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Lithium bridged cyclosiloxy-niobium(v) and -tantalum(v) complexes: thermal decomposition, solid-state and solution structural studies†

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Treatment of MCl_5 (M = Nb or Ta) with 3 equivalents of dilithium tetraphenyldisiloxanediolate, $[(Ph_2SiOLi)_2O]$, gave the lithium-bridged metallasiloxane complex, $[M\{O(SiPh_2O)_2\}_3]$-μ-$[Li(L)_2]$ (M = Nb **1** or M = Ta **2**; L = pyridine). The solid-state structure of compound **2** determined by single crystal X-ray diffraction is reported. Variable-temperature ^7Li NMR of **2** revealed two separate exchange processes which may account for the equilibration of non-equivalent silicon environments in **1** and **2**. Preparative scale thermal decomposition of the solid samples with L = tetrahydrofuran (thf) gave crystalline $LiNbO_3$ and $LiTaO_3$.

The chemistry of metallasiloxanes has received considerable attention in recent years.[1] This is due, in part, to their use as mechanistic models for heterogeneous SiO_2-supported catalytic systems,[2–5] as well as precursors for metal oxides and silicates.[6,7] Tetraorganodisiloxanediolate ligands, $[(R_2SiO)_2O]^{2-}$, in metallasiloxane complexes co-ordinate in a variety of modes,[1] with bridging[8] and chelate-bridging[9] being preferred. Our investigations into the reactions of $[(Ph_2SiOM')_2O]$ (M′ = Li or Na) with transition-metal chlorides gave rise to a range of interesting and sometimes unexpected products.[9–13]

Although an oxovanadium(IV) siloxane complex is known,[14] no monomeric chelate-bridging nioba- or tantala-siloxanes have so far been reported. In this paper, we now report on the synthesis of lithium-bridged cyclosiloxyniobium, $[Nb\{O(SiPh_2O)_2\}_3]$-μ-$[Li(py)_2]$ (py = pyridine) **1** and cyclosiloxytantalum, $[Ta\{O(SiPh_2O)_2\}_3]$-μ-$[Li(py)_2]$ **2** complexes, along with their solid-state and solution-phase structures and their use as single-source precursors for $LiNbO_3$ and $LiTaO_3$.

Results and Discussion

Synthesis and characterisation of $[M\{O(SiPh_2O)_2\}_3]$-μ-$[Li(py)_2]$ (M = Nb 1 or M = Ta 2)

Reaction of anhydrous MCl_5 (M = Nb or Ta) with 3 molar equivalents of dilithium tetraphenyldisiloxanediolate, $[(Ph_2SiOLi)_2O]$ yielded colourless crystals of $[M\{O(SiPh_2O)_2\}_3]$-μ-$[Li(py)_2]$ (M = Nb **1** or M = Ta **2**) after recrystallisation from a toluene–pyridine mixture. The X-ray structure analysis of the tantalum compound revealed the presence of lattice-held solvents of crystallisation and the structural formula of $[Ta\{O(SiPh_2O)_2\}_3]$-μ-$[Li(py)_2]\cdot 0.5C_6H_5Me\cdot C_5H_5N$, **2**·$C_6H_5Me\cdot C_5H_5N$. The molecular structure of compound **2** is shown in Fig. 1. Selected bond distances and angles for **2** are given in Table 1. Partial solution of the X-ray structure analysis of compound **1** (current *R* factor at 12% and therefore, geometrical data are not presented in this paper) revealed an identical molecular structure to that found for compound **2**. On completion the full data for **1** will be deposited at the Cambridge Crystallographic Data Base.

