III and Tables SI and SII (supplementary material).

Extended Hückel MO Calculations. The calculations on the model compound $(NH_3)(PH_3)_3MCl$, M = Co, Ni, were performed by using the program ICON[23] and the routine FMO for the fragment orbital analysis.[24] The atomic parameters for N, C, H, Cl, Co, and Ni were taken from ref 25 and those for P from ref 26. M–P, M–Cl, N–H, and P–H were fixed at 2.25, 2.30, 1.1, and 1.1 Å, respectively.

Acknowledgment. Thanks are expressed to Franco Cecconi for drawings.

Registry No. $(np_3)CoBr$, 93684-10-7.

Supplementary Material Available: Listings of observed and calculated structure factors, final thermal parameters (Table SI), and hydrogen coordinates (Table SII) (12 pages). Ordering information is given on any current masthead page.

---

(23) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 3179.

(24) Fujimoto, H.; Hoffmann, R. *J. Phys. Chem.* **1974**, *78*, 1167.

(25) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

(26) Dubois, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1977**, *1*, 479.

Contribution from the Max-Planck-Institut für Festkörperforschung,
D-7000 Stuttgart 80, West Germany

$Nb_6I_8(NH_2CH_3)_6$: The Lowest Oxidation State in a Niobium Cluster Compound and Its Topochemical Formation

F. STOLLMAIER and A. SIMON*

Received May 1, 1984

Nb_6I_{11} reacts topochemically with a solution of methylamine in ethanol, yielding a product with the composition $Nb_6I_8(NH_2CH_3)_6$. The diamagnetic behavior as well as structural details and analytical data is consistent with a 22-electron cluster system containing the metal in the lowest oxidation state (1.33+) observed in niobium clusters until now. $Nb_6I_8(NH_2CH_3)_6$ crystallizes in the triclinic space group $P\bar{1}$, with $Z = 2$ and lattice constants $a = 1031.5$ (5) pm, $b = 1104.4$ (5) pm, $c = 1522.0$ (10) pm, $\alpha = 82.00$ (5)°, $\beta = 80.17$ (5)°, and $\gamma = 81.05$ (5)°. The structure contains two crystallographically independent clusters that exhibit distinctly different geometries. The mean Nb–Nb distances are identical for both clusters ($\bar{d}$(Nb–Nb) = 275 pm).

Introduction

The compound Nb_6I_{11} consists of a three-dimensional network of Nb_6I_8 clusters linked via I bridges.[1,2] The structure has two interesting aspects: (a) Nb_6I_8 clusters occur in spite of the pronounced electron deficiency. Only 19 instead of 24 electrons are available for M–M bonding in the Nb_6 octahedron. (b) The I bridges are strained, especially those involved in bonding layers of the MoX_2 type structure ($Mo_6X_8X_{4/2}X_2$) according to $Nb_6I_8I_{4/2}I_{2/2}$.[1,2] Both characteristics are responsible for an interesting physical property of the compound, namely the spin-crossover transition occurring at 274 K.[2-4] Both characteristics are also reflected in a peculiar topochemical reaction.

Crystals of Nb_6I_{11} react with aqueous ammonia, gaining volume along the [0, 1, 0] direction and splitting into extremely thin lamellae within seconds. As the orientation of the lamellae is parallel to the MoX_2 type layers in the crystal of Nb_6I_{11}, this "accordion" reaction has been interpreted in terms of a $(I_{2/2})$ bond breakage.[1] To prove this assumption, it must be shown that intermediate or final products of the reaction still contain the same kind of clusters as Nb_6I_{11} itself.

Unfortunately, the reaction product of Nb_6I_{11} and aqueous ammonia quickly decomposes to yield a white amorphous precipitation. Working with liquid ammonia in closed ampules obviously results in a similar topochemical reaction. After some weeks, large dark brown crystals form, but these easily become amorphous and cannot be characterized further.[5] Fortunately the topochemical reaction also occurs with amines. The primary product of the reaction of Nb_6I_{11} with a solution of CH_3NH_2 in ethanol gradually dissolves, and dark brown crystals form that are stable at room temperature and atmospheric pressure. Single-crystal X-ray and conventional chemical analyses result in a composition $Nb_6I_8(NH_2CH_3)_6$ for this compound, which in fact still contains the Nb_6I_8 cluster.

