Synthesis of Niobium(v) Porphyrinates. Crystal Structures of Tri-μ-oxo-bis[5,10,15,20-tetraphenylporphyrinatoniobium(v)] and Acetato-oxo-(5,10,15,20-tetraphenylporphyrinato)niobium(v)–Acetic Acid (1/1)

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The action of $NbCl_5$ on a porphyrin (H_2L) followed by hydrolysis leads to a complex $[(NbL)_2O_3]$. When treated with acetic acid this complex in turn yields a metalloporphyrin of general formula $[NbL(O)(O_2CMe)]\cdot xMeCO_2H$. The crystal structures of $[\{Nb(tpp)\}_2O_3]\cdot 4C_2H_4Cl_2$ (1b) and $[Nb(tpp)O(O_2CMe)]\cdot MeCO_2H$ (2b) (tpp is the dianion of 5,10,15,20-tetraphenylporphyrin) have been solved by *X*-ray diffraction methods. Crystals of (2b) are triclinic, space group $P\bar{1}$, with a = 16.645(6), b = 11.332(4), c = 11.868(4) Å, α = 105.93(6), β = 100.54(4), γ = 105.05(4)°, and Z = 2. Crystals of (1b) are orthorhombic, space group *Pccn*, with a = 31.802(9), b = 11.595(5), c = 23.431(7) Å, and Z = 4. Both structures have been determined from diffractometer data by direct and Fourier methods and refined by full-matrix least-squares calculations to R 0.053 for (2b) (4 038 reflections) and R 0.076 for (1b) (1 555 reflections). In both complexes the niobium atom is seven-co-ordinated by the four nitrogen atoms of the porphyrin and by three oxygen atoms; the co-ordination polyhedron is of the 4 : 3 type and the niobium atom lies 1.00(1) and 0.99(2) Å respectively from the 4 N plane of (2b) and (1b). A comparative study with $[\{Nb(tpp)\}_2O_3]\cdot CHCl_3$ is made. A high-resolution n.m.r. study of both complexes shows the anisochrony of the methylenic protons of $[\{Nb(oep)\}_2O_3]$ and $[Nb(oep)O(O_2CMe)]\cdot MeCO_2H$ induced by the out-of-plane position of the metal atom.

ALTHOUGH most metals co-ordinate to porphyrin and such systems have been studied extensively, the results relating to niobium are very limited.[1,2] Buchler and his co-workers[1] have studied the action of niobium pentachloride on octaethylporphyrin (H_2oep) and obtained a product with formula $[\{Nb(oep)\}_2O_3]$ the structure of which was not established. The action of $NbCl_5$ on the porphyrins H_2L (L = oep, tpp, tptp, or omp) † leads to complexes with a molecular formula identical to that proposed by Buchler, *i.e.* $[(NbL)_2O_3]$ (1). These complexes when dissolved in hot acetic acid give rise to systems with formula $[NbL(O)(O_2CMe)]\cdot xMeCO_2H$ (2).

In two preliminary notes we pointed out that in the systems $[\{Nb(tpp)\}_2O_3]$ [3] and $[Nb(tpp)O(O_2CMe)]\cdot MeCO_2H$ [4] the metal atom is seven-co-ordinated. Johnson and Scheidt [5] have also published work on one of these products, $[\{Nb(tpp)\}_2O_3]$. In this paper we present results for a series of complexes (1) and (2) as well as the definitive structural data for $[Nb(tpp)O(O_2CMe)]\cdot MeCO_2H$ and $[\{Nb(tpp)\}_2O_3]$.

EXPERIMENTAL

The porphyrins H_2L were prepared as described previously.[6-9]

TABLE 1

Experimental data and yields

Complex	Reaction time (t/h)	Eluant	Recrystallization solvent	Yield (%)	Analysis (%) *			
					C	H	N	Nb
(1a) $[\{Nb(oep)\}_2O_3]$	4	$CHCl_3$–C_6H_6 (1 : 2) then $CHCl_3$–MeOH (4 : 1)	MeCN	71	66.7 (66.55)	6.8 (6.8)	8.3 (8.65)	14.5 (14.3)
(1b) $[\{Nb(tpp)\}_2O_3]$	20		C_6H_6	96	72.5 (72.45)	3.9 (3.85)	8.0 (7.7)	12.8 (12.75)
(1c) $[\{Nb(tptp)\}_2O_3]$	20	$CHCl_3$–MeOH (20 : 1)	$CHCl_3$–MeOH (1 : 1)	58	73.2 (73.35)	4.7 (4.65)	6.8 (7.15)	11.7 (11.8)
(1d) $[\{Nb(omp)\}_2O_3]$	40	$CHCl_3$–MeOH (20 : 1)	C_6H_5Me–MeOH (1 : 1)	76	62.2 (62.55)	5.4 (5.25)	10.5 (10.4)	17.7 (17.3)
(2a) $[Nb(oep)O(O_2CMe)]\cdot MeCO_2H$				65	63.1 (63.15)	6.8 (6.75)	7.3 (7.35)	12.5 (12.2)
(2b) $[Nb(tpp)O(O_2CMe)]\cdot MeCO_2H$				92	68.6 (68.55)	4.4 (4.2)	6.8 (6.65)	11.0 (11.05)
(2c) $[Nb(tptp)O(O_2CMe)]$				61	71.8 (71.75)	4.7 (4.7)	6.6 (6.7)	10.5 (11.1)
(2d) $[Nb(omp)O(O_2CMe)]\cdot MeCO_2H$				58	59.3 (59.25)	5.4 (5.45)	8.5 (8.65)	14.4 (14.3)

* Calculated values are given in parentheses.

Preparation of the Complexes $[(NbL)_2O_3]$ (1).—These products were prepared according to the following general method. A solution of $NbCl_5$ (0.03 mol) in benzonitrile (165 cm^3) was introduced under argon in a reactor provided

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† Abbreviations: tpp = 5,10,15,20-tetraphenylporphyrinate(2−); oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−); omp = 2,3,7,8,12,13,17,18-octamethylporphyrinate(2−); tptp = 5,10,15,20-tetra-*p*-tolylporphyrinate(2−).

with a glass stirring rod. A solution of the porphyrin H_2L (0.01 mol) in the same solvent (150 cm^3) was then added over 15 min. The mixture was heated under reflux and hydrolysed with water (50 cm^3), extracted with $CHCl_3$, washed with water, and dried. The resulting solid was chromatographed and recrystallized.

Preparation of the Complexes $[NbL(O)(O_2CMe)]\cdot xMeCO_2H$ (2).—The products (1) were dissolved while hot (118 °C) in the minimum quantity of acetic acid and, after cooling, the complexes were isolated ($x = 1$ for L = oep, tpp, omp; $x = 0$ for tptp).

The reaction conditions, yields, and elemental analyses for all the complexes are summarized in Table 1.