Two rare examples of niobium compounds having siloxy ligands which have been characterised by X-ray crystallography are $[Nb(EtC_5Me_4)Cl(\mu\text{-}O)_2[Nb\{OSiBu^t_2(OH)\}_2]_2(\mu_3\text{-}O)(\mu\text{-}Cl)]$[16] and $[NBu^n_4]_3[Nb_2W_4(\mu_6\text{-}O)(\mu\text{-}O)_{12}O_5\{OSiBu^t(Me_2)\}]$.[17] Monomeric tantalum(v) siloxides such as $[TaCl_4\{OSi(C_6H_4Me\text{-}2)_3\}]$[18]

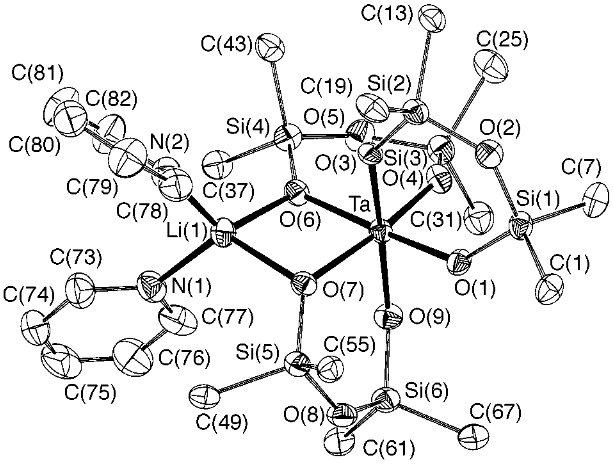

Fig. 1 Molecular structure of compound **2** drawn using PLATON[15] (thermal ellipsoids at the 50% probability level)

and $[TaMe_3Cl\{OSi(C_6H_4Me\text{-}2)_3\}]$[19] have been structurally characterised, as have dimeric species such as $[\{TaH_2(OSiBu^t_3)_2\}_2]$,[20] $[\{Ta(OSiBu^t_3)_3\}_2]$[21] and $[\{Ta(C_5Me_5)Cl\}_3(\mu\text{-}O)_2(\mu_3\text{-}O)(\mu\text{-}Cl)O_2SiBu^t_2]$.[16] Niobium-[22] and tantalum-(v)[23] compounds with a wide range of other oxy-ligating groups such as alkoxides, phenoxides, carbamates and acetates have been structurally characterised.

In compounds **1** and **2** the niobium and tantalum centres are in distorted octahedral environments, being surrounded by six oxygen atoms of the chelating tetraphenyldisiloxanediolate ligands. This anionic species retains one lithium counter ion which bridges an edge of the central octahedron (Fig. 1). The lithium atom itself occupies a distorted tetrahedral environment. There are two distinct categories of Ta–O distances in **2**. For example, the bond lengths for metal to lithium-co-ordinated oxygen, M–O (Li) [Ta–O(6) 2.027(3), Ta–O(7) 2.038(4), Å], are considerably longer than the remaining four M–O bond distances [Ta–$O_{ave.}$ 1.947(4) Å]. These bond distances are in close agreement with those found in known niobium and tantalum siloxide species.[16–22]

The position of the lithium counter ion also influences other internal parameters. The two Si–O (Ta) and two Si–O (Si) distances are identical in the TaOSiOSiO ring where the chelating oxyanions are not additionally co-ordinated to lithium [Si(1)–O(1) 1.613(3), Si(2)–O(3) 1.614(3), Si(1)–O(2) 1.634(4) and Si(2)–O(2) 1.637(4) Å]. The Si–O distances within the other two TaOSiOSiO rings indicate unsymmetrical polarisation

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† Dedicated to the memory of Professor Sir Geoffrey Wilkinson; A. C. S. and M. M. are privileged to have been co-workers and were enriched by the experience.

