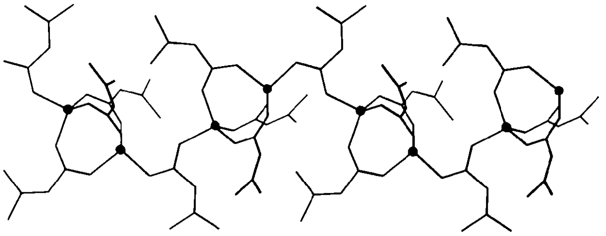

Fig. 3. The polymeric chain structure of (1).

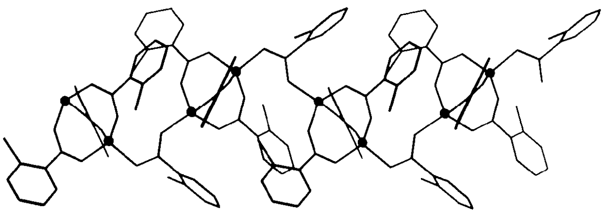

Fig. 4. The polymeric chain structure of (2). Only one component of the disordered ligand is shown.

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Structure of Oxotris(8-quinolinolato-*N*,*O*)niobium(V) Chloroform Solvate

By S. García-Granda, M. R. Díaz, L. Serra, A. Sanz-Medel and F. Gómez-Beltrán

Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Julián Clavería s/n, 33006 *Oviedo, Spain*

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Abstract. $[\mathrm{Nb(C_9H_6NO)_3O}]\mathrm{.CHCl_3}$, $M_r = 660{\cdot}74$, triclinic, $P\bar{1}$, $a = 9{\cdot}142\,(2)$, $b = 9{\cdot}693\,(2)$, $c = 16{\cdot}523\,(6)$ Å, $\alpha = 84{\cdot}01\,(2)$, $\beta = 73{\cdot}18\,(2)$, $\gamma = 73{\cdot}42\,(2)^\circ$, $V = 1342{\cdot}9\,(7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}63$ Mg m^{-3}, Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0{\cdot}71073$ Å), $\mu = 0{\cdot}769$ mm^{-1}, $T = 293$ K, $F(000) = 664$. Final conventional R factor = 0·042 for 3501 observed reflections and 428 variables. No unusual geometric features are present in the molecule. The central niobium is heptacoordinated, with one oxo and three 8-quinolinol ligands. The Nb—O(1) distance, 1·719 (3) Å, indicates a double bond. The average distance Nb—O(8-quinolinol) is 2·053 (3) Å. The Nb—N average distance is 2·385 (3) Å and the average bite angle, N—Nb—O, is 70·8 (1)°.

Introduction. In the course of our structural researches on Ni$^{\mathrm{II}}$ complexes we carried out the determination of the crystal structures of complexes containing 8-quinolinol derivatives as ligands (García-Granda & Gómez-Beltrán, 1986; García-Granda, Beurskens, Behm & Gómez-Beltrán, 1987; García-Granda, Jansen, Beurskens, Behm & Gómez-Beltrán, 1988). The present paper extends such investigations to a niobium complex with 8-quinolinol. It is well known that organic reagents, particularly the 8-hydroxyquinoline or its dihalogen derivatives, are of major importance in the analytical chemistry of niobium. This analytical chemistry includes separations (Gibalo, 1970), quantitative gravimetric analysis (Sanz-Medel, 1973), spectrophotometric (Motojima & Hashitani, 1961; Sanz-Medel & Díaz-García, 1981), fluorimetric (Sanz-Medel, Fernández de la Campa & García Alonso, 1987) and phosphorimetric (Kirkbright, Thompson & West, 1970; Sanz-Medel, Martínez García & Díaz García, 1987) methods for the determination of the element.

This structural investigation was mainly undertaken in order to study the influence of the central positive ion (*e.g.* Ni^{2+} or NbO^{3+}) on the coordination distances and bond angles with the organic ligand 8-hydroxyquinoline. However, additional

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important data have been obtained which allow us to correlate the crystal structures of the 8-hydroxyquinoline–NbO complex obtained with the analytical properties of this chelating agent so extensively used in the analytical chemistry of niobium.