Experimental Section

Preparations. $\mathbf{Nb_6I_8(NH_2CH_3)_6}$ is prepared from 0.5 g of Nb_6I_{11} and 20 mL of a 20% solution of CH_3NH_2 in ethanol (dried and deoxygenated with Oxisorb[6] at room temperature. The reaction starts at once, leading to a suspension of brown lamellae (phase I) in a brown solution. The lamellae slowly vanish, and after about 6 days a mixture of two solids has formed that consists of black and in thin layers dark red platelets of hexagonal shape (title compound) covered by light brown amorphous solid (phase II). Frequent shaking of the solution during preparation helps to separate the two phases. The crystals of the title compounds are isolated by repeated washings with the mother liquor. Attention is necessary as the amorphous component (phase II) is pyrophoric when dry.

$Nb_6I_8(NH_2CH_3)_6$ is air sensitive and has to be handled under an inert atmosphere. It is only slightly soluble in alcohols, e.g. ethanol, slowly decomposing to light brown amorphous products. Analysis of C, H, N, and I was by combustion with V_2O_5 and Nb by ICP. Anal. Found (calcd): C, 4.14 (4.10); H, 1.73 (1.72); N, 4.80 (4.78); I, 56.6 (57.7); Nb, 31.7 (31.7). Reaction of N_6I_{11} and propylamine leads to the analogous compound.

$\mathbf{Nb_6I_8(NH_2C_3H_7)_6}$ is prepared from 2 g of Nb_6I_{11} and 10 mL of dry propylamine at room temperature. The reaction starts at once, leading to a dark red solution. After 4 days, the solution is decanted cautiously from a small amount of fine deposit. By diffusion of 2-propanol into the dark solution, brown crystals precipitate. No amorphous products are observed in the reaction with $C_3H_7NH_2$, but the oxidized product of the disproportionation reaction is soluble in the system. Anal. Found (calcd): C, 12.22 (11.22); H, 3.10 (2.82); N, 4.64 (4.36); I, 51.8 (52.7); Nb, 28.7 (28.9).

Investigations of $\mathbf{Nb_6I_8(NH_2CH_3)_6}$. Thermal Behavior. $Nb_6I_8(NH_2CH_3)_6$ was thermally decomposed at a basis pressure of 10^{-6} torr

---

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

(2) Imoto, H.; Simon, A. *Inorg. Chem.* **1982**, *21*, 308.

(3) Finley, J. J.; Nohl, H.; Vogel, E. E.; Imoto, H.; Camley, R. E.; Zevin, V.; Andersen, O. K.; Simon, A. *Phys. Rev. Lett.* **1981**, *46*, 1472.

(4) Finley, J. J.; Camley, R. E.; Vogel, E. E.; Zevin, V.; Gmelin, E. *Phys. Rev.* **1981**, *B24*, 1323.

(5) C. Bauspiess, Dissertation, Münster, 1977.

(6) Krauss, H. L.; Stach, H. DBP 1667129, 1968.

0020-1669/85/1324-0168$01.50/0

Table I. Final Positional Parameters for $Nb_6I_8(NH_2CH_3)_6$

Atom	x	y	z
Nb1	-0.0766 (3)	0.3511 (3)	0.5081 (2)
Nb2	0.1685 (3)	0.3987 (3)	0.5201 (2)
Nb3	-0.0441 (3)	0.4913 (2)	0.6321 (2)
Nb4	0.5236 (3)	-0.1636 (2)	0.0681 (2)
Nb5	0.3140 (3)	0.0208 (3)	0.0584 (2)
Nb6	0.5468 (3)	0.0708 (3)	0.0965 (2)
I1	-0.3178 (2)	0.4475 (2)	0.6257 (2)
I2	0.0436 (2)	0.2271 (2)	0.6634 (1)
I3	0.2162 (2)	0.5564 (2)	0.6476 (2)
I4	0.1481 (2)	0.2430 (2)	0.3829 (2)
I5	0.2765 (3)	-0.2286 (2)	0.0280 (2)
I6	0.3300 (2)	0.2734 (2)	0.0898 (2)
I7	0.7761 (3)	-0.1193 (2)	0.1133 (2)
I8	0.3821 (3)	-0.0765 (2)	0.2365 (1)
N1	-0.177 (3)	0.162 (3)	0.526 (2)
N2	0.385 (3)	0.284 (3)	0.551 (2)
N3	-0.113 (2)	0.477 (2)	0.791 (2)
N4	0.560 (3)	-0.358 (3)	0.158 (2)
N5	0.087 (3)	0.031 (3)	0.129 (2)
N6	0.629 (4)	0.159 (3)	0.215 (3)
C1	-0.186 (4)	0.090 (4)	0.454 (3)
C2	0.422 (5)	0.160 (4)	0.542 (3)
C3	-0.020 (3)	0.468 (3)	0.855 (2)
C4	0.582 (4)	-0.474 (4)	0.133 (3)
C5	0.007 (5)	0.139 (5)	0.163 (4)
C6	0.556 (5)	0.194 (5)	0.290 (4)

(NETZSCH thermobalance STA 429, tantalum crucible, orifice of 1-mm diameter, content of $Nb_6I_8(NH_2CH_3)_6$ about 30 mg, heating rate 5 °C/min in connection with a BALZERS quadrupole mass spectrometer QMG 511).