Table 1 Selected bond lengths (Å) and angles (°) for compound **2**

Ta–O(4)	1.918(4)	Si(1)–O(2)	1.634(4)
Ta–O(1)	1.945(3)	Si(2)–O(3)	1.614(3)
Ta–O(9)	1.951(4)	Si(2)–O(2)	1.637(4)
Ta–O(3)	1.974(3)	Si(3)–O(4)	1.624(4)
Ta–O(6)	2.027(3)	Si(3)–O(5)	1.638(4)
Ta–O(7)	2.038(4)	Si(4)–O(5)	1.629(4)
Li(1)–O(7)	1.997(9)	Si(4)–O(6)	1.633(4)
Li(1)–O(6)	1.999(10)	Si(5)–O(8)	1.618(4)
Li(1)–N(1)	2.031(9)	Si(5)–O(7)	1.619(3)
Li(1)–N(2)	2.075(10)	Si(6)–O(9)	1.604(4)
Si(1)–O(1)	1.613(3)	Si(6)–O(8)	1.646(4)
O(4)–Ta–O(1)	92.92(16)	O(4)–Si(3)–O(5)	106.14(19)
O(4)–Ta–O(9)	92.02(15)	O(5)–Si(4)–O(6)	110.2(2)
O(1)–Ta–O(9)	89.13(15)	O(8)–Si(5)–O(7)	109.35(19)
O(4)–Ta–O(3)	95.75(15)	O(9)–Si(6)–O(8)	108.3(2)
O(1)–Ta–O(3)	86.31(15)	Si(1)–O(1)–Ta	136.9(2)
O(9)–Ta–O(3)	171.18(11)	Si(2)–O(2)–Si(1)	131.6(2)
O(4)–Ta–O(6)	87.74(16)	Si(2)–O(3)–Ta	139.9(2)
O(1)–Ta–O(6)	175.77(13)	Si(3)–O(4)–Ta	141.1(2)
O(9)–Ta–O(6)	95.02(15)	Si(4)–O(5)–Si(3)	130.6(2)
O(3)–Ta–O(6)	89.47(14)	Si(4)–O(6)–Li(1)	129.0(3)
O(4)–Ta–O(7)	169.07(11)	Si(4)–O(6)–Ta	133.9(2)
O(1)–Ta–O(7)	97.58(16)	Li(1)–O(6)–Ta	96.5(3)
O(9)–Ta–O(7)	85.13(14)	Si(5)–O(7)–Li(1)	122.7(3)
O(3)–Ta–O(7)	87.99(14)	Si(5)–O(7)–Ta	132.7(2)
O(6)–Ta–O(7)	82.02(15)	Li(1)–O(7)–Ta	96.2(3)
O(7)–Li(1)–O(6)	83.8(4)	Si(5)–O(8)–Si(6)	132.0(2)
O(3)–Si(2)–O(2)	108.42(19)	Si(6)–O(9)–Ta	137.84(19)

within these rings. The Si–O–Si angles are within ranges previously observed. The Ta–μ_4-O–Si bond angles are wider than the Ta–μ_3-O–Si angles, for example, Ta–O(4)–Si(3), 141.1(2) and Ta–O(6)–Si(4), 133.9(2)°. Thus the co-ordinated lithium cation causes considerable polarisation within the structure of **2**. It is noteworthy that the structure of $LiNb(OEt)_6$ consists of helical polymers where the $Nb(OEt)_6$ octahedra are *cis*-linked by lithium.[22]

NMR spectroscopic studies of compound 2

The ^{7}Li and ^{29}Si NMR spectra of compound **2** were obtained in deuteriated toluene. Only one signal was observed in the ambient-temperature ^{29}Si NMR spectrum, suggesting that the magnetically distinct Si environments of the solid-state structure were equilibrated in solution. The equilibration may be accomplished by intramolecular lithium ion mobility. We have reported on similar cation mobility in the lithium-bridged hafnasiloxane $Li_2[Hf\{O(SiPh_2O)_2\}_3]\cdot3py\cdot3C_6H_6$.[12] The process of silicon-site equilibration in **2** was partly revealed by variable-temperature ^{7}Li NMR studies. At ambient temperature, a single resonance is observed. On cooling to 210 K, this resonance splits into two, with further splitting of one of these signals at 190 K (see Fig. 2). Thus two distinct exchange processes ($\Delta G^\ddagger$ = 34 and 38 kJ mol^{-1}) are indicated. We propose the equilibria shown in Fig. 2 to account for these processes.

