Notes

Synthesis and Characterization of Monocyclopentadienyl Niobium Derivatives. *X*-Ray Crystal Structure of Di-μ-chloro-μ-oxo-bis[dichloro(η-trimethylsilylcyclopentadienyl)niobium(V)], $[\{Nb(\eta\text{-}C_5H_4SiMe_3)Cl_2\}_2(\mu\text{-}O)(\mu\text{-}Cl)_2]$ †

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$[Nb(\eta\text{-}C_5H_4R)Cl_4]$ [R = H (**1**) or $SiMe_3$ (**2**)] are easily hydrolysed to give $[\{Nb(\eta\text{-}C_5H_4R)Cl_2\}_2(\mu\text{-}O)(\mu\text{-}Cl)_2]$ [R = H (**3**) or $SiMe_3$ (**4**)] and finally $[\{Nb(\eta\text{-}C_5H_4R)Cl_3(OH_2)\}_2(\mu\text{-}O)]$ [R = H (**5**) or $SiMe_3$ (**6**)]. The reduction of (**1**) and (**2**) with sodium amalgam in the presence of ligands allows isolation of $[Nb(\eta\text{-}C_5H_4R)Cl_3L_2]$ and $[Nb(\eta\text{-}C_5H_4R)Cl_2(CO)L_2]$ (R = H or $SiMe_3$; L_2 = $2PMe_3$, $2PMe_2Ph$, or $Ph_2PCH_2CH_2PPh_2$) which have been characterized by magnetic measurements and i.r. and n.m.r. spectroscopy. The crystal structure of (**4**) has been determined: monoclinic, space group $P2_1/n$ with $a = 26.805(7)$, $b = 7.310(2)$, $c = 13.400(3)$ Å, $\beta = 91.42(2)°$, and $Z = 4$. The structure was refined to $R = 0.063$ for 2 539 observed reflections.

η-Cyclopentadienyl trialkyltin derivatives are excellent reagents to prepare $[M(\eta\text{-}C_5H_5)Cl_4]$ (M = Nb or Ta) complexes[1,2] and the reactions of these complexes with various reducing agents in particular have been studied.[3–6] We report here the synthesis of $[Nb(\eta\text{-}C_5H_4SiMe_3)Cl_4]$, the hydrolytic reactions of $[Nb(\eta\text{-}C_5H_4R)Cl_4]$ [R = H (**1**) or $SiMe_3$ (**2**)], and the reduction with sodium amalgam to give new niobium-(III) and -(IV) complexes. We also report the *X*-ray crystal structure of $[\{Nb(\eta\text{-}C_5H_4SiMe_3)Cl_2\}_2(\mu\text{-}O)(\mu\text{-}Cl)_2]$.

Results and Discussion

Complex (**2**) can be isolated, according to equation (1)

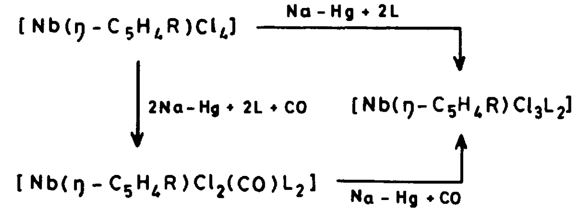
$$NbCl_5 + [M(\eta\text{-}C_5H_4SiMe_3)R_3] \longrightarrow [Nb(\eta\text{-}C_5H_4SiMe_3)Cl_4] + MR_3Cl \quad (1)$$

($M = Sn$, $R = Bu^n$; $M = Si$, $R = Me$), as red crystals soluble in benzene and CH_2Cl_2. This type of compound has been reported as polymeric or dimeric.[1,7] The i.r. spectrum of (**2**) shows ν(Nb–Cl) absorptions at 350—280 cm^{-1} and those expected for the η-cyclopentadienyl and the $SiMe_3$ groups.[8,9] The ^1H n.m.r. spectrum shows a singlet due to the $SiMe_3$ group and a complex multiplet due to the non-equivalent $\eta\text{-}C_5H_4$ protons[10] (see Table 1).

