0.035$ and $R_W = 0.035$, for all 3675 symmetry-independent reflections. The structure contains isolated $(Nb_6Cl_{12}^i)Cl_6^a$ clusters, separated by lithium and indium cations in a tetrahedral and a cubeoctahedral chloride coordination environment, respectively. Indium is present as In^+ with the $5s$ state being filled with two electrons, energetically lying at the bottom of the Nb $4d$ block. © 1994 Academic Press, Inc.

INTRODUCTION

A variety of structures and compositions of reduced niobium halides (1) are based on the binary Nb_6Cl_{14} (2) cluster with additional metal chloride. In most of these compounds, such as MNb_6Cl_{15} (M = Na, Cs) (3), $Ba_2Nb_6Cl_{18}$ (4), $M_4Nb_6Cl_{18}$ (M = Na, K, Cs) (5), and $MLnNb_6Cl_{18}$ (M = Na, K, Rb; Ln = lanthanide) (6), 16 electrons are present per [Nb_6] cluster; these occupy all available Nb–Nb bonding states as in the parent compound (Nb_6Cl_{14}). In $LnNb_6Cl_{18}$ (Ln = lanthanide) (7), however, these states are incompletely filled (15 electrons per cluster) and paramagnetic behavior is the result (8). Most of these compounds are moderately stable on exposure to air and dissolve in water and polar organic solvents (9).

The crystal structures of the last compounds exhibit isolated $[(Nb_6Cl_{12}^i)Cl_6^a]$ clusters, whereas direct chloride bridges between adjacent [Nb_6] clusters occur in Nb_6Cl_{14} and MNb_6Cl_{15}. Also, in $Nb_6Cl_{12}I_2$ (10) each of the six outer iodine atoms interconnect three [Nb_6] clusters. Still, in all these structures the [Nb_6] clusters are well separated from each other, and the electronic conditions are usually described by a molecular orbital treatment of a local $[(Nb_6Cl_{12}^i)Cl_6^a]$ cluster (11). Therefore, insulating to semi-conducting properties may be regarded. The valence orbital states of the former M cations are located clearly above the bonding niobium states in energy, and thus are empty, as they have donated their electrons to the Nb and halide states.

Reactions of group 13 metals with niobium halides under reducing conditions have so far remained unexplored. We found interesting results in the course of our study of reactions of group 13 metals with niobium chloride, with and without LiCl or sulfur. The synthesis and structure of a new compound ($In_2Li_2Nb_6Cl_{18}$) is presented in this paper.

EXPERIMENTAL

*Synthesis.* The new compound $In_2Li_2Nb_6Cl_{18}$ was prepared in high yield (about 80%) as black elongated hexagonal plate-like crystals from the reaction of stoichiometric amounts of $NbCl_5$, Nb powder, $InCl_3$ (or In metal), and LiCl [1]. The reaction took place in sealed Nb tubing at 820°C for 1 week, followed by slow cooling to 640°C and quenching in air. Because of the air- and moisture-sensitive nature of the reactants and product, all materials were handled under vacuum or argon atmosphere conditions.

$$2\ InCl_3 + 2\ LiCl + 2\ NbCl_5 + 4\ Nb \rightarrow In_2Li_2Nb_6Cl_{18}$$

$$[1]$$
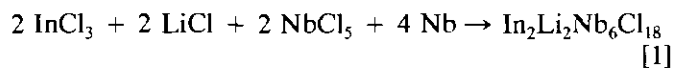
$In_2Li_2Nb_6Cl_{18}$ was characterized by X-ray powder diffraction (monochromated CuK_α radiation) obtained with an Enraf–Nonius (FR-552) guinier camera and α-quartz as an internal standard. Lattice parameters were determined from 65 indexed lines for the triclinic cell: $a = 922.0$ (2) pm, $b = 927.2$ (3) pm, $c = 926.7$ (2) pm, $\alpha = 119.28$ (2)°, $\beta = 96.51$ (2)°, $\gamma = 105.14$ (3)°.

