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# Preparation and Structure of $Nb_3Cl_8(CNCMe_3)_5$

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## Abstract

A trinuclear compound $Nb_3Cl_8(t\text{-}BuNC)_5 \cdot 2C_7H_8$ was obtained in *ca.* 30% yield by slow diffusion of t-BuNC into the solution of $Nb_2Cl_6(SMe_2)_3$ in toluene. It crystallizes in a monoclinic space group $P2_1/c$ with $a = 23.750(6)$, $b = 9.099(2)$, $c = 25.031(3)$ Å, $\beta = 95.59(2)°$, $V = 5383(3)$ Å$^3$ and $Z = 4$. The niobium atoms form an isosceles triangle with one short, 2.875(1) Å and two long, 3.207(1) and 3.220(1) Å, edges. One t-BuNC acts as an $\eta^2$, $\mu_3$ ligand while the others are terminal sigma donors. The molecule is paramagnetic with the formal positive charges on the niobium atoms being 2, 3 and 3. The reaction pathway leading to this trinuclear complex is proposed.

## Introduction

We have reported in a preliminary communication [1] that the nature of products obtained by reacting $Nb_2Cl_6(SMe_2)_3$ with t-BuNC is dependent upon how fast the reactants are brought to contact. If the process is carried out in a conventional way, with stirring, a complex of composition $Nb_2Cl_6(t\text{-}BuNC)_6$ is obtained in high yield. It contains a ligand resulting from coupling of two isocyanide molecules via the terminal carbon atoms. This reaction is of a general type and has been found [2] to occur for both Na and Ta with various alkyl isocyanides.

When, on the other hand, there is a slow interdiffusion of initially separated reactants a trinuclear product, $Nb_3Cl_8(t\text{-}BuNC)_5$, with one RNC acting as a six-electron two-center donor is isolated as the main product. While the molecule seems to be rather complex, a detailed analysis of its structure and magnetic properties provides a basis for a straightforward assignment of electronic configuration and rationalization of the mechanism of its formation. We present here a detailed report on this chemistry.

## Experimental

All manipulations were performed under an atmosphere of argon. Standard vacuum line and Schlenk techniques were used. The solvents were freshly distilled from benzophenone ketyl and Na/K alloy prior to use. t-Butyl isocyanide was purchased from Strem Chemicals, Inc., and used without further purification as a solution in toluene. $M_2Cl_6(SMe_2)_3$, M = Nb, Ta, were prepared by the literature method [2, 3].

ESR and IR spectra were recorded using an X-band Varian E-65 spectrometer and an IBM FT-IR/85 spectrometer, respectively.

### *Preparation of* $Nb_3Cl_8(t\text{-}BuNC)_5 \cdot 2C_7H_8$

The compound is obtained in the form of well developed crystals when the isocyanide is allowed to diffuse slowly into the toluene solution of the Nb complex. The following represents one of the typical experiments that have been carried out.

$Nb_2Cl_6(SMe_2)_3$ (0.9 g, 1.5 mmol) was dissolved in 80 ml of toluene in a 500 ml pear-shaped flask. 180 ml of a 1:1 toluene–hexane mixture was layered on top of that solution, followed by 6 ml of t-BuNC in toluene (18 mmol) diluted with 20 ml of hexane. Initially, the interface turned green but then became red–brown and upon interdiffusion of reactants crystalline material began to be deposited. After one week the solution was made homogeneous by shaking the flask, and the solid product was isolated by filtration. It consisted of thin, elongated rectangular crystals and an amorphous precipitate. The latter was quickly removed in air by repeated addition of dried degassed toluene and later hexane, and decantation of the suspension. The product was placed in a Schlenk tube which was then evacuated and filled with argon gas. Black crystals (0.31 g), red–brown in transmitted light, of $Nb_3Cl_8(t\text{-}BuNC)_5 \cdot 2C_7H_8$ were isolated. An additional crop of crystalline material was recovered by slow cooling of the post-reaction filtrate to −20 °C. Following purification by the described procedure, a combined yield of 0.36 g (0.31 mmol, 30%) of the product was obtained.