The decomposition of $Nb_6I_8(NH_2CH_3)$ starts at 100 °C. The first weak plateau is reached at 150 °C. The weight loss of 3.3% corresponds to a loss of two molecules of CH_3NH_2 per formula unit. A more pronounced plateau is reached at 230 °C, corresponding to a loss of two more CH_3NH_2 ligands (3.2%). The product still has the shape of the original crystal but is amorphous to X-rays (phase III; see below).

Further loss of methylamine is observed up to 360 °C, but no plateau occurs. Release of iodine is rapidly increasing above 290 °C. At ca. 900 °C a plateau corresponding to a total weight loss of 68.1% occurs (roughly equivalent to 4 I_2 + 6 NH_2CH_3). The residue consists of Nb_2C (carbon could originate from NH_2CH_3) according to its Guinier pattern compared with no. 15-147 of the ASTM file. The compound analytically proved to be free of nitrogen.

Magnetic Behavior. The magnetic susceptibility of $Nb_6I_8(NH_2CH_3)_6$ was determined by the Faraday method between -240 and +20 °C. No field dependence was observed up to 10 kG. The molar susceptibility varies between $\chi_{mol} = +8 \times 10^{-6}$ (33 K) and -2×10^{-6} cm^3 mol^{-1} (291 K), which means that the sample is nonmagnetic within experimental error (0.04 μ_B per $Nb_6I_8(NH_2CH_3)_6$ cluster). With a rough estimate of the diamagnetic contribution ($Nb^{1.33+}$ $\sim$-35 $\times 10^{-6}$, I^- -50 $\times 10^{-6}$,[7] CH_3NH_2 -27 $\times 10^{-6}$ cm^3 mol^{-1} [8]) a temperature-independent paramagnetic value $\chi_{TIP} \approx +770 \times 10^{-6}$ cm^3 mol^{-1} is obtained.

Photoelectron Spectroscopy. The photoelectron spectra (Al Kα, He I) of $Nb_6I_8(NH_2CH_3)_6$ and $Nb_6I_8(NH_2C_3H_7)_6$ were recorded on a Leybold-Heraeus spectrometer LHS-10. The results are given and discussed elsewhere.[9]

X-ray Investigations. Amorphous Products (Phases I–III). The diffuse patterns (Mo Kα) of phases I and III exhibit four intense structured maxima centered around d = 3.4, 2.1, 1.3, and 1.0. These maxima closely correspond to the maxima of the Fourier transform in the patterns of crystalline Nb_6I_{11} and $Nb_6I_8(NH_2CH_3)_6$ and reflect the presence of Nb_6I_8 clusters in all phases. In contrast, phase II yields a diffuse pattern with hardly any observable structure.

Powder Investigation. Powder patterns (modified Guinier technique;[10] 27 *hkl* with 4.7° < θ < 21.3°) lead to the lattice constants a = 1031.5 (5) pm, b = 1104.4 (5) pm, c = 1522.0 (10) pm, α = 82.00 (5)°, β = 80.17 (5)°, γ = 81.05 (5)°, space group $P\bar{1}$, Z = 2, ρ = 3.484 g cm^{-3}. From temperature-dependent powder patterns (+20 to -100 °C) a sharp and reversible phase transition at ca. -50 °C could be elucidated. Obviously the phase transition is of first order, as a single crystal of $Nb_6I_8(NH_2CH_3)$ is irreversibly destroyed when cooled below -55 (5) °C.

