atoms at the base of an approximate square pyramid. The antimony pyramids and phosphate tetrahedra interlock through corners to form the sheets, and again large spaces exist between the sheets. Thus the similarity between Sn(II) and Sb(III) structures follows from the presence of an ns^2 valence-electron configuration in both cases. The normally spherical s electrons are repelled in the presence of the strongly electronegative oxygen.

Edge or face sharing between tin(II) pyramids and phosphate or phosphite tetrahedra has not been observed probably because, with normal P–O distances and O–P–O angles and with a Sn–O distance of 2.2 Å, the O–Sn–O bond angle would be 70°. This is smaller than the ligand bond angles usually found for Sn(II) (Table VI).

Using Brown's[28] bond-valence description, which was also applied to the SnF_2 structure[29] in the first paper of this series, one finds the following. Disregarding Sn–O distances above 3.4 Å (corresponding to bond valences $S \lesssim 0.08$ valence unit), the tin atoms in $SnHPO_3$ are coordinated to 7 oxygen atoms and those in $SnHPO_4$ to 8 oxygen atoms. Individual bond valences for $SnHPO_3$ are 0.54, 0.53, 0.46, 0.14, 0.12, 0.10 and 0.08 vu, adding to a total bond valence of 1.97 for Sn(II) in $SnHPO_3$. This would correspond most closely to configuration C described by Brown, with three strong and three weak bonds (Brown's basic configurations are all six-coordinated octahedral). For $SnHPO_4$ the bond valences are 0.53, 0.40, 0.36, 0.22, 0.21, and 3 × 0.09 vu, for a total Sn(II) bond valence of 1.99 vu. As was the case for one of the tin atoms in SnF_2,[29] this configuration with one strong, four intermediate, and the rest weak bonds does not correspond to any of the ones listed by Brown for Sn–O compounds. Since this is apparently the second case of a configuration that does not fit easily into the bond-valence description, it might appear that a further refinement of these concepts is in order.

Acknowledgment. Support of this research by the National Institute of Dental Research under Grant DE-116 is gratefully acknowledged.

Registry No. $SnHPO_4$, 16834-09-6; $SnHPO_3$, 14332-39-9.

Supplementary Material Available: Final values of $|F_o|$ and $|F_c|$ for $SnHPO_3$ and $SnHPO_4$ (12 pages). Ordering information is given on any current masthead page.

---

(28) I. D. Brown, *J. Solid State Chem.*, **11**, 214 (1974).

(29) R. C. McDonald, H. H. K. Hau, and K. Eriks, *Inorg. Chem.*, **15**, 762 (1976).

Contribution from Ames Laboratory—DOE and Department of Chemistry,
Iowa State University, Ames, Iowa 50011

A More Reduced Nb_6I_8 Cluster. Synthesis and Structure of $CsNb_6I_{11}$ and Its Hydride $CsNb_6I_{11}H$

HIDEO IMOTO and JOHN D. CORBETT*

Received October 16, 1979

The title compound is formed by direct reaction of Nb_3I_8 or Nb_6I_{11} with Nb and CsI in a sealed Nb tube at 910 °C. The structure and composition were established by X-ray crystallography: space group $P6_322$, $Z = 2$, $a = 11.007$ (2) Å, $c = 11.894$ (2) Å, $R = 0.047$, and $R_w = 0.060$ for 777 independent reflections after correction for absorption and secondary extinction. The structure of $Cs^+[(Nb_6I^i{}_8)I^a{}_{6/2}]^-$ consists of distorted metal octahedra face-capped by I^i to give Nb_6I_8 clusters (D_{3d} symmetry) which are interconnected to other octahedra in a hexagonal close-packed arrangement through bridging I^a. The Nb–Nb distances range from 2.771 (2) to 2.940 (2) Å, the average of 2.825 Å being 0.025 (4) Å less than that in the known and closely related Nb_6I_{11} ($Nb_6I_8I_{6/2}$). The observed distortion of the octahedra in both phases can be understood in terms of packing and strain at the bridging iodine atoms. The title phase is converted to the isostructural $CsNb_6I_{11}H$ by H_2 at 400 °C, whereas Mo_6Cl_{12}, $Na_4M_6Cl_{18}$ (M = Nb, Ta), and Ta_6Cl_{15} do not react with hydrogen at 300–400 °C. Hydrogen absorption by halides of transition groups 5 and 6 and zirconium appears to require an oxidation state below 2.0. The upper limits of composition (oxidation state) found for group 3–6 halohydrides correspond closely to the upper limits found with the binary hydrides of the same metals.

