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A Dinuclear Niobium Oxo Compound $[Nb(OC_6H_3{}^iPr_2\text{-}2,6)_3O]_2$

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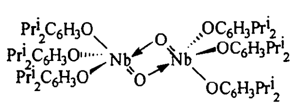
Abstract

In the compound hexakis(2,6-diisopropylphenoxy)-di-μ-oxo-diniobium(V), $[Nb(C_{12}H_{17}O)_3(\mu\text{-}O)]_2$, a distorted trigonal bipyramidal geometry is adopted around each Nb metal center by three terminal aryloxide O atoms and two non-symmetrically bridging oxo groups. Nb—O(bridging) = 1.807 (2), 2.117 (3) Å; Nb—O(aryloxide) = 1.874 (3), 1.877 (3), 1.880 (3) Å.

Comment

The number of studies of Group 5 metal–aryloxide complexes containing oxo ligands has recently increased (Yu, Fanwick, & Rothwell, 1992; Kee & Gibson, 1992). We report here the isolation and structural characterization of a dimeric aryloxide compound of niobium(V), $[Nb(OC_6H_3{}^iPr_2\text{-}2,6)_3O]_2$, (I), which is held together by two non-symmetrical bridging oxo groups.



(I)

Fig. 1 presents an *ORTEP* (Johnson, 1965) view of the title compound emphasizing the central coordination sphere. The molecule can be seen to adopt a distorted trigonal bipyramidal geometry about each Nb atom using three terminal aryloxide O atoms and two bridging oxo ligands.

The literature contains reports of three directly related oxo–aryloxide derivatives of Nb. The complex $[Nb(OC_6H_3Ph_2\text{-}2,6)_3O]$ (Yu, Fanwick & Rothwell, 1992) was shown to be monomeric in the solid state with a terminal Nb—O distance of 1.685 (9) Å. The two complexes $[Nb(OC_6H_3Me_2\text{-}2,6)_3O]$ and $[Nb(OC_6H_3{}^tBu_2\text{-}2,6)_3O]$ have also been isolated (Kee & Gibson, 1992) and assigned a monomeric structure on the basis of spectroscopic data. It is, therefore, surprising that the title compound obtained in this study adopts a dimeric structure in the solid state. It should also be noted that this compound exhibits extremely low solubility in hydrocarbon solvents, frustrating efforts to obtain solution NMR spectra.

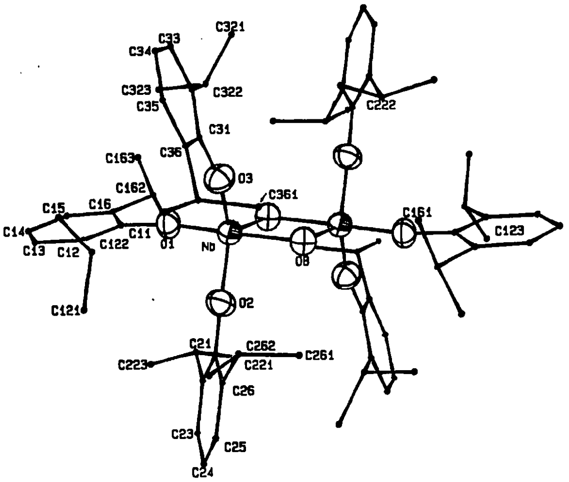


Fig. 1. A view of the molecule emphasizing the central coordination sphere. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

The two bridging groups can be seen (Table 2) to be asymmetrically bound to the two Nb metal centers. The short Nb—O(*B*) distance of 1.807 (2) Å is slightly longer than the typical values for terminal niobium(V) oxo ligands (Nugent & Mayer, 1987) while the long Nb—O(*B*) distance of 2.117 (3) Å is close to that found for simple dative bonds between O-atom donor ligands and Nb^V atoms, *cf.* a distance of 2.293 (2) Å for the Nb—O(thf) bond in $[Nb(OC_6H_3{}^iPr_2\text{-}2,6)_2(OC_6H_3{}^iPr\text{-}\eta^2\text{-}CMe{=}CH_2)(thf)]$ (Yu, Fanwick & Rothwell, 1990). The short Nb—O(*B*) bond occupies an equatorial position about the Nb atom. A similar pair of asymmetric bridging oxo ligands are present in $[(TPP)Nb(\mu\text{-}O)_3Nb(TPP)]$ (Johnson & Scheidt, 1978) which also contains a symmetric oxo bridge.

