133. Adducts of Niobium(V) and Tantalum(V) Halogenides. IX[1]). Relative Stability of the Adducts of the Chlorides and Bromides with Some Dialkylchalcogenides[2])

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(8. V. 74)

Summary. The relative stability of adducts formed by Nb(V) and Ta(V) pentachlorides and bromides with some dimethylchalcogenides and nitriles has been determined by ^{1}H-NMR. in dichloromethane at – 60°. The stabilities are explained in terms of the HSAB principle and *Jørgensen*'s symbiotic effect. A good correlation exists between the ionisation potential of the valence p orbital of the chalcogen atom in the ligand and the logarithm of the relative stability of the adduct formed with a given acid.

1. Introduction. – In dichloromethane and in chloroform, the dimeric Nb(V) and Ta(V) halides react quantitatively with *Lewis* bases to form monomeric, non-electrolyte adducts with 1:1 stoichiometry [2] [3]:

$$^1/_2\,(MX_5)_2 + L \rightleftarrows MX_5 \cdot L. \qquad (1)$$

In preceding communications of this series, various adducts of Nb(V) and Ta(V) chlorides have been studied, mainly with respect to their stability and kinetic behaviour. In this work, we examine by NMR. the stability of the adducts formed by Nb(V) and Ta(V) bromides and Ta(V) chloride, mainly with the dimethylchalcogenides.

2. Experimental Part. – The recording of NMR. spectra, the work in inert atmosphere and the purification of some of the products are described in [4]. $NbBr_5$ and $TaBr_5$ (*RIC/ROC*) were sublimed twice at 10^{-2} Torr and 130° and kept in sealed Pyrex tubes under vacuum. Diethylether (*Fluka*, puriss.) and diethylsulfide (*Fluka*, purum) were distilled over sodium.

Concentrations are expressed in molality (*m*). Chemical shifts[1]) ($\delta = (\nu - \nu_{TMS}) \cdot 10^6/\nu_{TMS}$) are given in ppm with respect to TMS as an internal reference.

The solid adducts are prepared under nitrogen and the conditions vary according to their solubility. As a rule, 40 mmol of MX_5 was added to 20 g of CH_2Cl_2 containing between 100 and 200 mmol of ligand (in order to allow the possible formation of a complex of the form $MX_5 \cdot 2L$). Upon dissolving, the solvent and excess ligand are evaporated at room temperature and 110 Torr. The adduct is then ground and dried for 1 h at $5 \cdot 10^{-2}$ Torr. The products were sealed under vacuum in Pyrex tubes.

The microanalyses have been performed by *Alfred Bernhardt*'s *laboratories*, 5251-Elbach, Germany. Each element is followed by the observed value in %.

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[1]) Part VIII: see [1].

[2]) Abstracted from the Ph. D. Thesis of *R. Good*, University of Lausanne, 1974.

[3]) In the preceeding communications of the series, δ was defined with the opposite sign. We now adopt the generally accepted sign convention for δ.

$\mathrm{NbCl_5 \cdot Me_2Se}$, brown.	Calc.	C 6.33,	H 1.59,	Se 20.8,	Cl 46.8,	Nb 24.5
	Found	C 6.36,	H 1.46,	Se 21.0,	Cl 46.5,	Nb 24.2
$\mathrm{TaCl_5 \cdot Me_2Se}$, yellow.	Calc.	C 5.14,	H 1.29,	Se 16.9,	Cl 37.9,	Ta 38.7
	Found	C 5.29,	H 1.37,	Se 16.8,	Cl 37.7,	Ta 38.9
$\mathrm{TaCl_5 \cdot Me_2Te}$, dark brown.	Calc.	C 4.66,	H 1.17,	Te 24.7,	Cl 34.4,	Ta 35.1
	Found	C 4.51,	H 1.24,	Te 25.0,	Cl 34.2,	Ta 34.8
$\mathrm{TaBr_5 \cdot Me_2O}$, yellow.	Calc.	C 3.83,	H 0.97,	Br 63.8,	Ta 28.9	
	Found	C 3.80,	H 1.05,	Br 63.7,	Ta 29.0	
$\mathrm{TaBr_5 \cdot Me_2Se}$, orange.	Calc.	C 3.46,	H 0.88,	Se 11.5,	Br 58.0	
	Found	C 3.26,	H 0.94,	Se 10.9,	Br 57.7	
$\mathrm{TaBr_5 \cdot Me_2Te}$, black.	Calc.	C 3.25,	H 0.82,	Te 17.3,	Br 54.1,	Ta 24.5
	Found	C 3.13,	H 0.92,	Te 17.5,	Br 53.9,	Ta 24.6