Characteristics of Complexes (1) *and* (2).—Characteristic i.r. bands (cm^{-1}, from CsI) and significant fragmentation patterns (relative intensity in parentheses) observed in the mass spectra are: $[\{Nb(oep)\}_2O_3]$ (1a), i.r. 702, *m/e* 1 298 (2) $[\{Nb(oep)\}_2O_3]^{+\cdot}$, 641 (100) $[Nb(oep)O]^+$; $[\{Nb(tpp)\}_2O_3]$ [(1b), i.r. 662, *m/e* 1 458 (4) $[\{Nb(tpp)\}_2O_3]^{+\cdot}$, 7.22 (100) $[Nb(tpp)(OH)]^+$; $[\{Nb(tptp)\}_2O_3]$ (1c), i.r. 718, *m/e* 1 570 (4) $[\{Nb(tptp)\}_2O_3]^{+\cdot}$, 778 (100) $[Nb(tptp)(OH)]^+$; $[\{Nb(omp)\}_2O_3]$ (1d), i.r. not observed, *m/e* 1 074 (100) $[\{Nb(omp)\}_2O_3]^{+\cdot}$, 529 (14) $[Nb(omp)O]^+$; $[Nb(oep)O(O_2CMe)]\cdot MeCO_2H$ (2a), i.r. 610, 692, 900, *m/e* 700 (7) $[Nb(oep)O(O_2CMe)]^+$, 641 (100) $[Nb(oep)O]^+$; $[Nb(tpp)O(O_2CMe)]\cdot MeCO_2H$ (2b), i.r. 582, 652, 900, *m/e* 781 (20) $[Nb(tpp)O(HO_2CMe)]^+$, 722 (100) $[Nb(tpp)(OH)]^+$; $[Nb(tptp)O(O_2CMe)]$ (2c), i.r. 580, 700, 910, *m/e* 837 (7) $[Nb(tptp)O(HO_2CMe)]^+$, 777 (100) $[Nb(tptp)(OH)]^+$; $[Nb(omp)O(O_2CMe)]$(2d), i.r. 608, 698, 900, *m/e* 588 (2) $[Nb(omp)O(O_2CMe)]^+$, 529 (100) $[Nb(omp)O]^+$.

Physical Measurements.—Elemental analyses were performed by the Service de Microanalyse du C.N.R.S. Mass spectra were recorded in the electron-impact mode with Finnigan 3300 and LKB 9000 spectrometers. Ionizing energy, 35—70 eV *; ionizing current, 0.4 mA; source temperature, 250 °C. Hydrogen-1 n.m.r. spectra were obtained on JEOL C 60 HL and CAMECA 250 spectrometers. Samples (40 mg) were dissolved in $CDCl_3$ (0.4 cm^3) with tetramethylsilane as internal reference. Infrared spectra were recorded on a Perkin-Elmer 325 or Beckman IR 4240 spectrometer. Samples were 1% dispersions in CsI pellets.

Determinations of Crystal and Molecular Structure.—(*a*) $[Nb(tpp)O(O_2CMe)]\cdot MeCO_2H$ (2b). *Crystal data.* $C_{46}H_{31}N_4NbO_3\cdot C_2H_4O_2$, Triclinic, $M = 844$, $a = 16.645(6)$, $b = 11.332(4)$, $c = 11.868(4)$ Å, $\alpha = 105.93(6)$, $\beta = 100.54(4)$, $\gamma = 105.05(4)°$, $U = 1\ 999$ Å^3, $Z = 2$, $D_c = 1.39$ g cm^{-3}, $F(000) = 864$, space group $P\bar{1}$, nickel-filtered Cu-K_α radiation, $\lambda = 1.542\ 42$ Å, $\mu(Cu\text{-}K_\alpha) = 30.4$ cm^{-1}, crystal size $0.1 \times 0.1 \times 0.2$ mm.

Purple crystals of (2b) were obtained by recrystallization in acetic acid. The diffraction intensities were collected on a three-circle CAD 3 Enraf-Nonius diffractometer in the θ—2θ scan mode. During the intensity measurements one reflection was used for periodic checking (every 50 reflections) of the alignment and possible deterioration of the crystal; no statistically significant deviations were observed. A total of 6 042 reflections was measured in half of the diffraction sphere with $4 < \theta < 60°$, and 4 038 reflections having $\sigma(I)/I < 0.20$ were used to solve and to refine the structure. Each reflection was corrected for Lorentz and polarization effects. Absorption corrections were not applied.

Solution and refinement. The crystal structure was solved by direct methods using the MULTAN [10] computer program. Fourier methods were applied to the best set of phases and gave the approximate positions of the niobium atom, the three oxygen atoms, and the four pyrrole groups (*R* 0.285). Fourier syntheses then yielded the co-ordinates of the missing atoms of the complex and those of the solvent molecule (with poor accuracy). A least-squares procedure, using the diagonal-matrix method, was first applied [4] followed by least-squares refinements using the ORXFLS [11] computer program without any weighting scheme. During the refinement process the thermal parameters of the solvent molecules were very large so that the bond lengths

TABLE 2

Positional parameters of complex (2b)

	$10^4x/a$	$10^4y/b$	$10^4z/c$
Nb	2 195(1)	7 655(1)	6 205(1)
C(1)	3 416(4)	5 908(7)	6 086(6)
C(2)	3 806(5)	5 301(8)	5 224(6)
C(3)	3 274(5)	5 021(7)	4 072(6)
C(4)	2 566(4)	5 466(7)	4 249(6)
C(5)	1 818(4)	5 190(6)	3 340(6)
C(6)	1 085(4)	5 493(6)	3 572(6)
C(7)	270(5)	5 081(7)	2 664(6)
C(8)	−244(5)	5 704(7)	3 171(6)
C(9)	256(4)	6 498(6)	4 402(6)
C(10)	−21(4)	7 368(6)	5 178(6)
C(11)	383(4)	7 954(6)	6 436(6)
C(12)	24(4)	8 635(7)	7 309(6)
C(13)	527(4)	8 829(7)	8 442(6)
C(14)	1 198(4)	8 275(7)	8 256(5)
C(15)	1 796(4)	8 187(7)	9 192(6)
C(16)	2 436(4)	7 621(7)	9 045(6)
C(17)	3 030(5)	7 489(8)	10 016(6)
C(18)	3 575(5)	6 930(8)	9 487(6)
C(19)	3 300(4)	6 717(7)	8 195(6)
C(20)	3 708(4)	6 208(7)	7 342(6)
N(21)	2 671(3)	6 071(5)	5 493(4)
N(22)	1 039(3)	6 299(5)	4 657(4)
N(23)	1 128(3)	7 785(5)	7 016(4)
N(24)	2 611(3)	7 145(5)	7 936(5)
C(25)	1 751(4)	4 491(7)	2 032(6)
C(26)	1 676(5)	3 185(8)	1 637(6)
C(27)	1 569(6)	2 523(9)	392(8)
C(28)	1 536(6)	3 238(10)	−418(7)
C(29)	1 625(6)	4 534(10)	−22(7)
C(30)	1 723(6)	5 170(9)	1 221(6)
C(31)	−805(4)	7 669(6)	4 663(6)
C(32)	−726(4)	8 510(7)	3 990(6)
C(33)	−1 449(4)	8 815(8)	3 510(7)
C(34)	−2 245(5)	8 285(7)	3 712(6)
C(35)	−2 320(5)	7 470(8)	4 387(7)
C(36)	−1 590(5)	7 161(8)	4 871(7)
C(37)	1 716(4)	8 699(7)	10 475(6)
C(38)	1 080(5)	7 970(8)	10 847(7)
C(39)	1 014(7)	8 409(10)	12 044(8)
C(40)	1 584(6)	9 573(9)	12 848(7)
C(41)	2 199(6)	10 327(9)	12 481(7)
C(42)	2 286(6)	9 882(8)	11 268(7)
C(43)	4 521(6)	5 936(7)	7 830(6)
C(44)	5 288(5)	6 938(9)	8 347(8)
C(45)	6 051(6)	6 721(10)	8 852(9)
C(46)	6 027(5)	5 502(9)	8 817(8)
C(47)	5 270(7)	4 461(10)	8 252(10)
C(48)	4 500(6)	4 689(9)	7 781(9)
O(1)	2 274(3)	8 544(5)	5 242(4)
O(2)	3 606(3)	8 627(5)	6 901(4)
O(3)	2 775(3)	8 562(5)	7 693(4)
C(49)	3 532(5)	9 593(7)	7 644(6)
C(50)	4 320(7)	10 713(11)	8 465(10)
O(4)	3 803(13)	−352(20)	4 036(18)
O(5)	4 059(11)	1 229(18)	5 750(16)
C(51)	4 732(11)	1 528(18)	4 441(15)
C(52)	3 637(9)	208(15)	4 795(14)

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

in the solvent molecule are given with very low accuracy. Each atom, except those of the solvent molecule, was refined anisotropically; a correction for anomalous scattering was made for the niobium atom ($\Delta f' = -0.6$, $\Delta f'' = 2.7$) and the atomic scattering factors were taken from ref. 12. The final conventional R index was 0.053. Final positional parameters are listed in Table 2.

