Crystal Structure of Fluoro(2,3,7,8,12,13,17,18-octaethylporphyrinato)oxoniobium; Demonstration of the Presence of Six-co-ordinated Niobium

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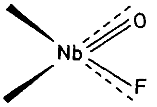
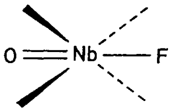
When HF is bubbled through a solution of $[Nb_2L_2O_3]$ (L = porphyrinate), porphyrinatoniobium oxide fluoride complexes are formed. The structures of some of these complexes have been studied from analytical and spectroscopic data. The title compound has been determined by *X*-ray diffraction methods. Crystals are monoclinic space group $P2_1/c$ with a = 15.007(3), b = 22.257(4), c = 10.058(2) Å, β = 77.85(2)°, and Z = 4.

In a recent communication [1] we have shown that the metalloporphyrinic system [Nb(oep)(O)F],† (1), could be used as a precursor for the preparation of low-oxidation-state niobium porphyrinates. The synthesis of compound (1) was first reported by Buchler and Rohbock; [2] two isomeric forms *cis* or *trans* are possible (see below), but its configuration was not, however, established.



cis



trans

In this paper we describe the preparation of the complexes [NbL(O)F] (1)—(4) [with L = oep (1), tpp (2), omp (3), and ttp (4)] and the *X*-ray structural determination of (1).

EXPERIMENTAL

The $[Nb_2L_2O_3]$ compounds (L = oep, ttp, tpp, omp) were prepared according to the methods previously reported.[3]

Preparations of the [NbL(O)F] *Complexes.*—The [NbL(O)F] compounds were prepared according to a procedure similar to that described for [Nb(oep)(O)F] (1).

Gaseous HF (6 cm^3 min^{-1}) was bubbled through a solution of $[Nb_2(oep)_2O_3]$ (0.19 mmol) in anhydrous benzene (50 cm^3) for 15 min. To the mixture maintained under a gaseous HF atmosphere, anhydrous hexane (300 cm^3) was added in six portions over a period of 30 min. The red precipitate obtained was filtered off, dried, and recrystallised from anhydrous toluene (30 cm^3) yielding [Nb(oep)(O)F], (1) (200 mg, 80%). The yields of the other compounds obtained under similar conditions were as follows: [Nb(tpp)(O)F] (2), 80; [Nb(omp)(O)F] (3), 50; and [Nb(ttp)(O)F] (4), 70%. Elemental analyses agreed with calculated values within ±0.5%.

During the preparation of the [NbL(O)F] complexes, under slightly modified experimental conditions, we obtained a second derivative. The synthesis of this second compound (1a; L = oep) is as follows. A stream of gaseous HF (15—30 cm^3 min^{-1}) was bubbled for 30 min through a solution of $[Nb_2(oep)_2O_3]$ (0.19 mmol) in anhydrous toluene (70 cm^3). This solution, allowed to stand at room temperature for a few days, yielded (1a) (150 mg, 60%). Spectral data: mass spectrum, *m/e* 660, $[Nb(oep)(O)F]^{\cdot+}$, 100%; 641, $[Nb(oep)O]^+$, 70%; ^1H n.m.r. ($CDCl_3$), 1.76(t, Me), 3.92(m, CH_2), and 10.52 p.p.m. (s, *meso*-H) relative to $SiMe_4$; i.r., ν(Nb–F) at 480 cm^{-1}. The essential information concerning the structure of (1a) cannot be gained from these data.

Physical Measurements.—Elemental analyses were performed by the Service de Microanalyses du C.N.R.S. Mass spectra were recorded in the electron-impact mode with a Finnigan 3300 spectrometer; ionising energy 30—70 eV; ‡ ionising current 0.4 mA; source temperature 250—400 °C. Hydrogen-1 n.m.r. spectra were obtained on a JEOL FX 100 spectrometer. Samples (10 mg) were dissolved in $CDCl_3$ (0.4 cm^3) with tetramethylsilane as internal reference. Infrared spectra were obtained on a Beckman IR 4240 spectrometer. Samples were 1% dispersions in CsI pellets. Visible and u.v. spectra were recorded on a Perkin-Elmer 559 spectrophotometer using 10^{-6} mol dm^{-3} solutions of the compound in dry and oxygen-free toluene.