Introduction

The lowest iodide known for niobium, analytically $NbI_{1.83}$, presents an unusual pattern of both structure and reactivity. The principal structure features[1,2] are well described by the formulation $(Nb_6I_8)I_{6/2}$. This represents the presence of niobium metal octahedra with each face of the polyhedra capped with iodine to form the clusters $Nb_6I_8{}^{3+}$, and these are further interconnected into a three-dimensional structure by six additional iodine atoms at larger distances which bridge symmetrically between metal atoms in different clusters. This compound contains the only example of an octahedral niobium or tantalum cluster which is face capped rather than edge bridged by halide as it is in the more common $M_6X_{12}{}^{n+}$ units (n = 2, 3, 4). Simon[3] has also demonstrated the very unusual reaction of Nb_6I_{11} with H_2 near 400 °C to form $Nb_6I_{11}H$, the hydrogen atom being located *within* the cluster. More recent X-ray[4] and neutron[5] studies have confirmed the structures of Nb_6I_{11} and $Nb_6I_{11}H$ in more detail and have determined the characteristic vibration frequency of 1120 cm^{-1} for the hydrogen in the cluster.

The present work was undertaken for the purpose of examining other possible derivatives of this unusual cluster, for example, as the potential anion $Nb_6I_{14}{}^{3-}$. Previous work had reported only a brown solution of Nb_6I_{11} in molten NaI from which the phase may be recrystallized[1] and a lack of success in producing the iodide analogue of $CsNb_4Br_{11}$.[6] There was

---

(1) A. Simon, H.-G. von Schnering, and H. Schäfer, *Z. Anorg. Allg. Chem.*, **355**, 295 (1967).

(2) L. R. Bateman, J. F. Blount, and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1082 (1966).

(3) A. Simon, *Z. Anorg. Allg. Chem.*, **355**, 311 (1967).

(4) A. Simon, private communication, 1979.

(5) S. A. Barratt, B. Fender, and A. Simon, unpublished research, 1978.

(6) A. Broll, A. Simon, H.-G. von Schnering, and H. Schäfer, *Z. Anorg. Allg. Chem.*, **367**, 1 (1969).

0020-1669/80/1319-1241$01.00/0

also the possibility that new and more reduced anionic clusters might be formed. This feature has recently been discovered for several compounds of scandium, two of which have the simplified formulations $Sc^{3+}(Sc_6Cl_{12}^{3-})$[7] and $(ScCl_2^+)_\infty$-$(Sc_4Cl_6^-)_\infty$.[8] In fact, reaction of Nb_6I_{11} or its precursor Nb_3I_8 with a small amount of CsI in the presence of excess metal produces the more reduced $CsNb_6I_{11}$. This phase contains a similar Nb_6I_8 cluster unit in a more open structure and also takes up hydrogen to form $CsNb_6I_{11}H$. A number of other cluster synthesis and hydrogenation attempts are also described.

Experimental Section

Synthesis of $CsNb_6I_{11}$. Niobium sheets (ca. 0.5 × 7 × 40 mm) used in this work as a niobium source were obtained by cold rolling a rod of high-purity niobium (Ta = 116, C = 15, H = 0.6, N = 29, O = 24 ppm). Iodine (J. T. Baker) was sublimed into the reaction tube just before the reaction. CsI was recrystallized from 0.05 wt % HI solution and dried under vacuum at 350 °C. NbI_5[9] and Nb_3I_8[10] were prepared according to the literature except that Nb_3I_8 was purified by chemical transport in a fused silica container at 750 → 700 °C. The Nb_6I_{11} was obtained from the reduction of Nb_3I_8 with excess niobium in a sealed niobium tube at ca. 900 °C.[1]

The phase which crystallography showed to be $CsNb_6I_{11}$ was prepared by the reaction of Nb_3I_8 (0.5 g) or Nb_6I_{11} (5 g) with excess niobium and a 2–4% excess of CsI in an arc-welded niobium tube at ca. 910 °C for 10 days or longer. No impurity was evidenced in the Guinier pattern of either except that the two strongest lines of Nb_3I_8 were barely detectable. When the preparation was attempted from Nb_3I_8 on a larger scale (12 g of Nb_3I_8 and 2.0 g of CsI), it was necessary to reequilibrate after an intermediate grinding of the product and cleaning of the metal sheets in order to achieve complete reaction. The stoichiometries of the two synthesis reactions are $10Nb_6I_{11} + 6Nb + 11CsI \rightarrow 11CsNb_6I_{11}$ and $5Nb_3I_8 + 9Nb + 4CsI \rightarrow 4CsNb_6I_{11}$. One previous study[6] with the latter set of reactants yielded negative results in an attempt to prepare $CsNb_4I_{11}$ according to the reaction $5Nb_3I_8 + Nb + 4CsI \rightarrow CsNb_4I_{11}$ by transport in the neighborhood of 600–700 °C. The large difference only in the Nb coefficients necessary to obtain these two products is noteworthy.

Good crystals of the product were found in the form of blades sticking on the niobium sheets. These were shiny black as synthesized and very dark brown after being ground. The phase is moderately stable in air and is only partially decomposed after 1 day. It does not dissolve in, nor readily react with, H_2O, 1 M HCl, 1 M HI, acetone, or ethanol.