The Nb—O(aryloxide) distances of 1.874 (3)–1.880 (3) Å and large Nb—O—Ar angles of 165.2 (3)–173.6 (3)° are common for Nb^V and Ta^V aryloxide compounds (Steffey, Fanwick & Rothwell, 1990).

Experimental

The title compound was obtained in high yield during the hydrogenolysis of the dialkyl compound $[Nb(OC_6H_3{}^iPr_2\text{-}2,6)_3R_2]$ ($R = CH_2C_6H_4Me\text{-}4$) (Visciglio & Rothwell, 1993) over 24 h in cyclohexane solvent at 363 K and 8300 kPa of hydrogen. This sparingly soluble oxo compound was presumably formed during the reaction by traces of water.

Crystal data

$[Nb_2O_2(C_{12}H_{17}O)_6]$
$M_r = 1281.42$
Triclinic
$P\bar{1}$
$a = 11.9492\ (8)$ Å
$b = 13.313\ (7)$ Å
$c = 13.420\ (1)$ Å
$\alpha = 113.614\ (5)°$
$\beta = 96.978\ (6)°$
$\gamma = 111.101\ (5)°$
$V = 1734.6\ (6)$ Å^3
$Z = 1$
$D_x = 1.227$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 35\text{–}41°$
$\mu = 3.14$ mm^{-1}
$T = 293$ K
Block
0.25 × 0.22 × 0.13 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega\text{-}2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.51$, $T_{\max} = 1.00$
5107 measured reflections
5107 independent reflections
4149 observed reflections $[F > 3\sigma(F)]$
$\theta_{\max} = 60°$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 83.33 min
intensity variation: <3%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.044$
$S = 1.199$
4149 reflections
370 parameters
H-atom parameters not refined
$w = 1/[\sigma^2F + (0.02F)^2 + 1 - F]$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Nb	0.07220 (3)	0.08388 (2)	0.12716 (2)	3.141 (6)
O(1)	0.1974 (2)	0.1053 (2)	0.2434 (2)	4.11 (6)
O(2)	0.1641 (2)	0.2364 (2)	0.1351 (2)	4.49 (7)
O(3)	−0.0551 (2)	0.0511 (2)	0.1951 (2)	4.59 (7)
O(*B*)	−0.0679 (2)	0.0493 (2)	−0.0116 (2)	3.70 (6)
C(11)	0.2920 (3)	0.1490 (3)	0.3404 (3)	3.96 (9)
C(12)	0.3147 (4)	0.2560 (3)	0.4366 (3)	4.6 (1)
C(13)	0.4159 (4)	0.3001 (4)	0.5318 (4)	5.9 (1)
C(14)	0.4878 (4)	0.2403 (4)	0.5303 (4)	6.2 (1)
C(15)	0.4610 (4)	0.1326 (3)	0.4353 (4)	5.5 (1)
C(16)	0.3614 (4)	0.0827 (3)	0.3377 (3)	4.4 (1)
C(21)	0.2382 (3)	0.3411 (3)	0.1345 (3)	3.95 (9)
C(22)	0.3598 (4)	0.3617 (3)	0.1274 (3)	4.8 (1)
C(23)	0.4325 (4)	0.4704 (4)	0.1280 (4)	6.4 (1)
C(24)	0.3889 (5)	0.5532 (4)	0.1357 (4)	7.6 (2)
C(25)	0.2707 (5)	0.5315 (3)	0.1438 (4)	6.8 (1)
C(26)	0.1923 (4)	0.4250 (3)	0.1432 (3)	4.9 (1)
C(31)	−0.1229 (3)	0.0339 (3)	0.2669 (3)	4.4 (1)
C(32)	−0.1486 (4)	−0.0697 (4)	0.2809 (3)	5.4 (1)
C(33)	−0.2183 (5)	−0.0823 (5)	0.3551 (4)	7.8 (2)
C(34)	−0.2575 (5)	0.0033 (5)	0.4110 (4)	8.9 (2)
C(35)	−0.2323 (4)	0.1021 (5)	0.3946 (4)	7.4 (2)
C(36)	−0.1638 (4)	0.1213 (4)	0.3208 (3)	5.4 (1)
C(121)	0.3025 (6)	0.4431 (4)	0.4459 (4)	8.3 (2)
C(122)	0.2333 (4)	0.3211 (3)	0.4400 (3)	5.4 (1)
C(123)	0.1742 (5)	0.3334 (4)	0.5357 (4)	7.5 (2)
C(161)	0.4006 (6)	−0.0156 (5)	0.1529 (5)	9.2 (2)
C(162)	0.3273 (4)	−0.0364 (3)	0.2317 (4)	5.3 (1)
C(163)	0.3433 (6)	−0.1304 (4)	0.2601 (6)	9.8 (2)
C(221)	0.4076 (7)	0.1981 (5)	0.0017 (5)	12.2 (2)
C(222)	0.4097 (4)	0.2698 (4)	0.1184 (3)	5.3 (1)
C(223)	0.5345 (6)	0.3262 (6)	0.2021 (8)	17.0 (3)
C(261)	−0.0313 (5)	0.3444 (5)	0.0312 (5)	8.8 (2)
C(262)	0.0605 (4)	0.4015 (3)	0.1499 (4)	6.2 (1)
C(263)	0.0520 (5)	0.5130 (5)	0.2337 (6)	9.9 (2)
C(321)	−0.1987 (6)	−0.2939 (5)	0.1747 (4)	8.7 (2)
C(322)	−0.1008 (5)	−0.1613 (4)	0.2229 (3)	6.3 (1)
C(323)	0.0183 (5)	−0.1351 (5)	0.3045 (5)	8.9 (2)
C(361)	−0.2250 (4)	0.1817 (4)	0.1793 (4)	7.1 (1)
C(362)	−0.1407 (4)	0.2259 (4)	0.2965 (4)	5.9 (1)
C(363)	−0.1544 (5)	0.3324 (5)	0.3852 (6)	9.8 (2)