Characteristic i.r. bands (cm^{-1}, from CsI), absorption spectral data, and significant fragmentation patterns observed in the mass spectra of compounds [NbL(O)F] (1)—(4) are given in Table 1.

Determination of the Crystal and Molecular Structure.—*Crystal data.* [Nb(oep)(O)F], $C_{36}H_{44}FN_4NbO$ (1), Monoclinic, M = 660, a = 15.007(3), b = 22.257(4), c = 10.058(2) Å, β = 77.85(2)°, U = 3 284.5(1) $Å^3$, Z = 4, D_c = 1.335 g cm^{-3}, $F(000)$ = 1 468, λ = 1.540 51 Å, $\mu(Cu\text{-}K_\alpha)$ = 34 cm^{-1}, space group $P2_1/c$ ($h0l$, $l = 2n$; $0k0$, $k = 2n$).

Solution and refinement. The cell parameters were measured and adjusted by the least-squares method to the observed positions of 25 reflections on a CAD4F Enraf-Nonius diffractometer. Intensity data were collected on the same apparatus with nickel-filtered Cu-K_α radiation using a (σ, ω) scanning mode ($\sigma < \omega < 70°$). Three reflections were used for periodic checking on the alignment of the crystal (every 100 reflections) and three more for testing the possible deterioration of the compound. No statistically significant deviations were observed. A total

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

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

TABLE 1

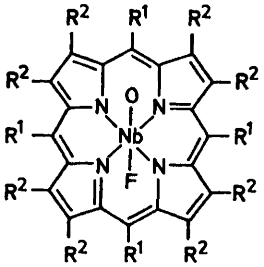
Infrared, u.v.–visible, and mass spectral data

Complex	I.r. (cm^{-1}, CsI pellets)		U.v.–visible*		Mass spectra		
	ν(Nb–F)	ν(Nb–O)	λ/nm	ϵ/dm^3 mol^{-1} cm^{-1}	m/e	Relative intensity	Fragmentation pattern
			568	30 000	661	100	[Nb(oep)(O)F + H]$^+$
(1)	540	910	530	9 800	642	71	[Nb(oep)O + H]$^{\cdot+}$
			404	195 000	641	65	[Nb(oep)O]$^+$
					739	93	[Nb(tpp)(O)F − H]$^+$
(2)	555	910	538	18 000	721	40	[Nb(tpp)O]$^+$
			420	316 000	720	100	[Nb(tpp)O − H]$^{\cdot+}$
			566	17 000	547	6.84	[Nb(omp)(O)F − H]$^+$
(3)	545	910	528	9 000	529	17.80	[Nb(omp)O]$^+$
			400	100 000	528	100	[Nb(omp)O − H]$^{\cdot+}$
					795		[Nb(ttp)(O)F − H]$^+$
(4)	550	910	541	23 000	777		[Nb(ttp)O]$^+$
			423	400 000	776		[Nb(ttp)O − H]$^{\cdot+}$

* Solvent = toluene for (1), (2), and (4), methylene chloride for (3).

TABLE 2

N.m.r. data *



Compound	R^1	R^2	Protons of R^1		Protons of R^2	
			multiplicity, intensity	δ	multiplicity, intensity	δ
					t, 24	1.76
(1)	H	C_2H_5	s, 4	10.52	m, 16	3.92
			M, 12	7.78		
(2)	C_6H_5	H	M, 8	8.22	s, 8	9.08
(3)	H	CH_3	s, 4	10.43	s, 24	3.63
			s, 12	2.70	s, 8	9.08
(4)	C_6H_4Me-*p*	H	M, 8	7.56		
			M, 8	8.06		

* s = Singlet, t = triplet, m = multiplet, and M = massive.