The hydrolysis of (**1**) and (**2**) in wet dichloromethane gave yellow or yellow-orange crystals of $[\{Nb(\eta\text{-}C_5H_4R)Cl_2\}_2(\mu\text{-}O)(\mu\text{-}Cl)_2]$ [R = H (**3**) or $SiMe_3$ (**4**)]. The structure of (**4**) has been determined by *X*-ray diffraction and is described below. Both (**3**) and (**4**) show comparable i.r. spectra with $\nu_{asym}(NbONb)$ absorption bands at 670 cm^{-1} in accord with a Nb–O–Nb angular structure.[11] The ^1H n.m.r. spectrum of (**4**) shows a singlet due to the $SiMe_3$ group and a multiplet due to the non-equivalent ring protons (see Table 1). The low solubility of (**3**) prevents n.m.r. study. Complexes (**3**) and (**4**) are stable under a dry atmosphere but they are transformed by stirring for a long time in wet dichloromethane or by long exposure to air into the orange aqua complexes $[\{Nb(\eta\text{-}C_5H_4R)Cl_3(OH_2)\}_2(\mu\text{-}O)]$ [R = H (**5**) or $SiMe_3$ (**6**)], probably similar to the previously reported complex with R = Me.[1,12]

The reduction of (**1**) and (**2**) with Na–Hg (10%) in the presence of different ligands gives new Nb^{III} and Nb^{IV} derivatives, as shown in the Scheme [dppe = 1,2-bis(diphenylphosphino)ethane]. Compounds (**10**),[12,13] (**12**),[5] and other carbonylniobium(III)[6,14] complexes have been reported previously. A complex related to (**8**) containing only one molecule of PMe_2Ph has also been isolated.[5] Complexes with the $\eta\text{-}C_5H_4SiMe_3$ group are comparatively more soluble than the $\eta\text{-}C_5H_5$ derivatives, which are scarcely soluble in toluene and very soluble in tetrahydrofuran (thf), chloroform, and dichloromethane. All the complexes are stable under an inert atmosphere in the solid but decompose slowly in solution. Complexes (**7**)—(**11**) are paramagnetic with $\mu_{eff.} = 1.41$—1.69 at room temperature, analogous to other Nb^{IV} derivatives reported previously.[15] The ν(CO) stretching frequency for (**12**)—(**16**) appears as a broad strong band at 1 878—1 925 cm^{-1} in the solid.

The ^{31}P n.m.r. spectrum for (**13**) shows a singlet indicating that the phosphorus atoms are equivalent, but a variable



Scheme.

R = H,L_2 = $2PMe_3$ (**7**)
R = H,L_2 = $2PMe_2Ph$ (**8**)
R = $SiMe_3$,L_2 = $2PMe_2Ph$ (**9**)
R = H,L_2 = dppe (**10**)
R = $SiMe_3$,L_2 = dppe (**11**)

R = H,L_2 = $2PMe_3$ (**12**)
R = H,L_2 = $2PMe_2Ph$ (**13**)
R = $SiMe_3$,L_2 = $2PMe_2Ph$ (**14**)
R = H,L_2 = dppe (**15**)
R = $SiMe_3$,L_2 = dppe (**16**)

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† *Supplementary data available* (No. SUP 56659, 5 pp.): experimental and simulated n.m.r. spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

pattern of signals is observed in the ^{1}H n.m.r. spectrum for the ligand methyl groups depending on the solvent and the resolution of the spectrometer. Each non-equivalent methyl group gives a triplet by coupling with ^{31}P of both *trans* phosphines.[16] The separation or superposition of these two triplets produces variable signals, as is known[5] for an analogous Ta complex. Experimental and simulated spectra agree very well. Complex (**14**) shows a ^{1}H n.m.r. spectrum consisting of a singlet for the $SiMe_3$ group, two multiplets (Ph and η-C_5H_4), and a triplet due to the virtual coupling of both *trans* ligands. The ^{31}P n.m.r. spectrum shows a singlet indicating that both phosphorus atoms are equivalent. These structural data suggest for (**12**)—(**14**) the same structure as that found for the tantalum derivative $[Ta(\eta\text{-}C_5H_5)Cl_2(CO)(PMe_2Ph)_2]\cdot$thf.[5] The ^{1}H n.m.r. spectra for (**15**) and (**16**) show the presence of dppe, along with the expected resonances of η-C_5H_4R.