Pyrolysis of compounds 1 and 2

Compounds **1** or **2** [L = tetrahydrofuran (thf)] were heated under vacuum [0.007 Torr (Torr ≈ 133.322 Pa)] in a quartz tube in stages to 500 °C. Volatile elimination products thf, biphenyl, and $(Ph_2SiO)_3$ were collected in a liquid nitrogen cooled trap. The amorphous residual black powders (analysed by X-ray powder diffraction crystallography) became colourless and crystalline on sintering at 700 °C for 2 h in a platinum boat. The measured powder diffraction data as shown in Tables 2 and 3 confirmed that $LiNbO_3$ and $LiTaO_3$ along with some other unidentified phases (probably silica) were formed in these pyrolyses. The observed *d* spacings match many of those calculated from published data on $LiNbO_3$[24] and $LiTaO_3$;[26] both observed patterns have additional unidentified underlying phases and there are considerable differences between the observed and calculated relative intensities particularly between the two $LiNbO_3$ patterns. The tantalum compound was also pyrolysed in air at 700 °C for 2 h. The X-ray powder diffraction data, Table 3, of the resulting white powder were consistent with monophasic $LiTaO_3$. A considerable number of recent reports have appeared[27] dealing with the formation (*via* sol–gel or chemical vapour deposition routes) of thin film lithium niobate and lithium tantalate from alkoxide precursors. Our single source precursors will be developed further in this respect.

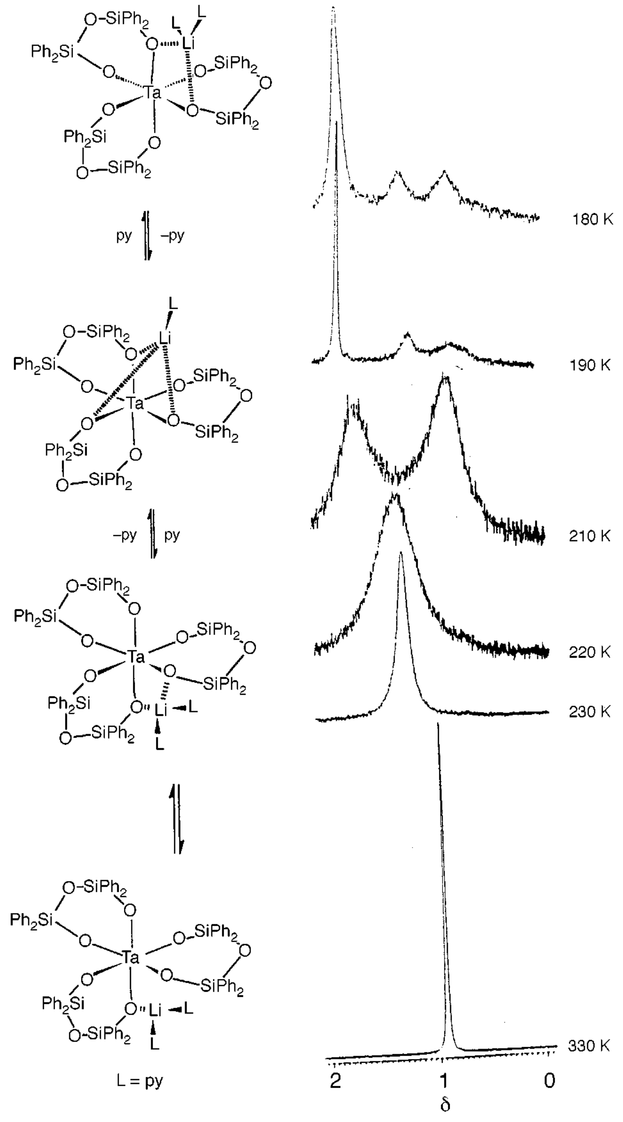

Fig. 2 Variable-temperature ^{7}Li NMR spectra and possible exchange processes for compound **2** in [$^2H_8$]toluene

Experimental

All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The chemicals $NbCl_5$ and $TaCl_5$ (Aldrich) were used as supplied. Infrared spectra were recorded using a Perkin-Elmer 1720X spectrometer (Nujol mulls between CsI plates); ^{1}H NMR spectra were recorded on a Bruker WH80 spectrometer with data listed in ppm downfield from $SiMe_4$; ^{29}Si and ^{7}Li NMR spectra were recorded on a Bruker AMX600 spectrometer with data listed in ppm downfield from $SiMe_4$ and LiCl in D_2O, respectively.

