Inorganica Chimica Acta, 12 (1975) 229–233

The Coordination Chemistry of Niobium and Tantalum Pentamethoxides: a General Discussion

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Received July 24, 1974

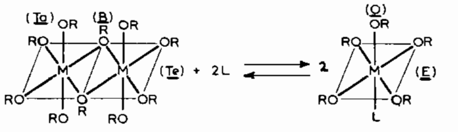
The coordination ability of about 40 potential monodentate and bidentate ligands with niobium and tantalum pentamethoxides has been investigated and is discussed.

Introduction

The coordination by some amines can be rationalized on a theoretical basis by considering the energy of the frontier orbitals, or on a practical basis, their pK_a values. For the oxo type ligands R_3MO (M = N,P,As), the charge on the oxygen atom, as evaluated from Faraday effect measurements or from infrared stretching frequencies, is determinant. Several predictions have been made and have received experimental confirmation. Steric factors are also important.

Results

It is well established that early transition metal alkoxides tend to auto-associate, rather than to form coordination compounds[1–3]. The coordination chemistry of niobium and tantalum pentamethoxides D has been investigated by low temperature NMR spectroscopy[3,4a,b]. The formation of octahedral complexes C is accompanied by the appearance of two new resonances in the methoxy region with an integration ratio of 4 to 1. The complexes C are in equilibrium with the dimer D (3 signals in 2/2/1 ratios) in solutions of toluene, dichloromethane or acetonitrile according to equation (1):



D C (1)

Only the following monodentate donors gave complexes with $Nb(OMe)_5$: NC_5H_5, NC_5H_{11} (piperidine), $NHOC_4H_8$ (morpholine), NH_3, NH_2CH_3, $NH(CH_3)_2$, $ON(CH_3)_3$, $OP(CH_3)_3$, $OAs(CH_3)_3$ and $OP[N(CH_3)_2]_3$ (HMPA) (formation constants, which are generally weak, are given in Tables I and II which accompany the discussion).

More than twenty other potential monodentate ligands including ethers [$O(CH_3)_2$, $O(C_2H_5)_2$, $O(CH_2)_4$ (THF), $O(CH)_4$ furane, $O(CH_2)_4O$ (dioxane), $O(CH_2)_4$ S]; the ketone $OC(CH_3)_2$; amines [$N(CH_3)_3$, $NH(CH_4)$ (pyrrole)]; nitriles [$NCCH_3$, $NCC(CH_3)_3$, NC_7H_5 (benzonitrile)]; sulfides [$S(CH_3)_2$, $S_2(CH_3)_2$, $S(CH)_4$ (thiophene), $SP(CH_3)_3$]; phosphines [$P(CH_3)_3$, $P[N(CH_3)_2]_3$]; phosphites, $P(OCH_3)_3$; phosphates, $OP(OCH_3)_3$; sulfoxides, $OS(CH_3)_2$, $OS(OCH_3)_2$ and arsines, $As(CH_3)_3$, gave no NMR-detectable amounts of complexes[3].

A range of bidentate ligands has now been investigated as well as some additional monodentate ligands. Among the potential bidentates, only ethylenediamine and *o*-phenanthroline gave complexes, while 2,2′-bipyridine, N,N,N′,N′-tetramethylenediamine, succinonitrile, tetramethylurea, monomethylcyclosilazane, hexamethylcyclotrisiloxane, octamethylphosphortriamide (OMPA) and diphosphine tetramethyldisulfide did not react with niobium and tantalum pentamethoxides.

The NMR spectrum recorded at –20° C on a solution of niobium pentamethoxide and ethylenediamine (en) in toluene (molar ratios Nb/To = 1.4×10^{-2}, en/Nb = 7.2) shows a sharp signal at 3.40 ppm for the methylene groups, and three peaks (1.18, 1.15 and 1.11 ppm) for the amino protons. The peak at 1.15 ppm was assigned to the free ligand. The two others, which always have equal area, can be attributed to a molecular species in which the amino groups are non-equivalent, which precludes a bridging[1] or chelating behaviour of the ligand. Furthermore, the pattern observed in the methoxy region, which consists of two signals at δ = 4.27 and 4.10 ppm with an integration ratio 1 to 4, is in agreement with the formation of an octahedral complex. These observations are thus consistent with the existence of a mononuclear complex in which ethylenediamine would behave as a monodentate ligand.

TABLE I. pK_a Values of the Ligand and Complexing Behaviour.