Reactions with In metal but without lithium at 800°C yielded black well crystalline material of $InNb_6Cl_{15}$ in high yield [2].

$$In + 3\ NbCl_5 + 3\ Nb \rightarrow InNb_6Cl_{15}$$

$$[2]$$
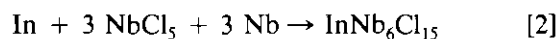
The latter was characterized by X-ray powder diffraction. Crystal data of $KZr_6Cl_{15}C$ were used for indexing the powder pattern of $InNb_6Cl_{15}$. Subsequent refinements of the orthorhombic lattice parameters (based on 17 indexed lines) lead to $a = 1781.8$ (9) pm, $b = 1342.2$ (6) pm, $c = 928.2$ (5) pm for $InNb_6Cl_{15}$.

Crystallography. Suitable single crystals of $In_2Li_2Nb_6Cl_{18}$ were sealed in thin-walled glass capillaries in a glove box. Rotation and precession photographs of a plate-like crystal revealed low Laue symmetry ($\bar{1}$). This was confirmed by X-ray diffraction data collected on a four-circle diffractometer (Siemens-Stoe AED 2), using graphite-monochromated MoK_α radiation. $In_2Li_2Nb_6Cl_{18}$ was found to crystallize in the triclinic system $P\bar{1}$ ($Z = 1$) with cell parameters $a = 923.6$ (2) pm, $b = 929.1$ (2) pm, $c = 928.2$ (2) pm, $\alpha = 119.50$ (3)°, $\beta = 96.50$ (3)°, $\gamma = 105.17$ (3)°, $V = 642.4 \times 10^6$ pm^3. Reflection data in a complete Ewald sphere ($2° \le 2\theta \le 60°$) were collected, and ten Ψ-scans were utilized for an empirical absorption correction. All 3675 symmetry-independent reflections ($F > 0$) out of 7320 measured were considered in subsequent calculations in the space group $P\bar{1}$ ($R_{av.} = 0.015$). The structure was solved using direct methods of the SHELXS-86 (12) program, and successive cycles of least-squares refinement and Fourier map synthesis using SHELX-76 (13). The anisotropic refinement (scattering factors from (14)) of all atoms (127 parameters) converged at $R = 0.035$ and $R_w = 0.035$, respectively. The final difference map was flat, with the largest background electron residual being less than 1 $e/Å^3$ (70 pm from the In atom).

THE STRUCTURE OF $In_2Li_2Nb_6Cl_{18}$

Positional parameters of $In_2Li_2Nb_6Cl_{18}$ determined from a single crystal are given in Table 1, anisotropic temperature factors are given in Table 2, and some important distances and bond angles are given in Table 3.

The new $In_2Li_2Nb_6Cl_{18}$ is the first reduced niobium halide containing a group 13 metal. The potential for isotypic substitution with Ga or Tl instead of In, and Br instead of Cl, respectively, is presently studied. The $(Nb_6Cl^i_{12})Cl^a_6$ clusters form a distorted primitive arrangement, being centered at the inversion center at the corners of the triclinic unit cell, or, alternatively, at 0, 0, 1/2, as shown in Fig. 1. Two In^+ and two Li^+ ions are centered in cavities of this arrangement. As in other cluster compounds of the general formula $(M^+)_4Nb_6X_{18}$ ($X = Cl$, Br) there are no direct halide bridges between different [Nb$_6$] clusters, and adjacent [Nb$_6Cl_{18}$] clusters are linked by halide bridges via cations.

Lithium is situated in a distorted tetrahedral coordination environment formed by four (outer) Cl atoms of four different clusters at an average distance $\bar{d}_{Li-Cl} = 240.2$ (6)

pm. This is the distance we would expect, considering the sum of the ionic radii of Li^+ (59 pm for coordination number 4) and Cl^- (181 pm) (15). Indium occurs as In^+ with a coordination number of twelve, and is situated in a distorted cubeoctahedron of chloride (Fig. 2). Bonding In–Cl distances range between 322.7 (1) and 366.20 (9) pm, with an average distance $\bar{d}_{In-Cl} = 348.8$ (1) pm. The separation between adjacent indium atoms appears to be too large (478.42 (8) pm) for any $In^+–In^+$ interactions to occur.