Table 2. *Selected geometric parameters* (Å, °)

Nb—Nb	3.0498 (7)	Nb—O(*B*)	1.807 (2)
Nb—O(1)	1.877 (3)	O(1)—C(11)	1.368 (4)
Nb—O(2)	1.880 (3)	O(2)—C(21)	1.360 (4)
Nb—O(3)	1.874 (3)	O(3)—C(31)	1.368 (4)
Nb—O(*B*)	2.117 (3)		
Nb—Nb—O(1)	140.70 (8)	O(2)—Nb—O(*B*)	86.5 (1)
Nb—Nb—O(2)	103.09 (9)	O(2)—Nb—O(*B*)	116.9 (1)
Nb—Nb—O(3)	102.39 (9)	O(3)—Nb—O(*B*)	86.8 (1)
Nb—Nb—O(*B*)	35.45 (6)	O(3)—Nb—O(*B*)	115.3 (1)
Nb—Nb—O(*B*)	42.83 (8)	O(*B*)—Nb—O(*B*)	78.3 (1)
O(1)—Nb—O(2)	95.3 (1)	Nb—O(*B*)—Nb	101.7 (1)
O(1)—Nb—O(3)	94.8 (1)	Nb—O(1)—C(11)	166.3 (2)
O(1)—Nb—O(*B*)	176.1 (1)	Nb—O(2)—C(21)	173.6 (3)
O(1)—Nb—O(*B*)	97.9 (1)	Nb—O(3)—C(31)	165.2 (3)
O(2)—Nb—O(3)	124.6 (1)		

The structure was solved using the Patterson heavy-atom method which revealed the position of one Nb atom. The remaining atoms were located using *DIRDIF* (Beurskens *et al.*, 1983) 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 by 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. Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964); the values for f' and f'' were those of Cromer (1974). There were 262 correlation coefficients greater than 0.50. The highest peak in the final difference Fourier map had an estimated error based on ΔF (Cruickshank, 1949) of 0.06. 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. All calculations were performed on a VAX computer. Refinement was performed using *MolEN* (Fair, 1990).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71772 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1066]