Table 1. *Fractional positional and thermal parameters with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2 × 10^2)
Nb(1)	0·02179 (5)	0·16034 (4)	0·24183 (3)	3·28 (1)
O(1)	−0·0712 (4)	0·0798 (4)	0·33205 (22)	4·66 (14)
O(18)	−0·0334 (4)	0·0779 (3)	0·14805 (22)	4·41 (13)
O(28)	−0·0228 (4)	0·3549 (3)	0·29573 (20)	3·62 (11)
O(38)	0·2175 (4)	0·0030 (3)	0·18448 (22)	4·50 (13)
N(11)	−0·2327 (4)	0·2954 (4)	0·23127 (25)	4·01 (15)
N(21)	0·0978 (4)	0·3299 (4)	0·13094 (24)	3·46 (14)
N(31)	0·2334 (5)	0·1481 (4)	0·3007 (3)	4·24 (16)
C(12)	−0·3319 (6)	0·4080 (6)	0·2766 (4)	4·84 (20)
C(13)	−0·4818 (7)	0·4766 (7)	0·2639 (4)	6·11 (24)
C(14)	−0·5300 (7)	0·4269 (7)	0·2059 (4)	6·20 (25)
C(15)	−0·4653 (8)	0·2416 (9)	0·0942 (4)	6·7 (3)
C(16)	−0·3573 (8)	0·1273 (8)	0·0509 (4)	6·5 (3)
C(17)	−0·2095 (8)	0·0674 (6)	0·0677 (4)	5·51 (25)
C(18)	−0·1700 (6)	0·1251 (5)	0·1284 (3)	4·14 (19)
C(19)	−0·2818 (5)	0·2457 (5)	0·1734 (3)	3·97 (18)
C(110)	−0·4303 (6)	0·3062 (6)	0·1566 (4)	5·00 (21)
C(22)	0·1554 (6)	0·3136 (6)	0·0474 (4)	4·62 (20)
C(23)	0·2002 (7)	0·4250 (6)	−0·0059 (4)	5·18 (22)
C(24)	0·1834 (7)	0·5543 (6)	0·0260 (4)	4·97 (22)
C(25)	0·1003 (6)	0·7055 (5)	0·1544 (4)	4·97 (22)
C(26)	0·0422 (7)	0·7117 (5)	0·2401 (4)	4·94 (22)
C(27)	0·0007 (7)	0·5952 (5)	0·2885 (4)	4·54 (21)
C(28)	0·0159 (5)	0·4702 (4)	0·2525 (3)	3·37 (16)
C(29)	0·0781 (5)	0·4589 (4)	0·1635 (3)	3·29 (16)
C(210)	0·1207 (5)	0·5768 (5)	0·1135 (3)	3·76 (17)
C(32)	0·2346 (7)	0·2264 (6)	0·3617 (4)	5·63 (24)
C(33)	0·3662 (8)	0·1991 (7)	0·3952 (5)	6·7 (3)
C(34)	0·4956 (8)	0·0895 (7)	0·3645 (5)	6·5 (3)
C(35)	0·6251 (7)	−0·1146 (7)	0·2655 (4)	6·30 (26)
C(36)	0·6126 (7)	−0·1909 (7)	0·2049 (4)	6·46 (26)
C(37)	0·4756 (7)	−0·1581 (6)	0·1752 (4)	5·55 (22)
C(38)	0·3506 (6)	−0·0412 (5)	0·2081 (3)	4·30 (19)
C(39)	0·3629 (5)	0·0373 (5)	0·2713 (3)	3·89 (17)
C(310)	0·5007 (6)	0·0038 (5)	0·3007 (4)	4·74 (20)
C(1)	0·7913 (9)	0·2731 (8)	0·5035 (5)	7·0 (3)
Cl(1)	0·8134 (3)	0·44306 (21)	0·51167 (14)	10·52 (11)
Cl(2)	0·8888 (4)	0·15183 (25)	0·56757 (16)	12·63 (14)
Cl(3)	0·5940 (4)	0·2762 (4)	0·53095 (20)	15·06 (18)