Table 1. Hydrogen-1 and ^{31}P n.m.r. spectra for monocyclopentadienylniobium complexes

Complex	$^{1}H^{a}$	J(P–H)/ Hz	Assignment	$^{31}P^{b}$
(**2**)	0.19 (2) [s]		$SiMe_3$	
	6.50 (4) [m]		C_5H_4	
(**4**)^{c}	0.39 (9) [s]		$SiMe_3$	
	7.09 (4) [m]		C_5H_4	
(**6**)^{c}	0.38 (9) [s]		$SiMe_3$	
	6.47 (4) [m]		C_5H_4	
	2.34 (2) [m]		H_2O	
(**12**)	1.30 (18) [t]	3.8	PMe_3	−14.55
	4.67 (5) [t]	2.4	C_5H_5	
(**13**)	4.28 (5) [t]	2.4	C_5H_5	
	7.01 (10) [m]		Ph	
	1.78 (12) [m]		PMe_2	−16.77
(**14**)	0.13 (4) [s]		$SiMe_3$	
	1.82 (12) [t]	3.8	PMe_2	+3.04
	4.20—4.42 (4) [m]		C_5H_4	
	6.97—7.28 (10) [m]		Ph	
(**15**)^{c}	2.67 (4) [m]		CH_2CH_2 (dppe)	
	5.97 [s], 7.24 [m] (20		Ph	
	4.74 (5) [s]		C_5H_5	
(**16**)^{c}	0.22 (9) [s]		$SiMe_3$	
	2.25 (4) [m]		CH_2CH_2 (dppe)	
	5.55 (4) [m]		C_5H_4	

^{a} Given as δ/p.p.m. (intensity) [multiplicity]. In C_6D_6; internal standard $SiMe_4$. ^{b} δ/p.p.m.; in thf; relative to H_3PO_4. ^{c} In $CDCl_3$.

Crystal Structure of $[\{Nb(\eta\text{-}C_5H_4SiMe_3)Cl_2\}_2(\mu\text{-}O)(\mu\text{-}Cl)_2]$ (**4**).—The structure of (**4**) shows (Figure) each niobium atom bonded to two terminal chlorine atoms, to one $C_5H_4SiMe_3$ group, and in addition two chlorine atoms; the oxygen atom bridges the two metal atoms. Relevant bond distances and angles are given in Table 2. Each Nb atom is in a distorted octahedral arrangement with the centroid of the η-$C_5H_4SiMe_3$ group occupying one apex, terminal chlorine atoms at two of the four equatorial sites, and the three remaining sites being associated with the bridging ligands. The oxide ligand is arranged at equatorial sites for both Nb atoms. The μ-O bridge is non-linear and is nearly symmetrical; both μ-Cl bridges are asymmetrical. The two shorter Nb–Cl bonds are longer than the terminal Nb–Cl bonds. The other two bonds in the Cl bridges, significantly the longest ones, are *trans* to the η-$C_5H_4SiMe_3$ rings, as observed previously in several complexes.[12,17] The Nb–Cl–Nb bridging angles are both acute [77.9(1) and 76.8(1)°]. The larger Nb–O–Nb and narrower Nb–Cl–Nb bridging angles observed in the present compound with respect to the bridging angles found in the dinuclear tantalum cation $[\{Ta(\eta\text{-}C_5Me_5)Cl_2\}_2(\mu\text{-}Cl)_3]^{+}$ [17] seem due to the necessity to accommodate the shorter Nb–O bonds compared with the Nb–Cl bonds across the bridge.

