References

Beveridge, K. A., Bushnell, G. W. & Kirk, A. D. (1985). *Acta Cryst.* C41, 899–902.
Clegg, W. (1985). *Acta Cryst.* C41, 1830–1831.
Cromer, D. T. & Liberman, D. (1970). *J. Phys. Chem.* 53, 1891–1898.
Lisgarten, J. N., Palmer, R. A. & Gazzi, D. M. (1990). *Acta Cryst.* C46, 396–399.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
Roberts, P. & Sheldrick, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
Rollett, J. S. (1965). Editor. *Computing Methods in Crystallography*, p. 22. Oxford: Pergamon Press.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure of a Tetrahedral Niobium Oxo Compound [$Nb(OC_6H_3Ph_2\text{-}2,6)_3(O)$]

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Abstract. Tris(2,6-diphenylphenoxy)oxoniobium(V), [$Nb(C_{18}H_{13}O)_3O$], $M_r = 844.82$, orthorhombic, $P2_12_12_1$, $a = 10.704$ (1), $b = 19.562$ (3), $c = 19.823$ (3) Å, $V = 4150$ (2) Å^3, $Z = 4$, $D_x = 1.35$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 3.22$ cm^{-1}, $F(000) = 1744.0$, $T = 293.15$ K, $R = 0.054$ for 1680 reflections with $I > 3.0\sigma(I)$. A tetrahedral geometry is seen to be adopted around the Nb-metal center with three aryl oxide O atoms and one terminal oxo group. Nb—O(terminal oxo group) = 1.685 (9) Å; Nb—O(aryl oxide) = 1.896 Å (av.).

Introduction. Recent years have seen a dramatic increase in the study of the synthesis, structure and reactivity of transition-metal compounds containing a terminal oxo group (Nugent & Mayer, 1987). We report here the isolation and structural characterization of a mononuclear aryl oxide compound of niobium(V) containing a terminal oxo group, [$Nb(OC_6H_3Ph_2\text{-}2,6)_3(O)$] ($OC_6H_3Ph_2\text{-}2,6$ = 2,6-diphenylphenoxide).

Experimental. The compound $Nb(OC_6H_3Ph_2\text{-}2,6)_3(O)$ was obtained in low yield during the room-temperature reduction of toluene solutions of the dichloride $Nb(OC_6H_3Ph_2\text{-}2,6)_3Cl_2$ (Chesnut, Durfee, Fanwick, Rothwell, Folting & Huffman, 1987) with sodium amalgam. This oxo compound was either formed during the reaction, by traces of water, or else was present in the original sample of the dichloride.

A yellow crystal of [$Nb(OC_6H_3Ph_2\text{-}2,6)_3(O)$], having approximate dimensions 0.28 × 0.25 × 0.22 mm, was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation on an Enraf–Nonius CAD-4 computer-controlled κ-axis diffractometer equipped with a graphite-crystal incident-beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $9 < \theta < 15°$, measured by the computer-controlled diagonal-slit method of centering.

The data were collected at a temperature of 293 K using the ω–2θ scan technique. The scan rate varied from 2 to 20° min^{-1} (in ω). The variable scan rate allows rapid data collection for intense reflections (where a fast scan rate is used) and assures good counting statistics for weak reflections (where a slow scan rate is used). Data were collected in a 2θ range of 4.00–45.00° with hkl limits of 0 to 11, 0 to 21 and 0 to 21, respectively. Systematic absences of $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$, and subsequent least-squares refinement, indicated space group $P2_12_12_1$. The scan range (°) was determined as a function of θ to correct for the separation of the $K\alpha$ doublet (*CAD-4 Operations Manual*, 1977); the scan width was calculated as ω-scan width $= (0.83 + 0.350\tan\theta)°$. Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak counting time to background counting time was 2:1. The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.0 to 2.4 mm; the vertical aperture was set at 4.0 mm. The diameter of the incident-beam collimator was 0.7 mm and the crystal to detector

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distance was 21 cm. For intense reflections, an attenuator was automatically inserted in front of the detector; the attenuator factor was 25.7.

A total of 3080 reflections were collected, all of which were unique and not systematically absent. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 3.2 cm^{-1} for Mo $K\alpha$ radiation. No absorption correction was made. Three standard reflections monitored every 5000 s showed no variation in intensity.