Reaction with Hydrogen. $CsNb_6I_{11}$ (3.61 g) was reacted with hydrogen at 640 torr and 350 °C, utilizing the apparatus described before.[11] After 6 h, the stoichiometry was $CsNb_6I_{11}H_{0.60}$. The temperature was then raised to 400 °C, and the composition $CsNb_6I_{11}H_{0.93}$ was obtained after 37 h more with final H_2 pressure of 602 torr. A second sample under 800 torr reached an essentially constant composition $CsNb_6I_{11}H_{0.91}$ after 9 days at 400 °C. This changed to $CsNb_6I_{11}H_{0.95(2)}$ at 300 °C (7 days), a change appropriate to a one-phase reaction.

The unit cell parameters for the two compounds, based on a least-squares fit of 2θ values for 30 lines measured from a Guinier film calibrated with NBS silicon as an internal standard, are as follows: for $CsNb_6I_{11}$ a = 11.007 (2) Å, c = 11.894 (2) Å, V = 1248.0 (4) Å^3; for $CsNb_6I_{11}H_{0.93}$ a = 11.021 (1) Å, c = 11.899 (2) Å, V = 1251.6 (4) Å^3. The difference for a is 0.014 (2) Å, for c 0.005 (3) Å, and for V 3.6 (6) Å^3.

Other Reactions. These are summarized in Table I. The starting materials Nb_3Br_8[10] and Ta_6Cl_{15}[12] were prepared as previously described. Reaction of Nb_3Br_8 (0.79 g), CsBr (~0.2 g), and excess Nb sheet in a sealed Nb tube gave $Cs_3Nb_2Br_9$[13] as identified by Weissenberg photographs. The analogous reaction of Nb_3I_8 (1.16 g), KI (0.26 g), and Nb gave Nb_6I_{11} and unreacted KI, not KNb_6I_{11}. Ta_6Cl_{15} (0.96 g), CsCl (0.20 g), and Ta strips (in Ta tube) yielded no new reduced products at 860 °C, which excludes $Cs_4Ta_6Cl_{18}$ known at lower temperatures (<800 °C)[14] as well. A small amount of a light yellow-brown phase was presumed to be a tantalum(V) or -(IV) double salt.

Table I. Results of Some Exploratory Synthesis Attempts

reactants	temp, °C	time, days	new products	H/cluster, mol
Nb_3I_8, CsI, Nb	910	10	$CsNb_6I_{11}$	
Nb_3Br_8, CsBr, Nb	910	33	$Cs_3Nb_2Br_9$	
Nb_3I_8, KI, Nb	900	34	Nb_6I_{11}, KI	
Ta_6Cl_{15}, CsCl, Ta	860	28	nil[a]	
Ta_6Cl_{15}, H_2 (1100 torr)	400	3	nil	<0.05
$Na_4Nb_6Cl_{18}$, H_2 (1700 torr)	350	3	nil	0.16 ± 0.06[a]
$Na_4Ta_6Cl_{18}$, H_2 (1000 torr)	300	1	nil[a]	<0.03
Mo_6Cl_{12}, H_2 (1900 torr)	300	10	nil	0.06 ± 0.12
	300	9	nil	0.15 ± 0.14

[a] See text.

The possible uptake of H_2 by several other clusters was also studied. The starting materials $Na_4Nb_6Cl_{18}$, $Na_4Ta_6Cl_{18}$,[15] and Mo_6Cl_{12}[16] were prepared as described in the literature. The conditions and measured H_2 uptake are also summarized in Table I. The initial $Na_4Nb_6Cl_{18}$ sample exhibited a weak ESR signal which got smaller on hydrogenation, indicating that an impurity in the diamagnetic $Na_4Nb_6Cl_{18}$ was probably responsible for the small H_2 uptake. A reaction of H_2 with Mo_6Cl_{12} previously reported[17] appears in error and must have been caused by impurities or leakage. The same report qualitatively noted that "Nb_6Cl_{14}" appeared to evolve H_2 to an extent corresponding to the composition $Nb_6Cl_{14}H_{1.2}$ if hydrogen had been present during the synthesis reaction (Nb + $NbCl_5$, 650 °C). However, the synthesis result could not be repeated. Only a small amount of impurity would have been necessary to desorb the indicated amount of hydrogen, e.g., finely divided NbH_x formed on cooling. Subsequent experience in other systems has also shown that the presence of hydrogen during synthesis reactions can cause disproportionation and considerably alter the distribution of products.[18]

The present results for Mo_6Cl_{12}, Nb_6Cl_{14}, and Ta_6Cl_{15} are in agreement with exploratory results cited by Simon.[3]

Crystal Selection and Data Collection. The crystal of $CsNb_6I_{11}$ used for data collection had the approximate shape of a hexagonal prism truncated by two bias faces at each end. The diameter of the prism was ca. 0.16 mm, and the longest length along the axis was 0.60 mm. The six side faces of the prism turned out to be the (100) set of faces generated by the principal axis of the hexagonal cell. Preliminary film work showed the structure belonged to the $6/mmm$ Laue group. The crystal was sealed in a 0.2-mm i.d. glass capillary in a nitrogen atmosphere and mounted with the c axis almost collinear with ϕ on a four-circle diffractometer designed and built in the Ames Laboratory. All procedures used for indexing and orientation of the crystal were as previously described.[19]

X-ray data were collected at ambient temperature by using Mo Kα radiation monochromatized with a graphite single crystal (λ 0.71002 Å). All reflections within a sphere defined at $2\theta \leq 60°$ in octants HKL and $H\bar{K}L$ were examined by using an ω-scan mode. The peak heights of three standard reflections were remeasured every 75 reflections to check on instrument and crystal stability; no decay of

---

(7) J. D. Corbett, R. L. Daake, K. R. Poeppelmeier, and D. H. Guthrie, *J. Am. Chem. Soc.*, **100**, 652 (1978).