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TABLE I. Crystal Data for $Nb_3Cl_8(t\text{-}BuNC)_5 \cdot 2C_7H_8$

| | |
|---|---|
| Formula | $Nb_3Cl_8N_5C_{39}H_{61}$ |
| Formula weight | 1162.30 |
| Space group | $P2_1/c$ |
| Systematic absences | $0k0, k \neq 2n; h0l, l \neq 2n$ |
| $a$ (Å) | 23.750(6) |
| $b$ (Å) | 9.099(2) |
| $c$ (Å) | 25.031(3) |
| $\alpha$ (°) | 90.0 |
| $\beta$ (°) | 95.59(2) |
| $\gamma$ (°) | 90.0 |
| $V$ (Å$^3$) | 5383(3) |
| $Z$ | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.434 |
| Crystal size (mm) | 0.5 × 0.3 × 0.03 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 10.313 |
| Data collection instrument | Enraf Nonius CAD-4 |
| Radiation (monochromated in incident beam) | MoK$\alpha$ ($\lambda_\alpha$ = 0.71073 Å) |
| Orientation reflections, number, range ($2\theta$) | 25; 16.2, 23.5 |
| Temperature (°C) | 22 |
| Scan method | $\omega - 2\theta$ |
| Data collection range, $2\theta$ (°) | $4 \leqslant 2\theta \leqslant 50$ |
| No. unique data, total with $F_o^2 > 3\sigma(F_o)^2$ | 5696, 3537 |
| Number of parameters refined | 375 |
| $R^a$ | 0.061 |
| $R_w{}^b$ | 0.072 |
| Quality-of-fit indicator$^c$ | 1.728 |
| Largest shift/e.s.d., final cycle | 0.47 |
| Largest peak (e Å$^{-3}$) | 0.829 |

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. $^c$Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

IR (THF solution, cm$^{-1}$), $\nu$(CN): 2210(m), 1623(s), 1612(m).

Analogous reactions with i-PrNC and $C_6H_{11}NC$ also produced red–brown compounds in contrast to blue or purple obtained when rapid mixing was employed. While this suggests that the trinuclear product was formed in these cases as well, only intractable oily material could be isolated. In the case of tantalum only the formation of dinuclear $Ta_2Cl_6(RNC)_6$ was observed and there was no indication of the presence of the niobium analogue.

### *X-ray Crystallography*

Single crystal X-ray analysis was carried out by application of general procedures that have been described elsewhere [4]*. Relevant crystallographic data are summarized in Table I. Polarization and Lorentz corrections were applied to the intensity data.

Owing to the complex nature of the Patterson map the structure was developed in the space group $P1$ by using a sequence of least-squares refinements and difference Fourier syntheses. After the position of niobium atoms was established the refinement was continued in the proper space group, *viz.* $P2_1/c$. The remaining non-hydrogen atoms were located by a series of isotropic least-squares refinements and from difference Fourier maps. Two of the five t-BuNC molecules present showed two distinctly different orientations of methyl groups around the tertiary carbon atom. They were refined with equal fractional occupancy of 0.5. Two molecules of the solvent, toluene, were also present. One of them was significantly distorted and the corresponding carbon atoms had relatively high thermal parameters.

Isotropic refinement of 61 atoms gave residuals $R$ and $R_w$ equal to 0.123 and 0.139, respectively. A correction for absorption by the method of Walker and Stuart [5] was applied at this stage. This reduced the residuals to 0.079 and 0.093. All atoms except those corresponding to methyl groups and solvent molecules in the lattice were refined anisotropically. The final values of $R$ and $R_w$ were 0.061 and 0.072, and no peaks of chemical significance were observed in the final difference Fourier map. See also 'Supplementary Material'.

## Results and Discussion

### *Molecular Structure*

The positional and isotropic-equivalent displacement parameters are given in Table II. Important bond distances and bond angles are presented in Tables III and IV, respectively. See also 'Supplementary Material'.