(*b*) $[\{Nb(tpp)\}_2O_3]\cdot 4C_2H_4Cl_2$ (1b). *Crystal data.* $C_{88}H_{56}N_8Nb_2O_3\cdot 4C_2H_4Cl_2$, Orthorhombic, $M = 1\,850$, $a = 31.802(9)$, $b = 11.595(5)$, $c = 23.431(7)$ Å, $U = 8\,640$ Å^3, $D_c = 1.42$ g cm^{-3}, $Z = 4$, $F(000) = 4\,530$, space group $Pccn$ ($h0l$, $l = 2n$; $0kl$, $l = 2n$; $hk0$, $h + k = 2n$), nickel-filtered Cu-K_α radiation, $\lambda = 1.542\,42$ Å, μ(Cu-K_α) = 48.30 cm^{-1}.

Red crystals of (1b) were recrystallized from 1,2-dichloroethane. Because of their rapid decay, probably by loss of solvent of crystallization, the crystal ($0.3 \times 0.1 \times 0.1$ mm) was sealed into a Lindemann glass capillary with a drop of its saturated solution. The intensity measurement techniques were similar to those described in (*a*). The intensity of the control reflection remained constant during the collection of the 4 600 reflections in a quarter of the diffraction sphere. However, owing to the presence of the saturated solution around the crystal, backgrounds were high and only 1 555 reflections with $\sigma(I)/I < 0.20$ were used to solve and to refine the structure. Each reflection was corrected for Lorentz and polarization effects.

Solution and refinement. Since (1b) crystallizes in the space group $Pccn$ with $Z = 4$, the asymmetric unit consists of the atoms of Nb(tpp)O in general crystallographic positions and of an oxygen in a special position on the two-fold axis or the inversion centre. The niobium atom and a part of the macrocycle were localized with the MULTAN [10] program. Fourier syntheses then defined the whole macrocycle (R 0.292). Precise study of the Fourier and difference-Fourier maps led to the position of the two solvent molecules and showed two very large electronic residues between the two macrocycles, corresponding to the oxygen atoms (R 0.170), one of which is on the two-fold axis. Refinement of the fractional co-ordinates and thermal parameters using the same least-squares procedure as in (*a*) led to a final conventional R index of 0.076. Definitive positions are given in Table 3.

Thermal parameters, observed and calculated structure factors, and details of the least-squares planes of both structures are listed in Supplementary Publication No. SUP 22493 (59 pp.).*

RESULTS

The reaction of $NbCl_5$ with the porphyrin bases (H_2L) in solution in benzonitrile leads to the complexes $[(NbL)_2O_3]$ (1). Analytically pure samples can be obtained by direct recrystallization or by chromatography on silica or alumina.

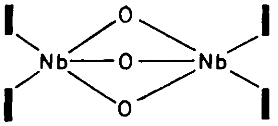
Isotopic distribution patterns relative to the highest observed m/e value in the mass spectra correspond to $[(NbL)_2O_3]^+$ and corroborate the molecular formula proposed on the basis of the elemental analyses. The base peak is either $[NbL(O)]^+$ or the recombination ion $[NbL(OH)]^+$. Characteristic fragmentations of the octaethyl- or tetraphenyl-porphinato systems are also observed: $-CH_2CH_3^{+\cdot} \longrightarrow -CH_2^+ + CH_3^\cdot$ and $[NbL(O) - xC_6H_5]^+$ respectively.

TABLE 3

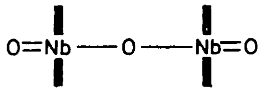
Positional parameters of complex (1b)

	$10^4x/a$	$10^4y/b$	$10^4z/c$
Nb	2 902(1)	8 363(2)	1 216(1)
N(21)	3 758(6)	8 103(13)	1 535(5)
N(22)	3 490(6)	8 495(14)	666(5)
N(23)	2 575(7)	9 977(14)	903(5)
N(24)	2 830(7)	9 548(13)	1 761(5)
C(1)	3 842(9)	8 011(16)	1 962(7)
C(2)	4 321(9)	7 313(17)	2 057(7)
C(3)	4 556(9)	6 946(17)	1 688(7)
C(4)	4 192(7)	7 442(15)	1 343(7)
C(5)	4 270(8)	7 284(17)	891(7)
C(6)	3 954(7)	7 779(17)	590(7)
C(7)	4 080(9)	7 717(19)	162(6)
C(8)	3 654(8)	8 380(19)	−56(6)
C(9)	3 310(8)	8 869(16)	285(7)
C(10)	2 866(8)	9 639(17)	188(7)
C(11)	2 537(9)	10 188(20)	483(7)
C(12)	2 114(9)	11 018(19)	385(7)
C(13)	1 857(8)	11 348(18)	753(7)
C(14)	2 163(10)	10 722(17)	1 080(6)
C(15)	2 066(9)	10 768(15)	1 509(9)
C(16)	2 390(8)	10 324(17)	1 827(7)
C(17)	2 331(9)	10 570(22)	2 271(6)
C(18)	2 710(8)	9 891(21)	2 487(7)
C(19)	3 068(9)	9 295(17)	2 162(7)
C(20)	3 486(9)	8 559(19)	2 264(8)
C(25)	4 783(8)	6 499(18)	788(6)
C(26)	4 653(10)	5 334(21)	689(7)
C(27)	5 108(12)	4 994(21)	548(7)
C(28)	5 686(10)	5 059(23)	531(7)
C(29)	5 782(10)	6 196(23)	626(8)
C(30)	5 319(10)	6 935(20)	786(8)
C(31)	2 548(13)	10 470(28)	−1 092(8)
C(32)	2 981(13)	11 132(22)	−855(9)
C(33)	2 285(11)	9 525(32)	−923(10)
C(34)	2 388(9)	9 201(23)	−486(8)
C(35)	3 016(12)	10 800(25)	−429(8)
C(36)	2 759(9)	9 917(22)	−279(7)
C(37)	1 538(8)	11 492(20)	1 630(6)
C(38)	1 027(8)	10 868(21)	1 680(8)
C(39)	561(10)	11 503(27)	1 810(9)
C(40)	563(10)	12 650(24)	1 888(8)
C(41)	1 017(10)	13 264(23)	1 814(8)
C(42)	1 542(10)	12 663(21)	1 713(8)
C(43)	3 641(12)	8 216(30)	2 743(7)
C(44)	3 917(11)	9 177(30)	2 909(9)
C(45)	4 086(12)	9 037(35)	3 345(12)
C(46)	3 915(15)	8 063(30)	3 506(9)
C(47)	3 598(15)	7 178(30)	3 388(11)
C(48)	3 403(13)	7 250(29)	2 923(13)
O(1)	2 500(0)	7 500(0)	808(7)
O(2)	2 141(7)	8 097(13)	1 411(7)
Cl(1)	4 321(4)	1 829(10)	271(3)
Cl(2)	5 353(5)	496(11)	878(5)
Cl(3)	1 547(5)	2 494(11)	3 134(3)
Cl(4)	269(5)	163(10)	2 879(4)
C(51)	997(15)	686(32)	2 938(16)
C(52)	949(18)	1 581(34)	3 051(16)
C(53)	4 667(16)	304(32)	848(14)
C(54)	4 252(20)	1 121(34)	702(13)