TABLE 3

Fractional co-ordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
C(1)	1 231(3)	4 442(2)	3 678(5)
C(2)	1 235(3)	3 863(2)	4 308(5)
C(3)	2 129(4)	3 725(2)	4 263(6)
C(4)	2 663(3)	4 221(2)	3 606(5)
C(5)	3 606(3)	4 263(2)	3 368(6)
C(6)	4 113(3)	4 722(2)	2 693(5)
C(7)	5 108(3)	4 765(2)	2 384(5)
C(8)	5 316(3)	5 277(2)	1 673(5)
C(9)	4 467(3)	5 563(2)	1 543(5)
C(10)	4 406(3)	6 078(2)	807(5)
C(11)	3 648(3)	6 350(2)	512(5)
C(12)	3 649(3)	6 845(2)	−417(5)
C(13)	2 777(3)	6 941(2)	−534(5)
C(14)	2 222(3)	6 518(2)	369(4)
C(15)	1 281(3)	6 470(2)	597(5)
C(16)	766(3)	6 037(2)	1 394(5)
C(17)	−213(3)	5 967(2)	1 591(5)
C(18)	−432(3)	5 472(2)	2 385(5)
C(19)	393(3)	5 242(2)	2 713(5)
C(20)	449(3)	4 726(2)	3 458(5)

TABLE 3 (*continued*)

Atom	x	y	z
N(21)	2 106(2)	4 659(2)	3 251(4)
N(22)	3 738(2)	5 219(2)	2 204(4)
N(23)	2 753(2)	6 160(2)	1 007(4)
N(24)	1 126(2)	5 592(2)	2 097(4)
C(25)	413(4)	3 486(3)	4 865(7)
C(26)	95(6)	3 139(4)	3 802(11)
C(27)	2 498(5)	3 167(3)	4 780(9)
C(28)	2 804(11)	2 713(6)	3 692(25)
C(29)	5 735(4)	4 315(3)	2 813(6)
C(30)	5 978(6)	4 455(4)	4 157(8)
C(31)	6 237(4)	5 549(3)	1 113(7)
C(32)	6 446(5)	6 049(4)	2 017(12)
C(33)	4 481(4)	7 178(3)	−1 124(6)
C(34)	4 759(6)	7 678(4)	−309(10)
C(35)	2 420(4)	7 365(3)	−1 444(7)
C(36)	2 213(9)	7 054(5)	−2 665(10)
C(37)	−828(4)	6 369(3)	995(7)
C(38)	−1 055(8)	6 137(7)	−277(10)
C(39)	−1 363(3)	5 192(2)	2 827(6)
C(40)	−1 503(5)	4 669(4)	1 940(10)
F	3 131(2)	6 224(1)	3 425(3)
O	1 624(2)	5 718(2)	4 481(3)
Nb	2 374(0)	5 628(0)	2 910(0)

TABLE 4

Bond distances (Å) and standard deviations

(*a*) Co-ordination polyhedron of the niobium atom

Nb–N(21)	2.208(4)	Nb–N(22)	2.217(3)	Nb–N(23)	2.220(4)
Nb–N(24)	2.197(4)	Nb–O	1.749(3)	Nb–F	1.888(3)
F–N(22)	2.622(4)	F–N(23)	2.615(5)	O · · · N(24)	3.672(5)
O–N(21)	2.690(5)	Nb · · · C(5)	3.636(5)	Nb · · · C(10)	3.473(4)
Nb · · · C(15)	3.635(5)	Nb · · · C(20)	3.466(4)	F · · · C(10)	2.930(5)
O · · · C(20)	3.131(6)	O–F	2.550(4)		

