

Preliminary communication

**Preparation and structural study
 of monocyclopentadienylalkoxoniobium(V) derivatives. Crystal
 structure of $\{[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}]_2(\mu\text{-O})(\mu\text{-OOC}_6\text{H}_4)_2\}$**

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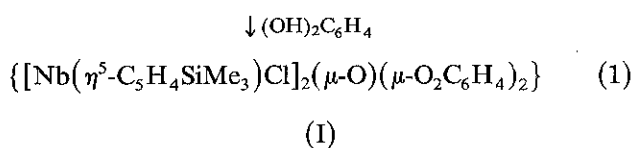
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Abstract

Alcoholysis with catechol or substitution reactions with NaOPh on $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cl}_4$ ($\text{R} = \text{H}, \text{SiMe}_3$) have given new alkoxoniobium(V) derivatives of the type $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cl}_3(\text{OPh})$ ($\text{R} = \text{H}, \text{SiMe}_3$) $\text{Nb}(\eta^5\text{-C}_6\text{H}_5)\text{Cl}_2(\text{O}_2\text{C}_6\text{H}_4)$ and $\{[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}]_2(\mu\text{-O})(\mu\text{-O}_2\text{C}_6\text{H}_4)_2\}$. The crystal structure of the last species has been studied. The two metal atoms, 3.079(1) Å apart, are symmetrically bridged by the oxo and the two catechol ligands. The two oxygen atoms of each catecholate group are coordinated to the metal atoms, one of them to one Nb atom and the other bridging the two Nb atoms. Chloride and CpSiMe_3 ligands complete the coordination sphere of both metal atoms.

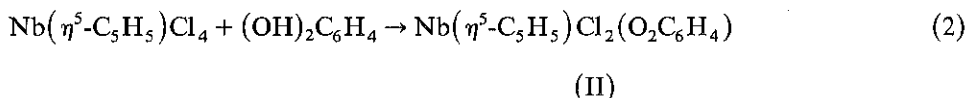
We have described the hydrolysis of $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Cl}_4$ with $\text{R} = \text{H}$ or SiMe_3 to give dimeric μ -oxo complexes, one of which was characterized by X-ray diffraction [1]. Here we report a study of the reactions of these compounds with catechol or with NaOPh to give new alkoxoniobium(V) species.

Dichloromethane solutions of $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_4$ are readily hydrolyzed [1]. Reaction with water preferentially takes place rather than alcoholysis, when catechol is added. Under these conditions catechol reacts with the resulting dinuclear μ -oxo complex to give the μ -oxo- μ -catecholate derivative I, according to eq. 1. The same



product is obtained by treating the previously isolated μ -oxo dimer with catechol.

In contrast, addition of catechol to a dichloromethane suspension of the insoluble $\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_4$ leads to direct alcoholysis to give the haloalkoxo complex II, according to eq. 2,



When NaOPh is used, exclusive substitution of the starting compound is observed for both halogeno compounds, according to eq. 3.



(III: R = H;
IV: R = SiMe₃)

No reaction took place between the μ -oxo dimers and NaOPh.

All the isolated complexes show the IR absorptions for the η^5 -cyclopentadienyl rings [2]. I and IV also show bands due to the SiMe₃ group [3]. The broad band observed for complex I at 650 cm⁻¹ must be assigned to the $\nu_{\text{asym}}(\text{Nb-O-Nb})$ vibration of an angular system [4]. The $\nu(\text{C-O})$ stretching vibration appears at 1240–1250 cm⁻¹, whereas absorptions due to $\nu(\text{M-O})$ are at 580 cm⁻¹.

¹H NMR spectra show a singlet for ($\eta^5\text{-C}_5\text{H}_5$) in complexes II and III, with the chemical shifts expected for niobium(V) derivatives [5], whereas a multiplet is observed for I and IV [6] along with a singlet due to the SiMe₃ protons. A complex signal is observed for the aromatic protons of both catecholate and phenyl groups*.