3. Results and discussion. – 3.1 *Stoichiometry and chemical shifts of the adducts.* At room temperature, the NMR. spectra of the adducts in the presence of an excess of ligand show only one signal owing to the rapidity of exchange (2)

$$\mathrm{MX_5 \cdot L + L^* \rightleftarrows MX_5 \cdot L^* + L.} \qquad (2)$$

At a sufficiently low temperature, the exchange is slowed down and two signals are observed. The signal corresponding to the coordinated ligand appears at lower field than the one of the free ligand. The chemical shifts δ of the adducts, together with the chemical shift differences $\Delta\delta$ due to complexation are reported in Table 1.

In the dimethylchalcogenides series, the chemical shifts δ are related to the electron density on the methyl group, as can be predicted from the electronegativity of the chalcogen atom. The decrease in chemical shift difference $\Delta\delta$ in passing from the oxide to the telluride indicates that the inductive effect on the methyl group caused by adduct formation is less important when the donor atom is polarisable.

Some of the adducts have been prepared in the solid state earlier [5]. For the remaining ones, the 1:1 stoichiometry has been established in the solid state by elemental analysis (see experimental part). In dilute solutions, the same stoichiometry is observed (Table 1) on the basis of the concentration of metallic halide known by weighing, and the concentration of complexed ligand determined by NMR. The latter quantity is determined by integration of the signal due to the coordinated ligand with respect to a quantitative reference (usually the signal due to the ^{13}C–H coupling of the solvent).

3.2 *Relative stability of the adducts.* We have determined by NMR. (*cf.* [7]) the constants $K_{a,b}$ for the competitive equilibria of type (3), in the case of slow exchange. The errors on the constants

$$\mathrm{MX_5 \cdot L_b + L_a \rightleftarrows MX_5 \cdot L_a + L_b} \qquad (3)$$

$$K_{a,b} = ([\mathrm{MX_5 \cdot L_a}]\,[\mathrm{L_b}]) \,/\, ([\mathrm{L_a}]\,[\mathrm{MX_5 \cdot L_b}]) \qquad (4)$$

are estimated as a function of the reproducibility of integrations, the number of determinations and the method used. As far as the conditions allowed, we have verified the value of $K_{a,b}$ by means of a cycle, measuring also $K_{a,c}$ and $K_{c,b}$, for which the product $K'_{a,b}$ must be equal to $K_{a,b}$. The values retained for the stability constants $K''_{a,b}$ have been obtained by taking into account both constants $K_{a,b}$ and

Table 1. *Chemical shifts* δ (ppm), *chemical shift differences* $\Delta\delta$ (ppm) *and stoichiometry of the adducts formed by* MX_5 (M = Nb, Ta; X = Cl, Br) *with a few nitriles and dimethylchalcogenides*, in CH_2Cl_2 at – 60°. Reference: internal TMS

Adduct	δ ($MX_5 \cdot L$)	$\Delta\delta = \delta(MX_5 \cdot L) - \delta(L)$	Stoichiometry M:L	Concentrations $[M]_t$	$[L]_t$
$TaCl_5 \cdot Me_2O$[a]	4.41 ± 0.01	0.98 ± 0.01	1 : 1.00 ± 0.08	0.03	0.12
$TaCl_5 \cdot Me_2S$	2.88 ± 0.01	0.75 ± 0.01	1 : 1.02 ± 0.02	0.03	0.12
$TaCl_5 \cdot Me_2Se$	2.76 ± 0.01	0.75 ± 0.01	1 : 0.99 ± 0.05	0.03	0.12
$TaCl_5 \cdot Me_2Te$	2.54 ± 0.01	0.62 ± 0.01	1 : 1.00 ± 0.03	0.05	0.11
$NbBr_5 \cdot MeCN$	2.61 ± 0.01	0.55 ± 0.01	1 : 1.07 ± 0.11	0.03	0.80
$NbBr_5 \cdot Me_3CCN$	1.57 ± 0.01	0.20 ± 0.01	1 : 1.00 ± 0.08	0.03	0.07–0.10
$NbBr_5 \cdot Me_2O$	4.20 ± 0.01	0.90 ± 0.01	1 : 0.98 ± 0.08	0.04	0.30
$NbBr_5 \cdot Me_2S$	2.71 ± 0.01	0.57 ± 0.01	1 : 0.98 ± 0.04	0.05	0.12–0.19
$TaBr_5 \cdot MeCN$	2.67 ± 0.01	0.60 ± 0.01	1 : 1.02 ± 0.02	0.03	0.20–0.40
$TaBr_5 \cdot Me_3CCN$	1.60 ± 0.01	0.22 ± 0.01	1 : 1.00 ± 0.06	0.03	0.07–0.10
$TaBr_5 \cdot Me_2O$	4.42 ± 0.01	1.11 ± 0.01	1 : 0.98 ± 0.03	0.04	0.12–0.30
$TaBr_5 \cdot Me_2S$	2.94 ± 0.01	0.81 ± 0.01	1 : 1.03 ± 0.03	0.05	0.11–0.20
$TaBr_5 \cdot Me_2Se$	2.82 ± 0.01	0.81 ± 0.01	1 : 0.98 ± 0.03	0.03	0.08
$TaBr_5 \cdot Me_2Te$	2.58 ± 0.01	0.67 ± 0.01	1 : 1.03 ± 0.04	0.02	0.05–0.09