(*b*) Macrocycle

C(1)–C(2)	1.437(7)	C(2)–C(3)	1.367(7)	C(3)–C(4)	1.439(7)
C(4)–C(5)	1.388(7)	C(4)–N(21)	1.380(6)	N(21)–C(1)	1.380(5)
C(5)–C(6)	1.366(6)	C(6)–N(22)	1.376(6)	C(6)–C(7)	1.463(6)
C(7)–C(8)	1.346(7)	C(8)–C(9)	1.455(7)	C(9)–N(22)	1.385(5)
C(9)–C(1)	1.379(7)	C(10)–C(11)	1.375(7)	C(11)–C(12)	1.444(7)
C(12)–C(13)	1.355(7)	C(13)–C(14)	1.445(6)	C(14)–N(23)	1.377(6)
C(11)–N(23)	1.397(5)	C(14)–C(15)	1.387(6)	C(15)–C(16)	1.381(6)
C(16)–C(17)	1.450(6)	C(17)–C(13)	1.359(7)	C(18)–C(19)	1.442(7)
C(19)–N(24)	1.384(5)	C(16)–N(24)	1.390(6)	C(19)–C(20)	1.383(7)
C(20)–C(1)	1.390(6)	C(2)–C(25)	1.500(7)	C(25)–C(26)	1.48(1)
C(3)–C(23)	1.497(9)	C(27)–C(28)	1.48(2)	C(7)–C(29)	1.498(8)
C(29)–C(30)	1.51(1)	C(8)–C(31)	1.506(7)	C(31)–C(32)	1.51(1)
C(12)–C(33)	1.497(7)	C(33)–C(34)	1.49(1)	C(13)–C(35)	1.491(8)
C(35)–C(36)	1.50(1)	C(17)–C(37)	1.498(8)	C(37)–C(38)	1.48(1)
C(18)–C(39)	1.51(6)	C(39)–C(40)	1.51(1)		

TABLE 5

Bond angles (°) and standard deviations

(*a*) Co-ordination polyhedron of the niobium atom

O–Nb–F	89.0(1)	N(21)–Nb–N(22)	76.9(1)	N(22)–Nb–N(23)	83.8(1)
N(23)–Nb–N(24)	77.5(1)	N(24)–Nb–N(21)	83.1(1)	N(21)–Nb–N(23)	131.3(1)
N(22)–Nb–N(24)	131.9(1)	O–Nb–N(21)	84.8(1)	O–Nb–N(24)	84.4(1)
F–Nb–N(23)	78.6(1)	F–Nb–N(22)	78.9(1)		

(*b*) Macrocycle

C(1)–C(2)–C(3)	106.4(4)	C(2)–C(3)–C(4)	107.0(4)	C(3)–C(4)–C(5)	125.5(5)
C(3)–C(4)–N(21)	110.5(4)	C(4)–N(21)–C(1)	105.1(4)	N(21)–C(1)–C(2)	111.0(4)
N(21)–C(1)–C(20)	124.8(4)	C(2)–C(1)–C(20)	124.1(4)	N(21)–C(4)–C(5)	123.9(4)
C(4)–C(3)–C(27)	125.8(5)	C(2)–C(3)–C(27)	127.3(5)	C(3)–C(27)–C(28)	112.3(10)
C(1)–C(2)–C(25)	125.9(5)	C(3)–C(2)–C(25)	127.7(5)	C(2)–C(25)–C(26)	112.8(6)
C(4)–C(5)–C(6)	125.3(5)	C(5)–C(6)–N(22)	123.5(4)	C(5)–C(6)–C(7)	126.2(4)
N(22)–C(6)–C(7)	110.3(4)	C(6)–C(7)–C(8)	106.3(4)	C(7)–C(8)–C(9)	107.9(4)
C(6)–C(7)–C(29)	124.8(4)	C(8)–C(7)–C(29)	128.9(4)	C(7)–C(29)–C(30)	114.0(5)
C(7)–C(8)–C(31)	129.2(5)	C(9)–C(8)–C(31)	122.9(5)	C(8)–C(9)–N(22)	109.5(4)
C(9)–N(22)–C(6)	105.9(3)	C(8)–C(9)–C(10)	124.8(4)	N(22)–C(9)–C(10)	125.6(4)
C(9)–C(10)–C(11)	129.3(4)	C(10)–C(11)–N(23)	124.5(4)	C(10)–C(11)–C(12)	126.0(4)
C(11)–C(12)–C(13)	107.8(4)	C(11)–C(12)–C(33)	124.9(5)	C(13)–C(12)–C(33)	127.3(5)
C(12)–C(33)–C(34)	114.2(5)	C(12)–C(13)–C(14)	106.4(4)	C(12)–C(13)–C(35)	129.1(4)
C(14)–C(13)–C(39)	124.4(4)	C(13)–C(14)–N(23)	110.9(4)	C(14)–N(23)–C(11)	105.4(3)
N(23)–C(14)–C(15)	123.2(4)	C(13)–C(14)–C(15)	125.9(4)	C(13)–C(35)–C(36)	111.9(6)
C(14)–C(15)–C(16)	125.2(5)	C(15)–C(16)–C(17)	125.6(4)	C(15)–C(16)–N(24)	124.2(4)
C(16)–N(24)–C(19)	105.8(3)	C(16)–C(17)–C(18)	106.4(4)	C(16)–C(17)–C(37)	124.9(4)
C(18)–C(17)–C(37)	128.7(4)	C(17)–C(37)–C(38)	114.2(7)	C(17)–C(18)–C(19)	108.0(4)
C(17)–C(18)–C(39)	127.1(4)	C(19)–C(18)–C(39)	124.9(4)	C(18)–C(39)–C(40)	112.3(4)
C(18)–C(19)–N(24)	109.7(4)	N(24)–C(19)–C(20)	125.3(4)	C(18)–C(19)–C(20)	124.9(4)
C(19)–C(20)–C(1)	127.8(4)				