While the molecular formula is established without ambiguity from the analytical and mass-spectral results, two structural arrangements (A) and (B) could be considered. The i.r. study was, *a priori*, likely to permit a choice between the (A) and (B) configurations. A characteristic band is observed in the spectra of $[(NbL)_2O_3]$ (L = oep,



(A)



(B)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

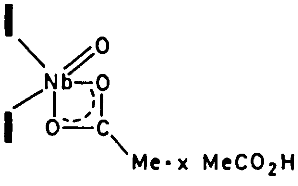
tpp, or tptp) respectively at 702, 662, and 718 cm^{-1}. This band may reasonably be assigned to a Nb–O single bond. Moreover, no band is observed in the 900 cm^{-1} region, which could have been attributed to a Nb=O double bond. These observations suggest that the niobium is seven-co-ordinate (A). However, these data are not sufficient to define the structural arrangement. Therefore we have studied the possibilities of transformation of these complexes in an attempt to specify these configurations.

When $[(NbL)_2O_3]$ (1) are treated with acetic acid, complexes of molecular formula $[NbL(O)(O_2CMe)]\cdot xMeCO_2H$ are obtained (2; $x = 1$ for L = oep, tpp, and omp; $x = 0$ for L = tptp). The yields of this reaction appear in Table 1. As for their precursors (1), the mass spectra, *a priori*, confirm the molecular formula (2), established from analytical results. The base peak of the products (2) corresponds either to $[NbL(O)]^+$ or to $[NbL(OH)]^+$, but the study does not allow the detection of the presence of a solvent molecule (when L = oep, tpp, or omp). The observed i.r. bands are listed in Table 4. Two bands appear in the range 580—700 cm^{-1} due to niobium-oxygen single bonds and one in the 900—910 region which may be attributed to a niobium–oxygen double bond. The spectral data may agree with the structures (C) and (D). The arrangement (C) is similar to the seven-co-ordination (A) proposed for the precursors (1) and the configuration (D) with an octahedral system of type (B). But unlike the precursors, the choice between these two structural models cannot be deduced from these data, since a Nb=O double bond and a niobium–acetate bond appear in each case.

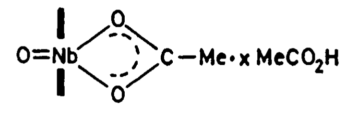
TABLE 4

Characteristic i.r. bands (cm^{-1}) of the complexes $[NbL(O)(O_2CMe)]\cdot xMeCO_2H$

Complex			
(2a) L = oep	(2b) L = tpp	(2c) L = tptp	(2d) L = omp
610	582	580	608
692	652	700	698
900	900	910	900



(C)



(D)

A ^{1}H n.m.r. study could give information allowing establishment of the structures of the complexes (1) and (2). In Table 5 are listed the n.m.r. characteristics of these complexes and the associated free bases. As already shown for metalloporphyrins,[13] in the case of the complexes (1) the co-ordination of the macrocycle to the niobium involves a shielding of all the protons ($\Delta\delta \leqslant 0.20$). For $[\{Nb(tpp)\}_2O_3]$ and $[\{Nb(tptp)\}_2O_3]$ the ambient-temperature n.m.r. spectrum exhibits coalescence of the *o*-, *m*-, and *p*-protons of the phenyl rings and also of the *o*- and *m*-protons of the tolyl groups. On the other hand, the n.m.r. spectra of complexes (2) are very similar to that of the associated free ligand, whatever the nature of the ligand.

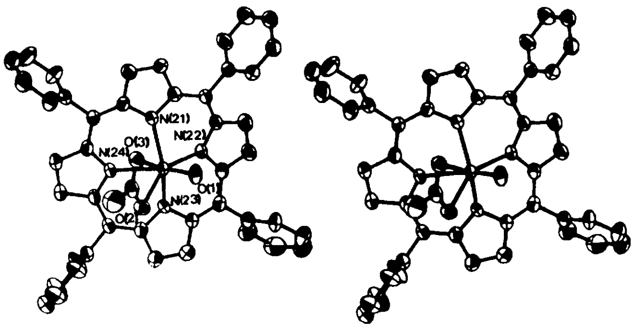


FIGURE 1 Stereoscopic view of complex (2b)

TABLE 5

N.m.r. data

	Compound	R¹ (*meso*)	R² (pyrrole)	Protons of R¹		Protons of R²	
				multiplicity, intensity	δ	multiplicity, intensity	δ
	H_2oep	H	C_2H_5	s, 4	9.97	t, 24	1.92
						q, 16	4.07
(1a)	$[\{Nb(oep)\}_2O_3]$	H	C_2H_5	s, 4	9.50	t, 24	1.56
						m, 16	4.05
(2a)	$[Nb(oep)O(O_2CMe)]\cdot MeCO_2H$	H	C_2H_5	s, 4	10.59	t, 24	1.92
						m, 16	4.25
	H_2tpp	C_6H_5	H	*m*-, *p*-H m, 12	7.75	s, 8	8.85
				o-H m, 8	8.20		
(1b)	$[\{Nb(tpp)\}_2O_3]$	C_6H_5	H	*m*-H m, 20	7.62	s, 8	8.39
(2b)	$[Nb(tpp)O(O_2CMe)]\cdot MeCO_2H$	C_6H_5	H	*m*-, *p*-H m, 12	7.75	s, 8	9.05
				o-H m, 8	8.18		
	H_2tptp	$C_6H_4CH_3$-*p*	H	*m*-H d, 8	7.55	s, 8	8.86
				o-H d, 8	8.10		
				p-CH_3 s, 12	2.70		
(1c)	$[\{Nb(tptp)\}_2O_3]$	$C_6H_4CH_3$-*p*	H	*o*-, *m*-H m, 16	7.37	s, 8	8.32
				p-CH_3 s, 12	2.73		
(2c)	$[Nb(tptp)O(O_2CMe)]$	$C_6H_4CH_3$-*p*	H	*m*-H m, 8	7.56	s, 8	9.08
				d-H m, 8	8.06		
				p-CH_3 s, 12	2.71		
	H_2omp	H	CH_3				
(1d)	$[\{Nb(omp)\}_2O_3]$	H	CH_3	s, 4	9.61	s, 24	3.45
(2d)	$[Nb(omp)O(O_2CMe)]\cdot MeCO_2H$	H	CH_3	s, 4	10.41	s, 24	3.68

However, even with all the observed spectroscopic data it is not possible to establish with certainty the structure of complexes (2). An *X*-ray study was then necessary for an example of each of these two types of complex.