The dimensions of the $(Nb_6Cl^i_{12})Cl^a_6$ cluster do not deviate much from other compounds containing this cluster unit. The Nb–Cl^i distances are significantly shorter than

TABLE 1
Atomic Positions in $In_2Li_2Nb_6Cl_{18}$

Atom	x/a	y/b	z/c
Nb1	0.14154 (5)	0.25132 (6)	0.57245 (6)
Nb2	0.14379 (5)	0.02202 (6)	0.70378 (6)
Nb3	0.13471 (5)	0.89153 (6)	0.34317 (6)
In	0.66173 (8)	0.51710 (9)	0.73243 (9)
Li	0.6201 (10)	0.1897 (11)	0.0498 (10)
Cl1	0.3261 (2)	0.9005 (2)	0.5561 (2)
Cl2	0.9896 (2)	0.8485 (2)	0.0770 (2)
Cl3	0.3247 (2)	0.1693 (2)	0.4010 (2)
Cl4	0.9921 (2)	0.5785 (2)	0.2333 (2)
Cl5	0.9972 (2)	0.2697 (2)	0.3463 (2)
Cl6	0.6655 (2)	0.6763 (2)	0.1725 (2)
Cl7[a]	0.3032 (2)	0.7512 (2)	0.1525 (2)
Cl8[a]	0.3307 (2)	0.0584 (2)	0.9664 (2)
Cl9[a]	0.6713 (2)	0.4344 (2)	0.3383 (2)

[a] Outer chloride.

TABLE 2
Temperature Factors in $In_2Li_2Nb_6Cl_{18}$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nb1	106 (2)	112 (2)	124 (2)	66 (2)	28 (2)	34 (2)
Nb2	104 (2)	123 (2)	112 (2)	66 (2)	22 (2)	37 (2)
Nb3	106 (2)	121 (2)	117 (2)	63 (2)	32 (2)	44 (2)
In	358 (3)	464 (3)	437 (3)	230 (3)	95 (2)	119 (3)
Li	433 (14)	394 (13)	258 (13)	197 (13)	138 (13)	200 (13)
Cl1	157 (5)	245 (6)	171 (5)	110 (5)	46 (4)	108 (4)
Cl2	189 (5)	238 (6)	133 (5)	100 (4)	51 (4)	103 (4)
Cl3	157 (5)	164 (5)	224 (6)	103 (4)	92 (4)	49 (4)
Cl4	184 (5)	138 (5)	217 (5)	75 (4)	79 (4)	61 (4)
Cl5	195 (5)	172 (5)	203 (5)	127 (4)	22 (4)	43 (4)
Cl6	155 (5)	166 (5)	177 (5)	91 (4)	−6 (4)	17 (4)
Cl7[a]	216 (6)	242 (6)	219 (6)	127 (5)	113 (5)	121 (5)
Cl8[a]	190 (5)	252 (6)	188 (5)	135 (5)	19 (4)	86 (5)
Cl9[a]	214 (6)	149 (5)	227 (6)	96 (5)	47 (5)	29 (4)

Temperature factors are given as $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^* + \ldots)]$; U_{ij} in pm^2.

[a] Outer chloride.

TABLE 3

Important Distances (pm) and Bond Angles (°) in $In_2Li_2Nb_6Cl_{18}$

Atoms	Distance	Atoms	Angle
Nb–Nb	292.70 (5)–293.61 (4)^a	Cl7–Li–Cl8	113.9 (3)
Nb–Cl^i	244.8 (1)–246.9 (1)^a	Cl7–Li–Cl8'	109.4 (3)
Nb–Cl^a	258.5 (1)–264.1 (1)^a	Cl7–Li–Cl9	118.6 (2)
		Cl8–Li–Cl8'	97.0 (2)
Li–Cl7	233.2 (7)	Cl9–Li–Cl8'	100.3 (2)
Li–Cl8	240.1 (5)	Cl9–Li–Cl8	114.1 (3)
Li–Cl8'	247.6 (6)		
Li–Cl9	240.0 (7)		
In–Cl1	351.6 (1)		
In–Cl2	348.9 (1)		
In–Cl3	352.7 (1)		
In–Cl3'	366.2 (1)		
In–Cl4	355.6 (1)		
In–Cl5	361.3 (1)		
In–Cl6'	352.9 (1)		
In–Cl6	359.2 (1)		
In–Cl7	322.7 (1)		
In–Cl8	352.2 (1)		
In–Cl9	326.4 (1)		
In–Cl9'	336.7 (1)		