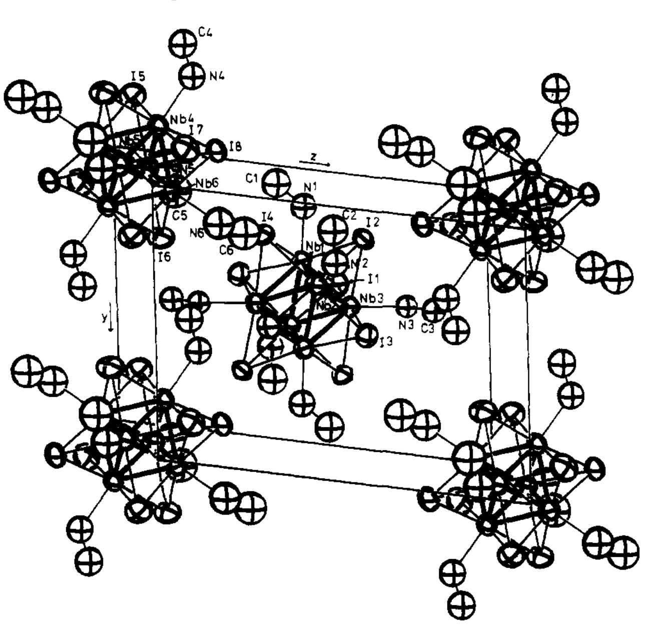

Figure 1. Unit cell of $Nb_6I_8(NH_2CH_3)_6$ (ORTEP plot[27]).

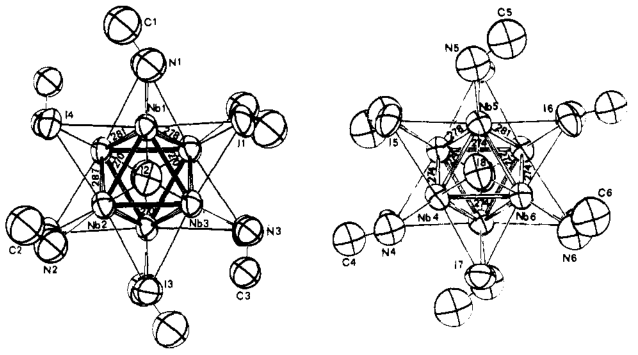

Figure 2. Independent $Nb_6I_8(NH_2CH_3)_6$ molecules. Atoms are drawn as ellipsoids of 50% probability.

Single-Crystal Investigation. Single crystals were sealed in glass capillaries under argon and measured on a P2$_1$ diffractometer (SYNTEX). The lattice constants were identical with the given values within 3σ; the crystal system was checked by precession photographs. A total of 4090 intensities were recorded at room temperature (Mo Kα, ω–2θ mode, 2$\theta \leq$ 44°, scan range 1°, variable scan speed between 0.75 and 29.3°/min), out of which 2870 had $I \leqslant 2\sigma(I)$ and were used for the calculations (program system SHELXTL, version 3[11]). An empirical absorption correction (ψ scan, μ = 87.46 cm^{-1}) was applied. The structure was solved by direct methods. Final reliability factors $R = \sum|F_o| - |F_c|/\sum|F_o| = 0.080$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.074$ ($w = 1/\sigma^2(F_o) + (0.0011F_o)^2$) were reached. The protons could not be located and were omitted in the calculations. Atomic form factors used correspond to neutral atoms.[12,13] A final difference map was flat to ±1.6 e Å^{-3}. The atomic parameters are summarized in Table I.

Results and Discussion

Description of the Crystal Structure. A projection of the crystal structure of $Nb_6I_8(NH_2CH_3)_6$ is shown in Figure 1. Relevant distances are summarized in Table II. The unit cell contains two crystallographically independent $Nb_6I_8(NH_2CH_3)_6$ units around the inversion centers. The structure is characterized by Nb_6I_8 clusters consisting of Nb_6 octahedra in the environments of I_8 cubes. Six methylamine ligands occupy corner positions of the Nb_6 core. The clusters are not linked in the structure of Nb$_6$-

---

(7) Simon, A. *Z. Anorg. Allg. Chem.* **1967**, *355*, 311.
(8) Haberditzel, W. "Magnetochemie"; Akademie-Verlag: Berlin, 1968.
(9) Geyer-Lippmann, J.; Simon, A.; Stollmaier, F. *Z. Anorg. Allg. Chem.* **1984**, *516*, 55.
(10) Simon, A. *J. Appl. Crystallogr.* **1970**, *3*, 11.
(11) Sheldrick, G. M. SHELXTL, Version 3 (unpublished), 1981.
(12) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.
(13) Cromer, D. T.; Libermann, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Table II. Interatomic Distances (Å) and Angles (deg)[a]