Experimental

All operations were carried out under vacuum or in an inert atmosphere using Schlenk-type glassware. $[Nb(\eta\text{-}C_5H_5)Cl_4]$,[1]

Table 2. Relevant bond distances (Å) and angles (°)* in complex (**4**)

(*i*) Involving the Nb atoms

Nb(1)–O	1.901(7)	Nb(1)–Cl(5)	2.533(4)	Nb(2)–O	1.924(7)	Nb(2)–Cl(5)	2.686(3)
Nb(1)–Cl(1)	2.408(4)	Nb(1)–Cl(6)	2.717(3)	Nb(2)–Cl(3)	2.383(4)	Nb(2)–Cl(6)	2.565(4)
Nb(1)–Cl(2)	2.374(4)	Nb(1)–Cg_1	2.101(13)	Nb(2)–Cl(4)	2.353(4)	Nb(2)–Cg_2	2.124(14)

Cl(1)–Nb(1)–Cl(2)	91.5(1)	Cl(6)–Nb(1)–O	72.4(2)	Cl(3)–Nb(2)–Cl(4)	94.0(2)	Cl(5)–Nb(2)–Cl(6)	71.8(1)
Cl(1)–Nb(1)–Cl(5)	82.6(1)	Cl(6)–Nb(1)–Cg_1	174.5(4)	Cl(3)–Nb(2)–Cl(6)	82.2(1)	Cl(5)–Nb(2)–O	72.3(2)
Cl(5)–Nb(1)–O	76.4(2)	Cl(1)–Nb(1)–Cg_1	104.9(4)	Cl(4)–Nb(2)–O	93.6(2)	Cl(5)–Nb(2)–Cg_2	174.1(5)
Cl(2)–Nb(1)–O	95.4(3)	Cl(2)–Nb(1)–Cg_1	104.7(4)	Cl(6)–Nb(2)–O	75.9(2)	Cl(3)–Nb(2)–Cg_2	105.0(4)
Cl(1)–Nb(1)–O	149.0(2)	Cl(5)–Nb(1)–Cg_1	105.2(4)	Cl(3)–Nb(2)–O	147.5(2)	Cl(4)–Nb(2)–Cg_2	105.6(4)
Cl(2)–Nb(1)–Cl(5)	150.0(1)	O–Nb(1)–Cg_1	102.5(5)	Cl(4)–Nb(2)–Cl(6)	150.6(1)	Cl(6)–Nb(2)–Cg_2	103.6(5)
Cl(6)–Nb(1)–Cl(1)	79.5(1)	Nb(1)–O–Nb(2)	118.2(4)	Cl(5)–Nb(2)–Cl(3)	78.3(1)	O–Nb(2)–Cg_2	103.2(5)
Cl(6)–Nb(1)–Cl(2)	78.2(1)	Nb(1)–Cl(6)–Nb(2)	76.8(1)	Cl(5)–Nb(2)–Cl(4)	78.9(1)	Nb(1)–Cl(5)–Nb(2)	77.9(1)
Cl(6)–Nb(1)–Cl(5)	71.8(1)						

(*ii*) Involving the trimethylsilylcyclopentadienyl groups

C(11)–C(21)	1.41(2)	C(11)–Si(1)	1.88(1)	C(22)–C(32)	1.45(2)	C(12)–Si(2)	1.88(1)
C(21)–C(31)	1.34(2)	Si(1)–C(61)	1.84(2)	C(32)–C(42)	1.36(3)	Si(2)–C(62)	1.88(2)
C(31)–C(41)	1.45(2)	Si(1)–C(71)	1.86(2)	C(42)–C(52)	1.50(3)	Si(2)–C(72)	1.91(2)
C(41)–C(51)	1.40(2)	Si(1)–C(81)	1.90(2)	C(12)–C(52)	1.43(2)	Si(2)–C(82)	1.87(2)
C(11)–C(51)	1.39(2)	C(12)–C(22)	1.39(2)				

