Preparation and Characterisation of some Niobium and Tantalum Penta-alkoxide Co-ordination Complexes

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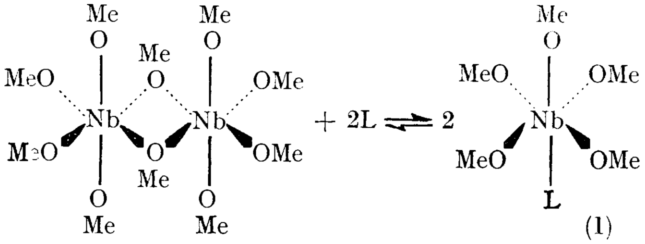
The first isolated niobium pentamethoxide complexes $Nb(OMe)_5,L$ (I; L = pyridine, γ-picoline, morpholine, hydrazine, trimethylamine oxide, and hexamethylphosphoramide) are reported, together with $Ta(OMe)_5,N_2H_4$. N.m.r. and i.r. spectra are discussed in terms of formation of octahedral six-co-ordinate niobium complexes. In these complexes hydrazine behaves as a unidentate ligand.

It is now well established that the early transition-metal alkoxides do not readily form co-ordination complexes but prefer to auto-associate into dimers, trimers, *etc.*[1-3] In the case of tantalum(v) methoxide, formation of a pyridine (py) complex was however postulated as early as 1956 by Bradley *et al.*[4] to account for ebullio-metric mass measurements carried out on the alkoxide in pyridine, but attempts to isolate the complex by evaporation of the solution failed. Only one tantalum alkoxide complex, $Ta_2(OPr^i)_{10},en$ (en = ethylenediamine), has been isolated so far but no structural data were given.[5]

An extensive n.m.r. study of the co-ordination chemistry of niobium and tantalum pentamethoxides in solution (more than 30 potential unidentate ligands were tested) confirmed that only ligands having a high charge density on the donor atom, such as amines and amine or phosphine oxides, dissociate the dimer alkoxides to some extent, according to (1). Equilibrium (1) generally lies on the side of the dimer.[2] On the


(II) (I) (1)

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other hand the exchange was found to be fast (causing a coalescence of all the methoxo-signals in the n.m.r. spectrum)[6] and thus prevents isolation of the complexes on evaporation of the solvent.

We now report the isolation and characterisation of the first niobium alkoxide complexes [I; L = pyridine (py), γ-picoline (pic), morpholine (mpl), trimethylamine oxide (tmo), hexamethylphosphoramide (hmpa), and hydrazine (hdz)], together with the tantalum pentamethoxide complex with hydrazine.

RESULTS AND DISCUSSION

Isolation of the Crystalline Complexes.—Solvent, concentration, and temperature conditions for precipitation of the crystalline complexes are critical and were found to depend considerably on the ligand. Slow precipitation of crystals from solutions containing niobium pentamethoxide and a several fold excess of pyridine (py), γ-picoline (pic), trimethylamine oxide (tmo), or hexamethylphosphoramide (hmpa) as ligand, and with toluene or acetonitrile as solvent, was achieved. After setting aside at —35 °C from 1 to 10 weeks, n.m.r. spectra of the supernatant liquors indicated the absence of both dimeric alkoxide and complex. With morpholine (mpl) the complex was precipitated immediately by addition of light petroleum to a toluene solution of the dimer and ligand. The adducts between either niobium and tantalum pentamethoxides and hydrazine (hdz) crystallised immediately on addition of the ligand in toluene or light petroleum. All the analytical data were in agreement with the formation of 1 : 1 adducts. Carbon disulphide or halogenated solvents gave side reactions and were avoided.

N.m.r. data (—40 °C) for the niobium and tantalum penta-alkoxide co-ordination complexes

Complex	Solvent	δ_e [a]	δ_0	Peak area (e/o)	δ_1	$\delta_{1'}$	Peak area (ligand/Nb)
$Nb(OMe)_5$,py	NC_5D_5	4·10	4·42	3·96	8·20		0·97
$Nb(OMe)_5$,pic	NC_5D_5	4·08	4·36	3·92	1·86	1·89	0·95
$Nb(OMe)_5$,mpl	NC_5D_5	4·13	4·30	3·58	3·41 2·50 1·80		0·98
$Nb(OMe)_5$,tmo	MeCN	3·96	4·04	3·85	3·31	3·26	0·92
$Nb(OMe)_5$,hmpa	MeCN	4·21	4·41	3·90	2·40 (9·9 Hz)	2·36 (10·1 Hz)	1·05
$Ta(OMe)_5$,hdz	MeCN	4·10	4·14	3·75	3·42	3·26	*b*

[a] In p.p.m., from Me_4Si as internal reference, e, o designating the equatorial methoxo-groups and the methoxo-group *trans* to the ligand in complex (I) respectively; 1 and 1′ denote the free and co-ordinated ligand signals respectively. [b] Measured before precipitation of the complex.