The molecule of $Nb_3Cl_8(t\text{-}BuNC)_5$, which is shown in Fig. 1, has a virtual mirror plane perpendicular to the Nb(1)–Nb(2) vector and incorporating the Nb(3) atom. In terms of composition and spatial distribution of ligands it resembles complexes of the type $M_3X_{13}$ with a central $M_3(\mu_3\text{-}X)(\mu_2\text{-}Y)_3$ core. However, it does not exhibit analogous cluster type metal–metal bonding and therefore has to be con-

TABLE II. Positional and Isotropic Equivalent Thermal Parameters for $Nb_3Cl_8(t\text{-}BuNC)_5 \cdot 2C_7H_8$

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$)$^a$ |
|---|---|---|---|---|
| Nb(1) | 0.33578(5) | 0.0283(1) | 0.14336(5) | 3.15(3) |
| Nb(2) | 0.24355(5) | 0.0262(1) | 0.20968(5) | 3.30(3) |
| Nb(3) | 0.21015(5) | 0.0071(1) | 0.08262(5) | 3.06(3) |
| Cl(1) | 0.3076(2) | 0.2294(4) | 0.1987(2) | 4.04(9) |
| Cl(2) | 0.1755(2) | 0.1785(4) | 0.1486(2) | 4.18(9) |
| Cl(3) | 0.2871(2) | 0.1825(4) | 0.0680(2) | 4.19(9) |

*(continued)*

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*Calculations were done on the VAX-11/780 computer at Department of Chemistry, Texas A&M University, College Station, TX, with the VAX-SDP software package.

TABLE II. *(continued)*

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$)[a] |
|---|---|---|---|---|
| Cl(4) | 0.4095(2) | −0.0305(5) | 0.2103(2) | 5.6(1) |
| Cl(5) | 0.3734(2) | −0.1205(5) | 0.0761(2) | 5.0(1) |
| Cl(6) | 0.2964(2) | −0.0299(5) | 0.2924(2) | 5.9(1) |
| Cl(7) | 0.1640(2) | −0.1246(5) | 0.2270(2) | 5.9(1) |
| Cl(8) | 0.1439(2) | 0.1013(5) | 0.0089(2) | 6.3(1) |
| N(1) | 0.2894(4) | −0.161(1) | 0.1752(4) | 2.8(2) |
| N(2) | 0.4412(5) | 0.268(1) | 0.1183(5) | 5.0(3) |
| N(3) | 0.1856(5) | 0.259(1) | 0.2957(5) | 5.1(3) |
| N(4) | 0.1127(5) | −0.253(1) | 0.0918(5) | 5.1(3) |
| N(5) | 0.2540(5) | −0.223(2) | −0.0084(5) | 5.6(4) |
| C(11) | 0.2554(5) | −0.111(1) | 0.1351(5) | 2.4(3) |
| C(12) | 0.2975(7) | −0.330(1) | 0.1866(6) | 5.0(4) |
| C(13) | 0.346(1) | −0.385(3) | 0.159(1) | 4.8(7)* |
| C(14) | 0.306(1) | −0.350(3) | 0.247(1) | 4.1(7)* |
| C(15) | 0.240(1) | −0.412(4) | 0.164(1) | 5.8(8)* |
| C(13A) | 0.290(1) | −0.406(3) | 0.131(1) | 4.6(7)* |
| C(14A) | 0.256(1) | −0.383(3) | 0.222(1) | 5.3(8)* |
| C(15A) | 0.361(1) | −0.343(4) | 0.209(1) | 6.5(9)* |
| C(21) | 0.4042(6) | 0.190(2) | 0.1256(6) | 4.5(4) |
| C(22) | 0.4909(7) | 0.364(2) | 0.1137(7) | 8.1(5) |
| C(23) | 0.482(2) | 0.508(5) | 0.148(2) | 10(1)* |
| C(24) | 0.540(2) | 0.286(4) | 0.157(2) | 7(1)* |
| C(25) | 0.496(2) | 0.415(7) | 0.062(2) | 16(2)* |
| C(23A) | 0.461(1) | 0.518(4) | 0.076(1) | 7.4(9)* |
| C(24A) | 0.506(2) | 0.430(4) | 0.167(2) | 9(1)* |
| C(25A) | 0.525(1) | 0.296(3) | 0.069(1) | 5.4(8)* |
| C(31) | 0.2060(7) | 0.182(2) | 0.2655(6) | 5.5(4) |
| C(32) | 0.1611(6) | 0.353(2) | 0.3347(6) | 7.9(5) |
| C(33) | 0.1177(9) | 0.256(2) | 0.3622(9) | 9.9(6)* |
| C(34) | 0.209(1) | 0.398(3) | 0.377(1) | 13.4(9)* |
| C(35) | 0.127(1) | 0.482(4) | 0.305(1) | 17(1)* |
| C(41) | 0.1438(6) | −0.158(1) | 0.0905(6) | 3.8(4) |
| C(42) | 0.0744(8) | −0.387(2) | 0.0956(8) | 8.3(6) |
| C(43) | 0.098(1) | −0.499(3) | 0.060(1) | 13.5(8)* |
| C(44) | 0.084(1) | −0.445(3) | 0.155(1) | 13.7(9)* |
| C(45) | 0.014(1) | −0.336(3) | 0.078(1) | 12.6(8)* |
| C(51) | 0.2403(6) | −0.143(2) | 0.0215(6) | 4.5(4) |
| C(52) | 0.2762(8) | −0.331(2) | −0.0470(7) | 9.4(6) |
| C(53) | 0.2272(9) | −0.379(3) | −0.085(1) | 11.1(7)* |
| C(54) | 0.317(1) | −0.428(3) | −0.018(1) | 16(1)* |
| C(55) | 0.316(1) | −0.240(3) | −0.081(1) | 11.2(7)* |
| C(61) | 0.4385(9) | 0.175(3) | 0.794(1) | 11.2(7)* |
| C(62) | 0.4223(8) | 0.166(2) | 0.8532(8) | 7.9(5)* |
| C(63) | 0.3696(9) | 0.204(2) | 0.8730(9) | 10.0(6)* |
| C(64) | 0.365(1) | 0.179(3) | 0.930(1) | 11.5(7)* |
| C(65) | 0.4102(9) | 0.131(3) | 0.960(1) | 10.8(7)* |
| C(66) | 0.4617(9) | 0.108(3) | 0.9433(9) | 10.8(7)* |
| C(67) | 0.4706(8) | 0.122(2) | 0.8895(8) | 9.1(6)* |
| C(71) | 0.988(1) | 0.116(4) | 0.066(1) | 19(1)* |
| C(72) | 0.9349(9) | 0.252(3) | 0.103(1) | 11.2(7)* |
| C(73) | 0.9434(9) | 0.301(3) | 0.1568(9) | 10.3(7)* |
| C(74) | 0.974(1) | 0.286(3) | 0.206(1) | 13.5(9)* |
| C(75) | 1.015(1) | 0.184(3) | 0.203(1) | 15(1)* |
| C(76) | 1.026(1) | 0.112(3) | 0.152(1) | 12.3(8)* |
| C(77) | 0.991(1) | 0.164(3) | 0.118(1) | 15(1)* |