Synthesis

$[Nb\{O(SiPh_2O)_2\}_3]$-μ-$[Li(py)_2]$ 1. To a slurry of $NbCl_5$ (0.43 g, 1.61 mmol) in toluene (20 cm^3) was slowly added a

Table 2 X-Ray powder data for the product of compound **1** pyrolysed under vacuum

$LiNbO_3$ (observed)		$LiNbO_3$[24,25]			
d/Å	*I* (%)	*h*	*k*	*l*	*d*/Å
5.9318	56				
4.6497	38				
3.7330	81	0	1	2	3.7497
3.4301	88				
3.2919	60				
2.7235	59	1	0	4	2.7362
2.7027	55				
2.6592	55				
2.5702	47	1	1	0	2.5740
2.4301	36				
2.3260	44	0	0	6	2.3105
2.2484	44	1	1	−3	2.2487
2.1045	100	2	0	2	2.1221
1.9829	42				
1.8712	39	0	2	4	1.8748
1.7160	44	1	1	6	1.7194
1.6516	40	2	1	1	1.6728
1.6380	35	1	2	2	1.6374
1.6334	35	2	1	−2	1.6374
1.6081	31	0	1	8	1.6152
1.5607	47	1	2	−4	1.5154
1.5115	34	2	1	4	1.5154
1.4888	54	3	0	0	1.4861
1.4453	31	2	1	−5	1.4400
1.3658	34	2	0	8	1.3681

solution of dilithium tetraphenyldisiloxanediolate (4.83 mmol) in tetrahydrofuran (25 cm^3), at 0 °C. After stirring for 12 h, all solvent was removed under reduced pressure and the residue extracted with toluene (30 cm^3). The clear, colourless filtrate was concentrated to ≈15 cm^3 and pyridine (3 cm^3) was added until the solution became turbid. On heating, the solution became clear and colourless crystals of **1** formed (1.68 g, 70.0%) on cooling to room temperature (m.p. 258 °C). The sample was dried under vacuum at 90 °C for several hours prior to analysis (Found: C, 65.3; H, 4.7; N, 1.7. Calc. for $C_{82}H_{70}LiN_2NbO_9Si_6$: C, 65.84; H, 4.72; N, 1.87%). IR (Nujol, cm^{-1}): 1592m, 1496m, 1306m, 1262m, 1216m, 1126s, 1116s, 1067s, 1033s, 1020s, 1007s, 992s, 953s, 897s, 728vs, 719s, 703vs, 697s, 573m, 526s, 483m, 465m, 431m, 398m, 286m and 227m. NMR: ^1H (C_6D_6, 298 K): δ 6.83 (m, 4 H, py), 7.23 (m, 36 H, Ph), 7.70 (m, 24 H, Ph), 7.85 (m, 2 H, py) and 8.00 (m, 4 H, py); ^7Li ([$^2H_8$]toluene, 297 K): δ 0.36 (s); ^{29}Si ([$^2H_8$]toluene, 300 K): δ −41.50 (s).

$[Ta\{O(SiPh_2O)_2\}_3]$-μ-$[Li(py)_2]$ 2. The reaction was performed by the same method described for the preparation of **1**, using $TaCl_5$ (0.58 g, 1.62 mmol) and dilithium tetraphenyldisiloxanediolate (4.83 mmol). A yield of 1.21 g (47.2%) of colourless crystals was obtained (m.p. >300 °C). The sample was heated under vacuum at 90 °C for several hours prior to analysis (Found: C, 62.0; H, 5.0; N, 1.9. Calc. for $C_{82}H_{70}LiN_2O_9Si_6Ta$: C, 62.18; H, 4.46; N, 1.77%). IR (Nujol, cm^{-1}): 1592m, 1496m, 1428m, 1305m, 1262m, 1157m, 1125s, 1115vs, 1070m, 1033s, 1005s, 989vs, 911vs, 728vs, 718s, 696vs, 625m, 556m, 529s, 482s, 465m, 431m, 397m, 305m, 287m and 224m. ^1H NMR (C_6D_6, 298 K): δ 6.85 (m, 4 H, py), 7.22 (m, 36 H, Ph), 7.70 (m, 24 H, Ph), 7.85 (m, 2 H, py) and 8.05 (m, 4 H, py); ^7Li NMR ([$^2H_8$]toluene, 300 K): δ 0.93 (s), (210 K) 1.93 (s) and 1.05 (s), (190 K) 1.97 (s), 1.44 (s) and 0.99 (s); ^{29}Si NMR ([$^2H_8$]toluene, 300 K): δ 41.30 (s).

