X-Ray Crystal Structure of Tetraphenylporphinatoniobium Oxide Acetate; Demonstration of the Presence of Seven-co-ordinated Niobium

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Summary The reaction of tetraphenylporphyrin with niobium pentachloride leads to a niobioporphyrin which, when treated with acetic acid, gives an acetate; an *X*-ray study shows that the metal is seven-co-ordinated in this acetate.

IN their work on metalloporphyrins, Buchler *et al.*[1] mention the possibility of seven-co-ordination of the metal, the three bonds which are not metal–nitrogen either all being on the same side of the porphyrin plane, or one bond being on the opposite side to the other two. We now report the synthesis and *X*-ray structure determination of the acetate $(TPPNbO)O_2CMe$[2] [$(TTP)H_2$ = tetraphenylporphyrin], the first metalloporphyrin for which seven-co-ordination has been demonstrated.

To a stirred solution of $NbCl_5$ (30 mmol) in benzonitrile (165 ml), $(TTP)H_2$ (10 mmol) in the same solvent (270 ml) was added dropwise, and the solution was heated under reflux for 20 h. The mixture was then hydrolysed with 50 ml of water, extracted with $CHCl_3$, washed with water, and dried. Recrystallisation from benzene of the solid obtained gave red crystals (96%), elemental analysis for which corresponded to the formula $C_{88}H_{56}N_8Nb_2O_3$ $[(TPPNbO)_2O]$. Recrystallization from acetic acid rather than benzene gave purple crystals (92%), elemental analysis for which corresponded to the formula $C_{46}H_{31}N_4NbO_3$,-$MeCO_2H$ $[(TPPNbO)O_2CMe,MeCO_2H]$; δ ($CDCl_3$; Me_4Si) 1·20 (m, Me), 7·75 (m, *m*- and *p*-Ph protons), 8·18 (m, *o*-Ph protons), and 9·50 (s, pyrrole-H).

The compound crystallizes in the triclinic system, space group $P\bar{1}$. *Crystal data*: $a = 16{\cdot}64 \pm 0.02$, $b = 11{\cdot}33 \pm 0{\cdot}01$, $c = 11{\cdot}57 \pm 0{\cdot}01$ Å; $\alpha = 105{\cdot}9 \pm 0{\cdot}2$, $\beta = 100{\cdot}5 \pm 0{\cdot}2$, $\gamma = 105{\cdot}1 \pm 0{\cdot}2°$, $Z = 2$, $D_c = 1{\cdot}25$ g cm^{-3}. Reflection intensities were recorded on a three-circle automatic diffractometer (CAD 3 Nonius) with Cu-K_α radiation. The structure was solved by direct methods, using the MULTAN

programme.[3] Block-diagonal least-squares refinement of all the atoms (including the solvent molecule leads to an R index of 0·06 for the 4038 non-zero reflections with

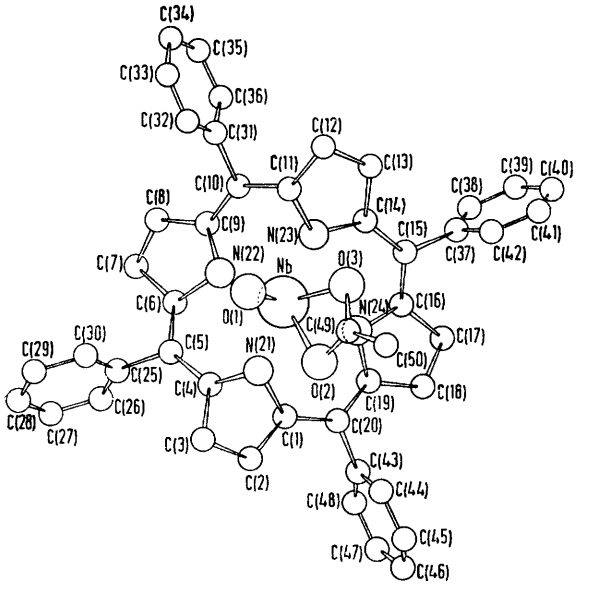

FIGURE. Structure of $(TPPNbO)O_2CMe,MeCO_2H$; the solvent molecule is not included.

$\sigma(I)/I < 0{\cdot}20$. The Figure shows a perspective view of the complex; the niobium atom is seven-co-ordinated, and lies within a polyhedron of symmetry close to C_s, with a square base defined by the four nitrogen atoms of the pyrrole rings and a triangular base, nearly parallel, defined by three oxygen atoms O(1), O(2), and O(3). The angle between the mean planes of these two bases is 1·1°; the metal is 1·0 Å out of the mean plane of the four nitrogen atoms and 1·35 Å out of the plane of the three oxygen atoms.

The acetate group is bonded to niobium through O(2) and O(3), which are exactly equidistant from the metal: Nb–O(2) 2·223(6) and Nb–O(3) 2·225(6) Å. The Nb–O(1) (1·716 Å) bond has the characteristics of a double bond. Significant differences are observed between the Nb–N distances: Nb–N(22) and Nb–N(24) [respectively 2·252(7) and 2·319(7) Å] are comparable to those already reported;[4] in contrast, Nb–N(21) and Nb–N(23) [respectively 2·173(7) and 2·187(7) Å] are much shorter. This difference can be related to the nitrogen–oxygen distances, N(22)–O(1) is 2·65(1) Å whereas N(24)–O(2) and N(24)–O(3) are 2·77(1) Å. Steric hindrance is thus important and causes a lengthening of the Nb–N(22) and Nb–N(24) bonds.

The most important Nb–ligand bond angles are: N(21)–Nb–N(22) 79·0(2); N(22)–Nb–N(23) 78·0(2); N(23)–Nb–N(24) 78·5(2); N(24)–Nb–N(21) 79·0(2); O(1)–Nb–O(3) 85·5(3); O(1)–Nb–O(2) 83·2(3); and O(2)–Nb–O(3) 58·5(2)°. The phenyl groups are planar and the angles between the mean plane of the four nitrogen atoms and the rings comprising C(25)—C(30), C(31)—C(36), C(37)—C(42), and C(43)—C(48) are respectively 60·3, 63·5, 70·7, and 72·2°. The phenyl groups are bonded to the macrocycle by single bonds whose mean length is 1·503 Å.

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[1] J. W. Buchler and K. Rohbock, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1073; J. W. Buchler, L. Puppe, K. Rohbock, and H. H. Schneehage, *Ann. N.Y. Acad. Sci.*, 1973, **206**, 116; M. Gouterman, L. K. Hanson, G. E. Khalil, J. W. Buchler, K. Rohbock, and D. Dolphin, *J. Amer. Chem. Soc.*, 1975, **97**, 3142.
[2] R. Guilard, B. Fliniaux, B. Maume, and P. Fournari, *Compt. rend.* (*C*), 1975, **281**, 461.
[3] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1970, **B26**, 274.
[4] G. Chavant, G. Constant, Y. Jeannin, and R. Morancho, *Acta Cryst.*, 1975, **B31**, 1823; C. Chavant, J. C. Paran, Y. Jeannin, G. Constant, and R. Morancho, *ibid.*, p. 1825.