A stereoscopic view of the complex [Nb(tpp)O(O_2CMe)]·$MeCO_2H$ (2b) is shown in Figure 1, and bond distances and angles with their standard deviations are listed in Tables 6 and 7. The niobium atom is seven-co-ordinated by the four nitrogen atoms, the oxygen O(1) which is double bonded to the niobium atom, and the two oxygen atoms O(2) and O(3) of the acetate group (Figure 2). The co-ordination is of the type 4 : 3: the niobium atom is inside a polyhedron of symmetry close to C_s. The polyhedron comprises a square base defined by the four nitrogen atoms and a triangular base defined by the three oxygens O(1), O(2), and O(3), nearly parallel to the former plane. The angle between the mean planes of the two bases is 1.1(2)°. The niobium atom lies 1.00(1) Å from the plane of the four nitrogen atoms and at 1.35(1) Å from that of the oxygen atoms. The O(1) atom double bonded to the niobium atom eclipses the N(22) atom. The bond length Nb–O(1) [1.720(6) Å] is identical with that in a seven-co-ordinated inorganic complex of niobium [1.710(10) Å].[14] The two oxygen atoms O(2) and O(3) of the acetate group yield bidentate co-ordination and the resulting bond lengths Nb–O(2) and Nb–O(3) are equal; Hoard *et al.*[15,16] have obtained similar results for [Zr(oep)(O_2CMe)$_2$]. The niobium–nitrogen bond lengths are quite different (Table 6) and this can be explained by steric hindrance (see below).

Tables 6 and 7 show that the bond distances and angles of the macrocycle are in good agreement with those given by Hoard.[16] Details of the least-squares planes, the distances of the atoms from these planes, and the dihedral angles are given in SUP 22493. The most important points can be summarized as follows. The pyrrole rings [N(21), C(6),

TABLE 6

Interatomic distances (Å) in complex (2b)

Nb–O(1)	1.720(6)	Nb–O(2)	2.219(4)
Nb–O(3)	2.217(4)	Nb–N(21)	2.171(6)
Nb–N(22)	2.249(4)	Nb–N(23)	2.186(6)
Nb–N(24)	2.318(6)		
N(21)–C(1)	1.393(9)	N(23)–C(11)	1.390(9)
C(1)–C(2)	1.425(11)	C(11)–C(12)	1.433(10)
C(2)–C(3)	1.389(10)	C(12)–C(13)	1.373(10)
C(3)–C(4)	1.423(11)	C(13)–C(14)	1.438(11)
C(4)–N(21)	1.403(8)	C(14)–N(23)	1.394(8)
C(4)–C(5)	1.390(9)	C(14)–C(15)	1.393(10)
C(5)–C(6)	1.403(11)	C(15)–C(16)	1.393(11)
C(6)–N(22)	1.387(8)	C(16)–N(24)	1.392(9)
C(6)–C(7)	1.442(9)	C(16)–C(17)	1.443(11)
C(7)–C(8)	1.364(12)	C(17)–C(18)	1.380(13)
C(8)–C(9)	1.443(8)	C(18)–C(19)	1.450(10)
C(9)–N(22)	1.375(9)	C(19)–N(24)	1.373(10)
C(9)–C(10)	1.387(10)	C(19)–C(20)	1.397(11)
C(10)–C(11)	1.406(8)	C(20)–C(1)	1.394(9)
C(5)–C(25)	1.505(9)	C(10)–C(31)	1.498(10)
C(25)–C(26)	1.388(11)	C(31)–C(32)	1.398(11)
C(26)–C(27)	1.415(11)	C(32)–C(33)	1.402(12)
C(27)–C(28)	1.419(16)	C(33)–C(34)	1.397(11)
C(28)–C(29)	1.372(16)	C(34)–C(35)	1.375(12)
C(29)–C(30)	1.410(11)	C(35)–C(36)	1.415(13)
C(30)–C(25)	1.389(12)	C(36)–C(31)	1.380(10)
C(15)–C(37)	1.517(10)	C(20)–C(43)	1.513(11)
C(37)–C(38)	1.384(12)	C(43)–C(44)	1.369(12)
C(38)–C(39)	1.406(12)	C(44)–C(45)	1.412(14)
C(39)–C(40)	1.370(11)	C(45)–C(46)	1.360(16)
C(40)–C(41)	1.371(14)	C(46)–C(47)	1.383(11)
C(41)–C(42)	1.435(12)	C(47)–C(48)	1.418(16)
C(42)–C(37)	1.379(9)	C(48)–C(43)	1.390(13)
C(49)–O(2)	1.263(9)	C(49)–O(3)	1.262(9)
C(49)–C(50)	1.506(10)	C(51)–C(52)	2.20(6)
C(52)–O(4)	1.08(5)	C(52)–O(5)	1.30(5)
Nb–C(5)	3.585(6)	Nb–C(10)	3.563(6)
Nb–C(15)	3.642(6)	Nb–C(20)	3.601(6)

TABLE 7

Bond angles (°) in complex (2b)

O(1)–Nb–N(22)	85.2(2)	O(2)–Nb–N(24)	74.5(2)
O(2)–Nb–O(3)	58.2(2)	O(3)–Nb–N(24)	75.5(2)
O(1)–Nb–O(3)	85.4(2)	O(2)–Nb–O(1)	83.8(2)
O(3)–Nb–N(23)	77.8(2)	O(2)–Nb–N(21)	78.2(2)
N(21)–Nb–N(22)	79.2(2)	N(21)–Nb–N(24)	78.8(2)
N(21)–Nb–N(23)	133.2(2)	N(22)–Nb–N(24)	121.2(2)
N(22)–Nb–N(23)	78.2(2)	N(23)–Nb–N(24)	78.8(2)
C(1)–N(21)–C(4)	104.8(5)	C(11)–N(23)–C(14)	105.0(5)
C(1)–C(2)–C(3)	107.2(7)	C(11)–C(12)–C(13)	106.9(6)
C(2)–C(3)–C(4)	106.6(7)	C(12)–C(15)–C(14)	107.0(6)
C(3)–C(4)–N(21)	110.7(6)	C(13)–C(14)–N(23)	110.2(6)
N(21)–C(1)–C(2)	110.5(6)	N(23)–C(11)–C(12)	110.7(6)
N(21)–C(4)–C(5)	123.9(6)	N(23)–C(14)–C(15)	125.7(6)
C(3)–C(4)–C(5)	124.9(7)	C(13)–C(14)–C(15)	123.9(6)
C(4)–C(5)–C(25)	120.2(6)	C(14)–C(15)–C(37)	117.1(6)
C(4)–C(5)–C(6)	123.4(5)	C(14)–C(15)–C(16)	125.6(7)
C(25)–C(5)–C(6)	116.4(6)	C(37)–C(15)–C(16)	117.3(6)
C(5)–C(6)–C(7)	124.1(6)	C(15)–C(16)–C(17)	125.1(7)
C(5)–C(6)–N(22)	126.5(6)	C(15)–C(16)–N(24)	124.3(6)
N(22)–C(6)–C(7)	109.2(6)	N(24)–C(16)–C(17)	110.6(6)
C(6)–C(7)–C(8)	107.5(7)	C(16)–C(17)–C(18)	106.3(7)
C(7)–C(8)–C(9)	106.4(7)	C(17)–C(18)–C(19)	106.8(7)
C(8)–C(9)–N(22)	110.3(6)	C(18)–C(19)–N(24)	110.5(6)
C(9)–N(22)–C(6)	106.1(5)	C(19)–N(24)–C(16)	105.8(6)
C(9)–C(10)–C(31)	118.6(6)	C(19)–C(20)–C(43)	116.8(6)
C(31)–C(10)–C(11)	118.2(6)	C(43)–C(20)–C(1)	117.9(6)
C(9)–C(10)–C(11)	123.2(6)	C(19)–C(20)–C(1)	125.3(7)
C(10)–C(11)–C(12)	125.0(6)	C(20)–C(1)–C(2)	124.3(7)
C(10)–C(11)–N(23)	123.6(6)	C(20)–C(1)–N(21)	125.0(6)
C(10)–C(9)–C(8)	123.6(6)	C(20)–C(19)–C(18)	124.6(7)
N(22)–C(9)–C(10)	126.1(6)	N(24)–C(19)–C(20)	124.8(6)
C(26)–C(25)–C(30)	120.9(7)	C(38)–C(37)–C(42)	120.4(7)
C(25)–C(26)–C(27)	120.1(8)	C(37)–C(38)–C(39)	120.6(8)
C(26)–C(27)–C(28)	117.7(9)	C(38)–C(39)–C(40)	119.6(9)
C(27)–C(28)–C(29)	122.1(9)	C(39)–C(40)–C(41)	120.5(9)
C(28)–C(29)–C(30)	119.2(9)	C(40)–C(41)–C(42)	120.7(9)
C(29)–C(30)–C(25)	120.0(8)	C(41)–C(42)–C(37)	118.2(8)
C(31)–C(32)–C(33)	119.8(7)	C(43)–C(44)–C(45)	120.7(8)
C(32)–C(33)–C(34)	120.0(7)	C(44)–C(45)–C(46)	119.8(9)
C(33)–C(34)–C(35)	120.2(7)	C(45)–C(46)–C(47)	120.7(9)
C(34)–C(35)–C(36)	119.9(8)	C(46)–C(47)–C(48)	119.2(1.0)
C(35)–C(36)–C(31)	120.3(7)	C(47)–C(48)–C(43)	120.0(9)
C(36)–C(31)–C(32)	119.8(7)	C(48)–C(43)–C(44)	119.4(8)
O(3)–C(49)–O(2)	117.7(7)	O(2)–C(49)–C(50)	120.0(8)
O(3)–C(49)–C(50)	122.2(8)		