The structure of complex I has been determined by X-ray diffraction as discussed below. We have no structural data which permit a definitive assignment for complexes II–IV, but in view of the structure observed for complex I, we suggest a similar dimeric structure for complex II, containing pseudo-octahedral niobium atoms sharing one of the oxo-catecholate groups, with formation of two μ -oxo bridges along with two terminal Nb–Cl bonds. Complexes III and IV should probably have dimeric or polymeric structures.

Crystals of I suitable for X-ray diffraction were obtained by liquid diffusion of hexane into a saturated toluene solution of the complex.

Crystal data for I. C₂₈H₃₄Cl₂Nb₂O₅Si₂, $M = 762.98$, monoclinic, space group C2/c, a 23.933(2), b 9.256(5), c 14.740(4) Å, β 98.56(2)°, U 3229 Å³, $Z = 4$, $D_c = 1.45$ g cm⁻³, $F(000) = 1544$, $\mu(\text{Mo-K}\alpha) 9.52$ cm⁻¹, 1638 reflections measured on a Nicolet R3m 4-circle diffractometer. The structure was solved by the heavy atom method followed by Fourier synthesis, and refined by full matrix-least squares methods to $R = 0.032$ and $R_w = 0.033$ for 1428 observed reflections ($F > 3\sigma(F)$).

The molecule lies on a crystallographic two-fold axis, O(3) is situated in a special position, and only half a molecule is observed in the asymmetric unit. The molecular

* Spectroscopic data: (a) for $\{[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}]_2(\mu\text{-O})(\mu\text{-O}_2\text{C}_6\text{H}_4)_2\}$. ¹H NMR (C₆D₆): 6.00–7.00(mc) ($\eta^5\text{-C}_5\text{H}_4$); 0.30(s) (SiMe₃); 6.00–7.00(mc) (O₂C₆H₄); (b) for $\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{O}_2\text{C}_6\text{H}_4)$. ¹H NMR (C₆D₆): 6.37(s) ($\eta^5\text{-C}_5\text{H}_5$); 6.00–7.00(mc) (O₂C₆H₄); (c) for $\text{Nb}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_3(\text{OPh})$. ¹H NMR (C₆D₆): 6.20(s) ($\eta^5\text{-C}_5\text{H}_5$); 6.32–7.31(mc) Ph(OPh); (d) for $\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}_3(\text{OPh})$. ¹H NMR (C₆D₆): 6.00–7.00(mc) ($\eta^5\text{-C}_5\text{H}_4$); 0.35(s) (SiMe₃); 6.00–7.00(mc) (O₂C₆H₄).