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a) Measured in $CHCl_3$ by *Merbach & Bünzli* [6].

Table 2. *Relative stability constants for the adducts $MX_5 \cdot L$ (M = Nb, Ta; X = Cl, Br) involving various nitriles and dimethylchalcogenides*, in CH_2Cl_2 at – 60°. $MX_5 \cdot L_b + L_a \rightleftarrows MX_5 \cdot L_a + L_b$, $K_{a,b}$

MX_5	L_a	L_b	method	n[a]	$K_{a,b}$	L_c	$K'_{a,b}$[b]	$\log K''_{a,b}$[c]
$TaCl_5$[d]	Me_2Te	Me_2Se	direct	4	1.8 ± 0.2	Me_2S	1.7 ± 0.3	0.25
		Me_2S	direct	4	2.0 ± 0.2	Me_2Se	2.2 ± 0.3	0.31
	Me_2Se	Me_2S	direct	3	1.2 ± 0.1	Me_2Te	1.1 ± 0.2	0.06
	Me_2S	Me_2O	direct	3[e]	5.5 ± 0.8			0.72
$NbBr_5$[f]	Me_2S	Me_3CCN	indirect[g]	3	33 ± 4			1.52
	Et_2S	Me_3CCN	indirect[g]	1	3.9 ± 0.5			0.59
	$OP(NMe_2)Cl_2$	MeCN	direct	1[i]	5.3 ± 0.9			
		Me_3CCN	direct	1[i]	6.8 ± 1.0			
	MeCN	Me_3CCN	direct	4	1.4 ± 0.2	$OP(NMe_2)Cl_2$	1.3 ± 0.4	0.15
	Me_3CCN	Me_2O	semi-direct[j]	4	48 ± 5			1.68
$TaBr_5$[k]	Me_2Te	Me_2Se	direct	3	8.9 ± 1.5			0.95
	Me_2Se	Me_2S	direct	4	2.7 ± 0.2	Me_3CCN	2.8 ± 0.6	0.43
		Me_3CCN	direct	2	4.7 ± 0.5			0.67
	Me_2S	Me_3CCN	direct	5	1.7 ± 0.3			0.24
	$OP(NMe_2)Cl_2$	Me_3CCN	direct	1[i]	18 ± 3			
		MeCN	direct	1[i]	30 ± 4			
	Me_3CCN	MeCN	direct	3	1.3 ± 0.1	$OP(NMe_2)Cl_2$	1.7 ± 0.6	0.11
		Et_2S	indirect[h]	1	2.5 ± 0.4			0.39
		Me_2O	semi-direct[j]	3	52 ± 5			1.72

[a] Number of determinations. [b] $K'_{a,b} = K_{a,c} \cdot K_{c,b}$. [c] $K''_{a,b}$ is the definitive value of $K_{a,b}$ adopted, taking into account the various constants determined. [d] $[Ta]_t \simeq 0.04$ *m*, $[L_a]_t + [L_b]_t \simeq 0.08$ *m*. [e] Determined in $CHCl_3$ by ***Merbach & Bünzli*** [6]. [f] $[Nb]_t \simeq 0.05$ *m*, $[L_a]_t + [L_b]_t \simeq 0.1$ to 0.6 *m*. [g] Integrations on L_a. [h] Integrations on L_b. [i] Determined by *Favez* [9]. [j] The signal of $MX_5 \cdot L_b$ is integrated with respect to the signal given by the ^{13}C–H coupling of the solvent; this serves as an internal standard.