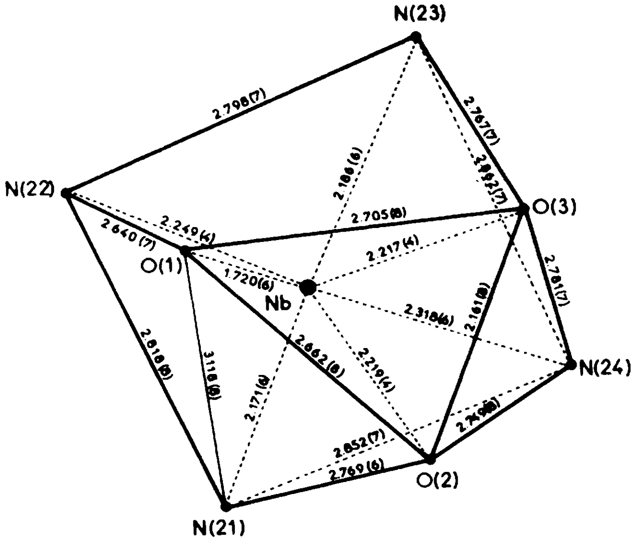


FIGURE 2 Co-ordination polyhedron of complex (2b)

C(7), C(8), C(9)] and [N(24), C(16), C(17), C(18), C(19)] are tilted respectively by 11 and 16° with respect to the least-squares plane of the macrocycle; it follows that the displacements of the atoms from this plane are larger than 0.4 Å. The four nitrogen atoms are not coplanar: their distances from the corresponding least-squares plane are larger than 0.1 Å. Except for C(16), C(17), C(18), C(19), N(24), the pyrrole rings are not quite planar. However, the four carbon atoms of each of the three rings lie in perfect planes; the nitrogen atoms are displaced significantly from these planes [0.087 Å for N(22) in an opposite direction to that of the niobium atom and by 0.060 Å for N(21) and N(23) towards the metal atom]. Finally, as expected, the distances C(49)–O(2) and C(49)–O(3) are equal [1.263(9) and 1.262(9) Å].

Although the spectroscopic results for complexes (1) suggest that they present the same type of co-ordination as (2), it was necessary to verify this by determining the crystal structure of [{Nb(tpp)}$_2$O$_3$]·4C$_2$H$_4$Cl$_2$ (1b). As indicated before, Johnson and Scheidt[5] published the crystal structure of [{Nb(tpp)}$_2$O$_3$]·CHCl$_3$ at the same time as our preliminary communication.[3]

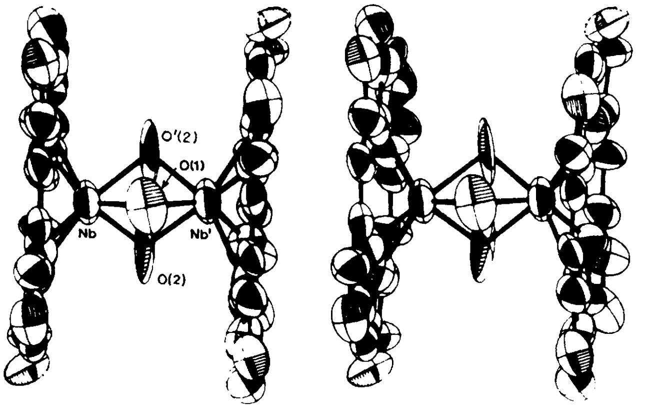


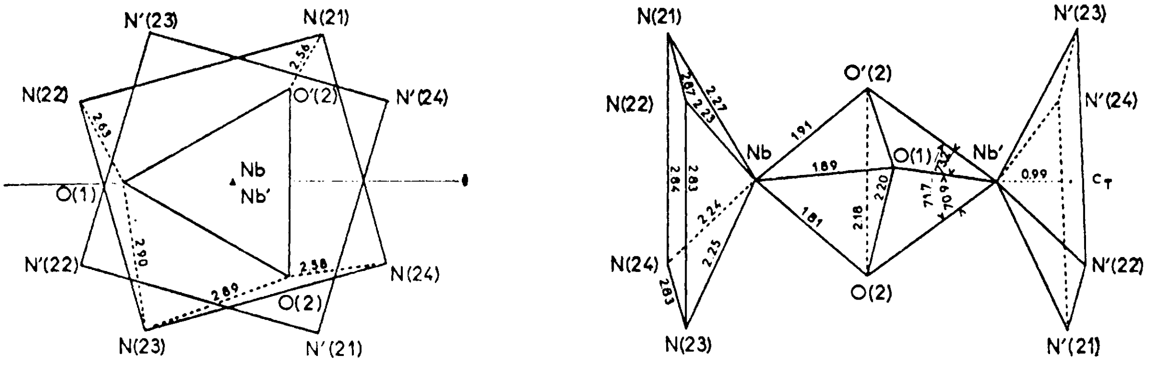
FIGURE 3 Stereoscopic view of complex (1b)

Figure 3 shows a spectroscopic view of complex (1b) and Tables 8 and 9 give the bond distances and angles and their standard deviations. The complex is tri-μ-oxo-bridged. As for (2b), the niobium atom is seven-co-ordinated and the resulting polyhedron, of symmetry C_s, is shown in Figure 4. The least-squares plane containing the four nitrogen atoms is parallel to the plane defined by the three bridging oxygen atoms. The distances from the niobium atom to these planes are respectively 0.99(2) and 1.37(3) Å. The three oxygen atoms are bonded to the metals by single bonds whose mean length is 1.87(3) ± 0.06 Å (Table 8).

Contrary to what is observed in the case of complex (2b), the niobium–nitrogen distances in (1b) are equal and the four nitrogen atoms are perfectly coplanar, the most important displacement being 0.01 Å. Both porphyrin macrocycles are staggered in order to reduce the steric interaction of the phenyl groups. The solvent molecules lie in the holes of the structures without apparent interaction with the complex molecule, which could explain the rapid deterioration of the crystal.