The structure was solved using the Patterson heavy-atom method which revealed the position of the Nb atom. The remaining atoms were located using *DIRDIF* (Beurskens *et al.*, 1984) and in succeeding difference Fourier syntheses. H atoms were located and added to the structure-factor calculations, but their positions were not refined. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w was as defined by the Killean & Lawrence (1969) method with terms of 0.020 and 1.0.

Scattering factors were taken from Cromer & Waber (1974). Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964); the values for f' and f'' were those of Cromer (1974). Only the 1680 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 262 variable parameters and converged (largest parameter shift was 0.02 e.s.d.) with unweighted and weighted agreement factors of $R = 0.054$ and $wR = 0.078$. The standard deviation of an observation of unit weight was 1.20. There were no correlation coefficients greater than 0.50. The highest peak in the final difference Fourier map had a height of 0.43 e Å^{-3} with an estimated error based on ΔF (Cruickshank, 1949) of 0.08. The factor for the determination of the enantiomorph (Rogers, 1981) refined to 1.56. Plots of $\sum w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices, showed no unusual trends.

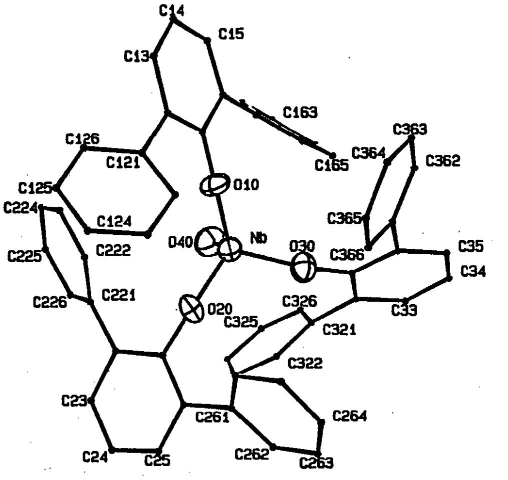

Fig. 1. *ORTEP* (Johnson, 1965) view of [Nb(OC$_6$H$_3$Ph$_2$-2,6)$_3$(O)] with thermal ellipsoids drawn at the 50% probability level.

Table 1. *Fractional coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2)

C atoms were refined isotropically. Nb and O atoms were refined anisotropically.