Interatomic distances

Nb1	- Nb3	269.5 (5)
Nb2	- Nb3	269.7 (4)
Nb1	- Nb2	270.2 (5)
Nb1	- Nb2a	277.7 (4)
Nb1	- Nb3a	280.5 (4)
Nb1	- Nb3a	287.0 (4)
Nb5	- Nb6	271.7 (5)
Nb4	- Nb6	273.6 (4)
Nb4	- Nb5	273.8 (4)
Nb6	- Nb4a	274.4 (4)
Nb5	- Nb6a	277.5 (4)
Nb5	- Nb4a	280.6 (4)
I1	- Nb1	295.2 (4)
I1	- Nb3	295.7 (4)
I1	- Nb2a	296.3 (4)
I2	- Nb3	291.5 (3)
I2	- Nb1	292.8 (4)
I2	- Nb2	294.2 (3)
I3	- Nb2	292.8 (4)
I3	- Nb3	294.0 (4)
I3	- Nb1a	296.1 (4)
I4	- Nb2	293.7 (4)
I4	- Nb1	294.8 (3)
I4	- Nb3a	295.5 (3)
I5	- Nb4	293.4 (5)
I5	- Nb5	294.9 (4)
I5	- Nb6a	297.3 (4)
I6	- Nb6	291.1 (4)
I6	- Nb4a	292.0 (4)
I6	- Nb5	292.9 (4)
I7	- Nb6	292.9 (4)
I7	- Nb4	293.2 (5)
I7	- Nb5a	293.3 (4)
I8	- Nb4	293.2 (3)
I8	- Nb5	293.3 (4)
I8	- Nb6	295.5 (4)
Nb1	- N1	243.4 (35)
Nb2	- N2	247.5 (30)
Nb3	- N3	239.2 (29)
Nb4	- N4	239.4 (30)
Nb5	- N5	239.6 (29)
Nb6	- N6	248.8 (48)
N1	- C1	146.4 (60)
N2	- C2	138.3 (54)
N3	- C3	146.3 (44)
N4	- C4	136.1 (57)
N5	- C5	144.6 (61)
N6	- C6	132.6 (69)
I1	- I2	420.3 (3)
I1	- I3a	411.7 (3)
I1	- I4a	405.3 (3)
I2	- I3	425.2 (3)
I2	- I4	420.7 (2)
I3	- I4a	411.9 (3)
I5	- I6a	413.2 (4)
I5	- I7a	413.9 (3)
I5	- I8	416.1 (4)
I6	- I7a	410.5 (4)
I6	- I8	419.2 (3)
I7	- I8	416.0 (4)
N1	- I2	355.3 (35)
N1	- I1	367.5 (32)
N1	- I3a	380.8 (30)
N1	- I4	383.2 (29)
N2	- I3	360.2 (32)
N2	- I2	374.9 (30)
N2	- I1a	377.9 (30)
N2	- I4	394.0 (35)
N3	- I2	361.0 (25)
N3	- I1	362.7 (29)
N3	- I4a	379.5 (24)
N3	- I3	386.3 (22)
N4	- I8	360.1 (31)
N4	- I7	363.2 (34)
N4	- I6a	377.8 (29)
N4	- I5	379.4 (32)
N5	- I5	358.6 (31)
N5	- I8	365.9 (32)
N5	- I7a	376.8 (29)
N5	- I6	386.5 (34)
N6	- I7	363.5 (36)
N6	- I5a	366.5 (43)
N6	- I6	385.5 (44)
N6	- I8	386.0 (40)
C1	- I3a	398.0 (42)
C1	- I4	399.2 (43)
C1	- I2	480.6 (50)
C1	- I1	492.5 (46)
C2	- I4	394.9 (52)
C2	- I2	402.7 (47)
C2	- I1a	478.2 (42)
C2	- I3	491.5 (44)
C3	- I3	375.6 (28)
C3	- I2	412.0 (34)
C3	- I4a	470.6 (30)
C3	- I1	507.1 (39)
C4	- I6a	383.6 (42)
C4	- I5	420.5 (41)
C4	- I7	462.1 (47)
C4	- I8	489.9 (43)
C5	- I6	378.9 (54)
C5	- I7a	443.0 (56)
C5	- I8	444.5 (51)
C5	- I5	502.9 (51)
C6	- I8	395.6 (61)
C6	- I6	406.6 (61)
C6	- I7	473.5 (56)
C6	- I5a	483.6 (58)