X-Ray crystallography

Single crystal data. A single crystal was selected from the crop deposited from toluene–pyridine solutions of **2** and used without further drying. Data were recorded on the crystal sealed in a glass capillary under argon, on a Enraf-Nonius CAD4 diffractometer operating in the ω–2θ scan mode. The structure was solved by standard heavy atom techniques (SHELXS 90)[28] and refined by least squares (on F^2) using SHELXL 97.[29] Hydrogen atoms were included at fixed positions [phenyl and pyridine C−H, 0.93 Å, methyl on toluene C−H 0.96 Å (riding model)]. The methyl group on the toluene solvent molecule was modelled for disorder and consequently the hydrogen in the *para* position was omitted. Data were corrected for absorption using an empirical method (ψ scans), with $T_{min} = 0.7964$, $T_{max} = 0.9989$. Largest difference peak and hole = 0.893 and −1.098 e $Å^{-3}$.

CCDC reference number 186/639.

Table 3 X-Ray powder data for pyrolysed compound **2**

Compound **2** pyrolysed in air $LiTaO_3$ (observed)		Compound **2** pyrolysed under vacuum $LiTaO_3$ (observed)		$LiTaO_3$[26,27]				
d/Å	*I* (%)	*d*/Å	*I* (%)	*h*	*k*	*l*	*d*/Å	*I* (%)
		4.6724	21					
3.7235	100	3.7254	100	0	1	2	3.7465	100
		3.2901	25					
		3.0705	26					
2.7141	42	2.7103	49	1	0	4	2.7277	40
2.5683	35	2.5683	39	1	1	0	2.5747	29
		2.3241	19					
2.1102	25	2.1159	27	2	0	2	2.1233	16
1.8674	24	1.8693	27	0	2	4	1.8733	18
1.7084	28	1.7084	31	1	1	6	1.7149	33
1.6346	22	1.6365	26	1	2	2	1.6388	9
1.6043	16	1.6024	19	0	1	8	1.6074	8
1.5115	20	1.5115	22	2	1	4	1.5153	8
1.4888	17	1.4850	20	3	0	0	1.4879	10
1.3582	16	1.3601	16	2	0	8	1.3681	5

Crystal data for compound $2\cdot0.5C_6H_5Me\cdot C_5H_5N$. $C_{90.5}H_{79}LiN_3O_9Si_6Ta$, $M = 1708.49$, triclinic, space group $P1$, $a = 13.850(9)$, $b = 14.025(10)$, $c = 24.487(10)$ Å, $\alpha = 94.85(8)$, $\beta = 103.74(9)$, $\gamma = 111.39(7)°$; $U = 4224(4)$ $Å^3$, $Z = 2$, $D_c = 1.343$ g cm^{-3}, crystal size 0.25 × 0.17 × 0.15 mm, $\mu = 1.444$ mm^{-1}, λ(Mo-Kα) = 0.710 73 Å, $F(000) = 1749$. A total of 12 313 reflections were measured of which 11 731 were independent and 8939 observed. Final $R1 = 0.0486$, $wR2 = 0.1294$ [$I > 2\sigma(I)$] and $R1 = 0.0801$, $wR2 = 0.1369$ (all data) for 838 parameters $\{w = 1/[\sigma^2(F_o^2) + (0.0914P)^2 + 0.27P]$ where $P = (F_o^2 + 2F_c^2)/3\}$.

X-Ray powder diffraction crystallography

Powder diffraction data were collected at room temperature on an automated Phillips PW1050/30 X-ray diffractometer using Ni-filtered Cu-Kα radiation (λ = 1.5418 Å) in flat plate θ–2θ geometry. Data were collected in the range 2θ 5–70°, in 0.05° steps with a scan time of 2 s per step. For comparison, simulated powder patterns for $LiNbO_3$ (r3c)[24] and $LiTaO_3$ (r3c)[26] were generated using published crystal data and LAZY-PULVERIX.[25]

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