References

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

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. Birmingham: Kynoch Press. (Present distributor Kluwer Academics Publishers, Dordrecht.)
Cruickshank, D. W. T. (1949). *Acta Cryst.* **2**, 154–157.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
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.
Johnson, J. F. & Scheidt, W. R. (1978). *Inorg. Chem.* **17**, 1280–1287.
Kee, T. P. & Gibson, V. C. (1992). *Polyhedron*, **11**, 587–589.
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: Wiley.
Steffey, B. D., Fanwick, P. E. & Rothwell, I. P. (1990). *Polyhedron*, **9**, 963–968.
Visciglio, V. M. & Rothwell, I. P. (1993). In preparation.
Yu, J. S., Fanwick, P. E. & Rothwell, I. P. (1990). *J. Am. Chem. Soc.* **112**, 8171–8712.
Yu, J. S., Fanwick, P. E. & Rothwell, I. P. (1992). *Acta Cryst.* **C48**, 1759–1761.

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$[Nb(CH_2SiMe_3)(OC_6H_3Ph_2\text{-}2,6)(\mu\text{-}CSiMe_3)]_2$

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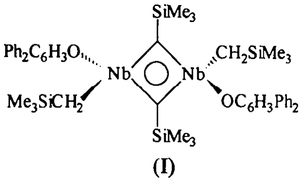
Abstract

The compound bis(2,6-diphenylphenoxy)bis(trimethylsilylmethane)bis(μ-trimethylsilylmethylidyne)diniobium has a crystallographic center of inversion with tetrahedral geometry adopted around each Nb metal center. Nb—Nb = 2.9082 (8), Nb—O = 1.909 (3), Nb—C(terminal alkyl) = 2.146 (5), Nb—C(bridging) = 1.979 (4) Å (average).

Comment

Recently, it has been shown that the Group 5 metal–alkylidyne bridged compounds $[(Me_3SiCH_2)_2M(\mu\text{-}CSiMe_3)]_2$ (N = Nb, Ta) (Mowat & Wilkinson, 1973) supported on silica will catalyze the exhaustive hydrogenation of a variety of aromatic substances (Profilet, Rothwell & Rothwell, 1993). Previously, our group had also shown that treatment of the tantalum compound with phenolic reagents led to a range of substitution products in which the central alkylidyne core was maintained (Fanwick, Ogilvy & Rothwell, 1987). We report here the isolation and structural characterization of a related dinuclear compound of niobium, $[Nb(CH_2SiMe_3)(OC_6H_3Ph_2\text{-}2,6)(\mu\text{-}CSiMe_3)]_2$, (I).



(I)

A view of the molecule is shown in Fig. 1. Earlier work has shown that all three of the possible substitutional isomers are formed when $[Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)]_2$ is reacted with two equivalents of 2,6-diphenylphenol (Fanwick, Ogilvy & Rothwell, 1987). The solid-state structure of the title niobium compound (Fig. 1) shows it to contain the *anti*-1,2-substituted isomer with a crystallographically imposed center of inversion. The Nb—Nb distance of 2.9082 (8) Å is only slightly longer than the distance of 2.897 (2) Å in $[(Me_3SiCH_2)_2Nb(\mu\text{-}CSiMe_3)]_2$. The Nb—O distance of 1.909 (3) Å and large Nb—O—C angle of 167.4 (3)° are typical for aryloxide ligands bound to niobium(V) metal centers (Steffey, Fanwick & Rothwell, 1990).

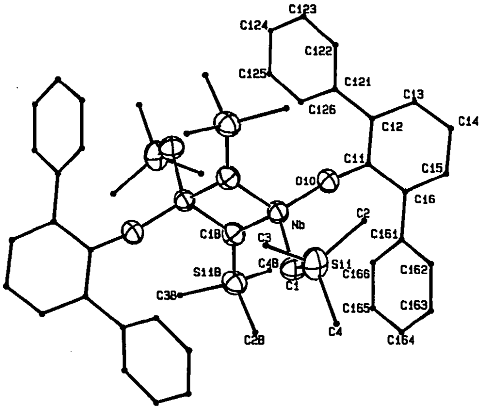


Fig. 1. A view of the molecule emphasizing the central coordination sphere. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Experimental

The title compound was prepared, in moderate yield, by addition of two equivalents of 2,6-diphenylphenol to a toluene solution of $[Nb(CH_2SiMe_3)_2(\mu\text{-}CSiMe_3)]_2$ and heating at 373 K