(8) K. R. Poeppelmeier and J. D. Corbett, *J. Am. Chem. Soc.*, **100**, 5039 (1978).

(9) J. D. Corbett and P. X. Seabaugh, *J. Inorg. Nucl. Chem.*, **6**, 207 (1958).

(10) A. Simon and H.-G. von Schnering, *J. Less-Common Met.*, **11**, 31 (1966).

(11) A. W. Struss and J. D. Corbett, *Inorg. Chem.*, **16**, 360 (1977).

(12) H. Schäfer, H. Scholz, and R. Gerken, *Z. Anorg. Allg. Chem.*, **331**, 154 (1964).

(13) A. Broll, H.-G. von Schnering, and H. Schäfer, *J. Less-Common Met.*, **22**, 243 (1970).

(14) A. Broll, D. Juza, and H. Schäfer, *Z. Anorg. Allg. Chem.*, **382**, 69 (1971).

(15) F. W. Koknat, J. A. Parsons, and A. Vongvusharintra, *Inorg. Chem.*, **13**, 1699 (1974).

(16) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, NJ, 1970, p 456.

(17) A. W. Struss and J. D. Corbett, *Inorg. Chem.*, **17**, 965 (1978).

(18) H. Imoto and J. D. Corbett, submitted for publication in *Inorg. Chem.*

(19) R. A. Jacobson, *J. Appl. Crystallogr.*, **9**, 115 (1976).

Table II. Atomic and Thermal Parameters in $CsNb_6I_{11}$

atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Nb	0.1915 (1)	0.5157 (1)	0.3490 (1)	1.31 (4)	1.42 (4)	1.34 (4)	0.60 (3)	−0.02 (3)	0.05 (3)
I1[b]	0.0220 (1)	0.6516 (1)	0.3420 (1)	1.49 (3)	2.21 (3)	1.88 (3)	0.91 (3)	0.30 (2)	−0.15 (3)
I2[b]	$^1/_3$	$^2/_3$	0.5477 (1)	2.08 (3)	β_{11}	1.12 (4)	$\beta_{11}/2$	0	0
I3[c]	0	0.7187 (1)	0	1.99 (4)	2.08 (3)	2.48 (5)	$\beta_{11}/2$	−0.78 (4)	$\beta_{13}/2$
Cs	0	0	1/4	4.55 (9)	β_{11}	9.26 (27)	$\beta_{11}/2$	0	0

[a] $T = \exp[-4^{-1}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Inner iodine I^i. [c] Outer iodine I^a.

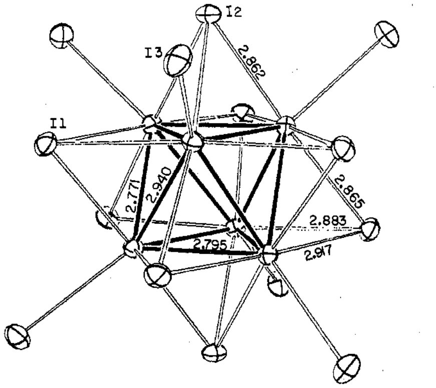

Figure 1. The cluster unit in $CsNb_6I_{11}$, with niobium atoms connected by heavy lines. The unit has D_{3d} symmetry; the exo iodine atoms shown also bond to other clusters (thermal ellipsoids at 50% probability).

diffraction intensity was noted. Cell parameters and their estimated standard deviations were obtained from tuned 2θ values for nine reflections in the range $30° < 2\theta < 40°$ which were obtained from the same crystal on the diffractometer. Their least-squares refinement yielded $a = 11.007$ (3) Å and $c = 11.899$ (4) Å, very close to the Guinier results given above.

Structure Determination and Refinement. Programs for data reduction, structure solution and refinement, and illustration were referenced before.[20] Atomic scattering factors for Cs^+, I^-, and Nb^{2+} (from the appropriate average of those for Nb^0 and Nb^{5+}) together with corrections for the real and imaginary parts of anomalous dispersion were taken from ref 21.