of 7 048 reflections was measured in a quarter of the diffraction sphere and 5 551 reflections having $\sigma(I)/I < 0.5$ were used to solve and refine the structure. Each reflection was corrected for Lorentz and polarisation effects. Absorption corrections were not applied ($\mu R_{\text{max.}} = 0.68$).

The structure was solved by the heavy-atom method; hydrogen atoms were located from difference-Fourier maps and all spatial and thermal parameters of the structure were refined with a full-matrix least-squares program [4a] to a *R* index of 0.050. All the non-hydrogen atoms were refined anisotropically. A correction for anomalous dispersion of the niobium atom was made ($\Delta f' = -0.65$, $\Delta f'' = 2.6$ e).[4b] Table 3 gives the spatial parameters, Tables 4 and 5 the bond distances and angles. Thermal parameters, fractional co-ordinates of the hydrogen atoms, observed and calculated structure factors, and least-squares planes are given in Supplementary Publication No. SUP 23183 (39 pp.).*

The Figure shows a projection of the structure on the four-nitrogen plane.

RESULTS AND DISCUSSION

Synthesis of Porphyrinatoniobium Oxide Fluorides.—The porphyrinatoniobium oxide fluorides [NbL(O)F] were prepared by treating a solution of $[Nb_2L_2O_3]$ in

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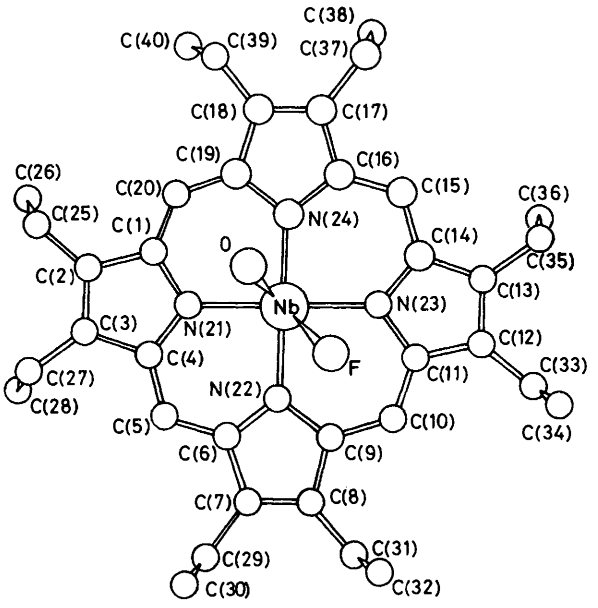
* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



Projection of [Nb(oep)(O)F](1) on the four nitrogen plane

anhydrous benzene with gaseous HF. Satisfactory yields (50—80%) were obtained.