N.M.R. Spectra.—Once crystallised, the niobium alkoxide complexes could only be redissolved in polar solvents, either non-complexing[2] such as acetonitrile (L = tmo or hmpa), or complexing such as py or hmpa (L = py, pic, or mpl). In all cases low-temperature proton n.m.r. spectra recorded on solutions of the isolated complexes were identical to those on equimolar mixtures of the penta-alkoxide and of the ligand in the same solvent and at the same concentration, as expected from equilibrium (1). When acetonitrile was used as solvent, the spectra showed in the MeO–Nb region, in addition to the signals of dimer (II), two signals (Table) having a 4 : 1 ratio, in agreement with the proposed octahedral structure (I). The co-ordinated ligand : niobium ratio was in accord with this formulation. When deuteriated py was used as solvent, the expected amount of non-deuteriated py or pic per niobium atom was found in the solution. The complex $Nb(OMe)_5$,py was further characterised by reaction of dry hydrogen chloride with a dilute solution of the complex in light petroleum, which gave the expected amount of pyridinium chloride. When the same experiment was undertaken in toluene it was possible to identify the mixed alkoxochloride $Nb(OMe)_3Cl_2$[7] (δ = 4·08 and 4·02 p.p.m. at —40 °C with peak-area ratio 1 : 2).

The complex of niobium pentamethoxide with hdz is an orange-brown slightly paramagnetic solid which is insoluble in all common solvents even those which complex the alkoxides. On the contrary, the tantalum analogue, which is yellow and diamagnetic, was found to be soluble in py and hmpa, in which solvents the n.m.r. spectra were those expected for the $Ta(OMe)_5$,py or $Ta(OMe)_5$,hmpa complexes respectively, while the amount of free hdz confirms a 1 : 1 Ta : hdz ratio. By slowly adding hdz to a solution of $Ta(OMe)_5$ in MeCN, a solvent in which the complex precipitates slowly enough to allow n.m.r. measurements to be carried out, it was however possible to recognise the two signals (4 : 1) expected for octahedral structure (I).

I.R. Spectra.—The most significant changes in the spectra were found for the complexed ligand when compared to the free ligand. Thus the ν(C=N) stretching vibration found at 1 578 cm^{-1} for free py[8-10] was shifted to 1 610 cm^{-1} on co-ordination. The py ring

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deformation vibration was also shifted to higher frequencies, 412 instead of 401 cm^{-1}.[8] The literature [11,12] reports the co-ordination-sensitive bands of pic to be those located at 1 608 (ν_{8a}), 1 224 (ν_{9a}), 997 (ν_1), 800 ($\nu_{10b} + \nu_{12}$), and 515 cm^{-1} (ν_{6a}). All these bands were found to be shifted to higher frequencies in the i.r. spectra of the Nb(OMe)$_5$,pic complex. The presence of the symmetric ring-breathing mode, shifted from 997 cm^{-1} in the free ligand to 1 005 cm^{-1} in the complex, is indicative of octahedral structure (I) for this complex.[11]

The ν(C–O–C) stretching frequency at 875 cm^{-1} in mpl remained unchanged in the complex Nb(OMe)$_5$,mpl, while the N–H stretching frequency was shifted from 3 340 to 3 270 cm^{-1}. This is in agreement with co-ordination of mpl through the nitrogen atom, as shown by other authors.[13,14] The ν(P=O) stretching frequency, at 1 217 cm^{-1} in free hmpa,[15] was lowered by 30 cm^{-1} on co-ordination, as expected for co-ordination through the oxygen atom,[15,16] while the two ν(P–N) frequencies shifted from 982 to 992 cm^{-1} and from 744 to 755 cm^{-1} [15] as an effect of the increase in delocalisation of the nitrogen electron pair towards the phosphorus atom. On the other hand there was only a small shift in the ν(N–O) frequency of tmo on co-ordination (from 925 [17] to 910 cm^{-1}). This observation is in agreement with other studies [18] and is attributed to the absence of π-bonding in the N–O bond as compared to the P–O bond.