C(21)–C(11)–C(51)	105.8(10)	C(11)–Si(1)–C(61)	109.3(6)	C(12)–C(22)–C(32)	109.0(12)	C(12)–Si(2)–C(62)	108.3(7)
C(11)–C(21)–C(31)	111.6(12)	C(11)–Si(1)–C(71)	110.5(6)	C(22)–C(32)–C(42)	107.8(14)	C(12)–Si(2)–C(72)	112.3(7)
C(21)–C(31)–C(41)	106.5(13)	C(11)–Si(1)–C(81)	101.6(6)	C(32)–C(42)–C(52)	109.3(13)	C(12)–Si(2)–C(82)	102.7(7)
C(31)–C(41)–C(51)	106.4(13)	C(61)–Si(1)–C(71)	114.3(7)	C(42)–C(52)–C(12)	104.6(12)	C(62)–Si(2)–C(72)	111.6(8)
C(41)–C(51)–C(11)	109.5(12)	C(61)–Si(1)–C(81)	110.8(7)	C(22)–C(12)–Si(2)	127.6(9)	C(62)–Si(2)–C(82)	112.7(7)
C(21)–C(11)–Si(1)	125.0(9)	C(71)–Si(1)–C(81)	109.7(8)	C(52)–C(12)–Si(2)	122.6(10)	C(72)–Si(2)–C(82)	109.0(8)
C(51)–C(11)–Si(1)	126.9(9)	C(22)–C(12)–C(52)	109.2(12)				

* Cg_1 = centroid of the C(11)—C(51) ring; Cg_2 = centroid of the C(12)—C(52) ring.

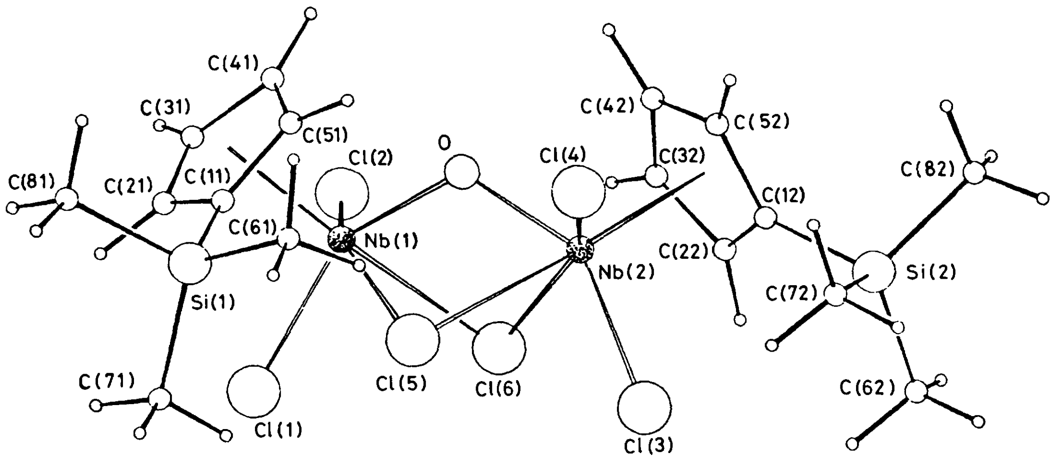

Figure. Molecular structure of (**4**) showing the atom numbering

Table 3. Analyses and physical properties of monocyclopentadienylniobium complexes

Complex	Found (calc.)/%		Colour	Yield (%)	$\mu_{eff.}$ (room temperature)
	C	H			
(**2**)	25.7 (25.8)	3.9 (3.4)	Red	80—85	
(**3**)	22.1 (22.0)	1.9 (1.8)	Yellow	90	
(**4**)	27.9 (27.8)	3.9 (3.7)	Yellow	90	
(**5**)	20.8 (20.6)	1.8 (1.7)	Orange		
(**6**)	26.9 (26.5)	4.5 (4.1)	Orange		
(**7**)	46.2 (46.6)	5.0 (4.9)	Red	60	1.53
(**8**)	31.6 (31.7)	5.5 (5.5)	Red	65	1.44
(**9**)	46.5 (47.0)	5.8 (5.7)	Brown	65	1.41
(**10**)	51.7 (51.4)	4.4 (4.1)	Violet	60	1.67
(**11**)	54.8 (55.5)	5.4 (5.0)	Violet	65	1.69
(**12**)	35.9 (35.2)	6.3 (5.6)	Red	60—62	
(**13**)	48.5 (49.5)	6.0 (5.0)	Red	80—80	
(**14**)	50.5 (49.5)	6.2 (5.7)	Red	60—75	
(**15**)	58.2 (58.6)	4.9 (5.5)	Green-brown	70—72	
(**16**)	58.0 (57.7)	5.8 (5.0)	Brown	70—70	