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^3B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{iso}/B_{eq}
Nb	0.1832 (1)	0.03505 (6)	0.23772 (6)	2.82 (2)
O(10)	0.182 (1)	0.1023 (4)	0.3053 (4)	3.3 (2)
O(20)	0.3549 (7)	0.0169 (4)	0.2160 (4)	3.1 (2)
O(30)	0.1131 (9)	0.0708 (4)	0.1577 (4)	3.4 (2)
O(40)	0.1109 (8)	−0.0361 (5)	0.2655 (4)	4.2 (2)
C(11)	0.144 (1)	0.1311 (7)	0.3635 (6)	3.2 (3)
C(12)	0.232 (1)	0.1654 (6)	0.4035 (6)	2.2 (3)
C(13)	0.191 (2)	0.1949 (6)	0.4635 (6)	3.5 (3)
C(14)	0.069 (1)	0.1894 (7)	0.4849 (7)	3.9 (3)
C(15)	−0.016 (1)	0.1557 (7)	0.4440 (7)	3.5 (3)
C(16)	0.017 (1)	0.1272 (6)	0.3829 (6)	2.5 (3)
C(21)	0.441 (1)	−0.0316 (7)	0.1997 (6)	3.0 (3)
C(22)	0.462 (1)	−0.0837 (6)	0.2445 (6)	2.6 (3)
C(23)	0.545 (1)	−0.1360 (7)	0.2210 (7)	3.9 (3)
C(24)	0.598 (1)	−0.1334 (7)	0.1576 (7)	3.9 (3)
C(25)	0.575 (1)	−0.0767 (7)	0.1169 (7)	3.7 (3)
C(26)	0.499 (1)	−0.0253 (7)	0.1371 (6)	3.0 (3)
C(31)	0.026 (1)	0.0754 (6)	0.1106 (6)	2.6 (3)
C(32)	−0.022 (1)	0.0141 (6)	0.0831 (6)	2.4 (3)
C(33)	−0.121 (1)	0.0195 (8)	0.0359 (8)	5.0 (4)
C(34)	−0.170 (2)	0.0830 (8)	0.0196 (8)	5.4 (4)
C(35)	−0.122 (2)	0.1419 (8)	0.0466 (8)	5.1 (4)
C(36)	−0.024 (1)	0.1385 (7)	0.0917 (7)	3.4 (3)
C(121)	0.366 (1)	0.1686 (7)	0.3844 (7)	3.2 (3)
C(122)	0.403 (1)	0.1842 (7)	0.3199 (7)	3.7 (3)
C(123)	0.529 (2)	0.1854 (8)	0.3052 (8)	5.1 (4)
C(124)	0.616 (2)	0.1705 (8)	0.3540 (8)	4.9 (4)
C(125)	0.580 (2)	0.1556 (8)	0.4169 (8)	4.9 (4)
C(126)	0.453 (2)	0.1543 (8)	0.4342 (7)	4.3 (4)
C(161)	−0.075 (1)	0.0891 (7)	0.3410 (7)	3.0 (3)
C(162)	−0.149 (1)	0.0386 (8)	0.3699 (6)	4.1 (3)
C(163)	−0.236 (1)	0.0038 (7)	0.3317 (7)	4.3 (4)
C(164)	−0.252 (1)	0.0202 (7)	0.2656 (8)	5.2 (4)
C(165)	−0.185 (2)	0.0725 (7)	0.2369 (8)	5.1 (3)
C(166)	−0.093 (1)	0.1075 (7)	0.2748 (7)	3.7 (3)
C(221)	0.416 (1)	−0.0872 (7)	0.3123 (7)	3.4 (3)
C(222)	0.415 (1)	−0.0299 (8)	0.3541 (6)	3.7 (3)
C(223)	0.375 (1)	−0.0312 (8)	0.4194 (7)	4.9 (3)
C(224)	0.330 (2)	−0.0915 (8)	0.4452 (8)	5.8 (4)
C(225)	0.331 (2)	−0.1494 (7)	0.4075 (7)	4.9 (4)
C(226)	0.370 (1)	−0.1474 (7)	0.3407 (7)	4.4 (4)
C(261)	0.488 (1)	0.0369 (8)	0.0944 (6)	3.8 (3)
C(262)	0.469 (1)	0.0289 (9)	0.0252 (7)	4.8 (3)
C(263)	0.470 (2)	0.0885 (9)	−0.0145 (8)	5.5 (4)
C(264)	0.488 (2)	0.1501 (9)	0.0115 (9)	6.5 (5)
C(265)	0.503 (2)	0.160 (1)	0.0781 (9)	7.0 (5)
C(266)	0.503 (2)	0.1018 (8)	0.1187 (7)	4.6 (4)
C(321)	0.028 (1)	−0.0544 (6)	0.1000 (6)	3.0 (3)
C(322)	0.156 (1)	−0.0675 (7)	0.0998 (7)	3.9 (3)
C(323)	0.205 (2)	−0.1304 (8)	0.1182 (7)	5.0 (4)
C(324)	0.120 (2)	−0.1802 (8)	0.1410 (8)	5.3 (4)
C(325)	−0.008 (2)	−0.1700 (9)	0.1395 (8)	5.6 (4)
C(326)	−0.049 (2)	−0.1066 (8)	0.1213 (7)	4.3 (4)
C(361)	0.030 (1)	0.2020 (7)	0.1221 (7)	4.2 (4)
C(362)	−0.053 (2)	0.2489 (8)	0.1514 (8)	4.7 (4)
C(363)	−0.002 (2)	0.3100 (9)	0.1789 (9)	6.0 (5)
C(364)	0.119 (2)	0.3229 (9)	0.1763 (9)	6.3 (5)
C(365)	0.202 (2)	0.2783 (9)	0.1471 (9)	7.3 (5)
C(366)	0.155 (2)	0.2154 (7)	0.1203 (7)	4.7 (4)

All calculations were performed on a VAX computer using *SDP* (Frenz, 1978).