Experimental. The niobium oxinate was prepared as previously described (Sanz-Medel, 1973). Suitable crystals were obtained from chloroform solutions. These specimens were quite unstable and were covered with an Araldite film during data collection to avoid destruction. A yellow crystal of approximate size 0·10 × 0·10 × 0·20 mm was used during the measurements. Throughout the experiment Mo $K\alpha$ radiation was used with a graphite crystal monochromator on a Nonius CAD-4 single-crystal diffractometer. The unit-cell dimensions were determined from the angular settings of 25 reflections ($\theta > 20°$). The intensity data of 17 937 reflections in the *hkl* range (−12, −13, −23) to (12, 13, 23), and θ limits ($0 < \theta < 30°$) were measured, using the ω–2θ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. The final drift correction factors were between 0·993 and 1·146. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction was applied, using ψ scans (North, Phillips & Mathews, 1968), μ(Mo $K\alpha$) = 0·769 mm^{-1} (correction factors were in the range 0·96–1·00). Symmetry equivalent reflections were averaged, $R_{\rm int} = \Sigma(I - \langle I\rangle)/\Sigma I = 0{\cdot}036$, resulting in 7815 unique reflections of which 3501 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and Fourier synthesis. Isotropic least-squares refinement, using *SHELX*76 (Sheldrick, 1976), converged to $R = 0{\cdot}10$. At this stage additional empirical absorption correction was applied (Walker & Stuart, 1983). The maximum and minimum absorption correction factors were, respectively, 1·22 and 0·63. Further anisotropic refinements followed by difference Fourier synthesis allowed the location of all H atoms. Final least-squares refinements involved positions and anisotropic thermal parameters for all non-H atoms. All H atoms were isotropically refined. The final conventional agreement factors were $R = 0{\cdot}042$ and $wR = 0{\cdot}043$ for 3501 observed reflections and 428 variables. The function minimized was $\Sigma w(F_o - F_c)^2$, $w = 1/[\sigma^2(F_o) + 0{\cdot}00080F_o^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift to e.s.d. ratio in the last full-matrix least-squares cycle was less than 0·06. The final difference Fourier map showed no peaks higher than 0·71 e Å^{-3} or deeper than −0·73 e Å^{-3}. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1974). Fig. 1, which shows the niobium coordination and the atomic numbering scheme, was drawn with *PLUTO* (Motherwell, 1976). Geometrical parameters were calculated with *PARST* (Nardelli, 1983).

Discussion. Final positional and thermal parameters are given in Table 1*. A selection of the molecular geometry data is collected in Table 2. A view of the complex showing the geometry and the atomic numbering scheme is given in Fig. 1. Values for angles between least-squares planes and lines and selected torsion angles have been deposited.

The central niobium is heptacoordinated, with three 8-quinolinol ligands and an oxo ligand. The Nb—O(1) distance is 1·719 (3) Å, very similar to the

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, hydrogen-bond distances and angles, least-squares-planes data and principal torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52542 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Nb(1)—O(18)	2·058 (3)	Nb(1)—O(1)	1·719 (3)	Nb(1)—N(11)	2·368 (3)
Nb(1)—O(28)	2·055 (3)	Nb(1)—N(21)	2·414 (3)	Nb(1)—N(31)	2·374 (3)
Nb(1)—O(38)	2·047 (3)				

O(18)—Nb(1)—O(28)	138·9 (1)	O(18)—Nb(1)—N(31)	142·7 (1)
O(18)—Nb(1)—O(38)	72·6 (1)	O(28)—Nb(1)—N(31)	72·4 (1)
O(28)—Nb(1)—O(38)	136·8 (1)	O(38)—Nb(1)—N(31)	70·2 (1)
O(18)—Nb(1)—O(1)	102·7 (1)	O(1)—Nb(1)—N(31)	90·1 (1)
O(28)—Nb(1)—O(1)	95·6 (1)	N(11)—Nb(1)—N(31)	145·7 (1)
O(38)—Nb(1)—O(1)	105·2 (1)	N(21)—Nb(1)—N(31)	93·9 (1)
O(18)—Nb(1)—N(11)	70·7 (1)	Nb(1)—O(18)—C(18)	124·6 (3)
O(28)—Nb(1)—N(11)	73·7 (1)	Nb(1)—O(28)—C(28)	123·8 (2)
O(38)—Nb(1)—N(11)	142·9 (1)	Nb(1)—O(38)—C(38)	125·1 (3)
O(1)—Nb(1)—N(11)	87·8 (1)	Nb(1)—N(11)—C(12)	128·5 (3)
O(18)—Nb(1)—N(21)	82·9 (1)	Nb(1)—N(11)—C(19)	113·6 (3)
O(28)—Nb(1)—N(21)	71·6 (1)	Nb(1)—N(21)—C(22)	130·3 (3)
O(38)—Nb(1)—N(21)	90·1 (1)	Nb(1)—N(21)—C(29)	110·9 (2)
O(1)—Nb(1)—N(21)	164·7 (1)	Nb(1)—N(31)—C(32)	128·5 (3)
N(11)—Nb(1)—N(21)	80·5 (1)	Nb(1)—N(31)—C(39)	113·2 (3)