Ligand	$pK_a(H_2O)$	pK_a(DMF)	Complexation (K_c in $l.mol^{-1}$ in toluene)
NC_7H_5 (benzonitrile)	−10.4[a]		no
$NCCH_3$	−10.0		no
$OC(CH_3)_2$	−7.2[a]		no
$S(CH_3)_2$	−5.3[a]		no
$O(CH_3)_2$	−3.8[a]		no
$O(CH_2)_4O$ (dioxane)	−3.4[a]		no
$O(CH_2)_4$ (THF)	−2.1[a]		no
$OCCH_3N(CH_3)_2$ (NDMA)	0.1[a]		no
$S(CH)_4$ (thiophene)	0.3[b]		no
$OC[N(CH_3)_2]_2$	0.4[b]		no
$OS(CH_3)_2$	1.4[b]		no
$N_2C_{12}H_8$ (*o*-phenanthroline)	3.2[c]		yes
$N_2C_{10}H_8$ (2,2′-bipyridine)	4.1[c]		no
NC_4H_5 (pyrrole)	5.0[d]		no
$[\{N(CH_3)_2\}CH_2]_2$ N,N,N′,N′-tetramethylenediamine	$\begin{cases} 5.8^{c} \\ 8.9 \end{cases}$		no
NC_5H_5	5.2[d]	3.0[e]	yes (0.04 at −60° C)
β-NC_6H_7 (β-picoline)	5.6[d]		yes (0.001 at −60° C)
α-NC_6H_7 (α-picoline)	5.9[d]		no
γ-NC_6H_7 (γ-picoline)	6.0[d]		yes (0.16 at −60° C)
N_2H_4	8.0[f]		yes
$NHOC_4H_8$ (morpholine)	8.2[g]		yes (0.003 at −50° C)
$P(CH_3)_3$	8.7[h]		no
NH_3	9.2[d]	9.5[e]	yes (0.30 at −45° C)
$N(CH_3)_3$	9.7[d]	9.0[e]	no
$NH_2(CH_2)_2NH_2$	9.9[d]	7.9[e]	yes (10.7 at −45° C)
NC_7H_{13} (quinuclidine)	10.55[i]		no
NH_2CH_3	10.6[d]	10.8[e]	yes (0.06 at −45° C)
$NH(CH_3)_2$	10.8[d]	10.1[e]	yes (0.07 at −45° C)
NHC_5H_{10}	11.1[d]	9.7[e]	yes (0.02 at −45° C)

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The reaction of *o*-phenanthroline is more complex. The NMR spectrum (−35° C) on solutions of $Nb(OMe)_5$ and *o*-phenanthroline in acetonitrile (molar ratios *o*-phen/Nb$\leq$1.2 and $Nb/CH_3CN > 0.10 \times 10^{-2}$) shows the existence of at least two new molecular species, the relative amounts of which depend on the dilution and on *o*-phen/Nb molar ratios. One set of signals (δ_o = 4.36 and δ_e = 4.09 ppm) which are in a surface ratio of 1 to 4, is tentatively assigned to an octahedral complex in which *o*-phenanthroline would behave as a monodentate ligand[5]. The other signals (δ_a = 4.01, δ_b = 3.40 and δ_c = 3.36, with a ratio of 1/2/2) could correspond to a heptacoordinated species. These two species are in dynamic equilibrium with the dimer. Further additions of ligand (*o*-phen/Nb> 1.2) increase the number of peaks in the methoxy region. The spectrum observed for the ligand is always poorly resolved and precludes more definite assignments from being made.

The purpose of the present paper is to discuss the various factors which are able to play a part in controlling the coordination chemistry of the niobium and tantalum pentamethoxides, and to establish a basis for the prediction of the complexing ability of potential ligands towards them.

Discussion

The coordination chemistry of niobium and tantalum pentamethoxides can obviously not be rationalised on the basis of the qualitative hard and soft model[6]: for example, the borderline base pyridine complexes these alkoxides, which are hard acids, while no coordination

TABLE II. Donor Strength of Phosphoryl Ligands and Ligand Behaviour.