$[Sn(\eta\text{-}C_5H_4SiMe_3)Bu^n{}_3]$, and $[Si(\eta\text{-}C_5H_4SiMe_3)Me_3]$ were synthesized according to refs. 18 and 19. Carbon and H analyses (Table 3) were performed with a Perkin-Elmer 240B microanalyzer. Hydrogen-1 and ^{31}P n.m.r. spectra were recorded on Varian FT-80A and Bruker WP-60CW instruments.

$[Nb(\eta\text{-}C_5H_4SiMe_3)Cl_4]$ (**2**).—A CH_2Cl_2 (30 cm^3) solution of $[Sn(\eta\text{-}C_5H_4SiMe_3)Bu^n{}_3]$ (8.70 g, 20 mmol) was added dropwise to a yellow CH_2Cl_2 (500 cm^3) solution of $NbCl_5$ (5.0 g, 18.5 mmol). The resulting red solution was stirred for 1 h, filtered, and then evaporated to dryness at room temperature under vacuum to give (**2**) as a microcrystalline red solid which was repeatedly washed with light petroleum (b.p. 40—60 °C). Yield 5.5 g (80%). The same procedure was carried out using $[Si(\eta\text{-}C_5H_4SiMe_3)Me_3]$.

$[\{Nb(\eta\text{-}C_5H_4R)Cl_2\}_2(\mu\text{-}O)(\mu\text{-}Cl)_2]$, (**3**) *and* (**4**); $[\{Nb(\eta\text{-}C_5H_4R)Cl_3(OH_2)\}_2(\mu\text{-}O)]$, (**5**) *and* (**6**).—A suspension of (**1**) or a solution of (**2**) (1.34 mmol) in water–saturated undistilled CH_2Cl_2 (50 cm^3) was stirred at room temperature for 3 h. Compound (**3**) was obtained as a yellow insoluble solid after filtration and drying under vacuum. Yield 90%. The resulting CH_2Cl_2 solution of (**4**) was evaporated to give the complex as a yellow crystalline solid. Yield 90%. Compounds (**5**) and (**6**) were obtained as orange solids when (**1**) or (**2**) in water–saturated undistilled CH_2Cl_2 were stirred at room temperature for 24 h. Yield 85%.

$[Nb(\eta\text{-}C_5H_4R)Cl_3L_2]$, (**7**)—(**11**).—Dimethylphenylphosphine (2.20 mol), PMe_3 (3.0 mmol, from 0.93 g of solid $AgI{\cdot}PMe_3$) or dppe (1.10 mmol) were added to a mixture of sodium amalgam (10%, 1.05 mmol) and (**1**) or (**2**) (1.0 mmol) in thf (30 cm^3). The mixture was vigorously stirred for 3 h at room temperature, then filtered and the solution evaporated to dryness under vacuum. The solid residues were washed with hexane (2 × 30 cm^3). Toluene was used to extract the residue for (**9**) and (**11**) and CH_2Cl_2 for (**7**) and (**8**), and (**10**). Compound (**10**) was obtained as violet crystals by addition of ethanol to the CH_2Cl_2 solution. All the remaining complexes were isolated by evaporation to dryness of the resulting solutions as red [(**7**) and (**8**)], brown [(**9**)], or violet [(**11**)] microcrystalline solids. Yields 60—65%.

$[Nb(\eta\text{-}C_5H_4R)Cl_2(CO)L_2]$, (**12**)—(**16**).—Carbon monoxide was bubbled for 3 h through a stirred thf (30 cm^3) solution containing a mixture of PMe_2Ph (2.20 mmol), PMe_3 (3.0 mmol), or dppe (1.10 mmol) with sodium amalgam (10%, 2.10 mmol) and (**1**) or (**2**) (1.00 mmol). The resulting solutions were filtered and then evaporated to dryness under vacuum. The solid residues were washed with hexane (2 × 30 cm^3) and then extracted with toluene or CH_2Cl_2 [for (**15**)]. Evaporation of these solutions to dryness yielded microcrystalline red [(**12**),(**13**),(**14**)] or brown [(**15**),(**16**)] solids. Yields 60—80%.