Data reduction yielded 3990 observed reflections ($I \geq 3\sigma(I)$) from 4182 measurements. Averaging of duplicate reflections gave 769 independent reflections. The only systematic absence observed was $00l$, $l \neq 2n$, which for the $6/mmm$ Laue group is consistent only with the space group $P6_322$. The positions of all atoms except Cs were determined from a Patterson map, and the Cs position was determined from a Fourier synthesis. Block-diagonal refinement with isotropic thermal parameters converged at $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.146$. Full-matrix least-squares refinement with anisotropic thermal parameters then gave convergence at $R = 0.08$ and $R_w = 0.10$ where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with $w = \sigma_F^{-2}$. At this stage the reflection data were corrected for absorption, the shape of the crystal being approximated with 10 faces. The volume absorption coefficient calculated[21] was 178.4 cm^{-1} and the transmission factors ranged from 0.087 to 0.172. Data reduction and averaging now yielded 777 independent reflections. Full-matrix least-squares refinement on this corrected data set converged at $R = 0.073$ and $R_w = 0.089$. A Fourier difference map at this state revealed sizable negative peaks at atom positions, and F_o was significantly less than F_c for the strongest reflections. The indicated secondary extinction correction was performed after which least-squares refinement gave $R = 0.047$ and $R_w = 0.063$. At this point the strongest and weakest groups of reflections were observed to have larger values of $w\Delta^2$ ($\Delta = |F_o| - |F_c|$), so the data set was reweighted in ten groups sorted according to F_o so that $w\Delta^2$ across the group was constant. The final refinement converged as residuals of $R = 0.047$ and $R_w = 0.060$ and gave a final difference Fourier map which was flat to ±2.0/Å.[3]

Table III. Bond Distances and Angles in $CsNb_6I_{11}$[a]

Distances (Å)			
Nb–Nb*a*	2.795 (2)	I1a–I1*c*	4.205 (2)
Nb–Nb*c*	2.940 (2)	I1a–I1*d*	3.790 (2)
Nb–Nb*d*	2.771 (2)	I1a–I2	4.146 (1)
Nb–Nb*e*	3.991 (2)	I1a–I3*a*	4.162 (2)
Nb–I1	2.917 (1)	I1a–I3*c*	3.929 (1)
Nb–I1*a*	2.883 (1)	I1a–I3*d*	4.383 (2)
Nb–I1*c*	2.865 (1)	I2–I3*c*	4.026 (1)
Nb–I2	2.862 (2)	I1a–I1*i*	3.783 (2)
Nb–I3	2.981 (1)	I1a–I2*i*	3.948 (1)
Cs–I1*a*	4.109 (1)	I1a–I3*e*	4.206 (1)
Cs–I3*a*	4.293 (1)		
Angles (Deg)			
Nb*a*–Nb–Nb*b*	60.00	I1–Nb–I1*c*	81.90 (4)
Nb*a*–Nb–Nb*d*	63.77 (4)	I1*c*–Nb–I1*a*	94.05 (4)
Nb*b*–Nb–Nb*c*	57.72 (4)	I1*a*–Nb–I2	92.39 (4)
Nb*c*–Nb–Nb*d*	58.51 (5)	I2–Nb–I1	91.67 (3)
Nb*a*–Nb–Nb*c*	88.16 (2)	I3*c*–Nb–I1	95.99 (4)
Nb*b*–Nb–Nb*d*	91.62 (2)	I3*c*–Nb–I1*c*	90.76 (4)
Nb*a*–Nb–I1*a*	61.82 (5)	I3*c*–Nb–I1*a*	84.12 (4)
Nb*a*–Nb–I2	60.78 (2)	I3*c*–Nb–I2	87.08 (4)
Nb*b*–Nb–I2	60.78 (3)	Nb–I1–Nb*a*	57.61 (5)
Nb*b*–Nb–I1	60.57 (5)	Nb–I1–Nb*c*	61.11 (4)
Nb*c*–Nb–I1	58.57 (4)	Nb*a*–I1–Nb*c*	57.64 (4)
Nb*c*–Nb–I1*c*	60.32 (3)	Nb–I2–Nb*a*	58.45 (4)
Nb*d*–Nb–I1*c*	61.50 (4)	Nb*a*–I3*d*–Nb	118.41 (6)
Nb*d*–Nb–I1*a*	60.87 (4)		

[a] Symmetry operations coded as follows: (*a*) $\bar{y}, x-y, z$; (*b*) $y-x, \bar{x}, z$; (*c*) $x, x-y, {}^1/_2-z$; (*d*) $y-x, y, {}^1/_2-z$; (*e*) $\bar{y}, \bar{x}, {}^1/_2-z$; (*f*) $y, y-x, {}^1/_2+z$; (*g*) $x-y, x, {}^1/_2+z$; (*h*) $\bar{x}, \bar{y}, {}^1/_2+z$; (*i*) $x-y, \bar{y}, \bar{z}$; (*j*) $y, x, \bar{z}$; (*k*) $\bar{x}, y-x, \bar{z}$ (unit translations not included).

