X-Ray Crystallographic Evidence for a Trinuclear Formulation for the 'Non-oxidized' Hexamethylbenzene–Niobium Chloride Cluster Complex, $[(Me_6C_6)_3Nb_3Cl_6]Cl$

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Summary A single-crystal *X*-ray diffraction study of $[(Me_6C_6)_3Nb_3Cl_6]Cl$ shows a trinuclear, rather than hexanuclear, formulation to be correct; the crystal is disordered, with the metal cluster lying on a site of crystallographic C_{6h} symmetry; the molecular symmetry approximates to D_{3h}, important internuclear distances being Nb—Nb = 3·334(6) and Nb—Cl (bridging) = 2·466(8) and 2·499(9) Å.

The diamagnetic complex $[(Me_6C_6)_3Nb_3Cl_6]Cl$ was originally reported by Fischer and Röhrscheid;[1] osmometric molecular weight determinations[1] were, however, ambiguous, suggesting some association of the cluster. More recently, King *et al.*[2] have shown that the $[(Me_6C_6)_3Nb_3Cl_6{}^{+}]_x$ ion can be oxidized to the $[(Me_6C_6)_3Nb_3Cl_6{}^{2+}]_x$ ion; since this latter 'oxidized' ion is also diamagnetic[2] it must contain an even number of electrons, the simplest formula thus being $[(Me_6C_6)_6Nb_6Cl_{12}{}^{4+}]$. It was further suggested[2] {by analogy with the hexametallic $[(Nb_6Cl_{12})Cl_6{}^{n-}]$ ions, n = 2,3,4}[3] that the 'non-oxidized' $[(Me_6C_6)_3Nb_3Cl_6{}^{+}]_x$ ion also had a hexanuclear structure, *i.e.*, was, in fact, $[(Me_6C_6)_6Nb_6Cl_{12}{}^{2+}]$. We have now undertaken a single-crystal *X*-ray diffraction study of the 'non-oxidized' species $[(Me_6C_6)_3Nb_3Cl_6]Cl$ and show that (in the solid state, at least) it is only trinuclear.

Crystal data: $C_{36}H_{54}Cl_7Nb_3$, M = 1013·71, hexagonal, space-group $P6/m$ (C_{6h}^1; No. 175), a = 12·2571(13), c = 8·0377(13) Å, U = 1045·8 Å^3, D_m = 1·60(2), D_c = 1·610 g cm^{-3} for Z = 1.

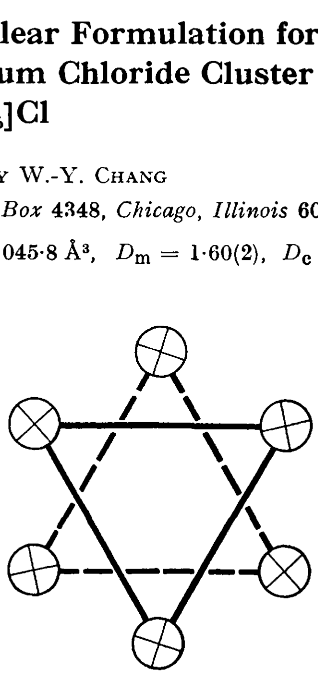

FIGURE 1. The pattern of disorder of the trinuclear species (Nb_3 clusters only).

Single crystals were obtained only after prolonged (6 months) storage of a concentrated solution in acetone at *ca.* −10 °C; they were very small hexagonal prisms of maximum dimension 0·05 mm. A *c*-axis rotation photograph (and other photographs) showed sharp Bragg reflections corresponding to *c ca.* 8 Å; there were, however, diffuse reflections at intermediate spacings, corresponding to an ill defined superlattice with c *ca.* 16 Å.

Diffraction data (sharp Bragg reflections only) were collected with a Picker FACS-1 diffractometer ($2\theta_{max} = 55°$; Mo-K_α radiation) and the structure was solved by Patterson, Fourier, and least-squares refinement techniques, the final R-factor being 12% for the 413 independent reflections with $I > 3\sigma(I)$.