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

TABLE III. Important Bond Distances (Å) for the Molecule of $Nb_3Cl_8(t\text{-}BuNC)_5 \cdot 2C_7H_8$

| | |
|---|---|
| Nb(1)–Nb(2) | 2.875(1) |
| Nb(1)–Nb(3) | 3.220(1) |
| Nb(2)–Nb(3) | 3.207(1) |
| Nb(1)–Cl(1) | 2.429(3) |
| Nb(1)–Cl(3) | 2.537(3) |
| Nb(1)–Cl(4) | 2.364(3) |
| Nb(1)–Cl(5) | 2.401(3) |
| Nb(1)–N(1) | 2.230(8) |
| Nb(1)–C(11) | 2.284(10) |
| Nb(1)–C(21) | 2.266(13) |
| Nb(2)–Cl(1) | 2.427(3) |
| Nb(2)–Cl(2) | 2.528(3) |
| Nb(2)–Cl(6) | 2.370(3) |
| Nb(2)–Cl(7) | 2.409(3) |
| Nb(2)–N(1) | 2.236(8) |
| Nb(2)–C(11) | 2.284(9) |
| Nb(2)–C(31) | 2.234(13) |
| Nb(3)–Cl(2) | 2.470(3) |
| Nb(3)–Cl(3) | 2.480(3) |
| Nb(3)–Cl(8) | 2.460(3) |
| Nb(3)–C(11) | 1.938(11) |
| Nb(3)–C(41) | 2.202(12) |
| Nb(3)–C(51) | 2.220(12) |
| N(1)–C(11) | 1.307(11) |
| N(1)–C(12) | 1.579(12) |
| N(2)–C(21) | 1.158(13) |
| N(2)–C(22) | 1.483(15) |
| N(3)–C(31) | 1.173(14) |
| N(3)–C(32) | 1.457(15) |
| N(4)–C(41) | 1.141(13) |
| N(4)–C(42) | 1.52(2) |
| N(5)–C(51) | 1.116(13) |
| N(5)–C(52) | 1.51(2) |