^{a} Range for bonding distances of the type Nb–Nb or Nb–Cl^i (i = inner) or Nb–Cl^a (a = outer).

the Nb–Cl^a bonds, and the Nb–Nb distances in the slightly distorted [Nb$_6$] octahedron of $In_2Li_2Nb_6Cl_{18}$ range between 292.70 (5) pm and 293.61 (4) pm (Table 3).

Electron count leads to 16 electrons per cluster, occupying Nb–Nb bonding states. Thus, all bonding cluster states (a_{1g}, t_{1u}, t_{2g}, a_{2u}) for idealized O_h symmetry of a local $[(Nb_6Cl^i_{12})Cl^a_6]^{4-}$ cluster) are filled.

THE ELECTRONIC STRUCTURE OF $In_2Li_2Nb_6Cl_{18}$

In compounds of the general formula $(M^+)_4Nb_6X_{18}$ (X = Cl, Br), with M = Na, K, Cs, empty M s orbitals are considered to be located well above the bonding Nb d block in energy. Therefore the electronic conditions for this class of compounds are usually described by molecular orbital treatment of an isolated $Nb_6X^{4-}_{18}$ cluster. In order to study the interactions of In atoms in the structure of $In_2Li_2Nb_6Cl_{18}$, we have performed a three-dimensional extended Hückel calculation (16) of the complete structure. See Appendix for details of the method.

The calculated density of states (DOS) (17) is shown in Fig. 3, with the contributions of Nb states to the total DOS highlighted in black. Chloride p states are responsible for a broad DOS maximum located between -12 eV and -17 eV. As shown in Fig. 3, the Nb (DOS) energy states of the title compound are qualitatively similar with the energy levels of an isolated $Nb_6X^{4-}_{18}$ cluster. A detailed analysis of orbital mixing and ordering of energy states of an isolated cluster has been provided in (18). As in
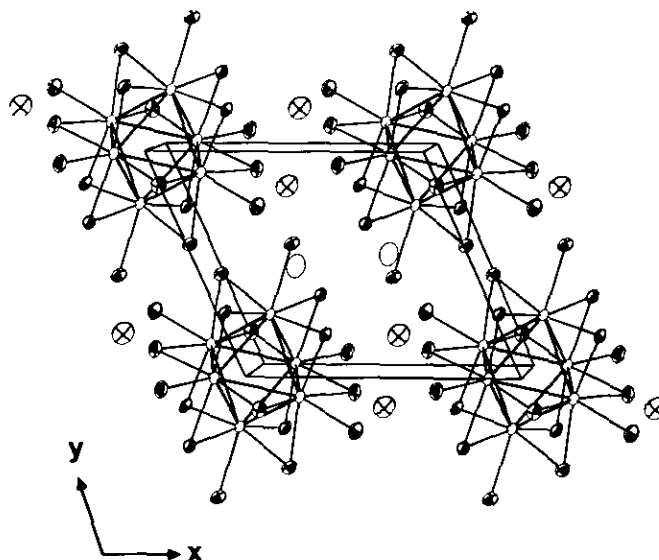

FIG. 1. Ortep drawing of the crystal structure of $In_2Li_2Nb_6Cl_{18}$, containing $(Nb_6Cl^i_{12})Cl^a_6$ clusters connected by indium (large empty ellipsoids) and lithium atoms (crossed ellipsoids).

other $Nb_6X^{4-}_{18}$ cluster compounds, eight metal-based bands are filled with electrons, corresponding with the a_{1g}, t_{1u}, t_{2g}, a_{2u} states (considering O_h point symmetry) with increasing energy. The a_{2u}-like band is the energetically highest Nb–Nb bonding state; it lies near the bottom of the antibonding Nb states (just below the Fermi level, ε_f). The Nb–Nb bonding nature of these states is shown by the computed crystal orbital overlap population (COOP) (17) in Fig. 3.