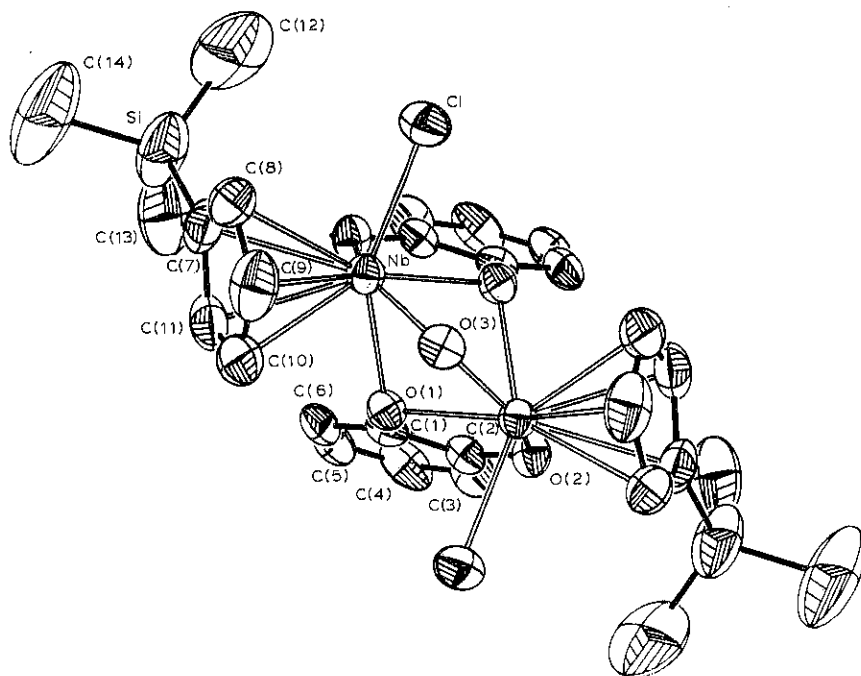


Fig. 1. The molecular structure of $\{[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}]_2(\mu\text{-O})(\mu\text{-O}_2\text{C}_6\text{H}_4)_2\}$ (I). Bond lengths: Nb–Nba 3.079(1); Nb–O(1) 2.224(3); Nb–O(1a) 2.173(3); Nb–O(2a) 1.970(3); Nba–O(1) 2.173(3); Nb–O(3) 1.926(3); Nb–C(7) 2.473(5); Nb–C(8) 2.456(5); Nb–C(9) 2.460(6); Nb–C(10) 2.411(5); Nb–C(11) 2.414(5) Å; bond angles Nb–O(1)–Nba 88.9(1); Nb–O(3)–Nba 106.2(2)°.

structure of $\{[\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Cl}]_2(\mu\text{-O})(\mu\text{-OOC}_6\text{H}_4)_2\}$ is shown in Fig. 1, together with some important bond parameters.

Compound I consists of a Nb dimer, bridged by one oxo-ligand and two dioxo-catecholate groups. Chloride and SiMe_3Cp complete the coordination sphere of each metal atom.

The distance between the two metal atoms is 3.079(1) Å, which is similar to Nb–Nb bond lengths in some compounds with two S ligands bridging the metal–metal bond [7,8]. There are few structural reports of other Nb compounds with oxygen as the bridging atom [9]. In $\{[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{NbCl}_3(\text{H}_2\text{O})_2](\mu\text{-O})\}$ [10] and $\{[(\eta^5\text{-Cp})_2\text{NbCl}_2\text{O}]^{2+}\}$ [11], the Nb–O–Nb angles, although significantly non-linear, have values approaching 180° (171.8(1) and 169.3(8)°), respectively. In I this angle is much smaller (106.2(2)°), but this must be due to the constraint imposed by the catechol ligands, which also bridge the two metal atoms. This behaviour has been observed in the case of oxo-bridged compounds of other metals. The Nb–O (oxo) distance of 1.926(3) Å is the same as that in $\{[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{NbCl}_3(\text{H}_2\text{O})_2\text{O}](\mu\text{-O})\}$ [10].

A small electronic density peak was observed next to O(3), the oxo bridge, and it was tentatively refined as a hydrogen atom, i.e. instead of an oxo bridge there would be an aquo bridge. The data refined properly, giving R and R_w the same as those obtained without the hydrogen. The hydrogen atom thus located would be within interaction distance (1.751(50) Å) of one of the niobium atoms. However, a detailed

study showed that this peak could be due to the vibration of the oxygen atom, and the absence of any spectroscopic evidence to the contrary make us think that it must be an oxo bridge.

The catecholate ligands are coordinated to both metal atoms through the two oxygen atoms. One of the oxygen atoms, O(2), is bonded to just one of the Nb atoms, with a bond length of 1.970(3) Å. The other oxygen atom in each of the catecholate ions bridges the two metal atoms in a nearly symmetrical fashion (bond lengths of 2.224(3) and 2.173(3) Å; these Nb–O distances are similar to that expected for a single bond (2.10–2.15 Å). In the case of the singly bonded oxygen, the bond length is intermediate between that for a single and that for a double bond (1.70 Å) [10]. The bonds between the metal and the bridging oxygen atoms, form angles of 70.9(1), 71.4(1), and 72.5(1)°.

The Nb–Cl bonds are 2.405(1) Å, a value similar to that in other niobium(V) complexes, such as NbCl₃[NCH₃C(S)CH₃]₂ [12]. The average C–C distance in the cyclopentadienyl rings is 1.393 Å, and the average C–C–C angle 107.6°. The Nb–C_{Cp} mean distance is 2.443 Å, not significantly different from other reported values [9].

Tables of atomic coordinates and a list of bond parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. They may be obtained on request from the Director by citing full literature reference for the communication.

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