sidered separately. The Nb atoms form an isosceles triangle with one short, 2.875(1) Å, and two long, 3.207(1) and 3.220(1) Å, edges. These two long distances preclude a direct metal–metal interaction and therefore two subunits, with some common atoms, can be distinguished in the molecule: mononuclear $NbCl_3L_3$ and dinuclear $Nb_2Cl_7L_3$ (at present charges are disregarded; they will be discussed below when the oxidation state is considered). The former has an octahedral geometry with a facial disposition of ligands. The dinuclear fragment is an edge-sharing bioctahedron with CN (assumed to occupy one coordination site) and Cl(1) defining the common edge. The equatorial plane is defined by seven atoms, *viz.* Nb(1), Nb(2), Cl(1), Cl(5), Cl(7), C(21) and C(31), which are positioned not more than 0.084 Å from it, while C(11) and N(1) are 0.539 Å and 0.764 Å above and below that plane. (See also 'Supplementary Material'.) Four chlorine atoms Cl(2), Cl(3), Cl(4) and Cl(6) define a second plane, which is perpendicular to the equatorial one with the dihedral angle between them equal to 90.9°. There is, however, a considerable distortion from an ideal

TABLE IV. Important Bond Angles (°) for the Molecule of $Nb_3Cl_8(t\text{-}BuNC)_5 \cdot 2C_7H_8$