Ligand	Charge Distribution Q_0 in e	character P⇆O bond	ν(P=O) (cm^{-1} in IR)	complexation K_c(–45° C)CH_3CN in l. mol^{-1}	RMN Data (ppm) on Complex C (–45° C) δ_e	δ_o
$OPH(CH_3)_2$	–1.038[a]	0.023[a]	1157	0.75 ± 0.10	3.92	3.98
$OP(CH_3)(OH)_2$			1160	reaction		
$OP(CH_3)_3$	–1.13	0	1182[c]	0.60 ± 0.10	3.88	3.96
$OP[N(CH_3)_2]_3$		0.200[d]	1194[d]	0.25 ± 0.05	3.95	3.98
$OP(C_6H_5)_3$	–0.827	0.370[b]	1195	no		
$OP(NC_4H_8O)_3$			1203[e]	no		
$OP(CH_3)[N(CH_3)_2]_2$			1203	0.04 ± 0.01	4.27	4.44
$OP(nC_4H_9)[N(C_2H_5)_2]_2$			1295[e]	0.004 ± 0.001	4.34	4.46
$OP(Cl)[N(C_2H_5)_2]_2$			1210[f]	no-redistribution.		
$OP(Cl)(CH_3)_2$	–0.953[a]	0.118[a]	1215	redistribution		
$OP(OCH_3)(CH_3)_2$	–0.847[a]	0.390[a]	1215	no		
$OP(OCH_3)[N(CH_3)_2]_2$			1225	no		
$OP(CH_3)(SCN)_2$			1235	redistribution		
$OP\{N(CH_3)_2\}_2]_2O$			1238[a]	no		
$OP(CH_3)(OCH_3)_2$	–0.623[a]	0.777[a]	1245	no		
$OP(OCH_3)_3$	–0.560	1.079[h]	1278	no		
	–0.399[a]	1165[a]				
$OP(O_3C_4H_8)$			1325	no		
$OP(CH_3)F_2$	–0.4447[a]	1.275[a]	1326	no-redistribution		

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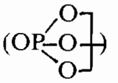
was noted with harder donors such as trimethylamine, ethers or methoxybisdimethylaminophosphine oxide. The quantitative approach of the HSAB concept by Drago[7,8] is no more effective and cannot afford a reliable way of predicting the behaviour of the ligands.

Nor is there an obvious relationship between the coordinative properties of the ligand and the existence of a delocalized π-system on it since pyridine and piperidine both complex the pentamethoxides.

Steric hindrance can explain why α-picoline, unlike the other picolines, does not complex the pentamethoxide. Nevertheless this factor alone certainly does not account for the non-complexing character of trimethylphosphate, quinuclidine or 4-phospha-1-methyl-3,5,7-trioxotricyclo(2,2,2)-heptane oxide  compared to hexamethylphosphortriamide, or trimethyl amine oxide.

Several approaches to the rationalization of our observations will now be discussed.

Frontier Orbitals

The mos attractive approach in accounting for the coordination chemistry of niobium and tantalum pentamethoxides is probably to consider the symmetry and energy of the frontier orbitals. Hollebone has investigated the electronic structures of several donors by photoelectron spectroscopy interpreted on the basis of a single center molecular orbital model[9]. This model is able to demonstrate that bridging bonds are stronger for alkoxides than for chlorides, because the former are better π-donors[10]. Further experimental evidence for this view is provided by mass spectral measurements which show that niobium pentamethoxide remains dimeric[11,12], while the pentachloride is dissociated in the gas phase under similar conditions[13].

On the other hand, when the donor is considered, ammonia is a very strong base according to Hollebone's model. Its highest occupied molecular orbital(HOMO) is localized on the donor atom and has the most favorable symmetry ($2a_1$) for overlapping with a σ-acceptor[10]; on the contrary in trimethylamine the HOMO (4pe) is stabilised by *ca.* 40 Kcal and acquires an antibonding character which diminishes its donor ability[14]. Further support for this interpretation of the complexing character of the aliphatic amines is provided by their first ionization potential values which are considered by Klopman as a measure of their softness (E)[15]. The electronic structure of dimethylether, which is not complexing, is similar to that of trimethylamine and its basicity is consequently low[14].

The preceding theoretical considerations appear to be promising in accounting for the ability of the ligand to coordinate niobium pentamethoxide. Unfortunately our knowledge of the energy gap between frontier orbitals is still limited.

pK_a Values

Another approach was to compare pK_a values of the ligands with their ability to coordinate $Nb(OMe)_5$ in Table I. It can be seen that formation of complexes generally occurs for high pK_a values. Nevertheless, no satisfying quantitative correlation could be found between formation constants and the pK_a values. This, in fact, is not surprising since the solvents used for our experiments are very different from those in which the pK_a values were measured.

Charge Distribution

An attempt was also made to correlate the ligand's behaviour with the charge distribution on its donor atom. This can only be reasonably expected in series of related compounds and for the same evaluation method of the charge distribution.

Such an evaluation was found to be possible in the case of the phosphoryl type compounds, for which one efficient method of determining electronic charges is afforded by Faraday effect measurements. These have confirmed Wagner's theoretical calculations[16] on the bond order in phosphoryl compounds, according to which the total bond order of the phosphoryl bond varies as a function of the substituent's electronegativity, from a nearly pure single bond in $(CH_3)_3PO$ to an almost triple bond in F_3PO. The situation is more complicated for phosphoramides[17]; however, Table II shows a correlation between the experimental formation constants and, when available, the charge distribution on the oxygen atom, and the π-bond order of the phosphoryl bond which, in turn, is reflected by its $\nu(P{=}O)$ frequency in the infrared spectra. The observation that it suffices to substitute one of the methyl or dimethylamino group in $OP(CH_3)_3$ or $OP[N(CH_3)_2]_3$ by a methoxy group to completely inhibit the coordination ability of the ligand toward $Nb(OMe)_5$ is consistent with the increase of the phosphoryl π-bond character. Similarly, the increase in the π-bond character of the $P \leftrightarrows O$ bond from hexamethylphosphortriamide to octamethylphosphortriamide, which is accompanied by an increase of 44 cm^{-1} of the infrared stretching frequency accounts for the non-complexing behaviour of this potential bidentate ligand.