DISCUSSION

These studies have clearly demonstrated a new geometry in the metalloporphyrin series; the metal is seven-co-ordinated and the resulting co-ordination polyhedron has a low symmetry C_s. A similar polyhedron of 4 : 3 geometry has been observed in tri-μ-chloro-bis[dicarbonylbis(trimethyl phosphite)molybdenum] tetrachloro(dimethyl phosphito)oxomolybdate[17]: the co-ordination sphere of each molybdenum atom of the cation also exhibits a 4 : 3 geometry. In fact, seven-co-ordination for a complex of Nb^{V} is not surprising since many other examples are known such as the ions [NbF$_7$]$^{2-}$,[18,19] [NbF$_6$O]$^{3-}$,[20] and [Nb(C$_2$O$_4$)$_3$O]$^{3-}$.[14] For all these complexes the co-ordination polyhedron is a more or less distorted pentagonal bipyramid or a capped trigonal prism. The diversity of the forms of the polyhedrons obtained is in agreement with the calculations and structural studies of Bradford Thompson and Bartell[21] and Hoffmann *et al.*[22] who have shown by using the Valence Shell Electron Pair Repulsion method[23] that seven co-ordination has in general a potential surface that is not distinguished by a deep minimum corresponding to one polytopal form. In the case of metalloporphyrins, the



O(1)-O(2)-O'(2) = 60.4
O'(2)-O(1)-O(2) = 59.2
Nb -O(2)-Nb' = 95.2

O(2)-O'(2)-O(1) = 60.4
Nb -O(1)-Nb' = 93.4
Nb -O'(2)-Nb' = 95.2

FIGURE 4 Co-ordination polyhedron of complex (1b) macrocycle imposes an almost square base to the polyhedron formed by the nitrogen atoms and thus only two kinds of polyhedron may exist [see structures (A)—(D)].

In fact, these two configurations are known in the metalloporphyrin series: the *trans* form in the case of [{Mo(tpp)O}$_2$O] [5] and the *cis* form for both complexes described in this paper. The difference between these forms is surprising if we refer to the ionic radii (0.66 for Nb^V and 0.63 for Mo^V) [24] of the metals. Presumably the same expansion energy for the macrocycle is required to allow each metal to enter the ' central hole ' but Mo^V has an electron in its 4*d* shell while for Nb^V this electronic shell is empty. In the case of a seven-co-ordinated niobium system there is no repulsive interaction between the metal electrons and those of the ligand; thus *cis* co-ordination is favoured because the expansion of the central hole is unnecessary (the metal lies 1.00 Å from the plane defined by the four nitrogen atoms), all the atomic orbitals interact, and a strong metal–oxygen ligand interaction appears. Nevertheless, this interaction is reduced by the repulsion between the nitrogen and oxygen atoms and can explain the differences in the Nb–N bond lengths in the acetato-complex.

In the case of both complexes the asymmetry induced by the ligands is enhanced by the out-of-plane position of the niobium atom. Moreover, for complex (1b) the presence of the three μ-oxo-atoms leads to a greater rigidity. Recently, Busby and Dolphin [25] have shown that the methylenic protons of metalloporphyrin systems are anisochronous resulting from the specific asymmetry of the metalloporphyrins, not from a hindered rotation of the lateral ethyl chains. Figure 5 reproduces part of the n.m.r. spectra (250 MHz) of [{Nb(oep)}$_2$O$_3$] (1a) and [Nb(oep)O(O$_2$CMe)]·MeCO$_2$H (2a). A triplet resonance pattern of the methylic protons ($J \simeq 7$ Hz)

TABLE 8

Interatomic distances (Å) in complex (1b)

Nb–Nb	2.75(4)	Nb–O(2)	1.81(2)
Nb–O(1)	1.89(1)	Nb–O′(2)	1.91(2)
Nb–N(21)	2.27(1)	Nb–N(22)	2.23(2)
Nb–N(23)	2.25(2)	Nb–N(24)	2.24(2)
N(21)–C(1)	1.38(2)	N(23)–C(11)	1.36(3)
C(1)–C(2)	1.42(3)	C(11)–C(12)	1.42(3)
C(2)–C(3)	1.36(3)	C(12)–C(13)	1.37(3)
C(3)–C(4)	1.50(3)	C(13)–C(14)	1.46(3)
C(4)–N(21)	1.41(2)	C(14)–N(23)	1.41(3)
C(4)–C(5)	1.46(3)	C(14)–C(15)	1.38(3)
C(5)–C(6)	1.34(3)	C(15)–C(16)	1.36(3)
C(6)–N(22)	1.39(2)	C(16)–N(24)	1.38(3)
C(6)–C(7)	1.35(2)	C(16)–C(17)	1.45(3)
C(7)–C(8)	1.44(3)	C(17)–C(18)	1.37(3)
C(8)–C(9)	1.47(3)	C(18)–C(19)	1.50(3)
C(9)–N(22)	1.35(3)	C(19)–N(24)	1.42(3)
C(9)–C(10)	1.41(3)	C(19)–C(20)	1.34(3)
C(10)–C(11)	1.37(3)	C(20)–C(1)	1.42(3)
C(5)–C(25)	1.54(3)	C(10)–C(31)	1.54(3)
C(25)–C(26)	1.42(3)	C(31)–C(32)	1.48(4)
C(26)–C(27)	1.37(3)	C(32)–C(33)	1.41(4)
C(27)–C(28)	1.42(4)	C(33)–C(34)	1.46(4)
C(28)–C(29)	1.37(4)	C(34)–C(35)	1.37(3)
C(29)–C(30)	1.47(4)	C(35)–C(36)	1.28(4)
C(30)–C(25)	1.35(3)	C(36)–C(31)	1.37(3)
C(15)–C(37)	1.54(3)	C(20)–C(43)	1.62(4)
C(37)–C(38)	1.41(3)	C(43)–C(44)	1.39(4)
C(38)–C(39)	1.38(3)	C(44)–C(45)	1.45(4)
C(39)–C(40)	1.35(4)	C(45)–C(46)	1.30(4)
C(40)–C(41)	1.30(4)	C(46)–C(47)	1.32(5)
C(41)–C(42)	1.45(3)	C(47)–C(48)	1.54(5)
C(42)–C(37)	1.38(3)	C(48)–C(43)	1.37(4)
Cl(1)–C(53)	1.60(4)	Cl(4)–C(51)	1.70(4)
Cl(2)–C(54)	1.62(4)	Cl(3)–C(52)	1.77(4)
C(53)–C(54)	1.43(6)	C(52)–C(51)	1.10(7)

TABLE 9

Bond angles (°) in complex (1b)