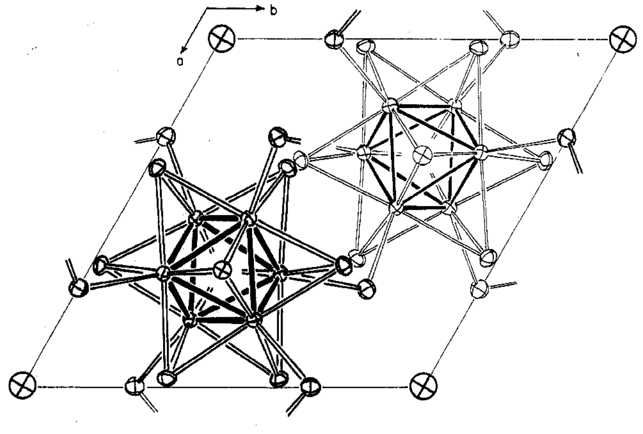

Figure 2. Contents of the unit cell of $CsNb_6I_{11}$ in infinite (001) projection, with cesium atoms located along 0, 0, z. The cluster in heavy outline is displaced by $c/2$ toward the viewer.

Results and Discussion

Description of Structure. Final positional and thermal parameters for $CsNb_6I_{11}$ are listed in Table II and important distances and angles, in Table III. Observed and calculated structure factor data are available as supplementary material.

The compound $CsNb_6I_{11}$ contains $Nb_6I_8^{2+}$ clusters in the form of niobium octahedra which are face capped by iodine, and each of these is bridged by six additional outer iodine atoms which bond evenly between metal atoms in different

---

(20) D. G. Adolphson, J. D. Corbett, and D. J. Merryman, *J. Am. Chem. Soc.*, **98**, 7234 (1976).

(21) "International Tables for X-ray Crystallography", Vols. III and IV, Kynoch Press, Birmingham, England, 1968 and 1974.

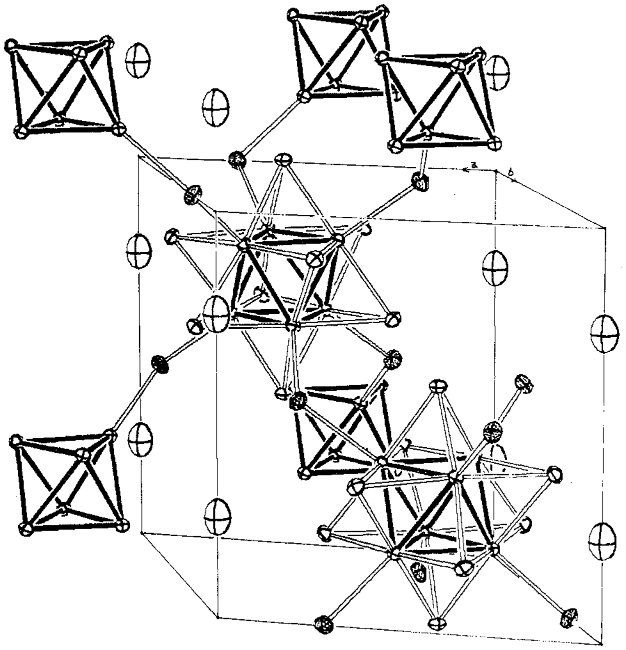

Figure 3. Interconnection of one cluster in $CsNb_6I_{11}$ to six neighbors through bridging I^a atoms (shown shaded). The I^i atoms lying outside the cell shown are omitted (50% thermal ellipsoids).

clusters, viz., $(Nb_6I^i_8)I^a_{6/2}$ according to a well-established scheme for the description of clusters (i = inner, a = outer).[22] Each cluster has rigorous D_{3d} (or 32) symmetry and an average Nb–Nb separation of 2.825 Å. Figure 1 shows this unit with unique distances labeled, and the contents of the unit cell are illustrated in Figure 2.

The distortion of the metal octahedron from local O_h symmetry arises from the rotation of one metal triangle by 6.1° about the C_3 axis relative to the other, this process generating alternating long and short distances (2.940 (2) and 2.771 (2) Å) between them compared with 2.795 (2) Å within the triangles. The I^i atoms follow this distortion and maintain relatively constant distances to the metal atoms. This in turn brings pairs of I^i atoms on faces which have the long Nb–Nb edge in common to within 3.79 Å of one another. The other short nonbonding distance, 3.78 Å, occurs between I^i atoms on adjoining clusters, as in center of Figure 2. Though these distances are short compared with twice the van der Waals radius of iodide ion (4.30 Å), the contrast is probably not so serious for iodine bonded with appreciable covalency.

The arrangement of clusters in the $CsNb_6I_{11}$ structure is best described in close-packed terms, although, again, the Nb–I bonding within and between the clusters is doubtlessly moderately covalent. The Nb_6I_8 units occur in hexagonally close-packed layers normal to *c*, with bridging iodine atoms I^a joining each cluster to three others in the layer above and to three of the same orientation in the layer below, as shown in Figure 3. Anything resembling close-packed iodine layers cannot be perceived in the structure since the niobium and inner iodine atoms in the face-capped octahedra are nearly coplanar, in contrast to the situation with edge-capped Zr_6I_{12} where metal atoms occur between close-packed iodine layers.[7] The cesium atoms also occupy positions of D_{3d} symmetry but lie in the layers of clusters rather than between them. The twelve nearer neighbors to cesium comprise (a) six I^i atoms at a distance of 4.110 Å, defining a trigonal antiprism which is flattened and somewhat twisted about the C_3 axis, and (b) six I^a at a slightly larger 4.293 Å distance in the form of an elongated trigonal antiprism. The relatively large cavity available to cesium compared with the van der Waals sum of 3.85 Å is evidently responsible for the somewhat large, though quite isotropic, thermal parameters found for that atom. However, an ion as small as sodium would appear necessary in order for the cation to pass the channel defined by the I^a atoms so ionic conduction does not seem likely in this phase. Formation of the potassium analogue was not achieved in an exploratory run (Table I).