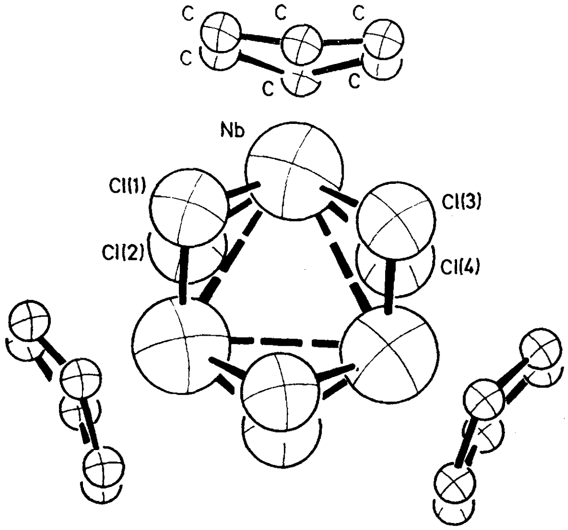

Figure 2. The geometry of the $[(Me_6C_6)_3Nb_3Cl_6^+$ ion. Methyl groups are omitted for the sake of clarity. (Note that the species has precise C_{3h} symmetry).

The cation is subject to a two-fold disorder in the crystal lattice, with the two Nb_3 triangles defining a 'Star of David' pattern (see Figure 1). The geometry of the $[(Me_6C_6)_3Nb_3Cl_6^+]$ cation is shown in Figure 2.

While the analysis is of low precision (because of the minute crystal size and disorder) the following points may be noted.

(1) The cluster is trinuclear and has precise C_{3h} (and approximate D_{3h}) symmetry.

(2) The niobium–niobium distance is 3·334(6) Å. This is consistent with the bond order of 1/3 (*i.e.*, 2 electrons shared by 3 niobium atoms) deduced by application of the noble-gas rule. [The Nb–Nb single bond in $[(C_5H_5)(C_5H_4)NbH]_2$, is 3·106(6) Å].[4]

(3) The niobium–(bridging chloride) distances are: Nb–Cl(1) = Nb–Cl(2) = 2·466(8) and Nb–Cl(3) = Nb–Cl(4) = 2·499(9) Å; angles around niobium are: Cl(1)–Nb–Cl(2) = 78·9(4), Cl(3)–Nb–Cl(4) = 77·7(4), Cl(1)–Nb–Cl(3) = Cl(2)–Nb–Cl(4) = 84·4(4), and Cl(1)–Nb–Cl(4) = Cl(2)–Nb–Cl(3) = 134·4(4)°. The Nb–Cl–Nb angles are each 84·4(3)°, the acuteness being further evidence for direct Nb–Nb bonding.

(4) The three crystallographically independent Nb–C-(benzene) distances are 2·53(3), 2·34(3), and 2·58(3) Å. However, disorder in the crystal precludes our claiming any significance in the apparent bending of the benzene nucleus.

Finally, it seems that the oxidation[2] of $[(C_6Me_6)_3Nb_3Cl_6^+]$ must also involve dimerization, see equation (1).

$$2[(C_6Me_6)_3Nb_3Cl_6^+] \xrightarrow{-2e} [(C_6Me_6)_6Nb_6Cl_{12}^{4+}] \qquad (1)$$

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[1] E. O. Fischer and F. Röhrscheid, *J. Organometallic Chem.*, 1966, **6**, 53.
[2] R. B. King, D. M. Braitsch, and P. N. Kapoor, *J.C.S. Chem. Comm.*, 1972, 1072.
[3] B. G. Hughes, J. L. Meyer, P. B. Fleming, and R. E. McCarley, *Inorg. Chem.*, 1970, **9**, 1343, and references contained therein.
[4] L. J. Guggenberger, *Inorg. Chem.*, 1973, **12**, 294.