Two (filled) indium 5s bands are centered around -9.1 eV, whereas the (empty) indium 5p states are located near -2.2 eV. Nearly as high in energy are the (empty) lithium 2s orbitals, depending on the energy parameters that are used (Table 4). The Fermi level (ε_f) marked in Fig. 3 is
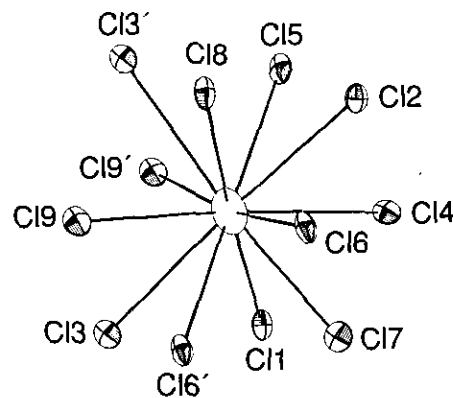

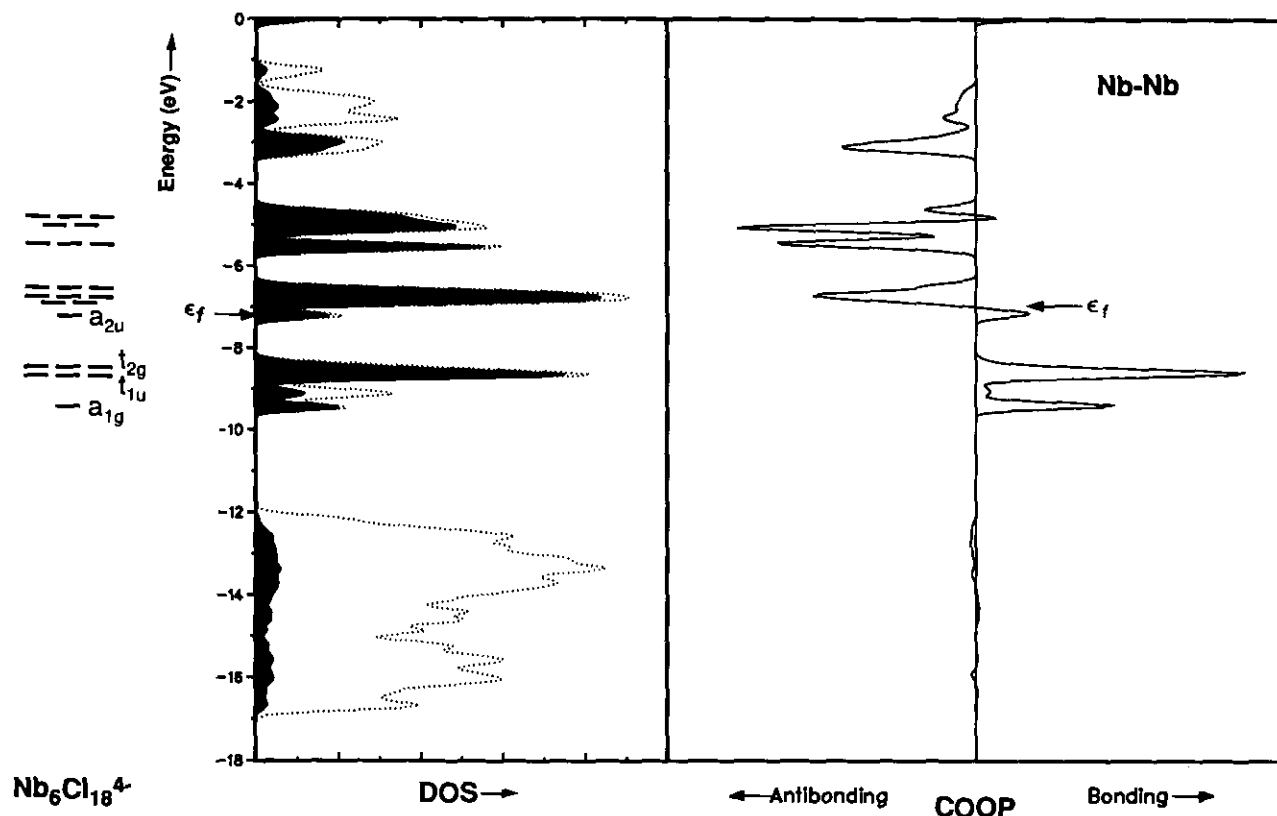FIG. 2. The coordination environment of the indium atom in $In_2Li_2Nb_6Cl_{18}$.