| | | | |
|---|---|---|---|
| Nb(2)–Nb(1)–Nb(3) | 63.19(3) | Cl(7)–Nb(2)–C(11) | 89.8(3) |
| Nb(1)–Nb(2)–Nb(3) | 63.66(3) | Cl(7)–Nb(2)–C(31) | 83.1(4) |
| Nb(1)–Nb(3)–Nb(2) | 53.14(3) | N(1)–Nb(2)–C(11) | 33.6(3) |
| Cl(1)–Nb(1)–Cl(3) | 82.9(1) | N(1)–Nb(2)–C(31) | 164.1(4) |
| Cl(1)–Nb(1)–Cl(4) | 89.6(1) | C(11)–Nb(2)–C(31) | 160.9(5) |
| Cl(1)–Nb(1)–Cl(5) | 165.4(1) | Cl(2)–Nb(3)–Cl(3) | 89.5(1) |
| Cl(1)–Nb(1)–N(1) | 101.7(2) | Cl(2)–Nb(3)–Cl(8) | 92.9(1) |
| Cl(1)–Nb(1)–C(11) | 101.2(3) | Cl(2)–Nb(3)–C(11) | 95.5(3) |
| Cl(1)–Nb(1)–C(21) | 82.4(3) | Cl(2)–Nb(3)–C(41) | 94.8(3) |
| Cl(3)–Nb(1)–Cl(4) | 154.8(1) | Cl(2)–Nb(3)–C(51) | 178.4(3) |
| Cl(3)–Nb(1)–Cl(5) | 87.9(1) | Cl(3)–Nb(3)–Cl(8) | 95.3(1) |
| Cl(3)–Nb(1)–N(1) | 119.1(3) | Cl(3)–Nb(3)–C(11) | 95.1(3) |
| Cl(3)–Nb(1)–C(11) | 85.6(3) | Cl(3)–Nb(3)–C(41) | 175.7(3) |
| Cl(3)–Nb(1)–C(21) | 77.3(3) | Cl(3)–Nb(3)–C(51) | 90.1(4) |
| Cl(4)–Nb(1)–Cl(5) | 94.0(1) | Cl(8)–Nb(3)–C(11) | 166.7(3) |
| Cl(4)–Nb(1)–N(1) | 86.0(3) | Cl(8)–Nb(3)–C(41) | 83.9(3) |
| Cl(4)–Nb(1)–C(11) | 119.6(3) | Cl(8)–Nb(3)–C(51) | 85.6(3) |
| Cl(4)–Nb(1)–C(21) | 77.9(3) | C(11)–Nb(3)–C(41) | 85.1(4) |
| Cl(5)–Nb(1)–N(1) | 92.7(2) | C(11)–Nb(3)–C(51) | 86.1(4) |
| Cl(5)–Nb(1)–C(11) | 89.4(3) | C(41)–Nb(3)–C(51) | 85.6(5) |
| Cl(5)–Nb(1)–C(21) | 84.5(3) | Nb(1)–Cl(1)–Nb(2) | 72.61(8) |
| N(1)–Nb(1)–C(11) | 33.6(3) | Nb(2)–Cl(2)–Nb(3) | 79.81(9) |
| N(1)–Nb(1)–C(21) | 163.3(4) | Nb(1)–Cl(3)–Nb(3) | 79.85(9) |
| C(11)–Nb(1)–C(21) | 161.9(4) | Nb(1)–N(1)–Nb(2) | 80.1(3) |
| Cl(1)–Nb(2)–Cl(2) | 83.4(1) | Nb(1)–N(1)–C(12) | 139.7(7) |
| Cl(1)–Nb(2)–Cl(6) | 88.8(1) | Nb(2)–N(1)–C(12) | 136.8(7) |
| Cl(1)–Nb(2)–Cl(7) | 165.0(1) | C(11)–N(1)–C(12) | 122(1) |
| Cl(1)–Nb(2)–N(1) | 101.6(2) | C(21)–N(2)–C(22) | 175(1) |
| Cl(1)–Nb(2)–C(11) | 101.2(3) | C(31)–N(3)–C(32) | 178(1) |
| Cl(1)–Nb(2)–C(31) | 83.2(4) | C(41)–N(4)–C(42) | 176(1) |
| Cl(2)–Nb(2)–Cl(6) | 154.1(1) | C(51)–N(5)–C(52) | 176(1) |
| Cl(2)–Nb(2)–Cl(7) | 87.4(1) | Nb(1)–C(11)–Nb(2) | 78.0(3) |
| Cl(2)–Nb(2)–N(1) | 119.3(3) | Nb(1)–C(11)–Nb(3) | 99.1(4) |
| Cl(2)–Nb(2)–C(11) | 85.8(3) | Nb(2)–C(11)–Nb(3) | 98.5(4) |
| Cl(2)–Nb(2)–C(31) | 76.1(4) | Nb(3)–C(11)–N(1) | 166.7(8) |
| Cl(6)–Nb(2)–Cl(7) | 94.5(1) | Nb(1)–C(21)–N(2) | 176(1) |
| Cl(6)–Nb(2)–N(1) | 86.4(3) | Nb(2)–C(31)–N(3) | 178(1) |
| Cl(6)–Nb(2)–C(11) | 120.0(3) | Nb(3)–C(41)–N(4) | 173(1) |
| Cl(6)–Nb(2)–C(31) | 78.4(4) | Nb(3)–C(51)–N(5) | 177(1) |
| Cl(7)–Nb(2)–N(1) | 93.2(2) | | |

bioctahedron since the central atoms are about 0.44 Å away from the axial plane.

The salient feature of the complex is the presence of $\eta^2,\mu_3$-t-BuNC ligand (see Fig. 2). Its bonding to the triangular $Nb_3$ unit can be described by beginning with the $R-\overset{+}{N}\equiv\overset{-}{C}$: resonance structure. The terminal C atom forms a strong donor bond to the Nb(3) atom while the two pairs of $\pi$ electrons form donor bonds to Nb(1) and Nb(2). C(11) is within bonding distance of all three metal atoms and the Nb(3)–C(11)–N(1) group is practically linear (angle at C(11) is 166.7(8)°). The C(11)–N(1)–C(12) fragment is markedly bent, with the angle of 122(1)°.

Compounds containing the $M_3$-$\eta^2,\mu_3$-(XY) moiety are already known for X = Y = C [6] and there are several examples of species with heteroatomic XY caps [7] but the six-electron two center mode of coordination by an unsaturated molecule presented here is very rare. An iron compound, $Fe_3(CO)_9$(t-BuNC) [8], with t-BuNC bonding in the same fashion as that observed here has been obtained. Other molecules like CO, RCN and $RC\equiv C^-$ have also been found [8] to form an analogous two center cap over a triangular array of metal atoms. In all these cases the diatomic X≡Y moiety is perpendicular to the shorter edge of an isosceles of the $M_3$ unit. However all previous examples are 18-electron low-valent carbonyl species while in $Nb_3Cl_8$(t-BuNC)$_5$ the metal atoms are in relatively high average oxidation states (av. = 2 2/3).

