246. Electron Transfer Spectra of Some Adducts of Niobium (V), Tantalum (V), Titanium (IV) and Zirconium (IV) Halides with Lewis Bases[1])

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(14. VII. 75)

Summary. The electron transfer spectra of adducts of the title metal halides with a series of ligands (nitriles, dialkylchalcogenides, phosphoryl and thiophosphoryl ligands and phosphines) have been studied. The effect of halogen substitution on the halogen metal transitions is discussed by comparing the spectra of the adducts with those of the hexahalometalates. The origin of the two ligand-metal transitions observed in most adducts is discussed and the splitting of the metal d levels in these almost octahedral adducts is estimated. For each metal halide, the series of adducts with dialkyl chalcogenides show a linear relationship of slope one between the ligand ionisation potential and the ligand-metal charge transfer energy. The ligand optical electronegativities have been estimated.

1. Introduction. – The structure, the relative stability and the kinetic behaviour of octahedral adducts $MX_5 \cdot L$ of niobium (V) and tantalum (V) halides with numerous *Lewis* bases have been investigated by NMR. spectroscopy [1–4]. In this study[2]) we discuss their electron charge transfer spectra, as well as those of adducts of titanium (IV) and zirconium (IV) chlorides with dimethylchalcogenides. In the previous papers of this series we have preliminarily investigated the hexachloro- and hexabromoniobate (V) and -tantalate (V) anions [5].

Since niobium (V) and tantalum (V) are d^o, the electronic spectra of the adducts $MX_5 \cdot L$ are made up of electron transfer solely. For MCl_6^- we observed essentially electron transfer between the chloride filled π levels ($1t_{1g}$, $2t_{1u}$, $1t_{2u}$ and $1t_{2g}$) and the vacant d orbitals of the metal ($2t_{2g}$). In the adducts one expects a splitting of the metal $2t_{2g}$ and $2e_g$ levels of the corresponding hexahalogenometalate, caused by a lowering of the molecular symmetry to C_{4v}. The results show that this splitting is small, as observed from the halogen to metal electron-transfer. We shall therefore classify the transitions in the adducts by analogy with the energy level diagram valid for MCl_6^- given in [5], adding the supplementary level due to the new ligand L.

2. Results. – 2.1. *Adducts with nitriles.* The spectra of adducts of $NbCl_5$ with a series of nitriles show (Table 1 and Fig. 1) that the nitrile-niobium electron transfer occurs at energies higher than 45 kK. These complexes therefore lend themselves

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[1]) Abstracted from the Ph. D. thesis of *M. Valloton*, University of Lausanne, 1974.

[2]) This paper is to be considered as part XI of the series. Part X: see [5].

Table 1. ***Electronic absorption spectra and assignments of adducts $NbX_5 \cdot L$ in methylenchloride*** (energies in kK, and $\varepsilon_{max} \cdot 10^{-3}$ in parentheses)

