Notes

Synthesis and Crystal Structure of Tris[bis(trimethylsilyl)amido]oxoniobium(V):† a Four-co-ordinated Oxo Niobium Precursor

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The reaction between $[NbCl_4(thf)_2]$ (thf = tetrahydrofuran) and $LiN(SiMe_3)_2$ affords, by oxygen abstraction of the thf ligand, the first non-chlorine oxoamido derivative of niobium, $[NbO\{N(SiMe_3)_2\}_3]$, (1). This novel compound could also be obtained directly from $(NbOCl_3)_n$, although in poor yield. Its monomeric nature was confirmed by *X*-ray analysis. The crystals are monoclinic, space group $P2_1/n$, with $a = 12.352(12)$, $b = 18.107(3)$, $c = 15.036(14)$ Å, $\beta = 101.83(5)°$, and $Z = 4$. The structure was solved and refined on the basis of 4 585 significant counter data to a final R of 0.034. The steric hindrance of the bis(trimethylsilyl)amido ligand stabilizes a low co-ordination number, with a terminal Nb=O bond. Compound (1) also represents the first authentic four-co-ordinate niobium compound structurally characterized.

Transition-metal dialkylamides display interesting reactivity, especially for C–H activation,[1] and are able to stabilize unusual geometries, co-ordination numbers, or oxidation states.[2] The bulky silylamides are more particularly appropriate for steric control of metal co-ordination[3] and were expected to reduce the ability of metal–metal bonding in low-valent Group 5 derivatives.[4] Moreover, in contrast to Group 4, silylamides remain limited to $[TaCl_3\{N(SiMe_3)_2\}_2]$[5] and its derivatives, and are unknown for niobium. We report here the synthesis and *X*-ray characterization of $[NbO\{N(SiMe_3)_2\}_3]$ an unusual four-co-ordinate niobium derivative, which is also the first oxoamido niobium species without chlorine atoms in the co-ordination sphere to be reported.

Results and Discussion

The reaction between $[NbCl_4(thf)_2]$ (thf = tetrahydrofuran) and bis(trimethylsilyl)amidolithium $LiN(SiMe_3)_2$ in hexane or toluene at room temperature for about 48 h yielded, after crystallization at −40 °C, white prisms, relatively air stable, as the less soluble species in aliphatic hydrocarbon solvents. It is obtained independently of the ligand-to-metal molar ratio, R, used (from 1 to 4), although its yield is favoured (*ca.* 40%) for $R = 3$, and has been characterized on the basis of an *X*-ray investigation as the novel niobium(V) compound $[NbO\{N(SiMe_3)_2\}_3]$, (1). The formation of a niobium(V) species as the major product (as evidenced by the ^1H n.m.r. spectrum of the diamagnetic reaction medium) is surprising, and may be due to accidental introduction of dioxygen or to oxygen abstraction from the tetrahydrofuran ligand. As compound (1) could also be obtained under strictly anaerobic conditions, the latter consideration is more likely. Moreover, formation of Group 5 oxo species from quinquevalent[6] or low valent[7] derivatives with oxygen-donor ligands has some precedents. The direct reaction between the polymeric oxohalide $(NbOCl_3)_n$ and $LiN(SiMe_3)_2$ is not a useful route to (1), as its yield is poor. Previous attempts to gain oxoamido species by aminolysis reactions have resulted in the formation of polymeric and poorly characterized species of type $[NbOX_2(NR_2)]$ and $[NbOX_2(NR_2)(NHR_2)]$ (X = Cl or Br; R = Et).[8,9]

The formation of compound (1), monomeric, volatile, and soluble in common solvents, including aromatic hydrocarbons, illustrates once more the ability of the bulky silylamido ligands to stabilize low co-ordination numbers and unusual geometry. This compound represents to our knowledge the first authentic four-co-ordinated niobium species structurally characterized. Its i.r. spectrum shows the presence of a terminal Nb=O bond as evidenced by an absorption band at 915 cm^{-1}, and also the characteristic $MNSi_2$ vibrations. The molecule is fluxional on the n.m.r. time-scale; the single peak at 0.34 p.p.m. (^1H spectrum in $CDCl_3$) is split at −11 °C into two peaks of equal area (δ = 0.33 and 0.23 p.p.m.). The free activation energy $\Delta G^\ddagger$ of the intramolecular process corresponds to 56.5 kJ mol^{-1}. This behaviour can probably be attributed to restricted rotation of each $N(SiMe_3)_2$ group about the Nb–N axis, giving at low temperature a frozen conformation of two types of three equivalent trimethylsilyl groups, proximal and distal, to the oxo moiety.