[k] $[Ta]_t \simeq 0.04$ *m*, $[L_a]_t + [L_b]_t \simeq 0.12$ to 0.50 *m*.

$K'_{a,b}$. The results are given in Table 2 and Figure 1. In the latter, we have also reported for comparison some results obtained by *Merbach & Bünzli* [6].

For the four metal halides, the stability of the adducts with the dimethylchalcogenides increases with the atomic number of the donor atom. These adducts are more stable when the donor atom is soft, which indicates, according to the HSAB principle, a relatively soft character for the Nb(V) and Ta(V) halides.

The relative softness of the donor atom is not however the only determining factor for the stability of an adduct. We notice, for example, that the adducts formed by diethylsulfide are markedly less stable than those formed by dimethylsulfide. In the scale of donor-acceptor interaction proposed by *Drago & Wayland* [8], the parameters C_b and E_b characterizing each of the two ligands are practically identical. This suggests that the enthalpic factors lead to similar stabilities, and the observed difference can safely be attributed to a steric effect.

Owing to the formation of mixed halogenides of general formula $MCl_nBr_{5-n} \cdot L$ $(0 \leqslant n \leqslant 5)$, the technique of competitive equilibria does not allow the determination of the relative stabilities of adducts formed by chlorides and bromides. Nonetheless, the comparison of the stability scales of Nb(V) and Ta(V) chlorides and bromides permits to show the existence of the symbiotic effect proposed by *Jørgensen* [10].

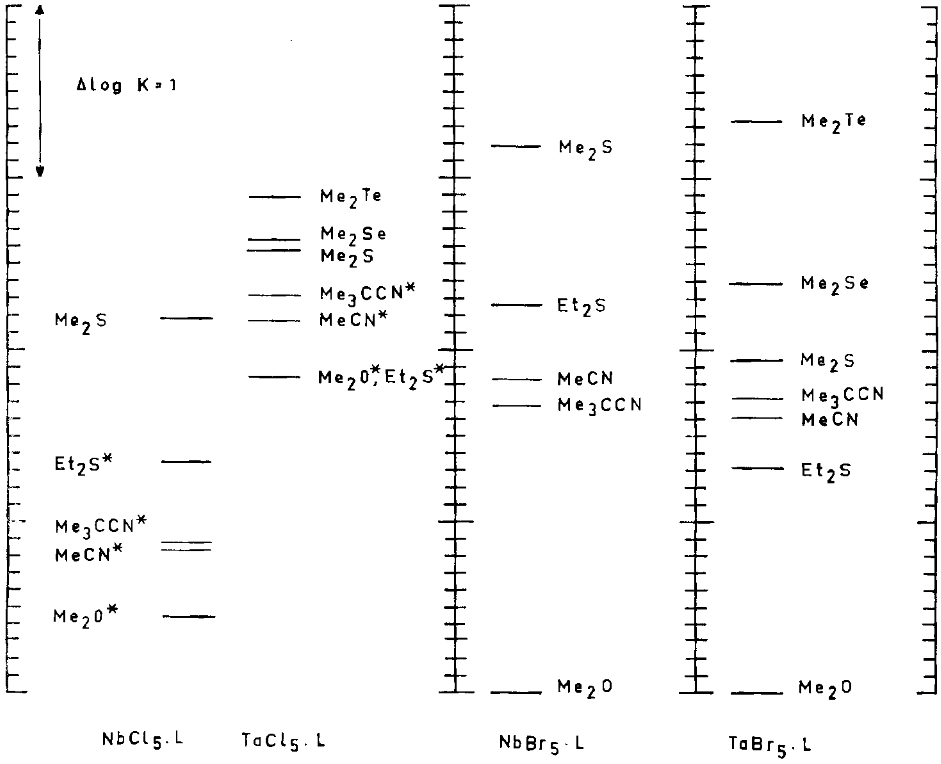

Fig. 1. *Relative stability of the adducts of niobium(V) and tantalum(V) chlorides and bromides* at – 60° in CH_2Cl_2 (or in $CHCl_3$: *). The relative position of the scales is known only for $NbCl_5$ and $TaCl_5$. The stability of the adducts increases from bottom to top.