Angles

Nb3	- Nb1	- Nb2	60.0 (1)
Nb3a	- Nb1	- Nb2	63.2 (1)
Nb3	- Nb1	- Nb3a	91.9 (1)
Nb2	- Nb1	- Nb2a	91.4 (1)
Nb2a	- Nb1	- Nb3	62.8 (1)
Nb2a	- Nb1	- Nb3a	57.8 (1)
Nb3	- Nb2	- Nb1	59.9 (1)
Nb3a	- Nb2	- Nb1	61.6 (1)
Nb3	- Nb2	- Nb3a	90.4 (1)
Nb1	- Nb2	- Nb1a	88.6 (1)
Nb1a	- Nb2	- Nb3	60.4 (1)
Nb1a	- Nb2	- Nb3a	57.0 (1)
Nb1	- Nb3	- Nb2	60.1 (1)
Nb1	- Nb3	- Nb1a	88.1 (1)
Nb1	- Nb3	- Nb2a	59.8 (1)
Nb2	- Nb3	- Nb1a	60.6 (1)
Nb2	- Nb3	- Nb2a	89.6 (1)
Nb1a	- Nb3	- Nb2a	56.9 (1)
Nb6	- Nb4	- Nb5	59.5 (1)
Nb6	- Nb4	- Nb6a	88.9 (1)
Nb6a	- Nb4	- Nb5	60.1 (1)
Nb5a	- Nb4	- Nb6	60.8 (1)
Nb5	- Nb4	- Nb5a	90.3 (1)
Nb6a	- Nb4	- Nb5a	58.6 (1)
Nb6	- Nb5	- Nb4	60.2 (1)
Nb6	- Nb5	- Nb6a	88.6 (1)
Nb6a	- Nb5	- Nb4	59.5 (1)
Nb4a	- Nb5	- Nb6	59.7 (1)
Nb4	- Nb5	- Nb4a	89.7 (1)
Nb6a	- Nb5	- Nb4a	58.7 (1)
Nb5	- Nb6	- Nb4	60.3 (1)
Nb5a	- Nb6	- Nb4	61.8 (1)
Nb5	- Nb6	- Nb5a	91.4 (1)
Nb4	- Nb6	- Nb4a	91.1 (1)
Nb4a	- Nb6	- Nb5	61.2 (1)
Nb4a	- Nb6	- Nb5a	59.5 (1)
Nb1	- I1	- Nb3	54.3 (1)
Nb1	- I1	- Nb2a	56.0 (1)
Nb3	- I1	- Nb2a	58.0 (1)
Nb3	- I2	- Nb1	54.9 (1)
Nb3	- I2	- Nb2	54.8 (1)
Nb1	- I2	- Nb2	54.8 (1)
Nb2	- I3	- Nb3	54.7 (1)
Nb2	- I3	- Nb1a	56.3 (1)
Nb3	- I3	- Nb1a	56.8 (1)
Nb2	- I4	- Nb1	54.7 (1)
Nb2	- I4	- Nb3a	58.3 (1)
Nb1	- I4	- Nb3a	56.7 (1)
Nb4	- I5	- Nb5	55.5 (1)
Nb4	- I5	- Nb6a	55.4 (1)
Nb5	- I5	- Nb6a	55.9 (1)
Nb6	- I6	- Nb4a	56.1 (1)
Nb6	- I6	- Nb5	55.5 (1)
Nb4a	- I6	- Nb5	57.3 (1)
Nb6	- I7	- Nb4	55.6 (1)
Nb6	- I7	- Nb5a	56.5 (1)
Nb4	- I7	- Nb5a	57.2 (1)
Nb4	- I8	- Nb5	55.7 (1)
Nb4	- I8	- Nb6	55.4 (1)
Nb5	- I8	- Nb6	55.0 (1)
C1	- N1	- Nb1	126.0 (23)
C2	- N2	- Nb2	123.4 (30)
C3	- N3	- Nb3	122.9 (16)
C4	- N4	- Nb4	129.3 (26)
C5	- N5	- Nb5	125.3 (29)
C6	- N6	- Nb6	125.6 (36)

[a] Atoms labeled with "a" are derived from the asymmetric unit by inversion symmetry.

$I_8(NH_2CH_3)_6$. One therefore would not expect considerable influence of the crystal lattice on the detailed geometry of the Nb_6 units as in the case of, e.g., Nb_6I_{11}.

Surprisingly, the crystallographically independent Nb_6I_8 clusters exhibit quite distinct differences in the structure of $Nb_6I_8(NH_2CH_3)_6$. The cluster made up of Nb1, Nb2, and Nb3 is the more distorted one, the Nb–Nb distances ranging from 270 to 287 pm. Distances in the cluster containing Nb4, Nb5, and Nb6 range from 272 to 281 pm. As shown in Figure 2 atoms Nb1, Nb2, and Nb3 (Nb1a, Nb2a, Nb3a) are arranged in equilateral triangles, forming an elongated trigonal antiprism. The triangles are shifted in a parallel mode, Nb1 and Nb1a approaching the pseudo-3-fold axis. Due to this shift the distance *d*(Nb2a–Nb3) is elongated to the largest extent in that cluster. In contrast, the cluster containing the atoms Nb4, Nb5, and Nb6 is characterized by a quadratic arrangement of the atoms Nb4, Nb6, Nb4a, and Nb6a. Atoms Nb5 (and Nb5a), which represent the apices of the distorted Nb_6 octahedron, are shifted away from the pseudo-4-fold axis toward atoms Nb4 and Nb6 (Nb4a, Nb6a).