The remaining ligands do not show any usual features. The terminal isocyanide molecules are linear with comparable Nb–C bond lengths. The Nb–Cl distances vary considerably depending on the mode

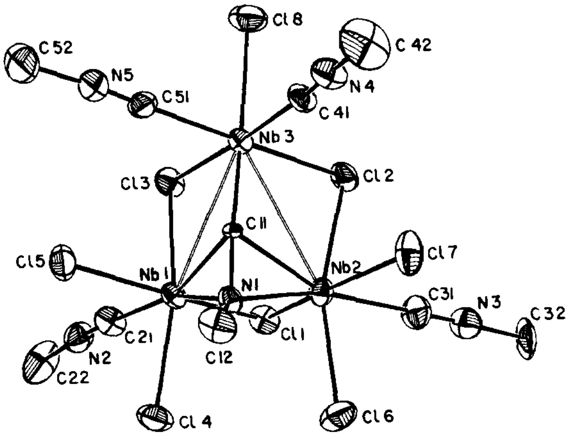

Fig. 1. ORTEP drawing of the $Nb_3Cl_8(t\text{-}BuNC)_5$ molecule. The ellipsoids are drawn at 30% probability level. Methyl carbon atoms have been omitted for the sake of clarity.

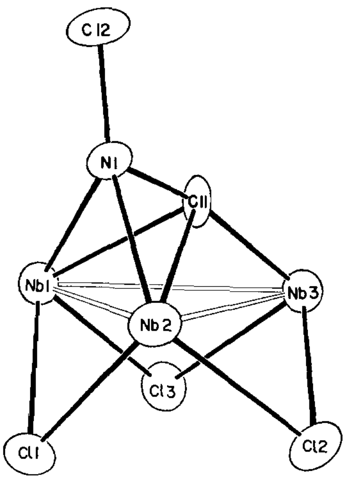

Fig. 2. Central portion of the $Nb_3Cl_8(t\text{-}BuNC)_5$ molecule.

of coordination and position with respect to other ligands. The Cl(1) bridge is equidistant from the Nb atoms it connects but the other two bridging Cl atoms are not. This can be attributed to their *trans* position to Cl atom on one side and to RNC on the Nb(3) side.

### *Spectroscopic Properties and Oxidation States*

The IR spectrum of $Nb_3Cl_8(t\text{-}BuNC)_5 \cdot 2C_7H_8$ in THF in the region where relevant CN vibrations are seen is shown in Fig. 3. The two prominent bands at 2210 cm$^{-1}$ and around 1620 cm$^{-1}$ (doublet) are assigned to C≡N stretching modes. The former is due to terminal RNC and as for the $Nb_2Cl_6(RNC)_6$ species it is shifted to higher energy with respect to a free ligand. The band around 1620 cm$^{-1}$ arises from the capping CN moiety. It is at a somewhat higher frequency, by *ca.* 60 cm$^{-1}$, than for the $Fe_3(CO)_9(t\text{-}BuNC)$ complex.

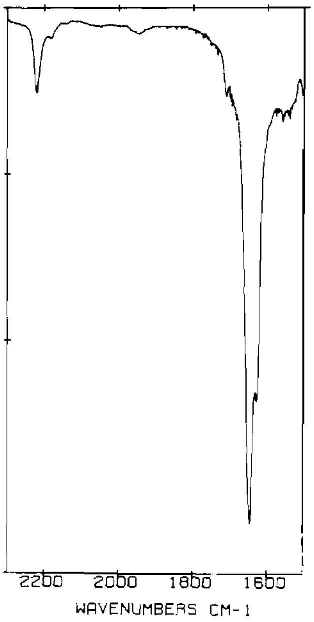

Fig. 3. IR spectrum of $Nb_3Cl_8(t\text{-}BuNC)_5 \cdot 2C_7H_8$ in THF in the region 1500–2300 cm$^{-1}$.