This effect can be summarized in the following way: hard bases (electronegative donor atoms) hold their valence electrons back when bound to a central atom, therefore rising its positive charge and making it a hard Lewis acid. Soft bases (donor atoms of low electronegativity) give part of their electrons to the central atom, thus reducing its positive charge and making it a soft *Lewis* acid. The bromide ion shows a softer behaviour than the chloride ion [11]. We therefore expect a greater stabilization of adducts formed with soft ligands in the case of bromides. Figure 1 indeed shows that the difference in stability between adducts formed with various dimethylchalcogenides strongly increases when passing from Nb(V) and Ta(V) chlorides to bromides.

In the series of dimethylchalcogenides, photoelectronic spectroscopy [12] showed that the s orbital of the valence shell of the chalcogenide is much more stable than the p orbital, thus it is the latter which forms the bond in an adduct. This point of view is verified by the excellent correlation found between the logarithm of relative stability of an adduct and the ionisation potential of the p orbital of the ligand. In Figure 2, the relative stability is given with respect to the adducts containing Me_2O. Since the series of ligands is the same in each case, it is possible to compare the slopes of the different straight lines (measurements with $NbCl_5$ and $NbBr_5$ have been restricted to two ligands for experimental reasons and the dotted lines give the probable orientation of the straight lines). This slope is proportional to the softness of a given acid. One can see that niobium is a softer acid than tantalum as *Merbach* & *Bünzli* [6] have suggested earlier. The same conclusion is reached by *Hammond* &

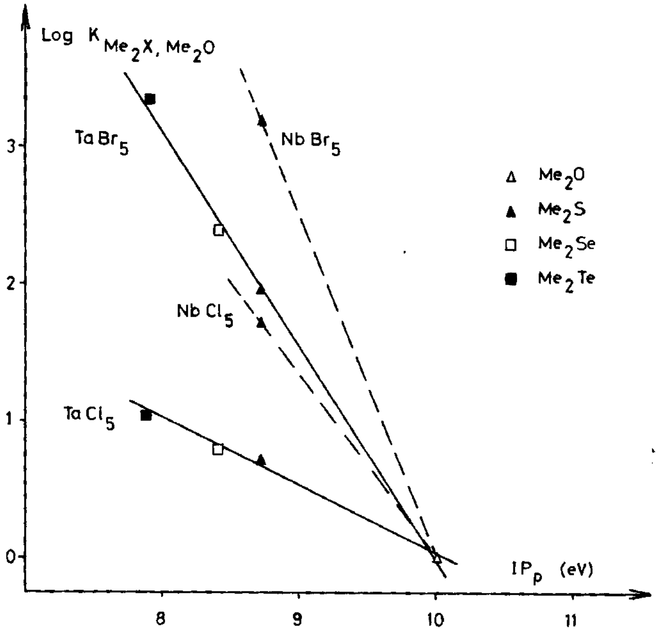

Fig. 2. *Correlation between the ionisation potential of the valence shell p orbital of the chalcogen in Me_2Y and the logarithm of the relative stability constant $K^{MX_5}_{Me_2Y, Me_2O}$ of the adducts at – 60°*

Lake [13] who investigated the formation constants of adducts formed by Nb(V) and Ta(V) chlorides with soft ligands as benzene. In a similar way, Figure 2 shows that bromides are softer than the corresponding chlorides; this was discussed above in terms of symbiotic effect.

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134. Synthesis of some Indanones having Nitrogen-containing Substituents

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Summary. The title compounds have been synthesized by a *Friedel-Crafts* acylation-alkylation between aromatic ethers and α,β-unsaturated carboxylic acids (or esters) having nitrogen-containing substituents. Polyphosphoric acid was used as condensing agent.

Introduction. – There have been a number of reports concerning the preparation of indanones by condensing an α,β-unsaturated carboxylic acid or derivative with an aromatic nucleus. Aluminum chloride [1], hydrogen fluoride [2] and polyphosphoric acid [3] have been used most frequently as condensing agents.

In this paper we describe the cyclisation between some α,β-unsaturated carboxylic acids or esters, having nitrogen-containing substituents, and aromatic ethers. Polyphosphoric acid was used as medium in these reactions. Indanones having nitrogen-containing substituents were obtained in moderate yields, and they were easily separated from their by-products or starting materials. In one case a β-hydroxy carboxylic acid was used instead of an α,β-unsaturated carboxylic acid.