In principle, the different geometries could be due to different valence electron concentrations in the two types of clusters. Partial replacement of CH_3NH_2 by CH_3NH^- can be ruled out from the results of the structure investigation, more precisely from Nb–N distances and thermal parameters of N atoms. But, an additional H atom located inside one of the Nb_6 units as in HNb_6I_{11} and $HCsNb_6I_{11}$, not detectable by X-ray or conventional chemical analyses, could result in different valence electron concentrations.

Magnetic measurements contradict this assumption, because $Nb_6I_8(NH_2CH_3)_6$ is essentially nonmagnetic. The result cannot be due to antiferromagnetic coupling between the well-separated clusters but gives evidence for an even number of electrons in M–M bonding states that are all spin paired in both cluster types in accordance with the expectation for 22-electron systems. As with other M_6X_8 or M_6X_{12} clusters the diamagnetic contributions are nearly compensated by a temperature-independent paramagnetism.[4,7,14] Less decisive, yet in agreement with the magnetic results, are the results of ESCA measurements.[9] The bond energies (BE) of the Nb $3d^{5/2}$ levels of different niobium iodides NbI_n (n = 5, 4, 2.67, 1.83) and niobium metal are linearly dependent on the oxidation number *n*. The relation is $BE(3d^{5/2}) = 201.8 + 1.07n$ (eV). The measured bond energies of the Nb $3d^{5/2}$ levels in the compounds $Nb_6I_8(NH_2CH_3)_6$ (203.3 eV) and $Nb_6I_8(NH_2C_3H_7)_6$ (203.1 eV) are in good agreement with the value 203.2 eV calculated from the above given relation with $n = 1.33+$. Last but not least, the assumption of 22-electron cluster systems is consistent with, though not proved by, the Nb–Nb distances in $Nb_6I_8(NH_2CH_3)_6$. The averaged distances are signficantly shorter than in any other compound containing Nb_6 units and, within standard deviations, identical for both cluster types ($\bar{d}$ = 275 pm). Mean distances in Nb_6I_{11} and $CsNb_6I_{11}$ are 285 and 282.5 pm, respectively.[1,17]

An exponential bond length–bond strength function[15] as suggested by Hönle and Yvon for the interpretation of Mo–Mo distances in Chevrel compounds[16] yields bond order sums $\sum n_i$ (calculated from $n = [d(1)/(d(n)]^5$, with a single-bond distance $d(1)$ = 270.8 pm for niobium[17]) as follows: Nb_6I_{11} (9.5 electron pairs) 9.36 (300 K) and 9.43 (110 K); $CsNb_6I_{11}$ (10 electron pairs) 9.63; $Nb_6I_8(NH_2CH_3)_6$ (11 electron pairs) 11.05 (cluster Nb1, Nb2, Nb3) and 11.08 (Nb4, Nb5, Nb6). Corbett[18] analyzed a great number of transition-metal cluster compounds and showed that a well-defined correlation between number of electrons occupying metal–metal bonding states, sum of Pauling bond order per electron pair PBO/e [calculated from $d(n) = d(1) - 0.6 \log (n)$ (n = bond order, $d(1)$ = single-bond distance)], and metal–metal distances exists. This relation leads for the compounds containing Nb_6I_8 to a wider range of bond order sums [PBO/e ranging from 0.76 for Nb_6I_{11} (300 K) to 0.98 for $Nb_6I_8(NH_2CH_3)_6$].