FIG. 3. The ordering of the lowest d levels of an isolated $Nb_6Cl_{18}^{4-}$ cluster, together with the DOS and the COOP of niobium states of the $In_2Li_2Nb_6Cl_{18}$ structure. Contributions of Nb states to the total DOS (dotted line) are projected in black. Note the filled indium 5s states centered near -9.1 eV, marked by the local maximum of the dotted line (total DOS). The Fermi level shown (ε_f) is consistent with 16 electrons occupying all bonding states of the $[Nb_6]$ cluster.

formally consistent with 16 electrons occupying Nb–Nb bonding states (eight energy bands). The Nb–Nb bonding interactions are marked by three bonding peaks in the COOP, of which the lowest and the highest represent an a-like state, and the center peak is consistent with two t-like states. All Nb states above the Fermi level exhibit antibonding Nb–Nb interactions. The computed Nb–In

and In–In overlap populations are antibonding. The lone pair for In^+ does not show a directional effect, as indicated by its nearly pure s character and the In–Cl distance parameters given in Table 3.

Note that this electronic situation is unique for compounds of this type with $[Nb_6]$ and $[Ta_6]$ clusters. In some of these, however, the a_{2u}-like level contains only one electron (e.g., in Nb_6F_{15} (19) or Ta_6Cl_{15} (20)).

CONCLUSION

The new $In_2Li_2Nb_6Cl_{18}$ may be a representative of a yet undiscovered family of mixed group 1 and 13 metal niobium halides. Lithium-containing compounds are of special interest because of their potential for ionic conductivity properties. The electronic conditions in these compounds are well understood, and may be altered by possible interactions between the group 13 cations. In $In_2Li_2Nb_6Cl_{18}$, however, no bonding In–In interaction is present.

The existence of compounds $(M^+)_4Nb_6X_{18}$ ($X =$ Cl or Br) with monovalent $M =$ Ga or In or Tl remains unknown. However, we have synthesized crystals of

TABLE 4
Extended Hückel Parameters

Atom	Orbital	H_{ii}(eV)	$\zeta_1{}^a$	ζ_2	$c_1{}^b$	c_2
Nb	$4d$	-8.26	4.08	1.64	0.6401	0.5510
	$5s$	-7.92	1.89			
	$5p$	-4.15	1.85			
Cl	$3s$	-26.30	2.18			
	$3p$	-14.20	1.73			
In (23)	$5s$	-12.60	1.90			
	$5p$	-6.19	1.68			
Li	$2s$	-5.400	0.65			
	$2p$	-3.500	0.65			

^{a} Slater type orbital exponent.
^{b} Coefficients in double zeta expansion.

$InNb_6Cl_{15}$, which have been studied, so far, only by powder and precession photographs. The indexed guinier pattern and the symmetry suggest this compound to be isotypic with $KZr_6Cl_{15}C$.

APPENDIX

The extended Hückel approach (16), within a tight-binding scheme (21) was employed in the theoretical calculations. A three-dimensional calculation of the complete structure was performed by applying translational symmetry to unit cell content $(In_2Li_2Nb_6Cl_{18})$ through the use of Bloch functions. A set of 8 k points of the triclinic Brillouin zone was used for the DOS calculations (17). The energy parameters (H_{ii}) and exponents used throughout the calculations are listed in Table 4. Off-diagonal matrix elements (H_{ij}) of the effective Hamiltonian were calculated according to the modified Wolfsberg–Helmholz formula (22).

ACKNOWLEDGMENTS

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