The analytical results and mass spectral data agree perfectly with the proposed molecular formulae. In the mass spectra the parent peak corresponds to $[NbL(O)F + H]^+$ or $[NbL(O)F - H]^+$ and an important fragment to fission between the niobium and fluoride atoms.

The presence of Nb=O [ν(Nb=O) at *ca.* 910 cm^{-1}] and Nb–F [ν(Nb–F) at *ca.* 540 cm^{-1}] bonds in the complexes was confirmed by comparison of the i.r. spectra of $[NbL(O)(O_2CMe)]$ [3] and $[NbLF_3]$.[2] The ^1H n.m.r. data and u.v. characteristics do not provide further information on the structural arrangement of these complexes and a choice between a *cis* or *trans* form could only be established by an *X*-ray structural determination.

Structure of [Nb(oep)(O)F], (**1**).—As in the Figure, the co-ordination sphere of the six-co-ordinate niobium atom exhibits a *cis* geometry of 4 : 2 type. The resulting polyhedron is nearly a trigonal prism, which belongs to the C_s point group. The non-crystallographic mirror plane contains the niobium, oxygen, fluorine, and *meso*-carbon C(10) and C(20) atoms, indeed all these atoms lie in the mirror plane within 0.005 Å. Consequently the oxygen and fluorine atoms perfectly eclipse the C(10) and C(20) *meso*-carbon atoms. The niobium atom lies at 0.906(3) Å from the perfect four-nitrogen plane and at 1.02(3) Å from the mean plane of the porphyrinic system. The niobium–oxygen distance has the characteristics of a double bond [1.749(3) Å]; the mean niobium–nitrogen distance is 2.210(3) ± 0.014 Å. All these values agree with those found previously [3] on seven-co-ordinate niobium porphyrins; Nb–N 2.25(2) Å (mean) in $[Nb_2(tpp)_2(\mu\text{-}O)_3]$, Nb–N 2.23(1) Å (mean) and Nb=O 1.720(6) Å in $[Nb(tpp)O(O_2CMe)]$. The Nb–F distance [1.888(3) Å] is slightly shorter than those observed in the $[NbF_7]^{2-}$ (1.95 Å) [5] and $[NbOF_6]^{3-}$ [2.04(3) Å] [6] ions but is in good agreement with those found in $[SeF_3]^+$ $[Nb_2F_{11}]^-$ (1.88 Å),[7] and in bis(8-hydroxyquinolinium) pentafluoroperoxoniobate [8] (1.92 Å). The O–Nb–F angle is almost a right angle [89.0(1)°] and imposes a short distance between the oxygen and fluorine atoms [2.550(4) Å]. Tables 4 and 5 show that the bond distances and angles of the complex are in very good agreement with those found in other metalloporphyrins.[9]

Details of the least-squares planes, distances of the atoms from these planes, and dihedral angles are given in SUP 23183. The most important points may be summarized as follows: (*a*) the four-nitrogen plane is a perfect plane within 0.007 Å; (*b*) the porphyrin ring is domed. The doming parameter, defined by Hoard [9] as the difference between the distance of the metal atom from the porphyrin macrocycle and that of the metal from the four-nitrogen plane, is 0.116(6) Å. As a consequence the pyrrole rings are tilted by 5° with respect to the least-squares planes of the macrocycle.

As pointed out before, the oxygen and fluorine ligands eclipse the *meso*-carbon atoms C(10) and C(20) in this six-co-ordinated complex and the niobium atom lies at 0.906(6) Å to the four-nitrogen plane. These results are different from those found in seven-co-ordinated niobium porphyrins [3] where the co-ordination polyhedron of the metal atom is of the 4 : 3 type, and the ligands eclipse two nitrogen atoms, and the niobium atom lies at 1.00 Å to the four-nitrogen plane. This latter geometry of the co-ordination sphere imposes a short distance between the ligands and the two eclipsed nitrogen atoms which enhances the distance of the metal to the porphyrin ring. In [Nb(oep)(O)F] no steric interactions between the macrocycle and ligands occur and the metal–macrocycle distance can be shorter (0.905 Å) than in seven-co-ordinated complexes.

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