The structure of $[NbO\{N(SiMe_3)_2\}_3]$ is shown in the Figure, which also defines the atom numbering scheme. Selected bond parameters are presented in Table 1. The effect of packing forces on the molecular geometry appears negligible (shortest intermolecular contacts C···H 3.05 and 3.13 Å) and the overall idealized geometry is C_3, with a four-co-ordinated niobium atom. The Nb=O distance [1.699(2) Å] is very close to that found for $NbOCl_3{\cdot}2L$ adducts [L = MeCN[10] or $P(NMe_2)_3O$[11]], and is consistent with a niobium–oxygen multiple bond.[12] This distance is shorter than the tantalum–oxo bond [1.725(7) Å][13] of the briefly mentioned $[TaO(NPr_2)_3]$. Although the difference in geometry between $[TaCl_3\{N(SiMe_3)_2\}_2]$[14] and $[NbO\{N(SiMe_3)_2\}_3]$ prevents a strict comparison, the metal–nitrogen bond lengths of compound (1) [av. 2.020(2) Å] are significantly longer than the values found for $[TaCl_3\{N(SiMe_3)_2\}_2]$ (av. 1.93 Å),[5] and account for lack of π-bonding (single Nb–N bond length is expected in the 2.04—2.08 Å range); this is in agreement with the observation that π

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

bonding is generally favoured for 5*d* compared with 4*d* elements. The planarity of the nitrogen atoms, and the nitrogen–silicon bond distances (av. 1.76 Å), suggest that the nitrogen lone pairs are mainly involved in N→Si π bonding.[3] The co-ordination polyhedron is a distorted tetrahedron owing to the steric requirements of the bis(trimethylsilyl)amido ligands, with an opening of the N-Nb-N angles to 116°, the niobium atom lying 0.416 Å from the average plane formed by the three nitrogen atoms, and is related to that of the $[MCl\{N(SiMe_3)_2\}_3]$ derivatives (M = Ti, Zr, or Hf).[14] The compression of the $Nb[N(SiMe_3)_2]_3$ group also results in an unsymmetrical alignment of the ligands with respect to the M-N bonds, with Nb-N-Si angles of *ca.* 115.5 (upper, *i.e.* proximal to O) and *ca.* 126° (lower, *i.e.* distal to O), and explains the fluxional behaviour in solution.

Compound (**1**) appears to be an interesting precursor to a variety of new niobium oxo derivatives.[15]

Experimental

The reactions were routinely performed under argon, using the Schlenk-tube technique, and solvents deoxygenated and dried by standard methods. Published methods were used for the synthesis of $NbOCl_3$,[16] $[NbCl_4(thf)_2]$,[17] and $LiN(SiMe_3)_2$.[18] Infrared spectra were recorded on a Perkin-Elmer 577 spectrometer as Nujol mulls, n.m.r. spectra on a Bruker WH-90 spectrometer, and mass spectra on a Ribermag R-10 spectrometer.