	$X \rightarrow 2t_{2g}$[a]				$L \rightarrow 2t_{2g}$	$L \rightarrow 2e_g$	Unassigned	$\Delta\nu$[b]
$NbCl_6^-$ [c]	28.9sh (<2.0)	31.8sh (11.4)	34.5 (28.9)	41.4 (6.4)				
$NbCl_5 \cdot CH_3CN$	26.0sh (0.48)		34.1 (23.2)	39.4 (8.3)	46.1 (6.6)			
$NbCl_5 \cdot CH_3CN$ [d]	25.0sh (0.50)		34.1 (22.1)	39.4 (8.7)	45.2 (7.5)			
$NbCl_5 \cdot ICH_2CN$ [d]	25.0sh (0.50)		34.0 (24.5)	39.3 (8.5)	46.3 (8.0)			
$NbCl_5 \cdot BrCH_2CN$ [d]			33.9 (16.5)	39.3 (6.0)				
$NbCl_5 \cdot ClCH_2CN$ [d]			34.3 (19.5)	39.8 (8.5)				
$NbCl_5 \cdot FCH_2CN$ [d]			33.9 (16.0)	39.4 (7.0)				
$NbCl_5 \cdot Cl_3PO$	25.8sh (0.42)		33.6 (18.9)		37.6 (11.4)		46.1 (8.2)	
$NbCl_5 \cdot (MeO)_3PO$	25.5sh (0.46)	30.8sh (9.9)	33.7 (20.8)		37.3 (19.8)		44.2 (9.7)	
$NbCl_5 \cdot (Me_2N)_3PO$		31.2sh (11.0)	34.0 (19.0)	41.0 (6.0)	36.4 (13.0)			
$NbCl_5 \cdot (Me_2N)_3PS$		30.9sh (9.4)	34.2 (22.5)		20.8 (1.9)		42.6 (10.3)	
$NbCl_5 \cdot Me_2O$			34.8 (18.0)				43.3 (8.6)	
$NbCl_5 \cdot Et_2O$		31.3sh (9.8)	34.1 (22.7)	41.0 (5.9)				
$NbCl_5 \cdot Me_2S$			34.2 (25.1)		24.6 (1.5)	43.7 (20.0)		19.1
$NbCl_5 \cdot Et_2S$			34.2 (23.3)		24.1 (1.2)	43.2 (17.0)		19.1
$NbCl_5 \cdot Me_2Se$			34.4 (22.1)		22.0 (1.6)	41.3 (24.8)	26.3 (0.53)	19.1
$NbF_5 \cdot Me_2S$					37.6 (1.0)			
$NbF_5 \cdot Me_2Se$					34.8 (1.1)			
$NbBr_6^-$ [b]	21.3sh (3.8)	22.8 (6.3)	27.2 (29.4)	35.7 (6.5)				
$NbBr_5 \cdot Me_2Se$		22.3 (3.8)	27.3 (14.8)		>22.3 [e]	38.8 (17.3)		<16.5

[a] The assignments for the hexahalides are respectively: $1t_{1g} \rightarrow 2t_{2g}$, $2t_{1u} \rightarrow 2t_{2g}$, $1t_{2u} \rightarrow 2t_{2g}$, $1t_{1u} \rightarrow 2t_{2g}$ [5].

[b] $\Delta\nu$: energy difference between the first and the second chalcogen-metal transition.

[c] In acetonitrile [5]. [d] In $CHCl_3$. [e] Absorption masked by the $Br \rightarrow 2t_{2g}$ transitions.

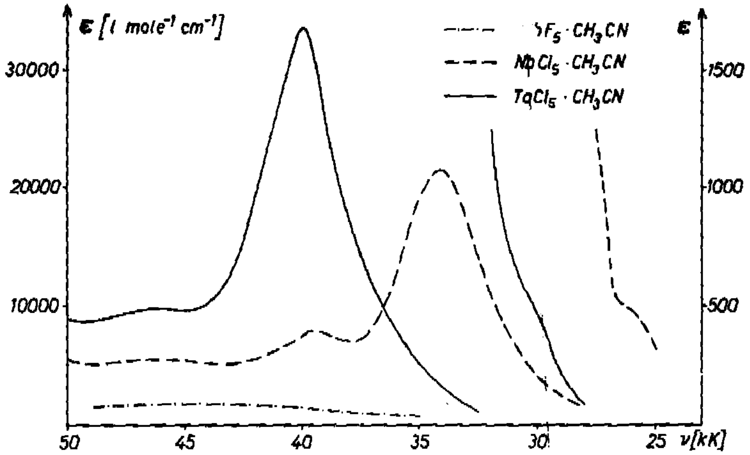

Fig. 1. *Electronic spectra of* $NbF_5 \cdot CH_3CN$, $NbCl_5 \cdot CH_3CN$, *and* $TaCl_5 \cdot CH_3CN$ *in* CH_2Cl_2