Discussion. Fig. 1 presents an *ORTEP* (Johnson, 1965) view of [Nb(OC$_6$H$_3$Ph$_2$-2,6)$_3$(O)] emphasizing the central coordination sphere. The molecule can be

Table 2. *Selected bond distances* (Å) *and angles* (°)

Nb—O(10)	1.878 (7)	O(10)—Nb—O(20)	107.3 (4)
Nb—O(20)	1.921 (8)	O(10)—Nb—O(30)	109.7 (4)
Nb—O(30)	1.890 (9)	O(10)—Nb—O(40)	110.0 (4)
Nb—O(40)	1.685 (9)	O(20)—Nb—O(30)	105.1 (4)
O(10)—C(11)	1.35 (1)	O(20)—Nb—O(40)	111.1 (4)
O(20)—C(21)	1.36 (1)	O(30)—Nb—O(40)	113.4 (4)
O(30)—C(31)	1.33 (1)	Nb—O(10)—C(11)	155.0 (9)
		Nb—O(20)—C(21)	146.0 (8)
		Nb—O(30)—C(31)	153.7 (9)

seen to adopt a tetrahedral geometry about the Nb atom using three aryl oxide O atoms and one terminal oxo ligand. Fractional coordinates and isotropic thermal parameters are collected in Table 1, while a listing of important bond distances and bond angles is given in Table 2.*

The Nb—O distance to the terminal oxo group, 1.685 (9) Å, compares well with the values reported for Nb monooxo complexes (Nugent & Mayer, 1987). The most common coordination number for Nb monooxo compounds is found to be six. A search in the Cambridge Structural Database for structural data for monomeric Nb monooxo fragments yielded 17 hits. Eleven entries show a distorted octahedral geometry of the central metal coordination sphere. It is, therefore, interesting to find that the complex [$Nb(OC_6H_3Ph_2\text{-}2,6)_3(O)$] has only four-coordinate Nb atoms with a slightly distorted tetrahedral arrangement of ligands around the metal center. The Nb—O(aryl oxide) distances of 1.878 (7)–1.921 (8) Å and large Nb—O—Ar angles of 146.0 (8)–155.0 (7)° are common for niobium(V) and tantalum(V) aryl oxide compounds (Steffey, Fanwick & Rothwell, 1990).

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55151 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU0405]

References

Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, Th. E. M., Prick, P. A. J., Noordik, J. H., Beurskens, G., Parthasarathi, V., Bruins Slot, H. J., Haltiwanger, R. C., Strumpel, M. & Smits, J. M. M. (1984). Tech. Rep. 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

CAD-4 Operations Manual (1977). Enraf-Nonius, Delft, The Netherlands.

Chesnut, R. W., Durfee, L. D., Fanwick, P. E., Rothwell, I. P., Folting, K. & Huffman, J. C. (1987). *Polyhedron*, **6**, 2019–2026.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.2. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B, p. 99. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cruickshank, D. W. T. (1949). *Acta Cryst.* **2**, 154–157.

Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 SDP–A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi. Delft Univ. Press.

Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781–782.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* **B25**, 1750–1752.

Nugent, W. A. & Mayer, J. M. (1987). *Metal-Ligand Multiple Bonds*, ch. 5, Table 5.2. New York: John Wiley.

Rogers, D. (1981). *Acta Cryst.* **A37**, 734–741.

Steffey, B. D., Fanwick, P. E. & Rothwell, I. P. (1990). *Polyhedron*, **9**, 963–968.

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Structure of Bis(hexafluoroacetylacetonato)bis(triphenylphosphine oxide)nickel(II)

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Abstract. [$Ni(C_5HF_6O_2)_2(C_{18}H_{15}OP)_2$], $M_r = 1029.4$, triclinic, $P\bar{1}$, $a = 9.266$ (3), $b = 11.385$ (3), $c = 12.606$ (3) Å, $\alpha = 112.72$ (2), $\beta = 99.90$ (2), $\gamma = 103.24$ (2)°, $V = 1142.7$ (5) Å^3, $Z = 1$, $D_x = 1.496$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.587$ mm^{-1}, $F(000) = 522$, $T = 298$ K, $R = 0.0661$ and $wR = 0.0480$ for 268 variable parameters ($S = 1.24$) and 3000 reflections with $F > 0$. The Ni atom possesses an octahedral geometry and forms bonds to two equatorial F_6acac ligands [Ni—O(1) =

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