X-Ray Crystal and Molecular Structures of Pentakisdimethylaminato- and Pentapiperidinato-niobium(v)

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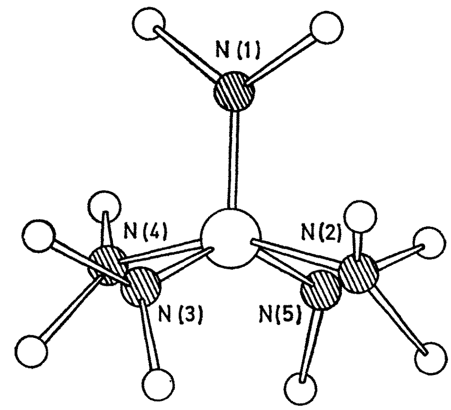
Summary X-Ray analysis shows the co-ordination geometries of the title compounds to be very similar and best described as distorted tetragonal pyramidal, with a shortened axial Nb–N bond.

IN an earlier publication,[1] we reported the structure of hexakisdimethylaminatotungsten(VI), in which the nitrogen atoms appeared to be involved in $p\pi \rightarrow d\pi$ bonding with the metal atom in a molecule of high symmetry (T_h). We are at present examining the effect that π-bonding might have on the geometry of dialkylamide molecules with other co-ordination numbers. We report here the structures of two Nb^V molecules, the dimethylamide [$Nb(NMe_2)_5$] and the piperidide [$Nb(NC_5H_{10})_5$].

Crystal data: $Nb(NMe_2)_5$, M 313·35, orthorhombic, $a = 13{\cdot}84(1)$, $b = 8{\cdot}19(1)$, $c = 14{\cdot}48(1)$ Å, $U = 1640$ Å^3, D_m *ca.* 1·3, $Z = 4$, $D_c = 1{\cdot}26$, μ(Cu-K_α) = 61·8 cm^{-1}, space group *Pbcn*. $Nb(NC_5H_{10})_5$, M 513·72, monoclinic, $a = 18{\cdot}275(8)$, $b = 9{\cdot}994(7)$, $c = 30{\cdot}841(10)$ Å, $\beta = 105{\cdot}29(10)°$, $U = 5433$ Å^3, D_m *ca.* 1·3, $Z = 8$, $D_c = 1{\cdot}26$, μ(Cu-K_α) = 39·2 cm^{-1}, space group $P2_1/c$.

Intensity data for the methylamide were recorded on a G.E. XRD6 manual diffractometer using the stationary crystal–stationary counter technique. Of a total of 1230 reflections measured out to a value of $2\theta = 120°$, only 696 had intensities significantly above background. Data for the piperidide were recorded on a Siemens A.E.D. using a 5-point measuring routine. For this compound, 2642 reflections out of a total of 3301 measured up to a value of 2θ of 80° had significant intensities.

Both structures were solved by Patterson and Fourier techniques, the piperidide with some difficulty due to pseudo-symmetry, and refined by full-matrix least-squares. R values are currently *ca.* 0·09 for both compounds.



FIGURE

The results of our analyses show a remarkable degree of similarity in co-ordination geometry between the dimethylamide and the two independent piperidide molecules. The Figure shows a molecule of the dimethylamide (hydrogen atoms not included), which has crystallographic two-fold symmetry, but the diagram could also represent the piperidide molecules if the methyl carbon atoms were considered to correspond to the α-carbon atoms of the piperidine ligands. The Table gives values of corresponding bond lengths and angles for the three molecules.

The co-ordination geometry is best described as distorted tetragonal pyramidal (TP) with the distortions tending to trigonal bipyramidal (TBP) geometry. One advantage of the TP description is that the Nb–N(1) bond, which is significantly shorter than the rest, coincides with the tetragonal axis. Calculations with all available experimental data suggest that a Nb–N single bond should have a length in the region 2·04—2·08 Å. On the basis of length alone, it would seem, therefore, that only one nitrogen atom is involved in any significant amount of π-bonding although all have approximate planar geometry [largest angle between the M–N bond and the NC_2 plane is 12° in one of the piperidine ligands; for tetrahedral geometry this would be *ca.* 35°]. It is possible, however, that the planarity of most of the amine groups arises from the rather tight packing of the ligands around the central metal atom, since preliminary calculations show that reorganisation to pyramidal geometry in the amine groups tends to increase steric interactions. In spite of the apparent differences between the dimethylamide and piperidine ligands, we consider them to be equivalent, sterically, since the β- and γ-carbon atoms in the latter are not involved in any intramolecular–interligand close contacts. Thus, if steric interactions do play a major part in deciding the geometry, it is not surprising that the two compounds are similar.

Molecular parameters for the NbN_5 *units*

	$Nb(NMe_2)_5$	$Nb(pip)_5$[1]	$Nb(pip)_5$[2]
Bond lengths (Å)			
Nb–N(1) (axial)	1·977(17)[a]	1·991(12)	1·981(13)
Nb–N(2) (basal)	2·044(14)	2·056(13)	2·043(15)
Nb–N(3) "	2·040(15)	2·051(14)	2·032(13)
Nb–N(4) "	2·044(14)	2·046(14)	2·048(16)
Nb–N(5) "	2·040(15)	2·055(14)	2·046(14)
Mean M–N (basal)	2·042	2·052	2·042
Bond angles (°)			
N(1)–Nb–N(2)	101·5(4)	100·5(5)	97·3(6)
N(1)–Nb–N(3)	109·1(4)	106·6(5)	109·0(5)
N(1)–Nb–N(4)	101·5(4)	100·2(5)	99·5(6)
N(1)–Nb–N(5)	109·1(4)	110·1(5)	112·0(5)
N(2)–Nb–N(3)	87·3(6)	87·9(6)	84·4(6)
N(2)–Nb–N(5)	86·1(6)	85·4(6)	88·8(6)
N(3)–Nb–N(4)	86·1(6)	86·0(6)	89·9(6)
N(4)–Nb–N(5)	87·3(6)	87·7(6)	85·0(6)

[a] E.s.d.'s in parentheses.

Nb^V is a d^0 system and on the basis of simple electron-pair repulsion arguments,[2] a NbX_5 species would be expected to have TBP geometry. As far as we know, no other d^0 MX_5 species have been examined crystallographically. The only compounds of this type, with spherically symmetrical d shells are the d^{10} species PX_5, AsX_5, SbX_5, and various isoelectronic ions, and the d^5 ion $[Fe(N_3)_5]^{2-}$.[3] Of these only $Sb(C_6H_5)_5$[4] and $[InCl_5]^{2-}$ [5] have TP geometry and no clear reasons have been suggested for these anomalies. All the other molecules examined have TBP geometry.

Thus, although it is clear that the existence of some multiple bonding between the metal and at least one of the ligands will have had some effect on the geometry, it is difficult to decide whether the structure actually found is a distortion from TP or TBP geometry since both symmetries will allow π-bonding of the required type. It is also difficult to decide whether electronic or steric factors are more important and in order to investigate this further, we are studying other derivatives with sterically different ligands.

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