An Eight-co-ordinated Metal Chelate with a D_4 Square Antiprismatic Configuration: Tetrakis(dipivaloylmethanato)niobium(IV)

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Summary The stereochemistry of $Nb[(Bu^tCO)_2CH]_4$ has been found by *X*-ray analysis to be based on a D_4 square antiprism.

IT is well established that metal complexes exhibiting discrete eight-co-ordination normally possess a stereochemistry based either on a D_{2d} dodecahedron or a D_{4d} square antiprism.[1–6] For metal tetrakis chelates in which the bidentate ligands are identical and symmetric, six dodecahedral and three square antiprismatic stereoisomers are possible, depending on which sets of edges the ligands span. Blight and Kepert[7] have recently evaluated the relative merit of the five stereoisomers in which the ligands span equivalent polyhedron edges by mapping the ligand–ligand repulsive energy for a range of normalized ligand bites. For bites $> 1{\cdot}25$, the favoured stereochemistry was the D_4 square antiprism (I). However, no example of this configuration has yet been observed. It was postulated that ordinary ligands with bites $> 1{\cdot}25$ would prefer to form polymeric structures rather than discrete M(bidentate)$_4$ complexes, because the interligand repulsions would be lower if the ligands bridged different metal atoms. We now report the first example of an M(bidentate)$_4$ complex whose stereochemistry is based on an idealized D_4 square antiprism (I).

$Nb[Bu^tCOCHCOBu^t]_4$ was prepared by the reaction of $NbCl_4$ and dipivaloylmethane in acetonitrile solution in the presence of triethylamine. Crystals, obtained from a benzene–acetonitrile solution, proved to be monoclinic, space group *Pc*, and to have cell dimensions of $a = 22{\cdot}30(5)$, $b = 11{\cdot}86(2)$, $c = 19{\cdot}58$ Å, $\beta = 107{\cdot}46(5)°$. The observed density ($1{\cdot}12$ g cm^{-3}) was identical to that calculated by assuming $Z = 4$, *i.e.*, 2 molecules per asymmetric unit. The intensities of 3667 independent reflections ($2\theta < 100°$) were measured on a Picker Diffractometer. The structure was solved using Patterson and Fourier methods and refined by full-matrix least-squares procedures with unit weights and anisotropic thermal parameters for the niobium and oxygen atoms. The final *R*-factor was 0·086.

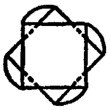
The Table presents polyhedron shape parameters for the two molecules (A and B) when viewed as D_4 square antiprismatic isomers and compares them to those calculated by Hoard and Silverton[1] for the most favoured polyhedron (MFP). The average values of the *l*, *s*, and θ parameters are in good agreement with those expected for the MFP Moreover, the sets of oxygens defining the idealized square faces deviate from planarity by less than 0·06 Å in molecule A and less than 0·02 Å in molecule B, and the planes are parallel or nearly parallel in the two molecules.

TABLE. D_4 *Square antiprismatic shape parameters*[a] *for* $Nb[(Bu^tCO)_2CH]_4$

	Molecule A	Molecule B	MFP
l	1·27	1·27	1·26[b]
s	1·18	1·18	1·19
l/s	1·08	1·08	1·06
θ, deg. ..	56·8	56·7	57·3
d_s (1), Å ..	0·058	0·015	0·00
d_s (2), Å ..	0·047	0·017	0·00
α_s, deg. ..	0·00	0·68	0·00

[a] The shape parameters are defined as follows: *l* and *s*, respectively, are the average lengths of the idealized lateral and square edges, normalized with respect to the average Nb–O bond distance; θ is the average angle formed between the Nb–O bonds and the idealized four fold rotation axis which passes through the Nb atom and the centroids of the best planes defining the idealized square faces; d_s is the average deviation of the four oxygen atoms from the best plane defining one of the two idealized square faces, α_s is the angle of intersection of the idealized square faces. [b] All values for the most favourable square antiprismatic polyhedron are from ref. 1.

The square antiprismatic description of the observed stereochemistry is a better approximation to the observed stereochemistry than a dodecahedron or a bicapped trigonal prism.[8] For the best dodecahedral approximation, the average deviation of the two sets of four oxygen atoms from the best planes defining the two interpenetrating idealized trapezoids is 0·26 Å for molecule A and 0·31 Å for molecule B. In a perfect bicapped trigonal prism, the triangular faces of the trigonal prism are parallel, whereas the corresponding faces in the most favoured square antiprism intersect at an angle of 25·7°. The smallest observed angle of intersection between opposite triangular faces in molecules A and B, respectively, was 19·3 and 22·9°.



(I)

The average Nb–O bond distances, ligand bites, and O–Nb–O angles of the chelate rings, respectively, are 2·12(5) A, 2·73(7) Å and 79·7(13)° for molecule A, and 2·12(4) Å, 2·74(5) Å and 80·2(4)° for molecule B.

Although the degree of distortion from a perfect D_4 square antiprism is greater for molecule A than for molecule B, the average ligand bite to Nb–O bond distance ratio is 1·29 ± 0·04 in both molecules. This value agrees with the normalized bite predicted by Blight and Kepert for a D_4 square antiprismatic configuration. However, the postulate that this configuration should be unstable with respect to a polymeric structure in which the ligands bridge different metal atoms could not be verified. In the absence of oxygen and moisture, the complex in dichloromethane solution is a stable, monomeric, very weak electrolyte in which the carbonyl groups of each ligand remain coordinated to niobium. It is possible that the steric requirements of the terminal t-butyl groups prohibit a polymeric structure. The acetylacetonates of several bivalent transition metal ions, for example, are oligomeric, whereas the dipivaloylmethanate derivatives are monomeric.[9]

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