well to the study of the modification of chloride to niobium charge transfer spectrum in passing from the hexachloro complex to the adduct. The most intense peak corresponding to the transition between the chloride non-bonding $1t_{2u}$ level and the metal $2t_{2g}$ level of $NbCl_6^-$ broadens and shifts slightly towards lower energy in the case of the adducts. The peak observed around 39.4 kK could have been attributed to a nitrile-niobium charge transfer; since its energy remains constant and we know that the stability of the adducts decreases by a factor of 10^4 from acetonitrile to the fluoroacetonitrile [2] we assign this peak to a $Cl^- \rightarrow 2t_{2g}$ transition. A decreasing stability would have to be interpreted by an increase in the nitrile-niobium charge transfer energy which is the case for the highest energy bands of the adducts with the nitrile and iodoacetonitrile; the fact that for the other nitriles this transition could not be observed can be accounted for by a new elevation of the energy which cannot be attained for instrumental reasons. Since no low energy band appeared in the adducts with $BrCH_2CN$ and ICH_2CN, it is clear that the ligand is coordinated through the nitrogen atom.

2.2. *Adducts with dialkylchalcogenides.* In the adducts of the niobium (V) halides two chalcogen-metal transitions are generally observed (Table 1 and Fig. 2). The energy of the first chalcogen-metal transition, $L \rightarrow 2t_{2g}$, decreases in passing from Me_2S to Et_2S and from Me_2S to Me_2Se and Me_2Te. In changing from $NbCl_5$ to NbF_5, this transition is displaced 14 kK towards higher energy. Since Me_2Se is not a better reducing agent than Br^-, it is impossible to distinguish the first selenium to metal-charge transfer of $NbBr_5 \cdot Me_2Se$ from the $Br^- \rightarrow 2t_{2g}$ transfer. The second chalcogen-metal transition, $L \rightarrow 2e_g$, is on the average ten times more intense than the first. As for $L \rightarrow 2t_{2g}$, its energy decreases in passing from Me_2S to Et_2S, and from Me_2S to Me_2Se and Me_2Te. In a given metal halide, the energy difference between the first and the second chalcogen-metal transition remains constant, irrespective of the chalcogen fixed on the metal, and is smaller for the bromides than for the chlorides. Looking at the chloride-niobium transitions we observe no change in the energy of the most intense transition, while the peak around 39.4 kK observed in $NbCl_5 \cdot RCN$ is hidden either by broadening of this last transition, or by the $L \rightarrow 2e_g$ transition.

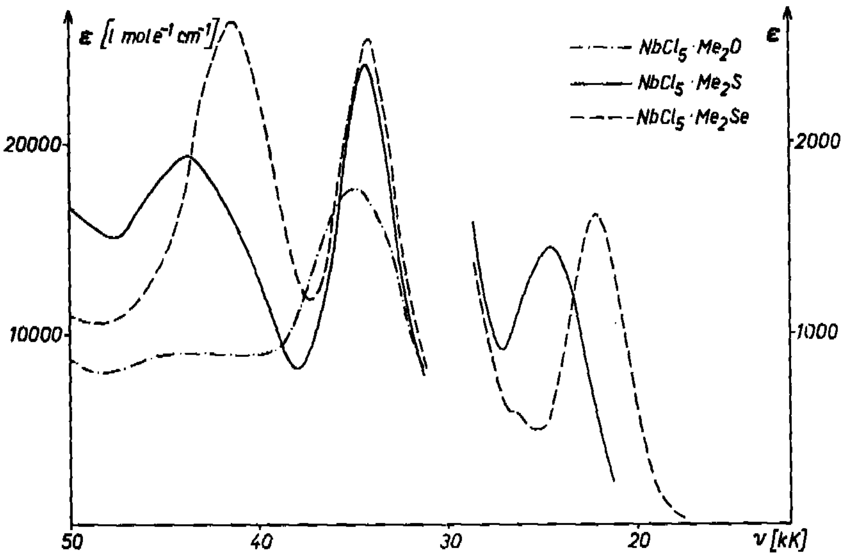

Fig. 2. *Electronic spectra of* $NbCl_5 \cdot Me_2O$, $NbCl_5 \cdot Me_2S$ *and* $NbCl_5 \cdot Me_2Se$ *in* CH_2Cl_2