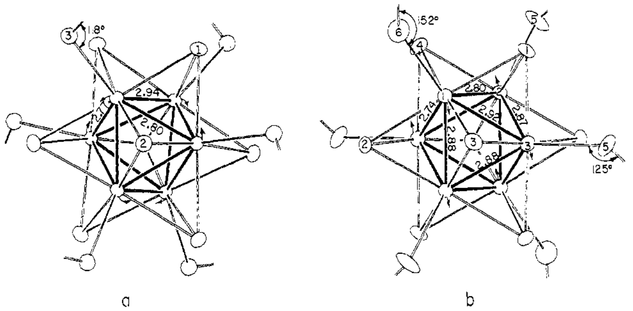

Figure 4. Comparison of the distortion of the clusters of (a) $CsNb_6I_{11}$, symmetry D_{3d}, and (b) Nb_6I_{11},[1,4] C_i, with displacements from an octahedron marked by arrows (infinite projection, 50% probability thermal ellipsoids).

Comparison with Nb_6I_{11}. The structure of Nb_6I_{11}[1,2] may be described as an orthorhombic distortion of a face-centered cube defined by Nb_6I_8 clusters except that clusters on the corners and faces are tilted in opposite directions through the operation of a series of glide planes. Two of the bridging I^a atoms link these clusters into puckered sheets $(Nb_6I^i_8)I^a_{4/2}$ and the third I^a links these into a three-dimensional array. Distances in $CsNb_6I_{11}$ are appropriately comparable to those in Nb_6I_{11}. For example, the average metal–metal distance of 2.825 (2) Å in the 20-electron cluster $Nb_6I_{11}^-$ is reasonable compared with an average of 2.850 (3) Å for the 19-electron analogue in Nb_6I_{11}, the latter being calculated from the results of a recent and more precise redetermination of the structure.[4] Distances for Nb–I^i in the cesium salt average 2.88 Å, 0.01 Å longer than in Nb_6I_{11}, each compound exhibiting a fairly small range in these distances, ±0.03 Å. On the other hand, the bridging I^a–Nb distances vary in the opposite way, a single 2.981 Å distance in the cesium salt vs. 2.925 Å in Nb_6I_{11}, again with a range of ±0.03 Å.

The two distinctly different modes of packing clusters of the formulation $(Nb_6I^i_8)I^a_{6/2}$ in $CsNb_6I_{11}$ and Nb_6I_{11} appear responsible for the observed distortions of the octahedra. The two Nb_6I_8 clusters are shown in infinite projection along the principal axes in Figure 4, the symmetry in $Nb_6I_{11}^-$ (left) being D_{3d} and that in the binary compound (right) only C_i. The latter is shown in the most nearly equivalent view normal to a pair of the least distorted triangles of a sensible parent octahedron which has edges of 2.883, 2.882, and 2.917 Å (σ = 0.003 Å). In $CsNb_6I_{11}$ the 6.1° twist on the top and bottom triangles of the "octahedron"—clearly visible in Figure 4a—is also accompanied by a further 4.6° displacement of I^a from the exo position normal to the polyhedron, that is, from the line through the center of the cluster and the niobium atom. It appears that packing of clusters to achieve van der Waals contacts between clusters at I^i, aided no doubt by the Cs^+ "glue", forces I^a outward from a normal bridging position, and this effect is relayed in a twisting of the top and bottom metal triangles in opposite directions throughout the structure via iodine bridging (Figure 3). The angle at I^a, 118.4°, is correspondingly less than the 124.6° found at I5 in Nb_6I_{11} (Figure 4b) which is taken to be the more nearly "normal" bridging angle in the formation of $Nb_6I_8I_{4/2}$ sheets.