Table 1. Selected bond distances (Å) and angles (°) in $[NbO\{N(SiMe_3)_2\}_3]$

Nb-O	1.699(2)	Si(1)-N(1)	1.756(2)
Nb-N(1)	2.018(2)	Si(2)-N(1)	1.766(2)
Nb-N(2)	2.021(2)	Si(3)-N(2)	1.751(2)
Nb-N(3)	2.021(2)	Si(4)-N(2)	1.758(2)
		Si(5)-N(3)	1.750(2)
		Si(6)-N(3)	1.777(2)
O-Nb-N(1)	101.97(7)	Nb-N(1)-Si(1)	126.2(1)
O-Nb-N(2)	101.63(7)	Nb-N(1)-Si(2)	115.5(1)
O-Nb-N(3)	102.05(8)	Si(1)-N(1)-Si(2)	117.5(1)
N(1)-Nb-N(2)	115.32(7)	Nb-N(2)-Si(3)	126.42(9)
N(1)-Nb-N(3)	115.16(7)	Nb-N(2)-Si(4)	115.53(9)
N(2)-Nb-N(3)	117.14(7)	Si(3)-N(2)-Si(4)	117.2(1)
		Nb-N(3)-Si(5)	125.6(1)
		Nb-N(3)-Si(6)	115.6(1)
		Si(5)-N(3)-Si(6)	118.71(1)

Synthesis of $[NbO\{N(SiMe_3)_2\}_3]$.—A solution of $LiN(SiMe_3)_2$ (2.68 g, 15.86 mmol) in hexane (25 cm^3) was added to a suspension of $[NbCl_4(thf)_2]$ (1.32 g, 3.48 mmol) in hexane (50 cm^3) at 0 °C. The reaction mixture, which becomes dark brown, was allowed to return to room temperature and stirred for 60 h. The insoluble products were removed by filtration and the filtrate was evaporated to dryness. The brown residue was extracted by hexane and the resulting solution concentrated to about 4 cm^3 and cooled to −50 °C, yielding, after crystallization and filtration, colourless parallepipeds of $[NbO\{N(SiMe_3)_2\}_3]$ (820 mg, 39%), moderately air-stable, soluble in common solvents including toluene (Found: C, 36.5, H, 9.2; Si, 25.1. $C_{18}H_{54}N_3NbOSi_6$ requires C, 36.65; H, 9.25; Si, 28.5%). I.r.: 1 255s (SiCH$_3$), 961m, 915s, 875vs, 852vs, 788vs, 755 (sh), 710s, 675s, 550m (Nb-N), and 300m cm^{-1} (Nb-N). N.m.r. (CDCl$_3$, 25 °C): δ_H 0.34 and δ_C 5.7 p.p.m. Mass spectrum: *m/z* 590 (100, M^+), 574 (64, $M - CH_4$ or $M - O$), 446 [36, $M - N(SiMe_3)_2 + NH_3$], 430 [34, $MH - N(SiMe_3)_2$], 162 [35, $NH_2(SiMe_3)_2$], and 147 (10%, $NSi_2C_5H_{17}$).

X-Ray Crystal Structure.—*Crystal data.* $C_{18}H_{54}N_3NbOSi_6$, $M = 590.07$, monoclinic, $a = 12.352(12)$, $b = 18.107(3)$, $c = 15.036(14)$ Å, $\beta = 101.83(5)°$, $U = 3291.5$ Å^3, $Z = 4$, $D_c =$