C(1)–N(21)–C(4)	106.4(1.4)	C(11)–N(23)–C(14)	103.6(1.6)
C(1)–C(2)–C(3)	108.4(1.8)	C(11)–C(12)–C(13)	107.9(1.9)
C(2)–C(3)–C(4)	106.1(1.8)	C(12)–C(13)–C(14)	104.8(1.8)
C(3)–C(4)–N(21)	107.6(1.5)	C(13)–C(14)–N(23)	110.2(6)
N(21)–C(1)–C(2)	110.5(1.6)	N(23)–C(11)–C(12)	112.7(1.9)
N(21)–C(4)–C(5)	125.7(1.6)	N(23)–C(14)–C(15)	110.9(1.7)
C(3)–C(4)–C(5)	126.7(1.7)	C(13)–C(14)–C(15)	127.1(2.0)
C(4)–C(5)–C(25)	112.3(1.6)	C(14)–C(15)–C(37)	113.5(1.3)
C(4)–C(5)–C(6)	125.5(1.8)	C(14)–C(15)–C(16)	128.4(2.0)
C(25)–C(5)–C(6)	122.2(1.8)	C(37)–C(15)–C(16)	118.0(1.9)
C(5)–C(6)–C(7)	123.9(1.9)	C(15)–C(16)–C(17)	126.4(2.0)
C(5)–C(6)–N(22)	124.3(1.8)	C(15)–C(16)–N(24)	123.3(1.9)
N(22)–C(6)–C(7)	111.5(1.7)	N(24)–C(16)–C(17)	110.3(1.7)
C(6)–C(7)–C(8)	107.2(1.8)	C(16)–C(17)–C(18)	108.3(1.9)
C(7)–C(8)–C(9)	103.5(1.9)	C(17)–C(18)–C(19)	106.3(1.8)
C(8)–C(9)–N(22)	111.5(1.7)	C(18)–C(19)–N(24)	107.7(1.6)
C(9)–N(22)–C(6)	106.2(1.6)	C(19)–N(24)–C(16)	106.9(1.6)
C(9)–C(10)–C(31)	119.0(1.3)	C(19)–C(20)–C(43)	123.4(2.0)
C(31)–C(10)–C(11)	116.9(1.4)	C(43)–C(20)–C(1)	113.2(1.9)
C(9)–C(10)–C(11)	124.1(1.9)	C(19)–C(20)–C(1)	123.4(2.0)
C(10)–C(11)–C(12)	123.8(2.0)	C(20)–C(1)–C(2)	125.3(1.9)
C(10)–C(11)–N(23)	123.4(2.0)	C(20)–C(1)–N(21)	123.2(1.8)
C(10)–C(9)–C(8)	119.4(1.8)	C(20)–C(19)–C(18)	122.3(1.9)
N(22)–C(9)–C(10)	129.1(1.8)	N(24)–C(19)–C(20)	129.5(2.0)
C(26)–C(25)–C(30)	123.5(2.0)	C(38)–C(37)–C(42)	119.2(2.0)
C(25)–C(26)–C(27)	115.0(2.1)	C(37)–C(38)–C(39)	115.7(2.1)
C(26)–C(27)–C(28)	126.4(2.3)	C(38)–C(39)–C(40)	125.2(2.5)
C(27)–C(28)–C(29)	115.8(2.3)	C(39)–C(40)–C(41)	120.1(2.5)
C(28)–C(29)–C(30)	120.8(2.3)	C(40)–C(41)–C(42)	118.2(2.3)
C(29)–C(30)–C(25)	118.1(2.2)	C(41)–C(42)–C(37)	120.6(2.1)
C(31)–C(32)–C(33)	112.8(2.5)	C(43)–C(44)–C(45)	113.0(2.7)
C(32)–C(33)–C(34)	123.3(2.5)	C(44)–C(45)–C(46)	113.0(2.7)
C(33)–C(34)–C(35)	127.1(2.4)	C(45)–C(46)–C(47)	137.0(3.3)
C(34)–C(35)–C(36)	114.0(2.3)	C(46)–C(47)–C(48)	113.4(3.0)
C(35)–C(36)–C(31)	120.3(2.7)	C(47)–C(48)–C(43)	108.6(2.8)
C(36)–C(31)–C(32)	121.7(2.7)	C(48)–C(43)–C(44)	133.1(2.8)
Nb–O(1)–Nb′	93.5(3)	O(1)–O(2)–O′(2)	60.4(7)
Nb–O(2)–Nb′	95.2(8)	O(2)–O(1)–O′(2)	59.3(7)
Cl(1)–C(53)–C(54)	123.7(2.1)	Cl(3)–C(52)–C(51)	112.0(2.5)
C(53)–C(54)–Cl(2)	126.5(2.0)	C(52)–C(51)–Cl(4)	127.9(2.4)

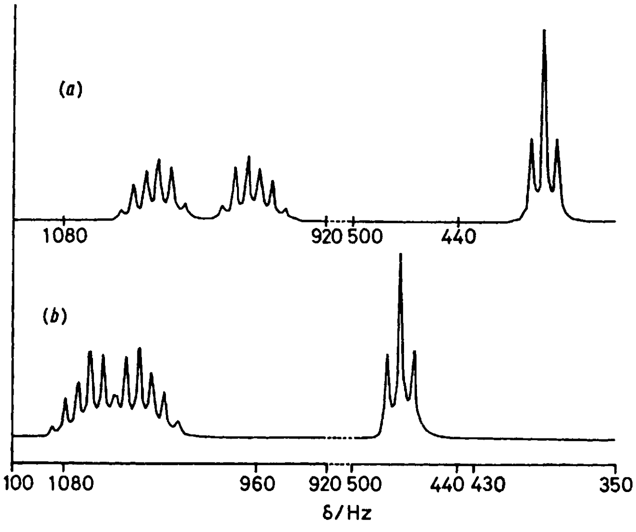


FIGURE 5 Part of the n.m.r. spectra of complexes (1a) (*a*) and (2a) (*b*)

and a multiplet with 12 lines for the methylenic protons are observed. This system, as for the case studied by Busby and Dolphin, can be explained by an ABX_3 system with $J_{AB} = -14$, $J_{AX} = J_{BX} = 7.5$ Hz for (1a) and $J_{AB} = -14.5$, $J_{AX} = J_{BX} = 7.6$ Hz for (2a).

Thus, from the present study and from that of Johnson and Scheidt[5] on [{Mo(tpp)O}$_2$O] it appears that no structural prediction can be made from the ionic radii, but a high-resolution n.m.r. study of the methylenic protons of a metal octaethylporphyrin system would allow of a prediction of the distance from the mean porphyrin plane to the metal atom and the *cis* or *trans* position of the ligands.

Finally it is of interest to compare both structures of [{Nb(tpp)}$_2$O$_3$] obtained from crystals grown from two recrystallization solvents: in structure (I) described by Johnson and Scheidt[5b] the angles defined by the straight line joining the two niobium atoms and the normals to both porphyrin macrocycles are 18 and 21°, while in structure (II) described here the Nb–Nb axis is nearly perpendicular to the planes of the macrocycles. From the data of Table 10, a significant difference between the niobium–niobium distances of both structures can be noted which leads to different niobium–oxygen bond lengths.

TABLE 10

	Structure of complex (1b)		
Distance (Å)	Slipped (I)		Staggered (II)
Nb–Nb	2.872(1)		2.751(4)
Nb–O	Nb(1)–O(2)	Nb(2)–O(3)	Nb–O(2)
	1.760(7)	1.782(7)	1.81(2)
	Nb(1)–O(1)	Nb(2)–O(1)	Nb–O(1)
	1.990(6)	1.910(6)	1.89(2)
	Nb(1)–O(3)	Nb(2)–O(2)	Nb–O′(2)
	2.278(7)	2.440(8)	1.91(2)

The complex [{Nb(tpp)}$_2$O$_3$] thus seems to be able to exhibit several stable configurations which could depend on the nature of the crystallization solvent. Consequently, the crystallographic results must be used with care when the spectroscopic data obtained from solutions are examined. This remark may be compared to that made by Buchler and Schneehage[26] for [{Sc(oep)}$_2$O] where a dissociation of the dimeric complex is observed as a function of the pH and the solvent. However, the i.r. characteristics of [{Nb(tpp)}$_2$O$_3$] are in agreement with the proposed structure since the band corresponding to a niobium–oxygen double bond (near 900 cm^{-1}) is missing.

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