The problem in Nb_6I_{11} focuses at the I6 atoms which bridge between Nb1 atoms in different sheets. Here the angle has

---

(22) H. Schäfer and H.-G. von Schnering, *Angew. Chem.*, **76**, 833 (1964).

opened to 152°, and the iodine is displaced 4° from the ideal exo position in addition to the observed polyhedral distortion. The evident strain gives a relative sideways displacement or push to the top and bottom triangles as shown in Figure 4b. An alternate description of the same result,[1,2] less convenient for the present comparison, recognizes the existence of a fairly regular waist for an octahedron (Nb2 and Nb3 with edges of 2.87 and 2.88 Å), with Nb1 displaced off the normal to this square to give short (2.80, 2.74 Å) and long (2.88, 2.92 Å) distances to the waist atoms, evidently because of the abnormally large "bite" forced on I6. The commonality observed for these distortion modes makes an explanation of that for Nb_6I_{11} in terms of a Jahn–Teller distortion[2] less plausible.[23]

The Cluster Hydrides. Hydrogenation of $CsNb_6I_{11}$ takes place about as easily as for Nb_6I_{11} itself and likewise in a one-phase reaction. The powder pattern of the $CsNb_6I_{11}H_{0.93}$ product was completely identical with that for $CsNb_6I_{11}$ except for very small shifts of the lines. Increases in the cell parameters of 0.015 (2) Å and 0.006 (3) Å on hydrogenation (Experimental Section) compare with changes 0.005 (4), 0.129 (8), and −0.088 (6) Å which occur in the orthorhombic axial lengths on deuteration of Nb_6I_{11}.[4] These correspond to very similar cell volume increases of 0.29% and 0.23%, respectively. In contrast, the volume increase on formation of ZrBrH from ZrBr, where the hydrogen is not constrained by a discrete cluster but the relative amount of hydrogen is greater, is 3.4%.

The formation of $CsNb_6I_{11}H$ makes it clear that the reaction of hydrogen with Nb_6I_{11} is not simply a result of the presence of an odd number of electrons binding the cluster. But other reasons for the hydrogen uptake in these particular Nb_6I_8 clusters are not at all obvious. They represent a very different situation from the metal itself with respect to electron density; the clusters contain 19 or 20 binding electrons, compared with only about $3^1/_3$ per octahedron of nearly the same size in close-packed niobium metal if a uniform spatial distribution of electron density is assumed over octahedral and tetrahedral volumes. Presumably only a small number of the metal–metal bonding states are totally symmetric and serve to bind hydrogen. In contrast to the hydrogen binding properties of the niobium iodide clusters, several other "electron-rich" niobium and tantalum chloride clusters with 14 or 15 electrons per octahedron, e.g., Ta_6Cl_{15}, $Nb_6Cl_{18}^{4-}$, and $Ta_6Cl_{18}^{4-}$, as well as Mo_6Cl_{12} (24 electrons) do not take up hydrogen under the conditions studied (Table I).

It would appear that the particularly low oxidation states involved in these two iodide clusters provide the best correlation with hydrogen reactivity, leading to the empiricism that no reduced halide of a group 5 or 6 metal with oxidation state of 2+ or higher is active with hydrogen. The same appears to apply to group 4 as well, at least for zirconium,[11,17] while a number of group 3 halides with oxidation states of 2+ or less do take up hydrogen. Thus only the very reduced halides in these groups which have a sufficiently high (Fermi) level or polarizability of electrons are able to dissociate and bind hydrogen either through extensive overlap with delocalized electrons or through the formation of H^-. The ability to bind hydrogen appears to vary with oxidation state and the number of electrons available for delocalized bonding in the same way as do the length and number of metal–metal bonds in the same compounds.[24]

Finally, the compositions achieved when hydrogen reacts with many reduced halides, namely, group 3 halides with oxidation states near 2+ or less and group 4, 5, and 6 halides below the oxidation state of 2+, correlate in a significant way with the limit of composition achieved in the simple binary hydrides of the same elements. Thus LaI_2H[17,18] compares with LaH_3 (and likewise with other rare earth elements), ZrXH[11] with ZrH_2, $ThI_2H_{1.7}$[17] with $ThH_{3.75}$, and $Nb_6I_{11}H$[3] with NbH_2, while there is no uptake when the oxidation state in the halide exceeds that of the highest hydride (Table I etc.). Some halohydrides do not achieve this limit ($CsNb_6I_{11}H$, $GdCl_{1.5}H_{0.9}$, $ScCl_{1.5}H_{0.7}$,[17] etc.), presumably for structural reasons. The similarities found for these upper limits suggest that substitution of halide for hydride is a small, not a major, change as far as stability. Further efforts to explain these factors would seem to have considerable merit.

Acknowledgment. Professor Simon and Dr. Fender generously provided us with unpublished structural data on Nb_6I_{11} and $Nb_6I_{11}H$. The authors are also indebted to Barb Helland and Professor R. A. Jacobson for assistance with the diffractometer and the programs. This work was in part supported by the U.S. Department of Energy, Contract No. W-7405-Eng-82, Division of Chemical Sciences, budget code AK-01-02-02-2.

Registry No. $CsNb_6I_{11}$, 73069-72-4; $Cs_3Nb_2Br_9$, 31853-72-2; Nb_3I_8, 12030-01-2; Nb_6I_{11}, 12196-47-3; Nb_3Br_8, 12049-24-0; $CsNb_6I_{11}H$, 73069-73-5.

Supplementary Material Available: A listing of structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

---

[23] The Nb_6I_{11} clusters do show substantial distortions at low temperature: H. Imoto and A. Simon, unpublished research.

[24] J. D. Corbett, unpublished research.