The assignment of the ν(M–N) and ν(M–O) co-ordination vibrations proved to be more difficult. Several authors [19-21] have located the metal–nitrogen vibration modes, for ligands such as py and picolines, between 250 and 150 cm^{-1}. Theoretical calculations by Bicelli [22] lead to the same conclusions. We have assigned the band at 178 cm^{-1} for the py complex, and that at 205 cm^{-1} for the pic complex, to metal–nitrogen stretching vibrations. This vibration appeared at 145 cm^{-1} in the spectra of the mpl complex, which further confirms that co-ordination occurs through the nitrogen atom.[19,20] This conclusion is also supported by the fact that no complexing was observed between the pentamethoxide and dioxan or tetrahydrofuran.[2] We tentatively assign the vibrations found respectively at 278 and 305 cm^{-1} for the hmpa and tmo complexes to the Nb–O bond,[23] although other authors report them at higher frequencies.[15,24]

The i.r. spectra of the complexes Nb(OMe)$_5$,hdz and Ta(OMe)$_5$,hdz were different: the stretching ν_s(N–N) frequency was found at 940 cm^{-1} for the tantalum compound, but at 975 cm^{-1} for the niobium derivative. Braibanti *et al.*[25] noted an increase in this frequency from hdz (875 cm^{-1}) to complexes containing unidentate hdz (930 cm^{-1}) to those containing bridging hdz (between 948 and 985 cm^{-1}).[26]

Unidentate behaviour may thus be assumed for hdz in the complex Ta(OMe)$_5$,hdz on the basis of the i.r. spectra. Further confirmation of an octahedral complex is borne out by the n.m.r. low-temperature study (Table). On the other hand, the great insolubility and the higher ν_s(N–N) frequency found for the Nb(OMe)$_5$,hdz compound are indicative of the presence of hdz bridges. The two complexes also absorb at 3 230 cm^{-1} [ν(NH$_2$)] and in the region 1 580—1 600 cm^{-1} [δ(NH$_2$)] [26] shifted towards free hdz. Assignment of the ν(M–N) vibration in hdz complexes is uncertain: the frequency is reported to occur between 340 and 614 cm^{-1}.[27,28] Assignment of this vibration to the bands at 395 (M = Nb) and 370 cm^{-1} (M = Ta) would seem the most reasonable.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. The metal alkoxides were prepared according to the literature.[29,30] Solvents were purified and dried by standards methods.[31] Hydrazine (hdz) (98%) was dried over potassium hydroxide for 3 days and repeated distillations over potassium hydroxide were carried out immediately before use. Trimethylamine oxide was prepared according to the literature.[32]

N.m.r. spectra were recorded on a C60-HL JEOL spectrometer equipped with a variable-temperature attachment. Tetramethylsilane (tms) was used as internal reference. Magnetic susceptibilities were measured on solid samples at room temperature with a Gouy-balance system. I.r. spectra were recorded on Perkin-Elmer 577 and Beckman IR 11 spectrometers as Nujol mulls between KBr or polyethylene discs. The wavenumbers reported are expected to be accurate to ± 5 cm^{-1} or better. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS. Metals were analysed as oxide. There appears to be a systematic error for the niobium determination.

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Preparations.—*Pentamethoxoniobium–pyridine* (1/1), $Nb(OMe)_5$,py. Niobium pentamethoxide (130 mg, 0·52 mmol) and pyridine (py) (2·28 g, 29·5 mmol) were dissolved in toluene (1·6 cm^3). The first crystals were observed to form after 8 days at room temperature. The solution was then cooled to −30 °C. After 2 months white *crystals* were filtered off, washed with toluene or light petroleum, and dried under vacuum at 25 °C for 48 h (138 mg, 83%), m.p. 138 °C (decomp. 140°) (Found: C, 36·5; H, 6·20; N, 4·6; Nb, 29·4. Calc. for $C_{10}H_{20}NNbO_5$: C, 36·7; H, 6·20; N, 4·80; Nb, 28·5%). The complex is very sensitive to air. It is insoluble in aliphatic hydrocarbons and toluene, slightly soluble in acetonitrile or light petroleum, and soluble in methanol or py.