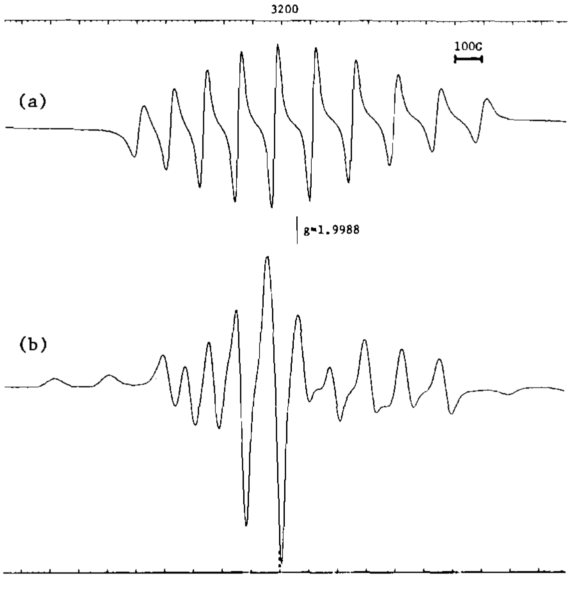

Fig. 4. ESR spectrum of $Nb_3Cl_8(t\text{-}BuNC)_5 \cdot 2C_7H_8$ in THF. The vertical line marks position of the standard (phosphorus doped into silicon) with $g = 1.9988$. (a) Room temperature; (b) liquid nitrogen temperature.

Based on composition a formal +8 charge is inferred for the $Nb_3$ unit. Since there are seven d electrons left in the metal core the complex must be paramagnetic. Accordingly its $^1H$ NMR spectrum consists of 3 broad resonances located between 6 and 9.5 ppm. The ESR spectrum, which is shown in Fig. 4, is a decet at room temperature, due to coupling to one Nb atom ($I = 9/2$) with typical average ⟨g⟩ and ⟨A⟩ values, 1.95 and 130 G, respectively. At −196 °C partial resolution of the components arising from the solid state anisotropy is observed. The obvious choice for localization of the unpaired electron(s) is the unique atom, namely Nb(3), which therefore has an oxidation state +2 or +4. Little is known about the ESR spectra of Nb(+2) [9] but a recent paper [10] indicates that they are similar to those observed for Nb(+4) species with $d^1$ configuration and the two states cannot be distinguished by this technique. From these considerations, there are two possible combinations of oxidation state for the three metal atoms: 3, 3, 2 and 2, 2, 4.

We think that the most reasonable account of the bonding and electron distribution in the molecule can be based on the formal starting point of a 3, 3, 2 distribution of formal metal valences. Thus, we have at Nb(3) an octahedral niobium(II) unit which supplies the bridging C≡NR ligand and one of the two chlorine ligands, Cl(2) or Cl(3) to the dinuclear niobium(III)–niobium(III) unit. Within the latter there would be a perturbed $\sigma^2\pi^2$ Nb=Nb bond. The perturbation would be mainly due to the interaction of the $\pi$ bond with Nb(III), thus weakening it a little. In this way the fact that the Nb(1)–Nb(2) separation of 2.875(1) Å is somewhat long for a double bond in an edge-sharing bioctahedron [11] could be explained.

The way in which this trinuclear molecule forms can only be a subject for speculation, but based on the above way of looking at the molecular structure and bonding, we can suggest a plausible pathway. Some of the $Nb_2Cl_6(SMe_2)_3$ starting material first reacts with t-BuNC to generate a reduced species such as $NbCl_2(CN{-}t{-}Bu)_3L$. The triple bond of one Nb–C≡N–R unit then adds across the Nb=Nb bond of another molecule of $Nb_2Cl_6(SMe_2)_3$, displacing the bridging $SMe_2$. From here, one requires only a few shifts in the positions of Cl atoms and replacement of terminal $SMe_2$ ligands by RNC ligands to complete the assembly of the product molecule. It would have to be assumed, and it is certainly not unreasonable to do so, that generation of the mononuclear Nb(II) species is the rate-controlling step, since the preparative reaction requires a long period of time and if rapid mixing is employed the completely different, dinuclear product $Nb_2Cl_6(RNC)_6$, is obtained.

## Supplementary Material

Full listing of bond distances and bond angles, tables of selected least-squares planes, anisotropic thermal parameters, observed and calculated structure factors (23 pages) are available. Copies may be obtained from author F.A.C.

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