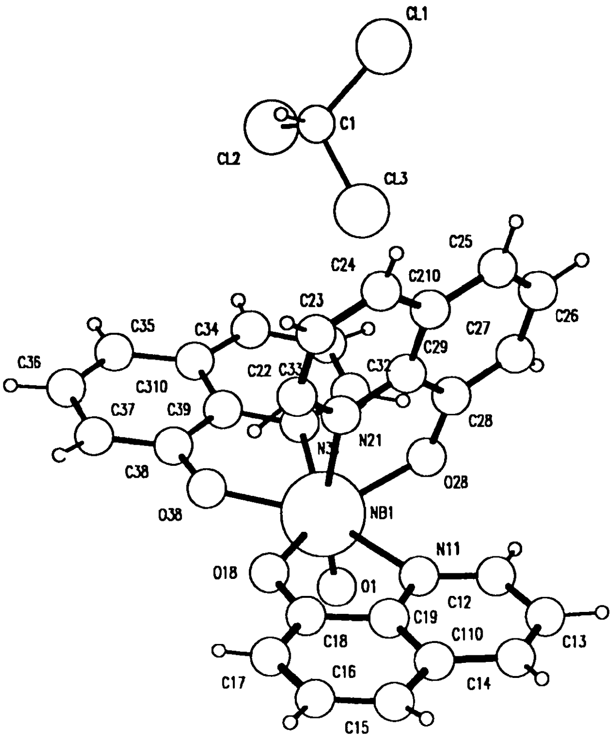

Fig. 1. A *PLUTO* (Motherwell, 1976) diagram showing the coordination of central niobium and the atomic numbering.

distance of 1·71 (1) Å found for the same bond in ammonium oxotrioxalatoniobate monohydrate (Mathern, Weiss & Rohmer, 1969). This Nb—O(1) distance indicates a double bond. The average distance Nb—O(8-quinolinol) of 2·053 (3) Å is similar to the corresponding Ni—O distance found in the nickel(II) compounds previously cited [from 2·016 (12) to 2·058 (12) Å]. On the contrary, the bonds Nb—N found are clearly longer [average of 2·385 (3) Å] than those found in the previously cited nickel complexes [range of 2·03 (1) to 2·09 (2) Å]. The N—Nb—O angle [average 70·8 (1)°] is also significantly smaller than the N—Ni—O angles normally found in nickel complexes [range 79·2 (6)–82·2 (3)°]. The chloroform molecule does not seem to have any other effect except to help the packing. Atoms in this molecule have high temperature factors, and loss of this molecule is probably responsible for the crystal deterioration with time. Compared with the nickel(II) 8-quinolinate complexes, the niobium complex shows greater differences when comparing their Nb—O and Nb—N bond distances. Whereas the nickel 8-quinolates show Ni—O and Ni—N distances reflecting similar strengths in the corresponding bonds, the different distances observed in the niobium complex therefore reflect very different bond strengths. Perhaps steric reasons contribute to the differences between bond distances found in the (NbO) 8-quinolinate. Nevertheless, this structural characterization contributes to our understanding of the chemical stabilization of the $(NbO)^{3+}$ cation mainly by complexing agents with oxygenated groups ($—OH^-$,$—COO^-$,...) (Alimarin & Savvin, 1966).

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