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# $\mu$-Oxo-bis{diethoxy[salicylaldoximato(2–)]niobium(V)}

**Mostafa M. Amini,[a] Mehdi Mirzaee[a] and Seik Weng Ng[b]***

[a]Department of Chemistry, Shahid Beheshti University, Tehran, Iran, and [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

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**Key indicators**

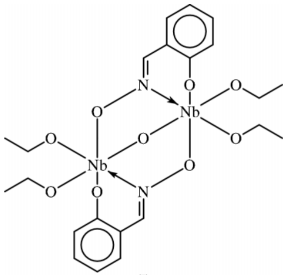
Single-crystal X-ray study
$T$ = 173 K
Mean $\sigma$(C–C) = 0.004 Å
$R$ factor = 0.021
$wR$ factor = 0.060
Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The doubly deprotonated ($C_7H_5NO_2$) groups in the title compound, [$Nb_2O(C_7H_5NO_2)_2(C_2H_5O)_4$], use the phenoxy O and imino N atoms to chelate to one Nb atom and the oximato O atom to bond to the other Nb atom; the two Nb atoms are six-coordinate in an octahedral geometry.

## Comment

Salicylaldoxime (2-hydroxybenzaldehyde oxime) is a ligand that chelates to metal ions through the phenolic O and oxime N atoms in its mono-deprotonated form (Smith *et al.*, 2002). As a reagent for inorganic analysis, it has been in use for some time (Chaudhuri, 1999), the compound being mentioned in a 1964 edition of Vogel's textbook of inorganic analysis. In the complexes, the free $OH_{oxime}$ group usually engages in hydrogen-bonding interactions that stabilize the structure, as noted in, for example, aquabis(salicylaldoximato)copper, whose two groups form hydrogen bonds to the coordinated water molecule (Potočňák *et al.*, 1997). Doubly deprotonated anions in polynuclear complexes are rare in the structural literature (Smith *et al.*, 2003).


(I)

The asymmetric unit of the title air-stable dinuclear $Nb^V$ derivative, (I), consists of a $(CH_3CH_2O)_2Nb-O-Nb(OCH_2CH_3)_2$ unit that is linked to two ($O-C_6H_4CH{=}N-O$) units. Each dianionic unit chelates to one Nb atom through its phenolic O and oximate N atoms, and each uses its oximate O atom to bind to the other Nb atom. The geometry of the metal atoms is octahedral; the two ethoxy groups are oriented *cis* to each other (Fig. 1). In the case of a second-row transition metal complex, the $[(C_6H_5NO_2)O_2Mo]_2O]^{2-}$ anion, the Mo—O—Mo skeleton displays a 131.5 (3)° angle at the bridging O atom (Liu *et al.*, 1989). The reason for the rather wide angle is attributed to the $C_6H_5NO_2$ group bonding to two Mo atoms to give rise to the formation of a five-membered Mo—O—Mo—N—O ring that is constrained to be coplanar with the six-membered Mo—O—C—C—C—N ring. Both pairs of terminal oxo atoms are oriented in a *cis* manner in the octahedral geometries of the two Mo atoms. The present neutral Nb

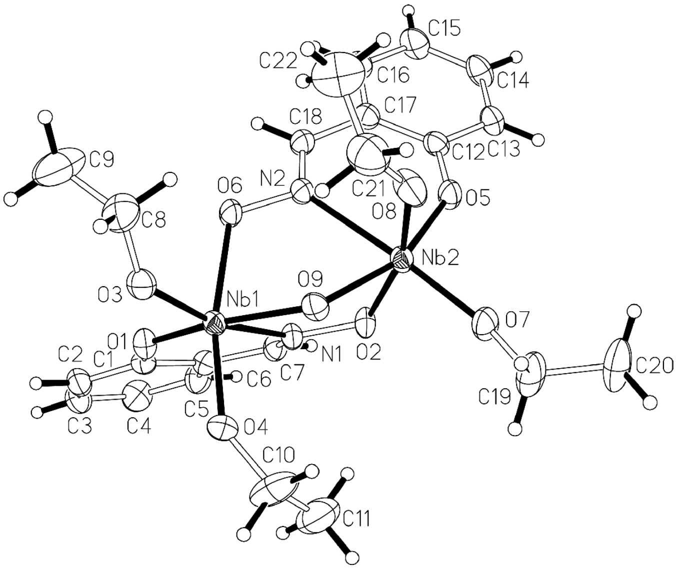


**Figure 1**
*ORTEP*II (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

compound adopts a similar structure, with the ethoxy groups in place of the terminal oxo ligands; the Nb—O—Nb angle is also large [129.4 (1)°]. The Nb—$O_{oxo}$ bond distances [Nb1—O9 = 1.940 (1) Å and Nb2—O9 = 1.930 (1) Å] are somewhat shorter than distances found in other oxodiniobium systems, *e.g.* in $[(C_3H_7\text{-}i)_2 2,6\text{-}C_6H_3]_6O_2Nb_2$ (Visciglio *et al.*, 1993). In solution, the Nb atoms retain their six-coordinate geometry, as shown by the $^{93}$Nb NMR shift (Amini & Sacks, 1990; Lee & Crayston, 1991).