Crystal Structure of Complex (**4**).—An elongated prismatic yellow-orange crystal of (**4**), of approximate dimensions 0.10 × 0.30 × 0.88 mm, was sealed in a Lindemann capillary under a nitrogen atmosphere and mounted on the diffractometer.

Crystal data. $C_{16}H_{26}Cl_6Nb_2OSi_2$, M = 689.08, monoclinic, a = 26.805(7), b = 7.310(2), c = 13.400(3) Å, β = 91.42(2)°, U = 2 625(1) $Å^3$ (by least-squares refinement from the θ values of 23 accurately measured reflections, λ = 0.710 69 Å), space group $P2_1/n$, Z = 4, D_c = 1.744 g cm^{-3}, $F(000)$ = 1 368, $\mu(Mo\text{-}K_\alpha)$ = 15.50 cm^{-1}.

Data collection and processing. A Siemens AED diffractometer (θ–2θ mode, niobium-filtered Mo-K_α radiation) was employed using the SHELX program system;[20] reflections in the range $3 \leqslant \theta \leqslant 24°$ were measured. Of 4 620 independent reflections, 2 539, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. A correction for absorption was applied (max. and min. transmission factors: 1.3446 and 0.6674).[21]

Structure analysis and refinement. Patterson and Fourier

Table 4. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Nb(1)	3 214(1)	1 709(2)	6 006(1)	C(41)	3 382(7)	3 929(22)	7 260(11)
Nb(2)	3 545(1)	3 262(2)	3 821(1)	C(51)	3 848(5)	3 323(21)	6 946(10)
Cl(1)	3 028(1)	−1 500(5)	6 158(2)	C(61)	4 970(6)	1 327(23)	6 452(11)
Cl(2)	2 361(1)	2 496(6)	6 176(3)	C(71)	4 407(6)	−2 263(20)	6 958(14)
Cl(3)	3 749(2)	1 054(5)	2 588(2)	C(81)	4 718(7)	432(25)	8 628(12)
Cl(4)	4 376(1)	4 225(6)	4 074(3)	C(12)	3 434(6)	5 119(17)	2 293(9)
Cl(5)	3 915(1)	522(4)	4 951(2)	C(22)	2 981(5)	4 288(18)	2 509(10)
Cl(6)	2 836(1)	1 000(5)	4 146(2)	C(32)	2 801(7)	5 028(22)	3 435(11)
Si(1)	4 520(1)	195(5)	7 260(3)	C(42)	3 138(9)	6 283(22)	3 774(12)
Si(2)	3 783(2)	4 991(6)	1 098(3)	C(52)	3 569(6)	6 350(17)	3 079(10)
O	3 370(3)	3 735(10)	5 181(5)	C(62)	3 463(7)	3 268(24)	259(11)
C(11)	3 915(4)	1 509(16)	7 220(8)	C(72)	4 470(6)	4 408(28)	1 318(12)
C(21)	3 481(5)	1 013(18)	7 733(9)	C(82)	3 732(7)	7 380(23)	606(11)
C(31)	3 147(6)	2 373(24)	7 733(10)				

methods, full-matrix least-squares refinement with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms; hydrogen atoms placed at their geometrically calculated positions and introduced in the final calculations with isotropic thermal parameters. Weighting scheme used in the last cycles: $w = K/[\sigma^2(F_o) + gF_o^2]$ with $K = 1.2067$ and $g = 0.001$. Final R and R' values 0.063 and 0.067. Programs for computer used and sources of scattering factors (Nb,Cl,Si) are given in ref. 22. All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna) and on the GOULD-SEL 32/37 computer of the Centro di Studio per la Structturistica Diffracttometrica del C.N.R. (Parma). Final atomic co-ordinates are given in Table 4.

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