For the adducts of tantalum (V) halides, $L \rightarrow 2t_{2g}$ is split (Table 2, Fig. 3). $L \rightarrow 2e_g$ is again ten times more intense than $L \rightarrow 2t_{2g}$ and the energy difference between these two transitions again stays constant in passing from one chalcogenide to another for a given metal halide. The halide-metal transitions show, as for niobium (V), only one broad intense band in these tantalum (V) adducts.

The series of adducts of titanium (IV) and zirconium (IV) chlorides with the dimethylchalcogenides have been prepared in order to see to what extent the results obtained with niobium (V) and tantalum (V) may be generalized. The adducts $TiCl_4 \cdot 2L$ with ethers [6] and sulfides [7] are known. It appears that most of them and in particular $TiCl_4 \cdot 2Me_2S$ have *cis* geometry in the solid state according to their infrared spectra [8] [10]. The syntheses and the IR. spectra of $ZrCl_4 \cdot 2Me_2O$ [9] and $ZrCl_4 \cdot 2Me_2S$ [10] are also known. The electronic spectra of the adducts of titanium (IV) chloride again show the two chalcogen-metal transitions, but with a smaller energy difference than for the adducts of niobium (V) and tantalum (V) (Table 3 and Fig. 3). We can also observe the $L \rightarrow 2e_g$ transition in $TiCl_4 \cdot 2Me_2O$ at 48.8 kK. The chloride to metal charge transfer bands in the adducts of titanium, corresponding to $1t_{2u} \rightarrow 2t_{2g}$ and $2t_{1u} \rightarrow 2t_{2g}$ in $TiCl_6^{2-}$, show an analogous behaviour to that found in the case of niobium (V); moreover these transitions are masked by the second chalcogen to metal charge transfer in the adducts with Me_2S and Me_2Se. For the zirconium complexes, we observe essentially the chalcogen-metal transitions, the halogen-metal transitions being of very high energy. The first chalcogen-metal charge transfer is split and the energy difference between the two chalcogen-metal transitions is larger than in the case of titanium, but can be estimated only in the adduct with Me_2Te.

Table 2. *Electronic absorption spectra and assignments of $TaX_5 \cdot L$ in methylenchloride* (energies in kK, and $\varepsilon_{max} \cdot 10^{-3}$ in parentheses)