## Experimental

Manipulations were performed under nitrogen, using standard Schlenk techniques. Niobium(V) pentaethoxide was purified by vacuum distillation (Amini & Sacks, 1990). To the reagent (1.28 g, 4 mmol) in benzene (10 ml) was added salicylaldoxime (0.55 g, 4 mmol). The mixture was stirred for a day, after which the solvent was removed under reduced pressure to furnish an orange solid that was not air-sensitive. The compound was crystallized from dichloromethane/hexane (6/1) in a refrigerator. The pure compound decomposes above 523 K. The compound was chemically characterized by mass spectroscopy (652 for the $M^+$ peak). UV ($CH_2Cl_2$): 231.5 ($\sigma$ to $\pi$*), 277.5 ($\pi$ to $\pi$*), 357.5 nm ($n$ to $\pi$*). IR: 3045, 2905, 1592, 1553 cm$^{-1}$. $^{93}$Nb NMR ($CDCl_3$, p.p.m.): 135 (referenced to $NbCl_6^-$). $^1$H NMR ($CDCl_3$, p.p.m.): 1.16 and 1.46 ($-CH_3$), 4.47 and 4.62 ($-CH_2-$), 6.8 to 7.4 ($-C_6H_4-$), 7.94 ($-CH{=}N-$).

*Crystal data*

$[Nb_2O(C_7H_5NO_2)_2(C_2H_5O)_4]$
$M_r$ = 652.30
Triclinic, $P\bar{1}$
$a$ = 10.8119 (7) Å
$b$ = 12.1443 (8) Å
$c$ = 12.2344 (8) Å
$\alpha$ = 63.679 (1)°
$\beta$ = 68.124 (1)°
$\gamma$ = 79.095 (1)°
$V$ = 1335.63 (15) Å$^3$
$Z$ = 2
$D_x$ = 1.622 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 7063 reflections
$\theta$ = 2.3–26.6°
$\mu$ = 0.91 mm$^{-1}$
$T$ = 173 (2) K
Block, orange
0.50 × 0.50 × 0.20 mm

*Data collection*

Siemens *P*4/SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.660, $T_{max}$ = 0.831
16 798 measured reflections
5367 independent reflections
4675 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.017
$\theta_{max}$ = 26.6°
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 15$
$l = -15 \rightarrow 15$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.060
$S$ = 1.03
5367 reflections
316 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.62 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.55 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Nb1—O1 | 1.971 (1) | Nb2—O2 | 2.061 (1) |
| Nb1—O3 | 1.896 (1) | Nb2—O5 | 1.969 (1) |
| Nb1—O4 | 1.890 (1) | Nb2—O7 | 1.882 (2) |
| Nb1—O6 | 2.071 (1) | Nb2—O8 | 1.897 (2) |
| Nb1—O9 | 1.940 (1) | Nb2—O9 | 1.930 (1) |
| Nb1—N1 | 2.333 (2) | Nb2—N2 | 2.337 (2) |
| | | | |
| O1—Nb1—O3 | 98.7 (1) | O2—Nb2—O5 | 89.0 (1) |
| O1—Nb1—O4 | 93.4 (1) | O2—Nb2—O7 | 94.2 (1) |
| O1—Nb1—O6 | 93.9 (1) | O2—Nb2—O8 | 164.8 (1) |
| O1—Nb1—O9 | 155.8 (1) | O2—Nb2—O9 | 81.9 (1) |
| O1—Nb1—N1 | 78.1 (1) | O2—Nb2—N2 | 77.3 (1) |
| O3—Nb1—O4 | 102.2 (1) | O5—Nb2—O7 | 99.3 (1) |
| O3—Nb1—O6 | 86.9 (1) | O5—Nb2—O8 | 95.3 (1) |
| O3—Nb1—O9 | 104.6 (1) | O5—Nb2—O9 | 155.5 (1) |
| O3—Nb1—N1 | 164.7 (1) | O5—Nb2—N2 | 78.0 (1) |
| O4—Nb1—O6 | 167.4 (1) | O7—Nb2—O8 | 99.5 (1) |
| O4—Nb1—O9 | 87.8 (1) | O7—Nb2—O9 | 104.0 (1) |
| O4—Nb1—N1 | 93.0 (1) | O7—Nb2—N2 | 171.0 (1) |
| O6—Nb1—O9 | 81.3 (1) | O8—Nb2—O9 | 88.3 (1) |
| O6—Nb1—N1 | 78.4 (1) | O8—Nb2—N2 | 89.3 (1) |
| O9—Nb1—N1 | 77.7 (1) | O9—Nb2—N2 | 77.9 (1) |

H atoms were placed at calculated positions (C—H = 0.95 Å for the aromatic and methine, 0.98 Å for the methylene and 0.99 Å for the methyl H atoms), and they were included in the refinement in the riding model approximation. The isotropic displacement parameters were set equal to $1.2U_{eq}$(C) for the aromatic, methyl and methylene H atoms, and $1.5U_{eq}$(C) for the methyl H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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