The distortion of Nb_6I_8 clusters in $Nb_6I_8(NH_2CH_3)_6$ is not comparable to that in the rhombohedral high-temperature Chevrel phases Mo_6S_8M (M = Pb, Ba)[19,20] containing the isoelectronic Mo_6S_8 clusters. The latter are elongated along a 3-fold axis, and the deviation of distances from a mean Mo–Mo distance is significantly smaller than in the case of the niobium compound. In the triclinic low-temperature phases of $Ni_{0.66}Mo_6Se_8$,[21] $Ni_{0.84}Mo_6Te_8$[22] and $Cu_{1.8}Mo_6S_8$,[23] the deviation is however of the same order of magnitude as in the niobium compound. The regularity as well as the rigidity of the M_6 unit is enhanced when the maximum number of 24 electrons is reached in the unit. In contrast to Nb_6I_{11} the isostructural phases $Mo_6Cl_{10}S$[24] and $Li_4Re_6S_{11}$[25] hardly show any distortion of the ideal M_6 octahedra, leading to the conclusion[25] that the distortion of M_6X_8 clusters is "mainly caused by different degrees of occupation of the electronic states" and interconnection (or, more generally, intercluster contacts) are less important. The structure of $Nb_6I_8(NH_2CH_3)_6$ demonstrates that even rather weak van der Waals interactions between adjacent clusters may lead to geometrically different but energetically more or less equivalent arrangements of the metal atoms. The strain acting on the clusters in $Nb_6I_8(NH_2CH_3)_6$ is visible with some of the non-metal positions. As one would expect, the Nb–I distances lie in a rather narrow range (between 291 and 297 pm). The scatter is significantly smaller than with the Nb–Nb distances. The mean Nb–I distance is significantly larger (+12 pm) than in the structure of Nb_6I_{11}. This result is easily understood in terms of the lower niobium oxidation state in $Nb_6I_8(NH_2CH_3)_6$. As a consequence, the intracluster I–I distances on the average are larger than in Nb_6I_{11} (between 405 and 425 pm), although the Nb_6 core is smaller. Obviously it is the approach between Nb and I atoms rather than I and I atoms that determines the dimension of the cluster. Interestingly, the shortest intercluster I–I distance (410 pm) occurs with atoms I2 and I7. Atom I2 follows the elongation of the cluster containing Nb1, Nb2, and Nb3 along the pseudo-3-fold axis and the position of I7 is intimately related to the characteristic distortion of the cluster containing Nb4, Nb5, and Nb6.

The mean Nb–N distance is 243 pm, which again is significantly longer than in compounds of Nb in a higher oxidation state like $NbOCl_2(OEt)(bpy)_2$ (232 pm).[26] Some influence of packing effects is also recognizable in the arrangement of the amine ligands, i.e. the limited rotational freedom relative to the Nb–N axes. According to expectation, the CH_3 group normally settles in the sterically favored position above the edge centers of the I_8 cubes. But, some of the C atoms (C3, C4, C5) rather approach cube corners, leading to the short C–I distances around 380 pm. The orientations of the amine ligands are not related to any of the pseudosymmetries found for the arrangements of atoms Nb1, Nb2, and Nb3 and Nb4, Nb5, and Nb6.

Acknowledgment. The experimental help of and discussions with R. Kremer, C. Mensing, E.-M. Peters, and W. Hönle are gratefully acknowledged. Thanks are due to the Fonds der Chemischen Industrie for financial support.

Registry No. $Nb_6I_8(NH_2CH_3)_6$, 93683-43-3; $Nb_6I_8(NH_2C_3H_7)_6$, 93714-40-0; Nb_6I_{11}, 12196-47-3.

Supplementary Material Available: Listings of all calculated atomic coordinates and thermal parameters and of observed and calculated structure factor amplitudes (*h, k, l*, F_o, F_c) (18 pages). Ordering information is given on any current masthead page.

---

(14) Spreckelmeyer, B. *Z. Anorg. Allg. Chem.* **1968**, *358*, 147.

(15) Brown, I. D. In "Structure and Bonding in Crystals"; O'Keeffe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol. II, p 1.

(16) Hönle, W.; Flack, H. D.; Yvon, K. *J. Solid State Chem.* **1983**, *49*, 157.

(17) Imoto, H.; Corbett, J. D. *Inorg. Chem.* **1980**, *19*, 1241.

(18) Corbett, J. D. *J. Solid State Chem.* **1981**, *39*, 56.

(19) Yvon, K. "Topics in Current Physics"; Fischer, O., Maple, M. B., Eds.; Springer-Verlag: Heidelberg, 1981; Vol. 32, Chapter 3.

(20) Nohl, N.; Klose, W.; Andersen, O. K. "Topics in Current Physics"; Fischer, O., Maple, M. B., Eds.; Springer-Verlag: Heidelberg, 1982; Vol. 33, Chapter 6.

(21) Guillevic, J.; Grandjean, D. *J. Solid State Chem.* **1973**, *6*, 335.

(22) Hönle, W.; Yvon, K. *Z. Kristallogr.* **1983**, *162*, 103.

(23) Baillif, R.; Yvon, K.; Flükiger, R.; Müller, J. *J. Low Temp. Phys.* **1979**, *37*, 231.

(24) Perrin, C.; Sergent, M.; le Traon, F.; le Traon, A. *J. Solid State Chem.* **1978**, *25*, 197.

(25) Bronger, W.; Miessen, H. J. *J. Less. Common. Met.* **1982**, *83*, 29.

(26) Kamenar, B.; Prout, C. K. *J. Chem. Soc. A.* **1970**, 2379.

(27) Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.