	$X \rightarrow 2t_{2g}$[a]				$L \rightarrow 2t_{2g}$	$L \rightarrow 2e_g$	Unassigned	$\Delta\nu$[b]
$TaCl_6^-$ [c]	34.8sh (5.8)	38.0 (23.8)	41.5 (38.0)	49.5 (11.0)				
$TaCl_5 \cdot CH_3CN$	30.8sh (0.14)		40.0 (38.5)	45.8 (9.6)				
$TaCl_5 \cdot (Me_2N)_3PS$	35.1 (8.3)	38.5 (19.5)	40.8 (27.3)		27.4 (3.4)			
$TaCl_5 \cdot (i\text{-}Pr)_3P$		38.5 (14.5)	41.0 (22.5)		25.2 (1.8)			
$TaCl_5 \cdot Me_2O$	35.1sh (4.8)	38.2sh (14.2)	40.8 (23.1)		43.1 (17.2)			
$TaCl_5 \cdot Et_2O$	34.5sh (4.6)	38.0sh (17.4)	40.8 (28.3)					
$TaCl_5 \cdot Me_2S$			40.5 (31.0)		29.6 (1.7)	$\geq$50.0[d]		$\geq$20.4
$TaCl_5 \cdot Et_2S$			40.5 (31.0)		28.7 (1.5)	$\geq$50.0[d]		$\geq$21.3
					30.9 (1.4)			
$TaCl_5 \cdot (i\text{-}Pr)_2S$					28.3 (1.0)			
$TaCl_5 \cdot Me_2Se$	35.9sh (7.0)		40.6 (29.7)		27.0 (1.9)	48.3 (25.7)		21.3
					29.4 (1.3)			
$TaCl_5 \cdot Me_2Te$		38.8sh (18.7)	41.5 (32.2)		22.6 (1.8)	43.7 (34.8)	29.9 (0.76)	21.1
					24.7sh (1.4)			
$TaBr_6^-$ [c]	22.7 (0.6)	26.0 (7.9)	32.0 (34.7)	41.5 (6.8)				
		29.8sh (15.0)	33.7 (32.5)					
$TaBr_5 \cdot Me_2Se$	23.7 (2.1)	27.2 (6.4)	31.4 (17.7)		$\geq$23.7[e]	44.4 (24.9)		$\leq$20.7
			33.9 (27.8)					
$TaBr_5 \cdot Me_2Te$	23.0 (2.5)	27.0 (5.4)	31.5sh (12.5)		19.8 (2.4)	40.6 (50)		<20.8
			34.1 (23)					

[a] The assignments for the hexahalides are respectively: $1t_{1g} \rightarrow 2t_{2g}$, $2t_{1u} \rightarrow 2t_{2g}$, $1t_{2u} \rightarrow 2t_{2g}$, $1t_{1u} \rightarrow 2t_{2g}$ [5].

[b] $\Delta\nu$: energy difference between the first and the second chalcogen-metal transitions.

[c] In acetonitrile [5].

[d] Transition too energetic to be measured.

[e] Absorption masked by the $Br \rightarrow 2t_{2g}$ transitions.

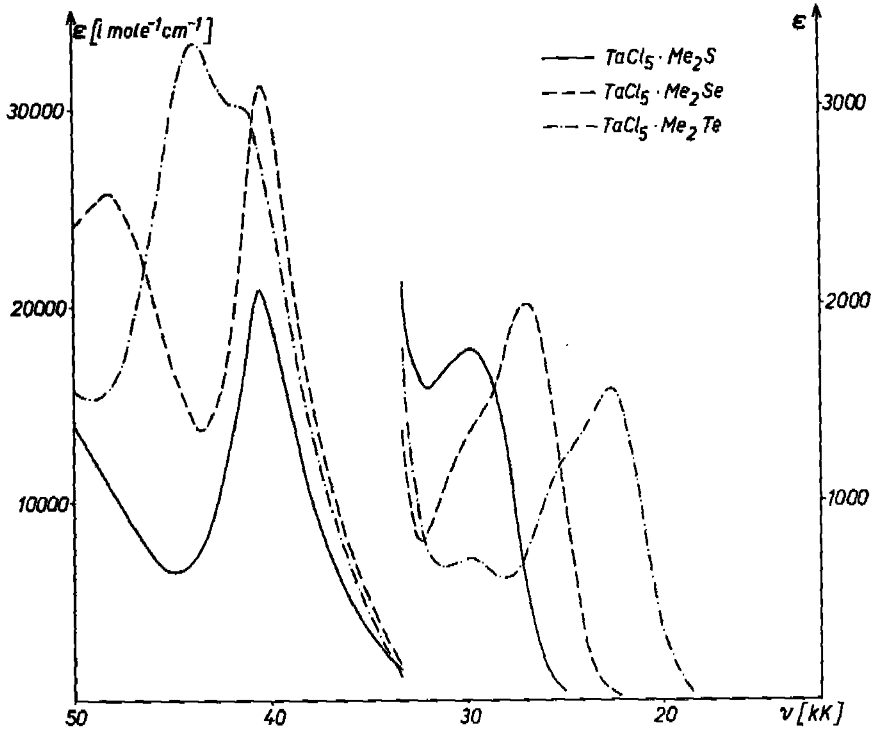

Fig. 3. *Electronic spectra of* $TaCl_5 \cdot Me_2S$, $TaCl_5 \cdot Me_2Se$ *and* $TaCl_5 \cdot Me_2Te$ *in* CH_2Cl_2