The same preparation undertaken in carbon disulphide led to a paramagnetic red-brown product ($\chi_{corr.} = 220 \times 10^6$ c.g.s. units at 25 °C) stable in air and insoluble in all common organic solvents, m.p. 200 °C (decomp. 210 °C) [Found: C, 30·2; H, 3·50; N, 3·4; Nb, 21·2; S, 27·1. $Nb(OMe)_4NC_5H_5,2CS_2$ requires C, 29·5; H, 3·8; N, 3·1; Nb, 20·7; S, 28·6%]. ν(C–O) at 1 085, 1 070, and 1 020 cm^{-1}; ν(Nb–O) at 518 cm^{-1}. A band at 342 cm^{-1} was tentatively attributed to a Nb–S stretching mode.[33]

Pentamethoxoniobium–γ-picoline (1/1), $Nb(OMe)_5$,pic. Niobium pentamethoxide (200 mg, 0·8 mmol) was added to a mixture of γ-picoline (pic) (2 g, 21·43 mmol) and toluene (8·4 cm^3). Crystallisation, observed after 2 months, was achieved by addition of light petroleum (5 cm^3). The colourless *precipitate* was isolated as above (232 mg, 85%), m.p. 132 °C (Found: C, 38·1; H, 6·40; N, 3·85; Nb, 28·05. Calc. for $C_{11}H_{22}NNbO_5$: C, 38·8; H, 6·50; N, 4·10; Nb, 27·2%). The complex possesses similar solubility properties to those of $Nb(OMe)_5$,py.

Pentamethoxoniobium–morpholine (1/1), $Nb(OMe)_5$,mpl. The same procedure applied to a mixture of niobium pentamethoxide (150 mg, 6·05 mmol), morpholine (mpl) (1·74 g, 20 mmol), toluene (5 cm^3), and light petroleum (4 cm^3) gave the *complex* $Nb(OMe)_5$,mpl (160 mg, 87%), m.p. 155 °C (Found: C, 30·9; H, 7·05; N, 3·90; Nb, 28·0. Calc. for $C_9H_{24}NNbO_6$: C, 32·1; H, 7·20; N, 4·20; Nb, 27·75%).

Pentamethoxoniobium–trimethylamine oxide (1/1), $Nb(OMe)_5$,tmo. Trimethylamine oxide (tml) (29·4 mg, 0·39 mmol) was added to a solution of niobium pentamethoxide (175 mg, 0·71 mmol) in acetonitrile (1·5 cm^3). After stirring, the solution was cooled to −30 °C. The *crystals* were filtered off after 2 weeks (200 mg, 90%), m.p. 105 °C (Found: C, 29·4; H, 7·25; N, 4·38; Nb, 29·25. Calc. for $C_8H_{24}NNbO_6$: C, 29·4; H, 7·40; N, 4·30; Nb, 28·7%).

Pentamethoxoniobium–hexamethylphosphoramide (1/1), $Nb(OMe)_5$,hmpa. Niobium pentamethoxide (220 mg, 0·88 mmol) was dissolved in hmpa (187 mg, 1·05 mmol and acetonitrile–toluene 2 : 1, 2·1 cm^3). The first crystals formed after 48 h at room temperature and precipitation was complete after 10 days. The *crystals* were isolated as above (320 mg, 85%), m.p. 97 °C (decomp.). The same product was obtained with pentane as solvent, but crystallisation was slower (Found: C, 28·95; H, 8·00; N, 23·85; Nb, 22·45; P, 7·0. Calc. for $C_{11}H_{33}N_3NbO_6P$: C, 29·0; H, 8·00; N, 23·95; Nb, 21·8; P, 6·70%).

Pentamethoxoniobium–hydrazine (1/1), $Nb(OMe)_5$,hdz. A solution of hydrazine (hdz) [94 mg, 2·92 mmol in light petroleum (10 cm^3)] was added at room temperature to a solution of niobium pentamethoxide (162 mg, 0·65 mmol) in anhydrous light petroleum (5 cm^3). An orange-brown crystalline *solid* precipitated immediately. It was filtered off, washed with dry light petroleum, and dried under vacuum (143 mg), decomp. 170 °C (Found: C, 21·1; H, 6·90; N, 10·55; Nb, 33·5. Calc. for $C_5H_{19}N_2NbO_5$: C, 21·4; H, 6·80; N, 10·0; Nb, 33·2%). The adduct was unstable in air and insoluble in all common organic solvents.

Pentamethoxotantalum–hydrazine (1/1), $Ta(OMe)_5$,hdz. The same procedure applied to $[Ta(OMe)_5]_2$ (150 mg, 4·28 mmol) gave the yellow *complex* $Ta(OMe)_5$,hdz (152 mg, 95%), m.p. 160 °C (decomp. 170 °C) (Found: C, 16·1; H, 5·20; N, 7·75; Ta, 51·25. Calc. for $C_5H_{19}N_2O_5Ta$: C, 16·3; H, 5·15; N, 7·60; Ta, 51·05%). The complex is insoluble in aliphatic hydrocarbons, toluene, light petroleum, acetonitrile, nitromethane, trimethyl phosphate and soluble in py or hmpa.

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