As a practical rule, it can be predicted that complexation occurs, in the absence of steric constraints, with phosphoryl ligands having $\nu(P{=}O)$ frequencies lower than 1210 cm^{-1} (Table II). On this basis, we could predict that $OP(CH_3)[N(CH_3)_2]_2$ ($\nu(P{=}O)$: 1203 cm^{-1}) and $OP(n\text{-}C_4H_9)[N(C_2H_5)_2]_2$ ($\nu(P{=}O)$: 1205 cm^{-1}) would complex $Nb(OMe)_5$, while $OP(CH_3)(SCN)_2$ ($\nu(P{=}O)$: 1235 cm^{-1}) and $OP(OCH_3)_3$ ($\nu(P{=}O)$: 1278 cm^{-1}) would not. These predictions were verified (Table II). However, triphenylphosphine oxide and trimorpholinephosphine oxide did not complex niobium pentamethoxide nor tantalum pentamethoxide, although their phosphoryl vibrations are lower than 1210 cm^{-1}. This may be due to their greater bulkiness[18]. In several cases, a redistribution[19] of the substituents between the phosphorus and niobium atoms was observed to occur. In some cases this phenomenon is too rapid to allow reliable conclusions.

Similar conclusions are probably valid for arsenic oxide donors, but the effects of the substituent's electronegativity on the charge of the oxygen atom and of the substituent's bulkiness is less pronounced[20]. Thus complexation takes place between niobium pentamethoxide and triphenylarsine oxide ($\nu(As{=}O)$: 880 cm^{-1}, $K_c(-40°C)CH_3CN = 0.50 \pm 0.05$ l. mol^{-1} or trimethylarsine oxide ($\nu(As{=}O)$: 904 cm^{-1}, $K_c(-40°)CH_3CN = 0.35 \pm 0.05$ l mol^{-1}) but no longer with dichloromethoxyarsine oxide ($\nu(As{=}O)$: 920 cm^{-1}) or methyldimethoxyarsine oxide ($\nu(As{=}O)$: 950 cm^{-1}).

Similarly the Faraday effect measurements[21] were interpreted to mean that the $S \leftrightarrows O$ π-bond order is high and the charge on the oxygen atom low ($\leq 0.64e$), which is consistent with the non-complexing character of such donors [$(CH_3)_2SO$, $(CH_3O)_2SO$, $(CH_3O)_2SO_2$].

The ability of the various ligands to complex niobium pentamethoxide is also valid for tantalum pentamethoxide, but the formation constants are generally higher for the tantalum complexes[3]. For instance, the values of the formation constants are 70 ± 10. l. mol^{-1} for $Ta(OMe)_5 \cdot OP(CH_3)_3$ or 0.55 ± 0.10 for $Ta(OMe)_5 \cdot OP[N(CH_3)_2]_3$ while they are only 0.60 ± 0.10 and 0.25 ± 0.05 for the corresponding niobium derivatives but finally the range of ligands which complexes $Ta(OMe)_5$ is no more extended than for Nb $(OMe)_5$.

Miscellaneous

Another promising approach could be the use of Gutmann's donor numbers D_n[22] as a measure of the ligand's donor strength, since ligands having a high donor number (pyridine and HMPA) were found to coordinate $Nb(OMe)_5$. Unfortunately, this approach is still limited by the small number of ligands whose D_n are available.

Experimental

All manipulations were carried out under dry nitrogen. The solvents were dried and purified by standard methods.

Niobium and tantalum pentamethoxides were prepared as described in the literature[23]. Quinuclidine was obtained from the hydrochloride[24]. 4-phospha-1-methyl-3,5,7-trioxatricyclo(2,2,2)heptane oxide was synthesized according to Verkade[25]. OMPA (Gift from Murphy Chemical) was purified by vacuum distillations. The phosphoryl ligands were prepared as described in the literature[26].

The NMR spectra were recorded on a JEOL C-60 HL spectrometer. The formation constants of the niobium pentamethoxide complexes were estimated from the NMR measurements as formerly described[3]. Ligand behaviour was examined on toluene, acetonitrile or dichloromethane solutions. The results are summarised in Tables I and II. Infrared spectra were obtained on a Beckman IR 577 spectrometer.

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