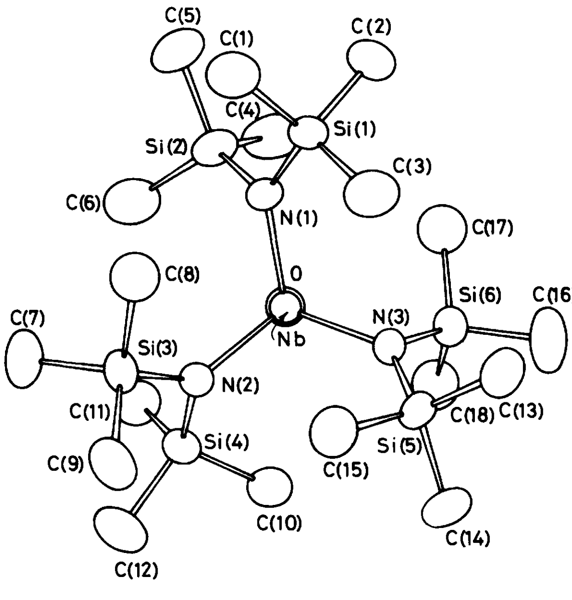

Figure. An ORTEP view of $[NbO\{N(SiMe_3)_2\}_3]$

Table 2. Final positional parameters of $[NbO\{N(SiMe_3)_2\}_3]$ with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Nb	0.230 21(2)	0.245 87(1)	0.528 52(1)	C(5)	0.5615(3)	0.3426(3)	0.4416(3)
O	0.3014(2)	0.2471(1)	0.6379(1)	C(6)	0.5193(3)	0.2093(3)	0.5402(4)
Si(1)	0.285 11(7)	0.370 23(5)	0.377 21(6)	C(7)	0.3636(3)	0.0341(2)	0.4135(3)
Si(2)	0.471 15(7)	0.304 68(6)	0.515 78(7)	C(8)	0.2625(3)	0.1662(2)	0.3137(2)
Si(3)	0.240 13(7)	0.095 40(5)	0.397 64(6)	C(9)	0.1182(3)	0.0392(2)	0.3432(2)
Si(4)	0.229 40(7)	0.077 54(5)	0.594 82(6)	C(10)	0.1354(3)	0.1105(2)	0.6677(2)
Si(5)	−0.044 13(6)	0.271 00(5)	0.475 20(6)	C(11)	0.3714(3)	0.0693(2)	0.6632(3)
Si(6)	0.094 00(7)	0.357 19(5)	0.631 12(6)	C(12)	0.1824(4)	−0.0180(2)	0.5615(3)
N(1)	0.3289(2)	0.3063(1)	0.4651(2)	C(13)	−0.1221(3)	0.3491(2)	0.4119(3)
N(2)	0.2254(2)	0.1366(1)	0.5006(2)	C(14)	−0.1320(3)	0.2301(2)	0.5482(3)
N(3)	0.0862(2)	0.2948(1)	0.5389(2)	C(15)	−0.0301(3)	0.2001(2)	0.3901(3)
C(1)	0.3386(3)	0.3514(2)	0.2718(2)	C(16)	−0.0298(4)	0.4175(2)	0.6195(3)
C(2)	0.3238(3)	0.4660(2)	0.4163(3)	C(17)	0.2116(4)	0.4208(2)	0.6375(3)
C(3)	0.1346(3)	0.3714(2)	0.3417(3)	C(18)	0.1073(4)	0.3095(3)	0.7410(2)
C(4)	0.4999(3)	0.3598(3)	0.6206(3)				

1.19 g cm^{-3}, $F(000) = 1\,264$, space group $P2_1/n$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,73$ Å, $\mu(\text{Mo-}K_\alpha) = 5.8$ cm^{-1}.

Intensity measurements. The crystal sample, of dimensions 0.69 × 0.55 × 0.40 mm, was mounted in a Lindeman capillary, and the intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer. Intensities were measured using the ω-scan technique, within the limits $1 < \theta < 25°$ (total number 6 227). Corrections for Lorentz and polarization effects were applied, but not for absorption, owing to the low value of the linear absorption coefficient. A set of 4585 independent significant reflections with $I > 3\sigma(I)$ was used in the structure solution and refinement.

Structure analysis and refinement. The structure was solved on a PDP 11-60 computer, using the Enraf-Nonius SDP package. The atomic positions of the 29 non-hydrogen atoms were found with the MULTAN program and subsequent Fourier-difference synthesis. Refinement of their co-ordinates and thermal parameters, first isotropic, and then anisotropic, led to R and R' values of 0.042 and 0.068, respectively. At this stage of the refinement, the positions of the 54 hydrogen atoms were calculated, and most of them were located on a Fourier-difference synthesis. Introduction of these atoms into the refinement, with fixed co-ordinates and isotropic thermal parameters of 5 Å^2, was significant. Two last cycles of refinement of the co-ordinates and anisotropic thermal parameters of the 29 non-hydrogen atoms led to final values of $R = 0.034$ and $R' = 0.051$. The weighting scheme used was $w = 1/\sigma^2(|F_o|)$.

The final positional parameters are reported in Table 2.

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