2.3. *Adducts with phosphoryl and thiophosphoryl ligands*[3]. In these adducts a single ligand-metal transition, $L \rightarrow 2t_{2g}$, is observed (Table 1 and 2). For the phosphoryl-niobium charge transfer, one sees a shift towards lower energy in passing from $OPCl_3$ to $OP(OMe)_3$ and $OP(NMe_2)_3$. This shift parallels the increase of the donor ability of the ligand. The effect is small, while the stability difference between the three adducts amounts to about 15 orders of magnitude.

2.4. *Adducts with phosphines.* The adduct with the trimethylphosphine was found to be unstable in dichloromethane at room temperature. On the other hand we succeeded with the triisopropylphosphine: at –60° the ^{1}H-NMR. spectrum shows, in the presence of an excess of ligand, a quadruplet due to the free phosphine [12], and at 0.4 ppm. to lower field a second quadruplet due to $TaCl_5 \cdot (i\text{-}Pr)_3P$. The electronic spectrum shows only one phosphorus-tantalum transition (Table 2).

3. Discussion. – 3.1. *Origin of the two chalcogen-metal transitions.* The two bands arise either from two different ligand orbitals susceptible to an electron transfer to the same metal orbital, or from a single ligand orbital from which an electron can transfer to two different metal orbitals. Fig. 5 shows the two situations if we assume that the $2t_{2g}$ and $2e_g$ levels of the octahedral complex are only slightly modified upon substitution of a halogen by a neutral *Lewis* base. X_π represent the π levels of the halides and L the donor orbitals of the chalcogen atom. The photoelectron spectra of

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[3] These adducts were characterized and their stability measured by NMR. [11].

Table 3. *Electronic absorption spectra and assignments of* $TiCl_4 \cdot 2L$ *and* $ZrCl_4 \cdot 2L$ *in methylenchloride* (energies in kK, and $_{max} \cdot 10^{-3}$ in parentheses)

	$Cl \rightarrow 2t_{2g}$[a])				$L \rightarrow 2t_{2g}$	$L \rightarrow 2e_g$	$\Delta\nu$[b])
$TiCl_6^{--}$[c])	25.0sh (1.3)	29.6sh (17.0)	31.8 (22.0)	43.8 (30.0)			
$TiCl_4 \cdot 2Me_2O$		30.1sh (5.4)	33.7 (9.4)	43.1 (8.4)		48.8 (14)	
$TiCl_4 \cdot 2Me_2S$		31.7sh (5.8)			26.0 (2.2)	37.0 (19.3)	11.0
$TiCl_4 \cdot 2Me_2Se$				43.9 (13.6)	23.3 (1.8)	35.3 (24.8)	12.0
$ZrCl_6^{--}$[d])			41.7				
$ZrCl_4 \cdot 2Me_2S$					39.7 (3.5)	$\geqslant$50.0[e])	10
$ZrCl_4 \cdot 2Me_2Se$					34.5sh (2.6)	$\geqslant$50.0[e])	15
					37.5 (3.5)		
$ZrCl_4 \cdot 2Me_2Te$			42.2 (14.6)		29.2 (2.2)	47.4 (30.6)	~18
					33.3 (2.0)		

[a]) The assignments for the hexahalides are respectively: $1t_{1g} \rightarrow 2t_{2g}$, $2t_{1u} \rightarrow 2t_{2g}$, $1t_{2u} \rightarrow 2t_{2g}$, $1t_{1u} \rightarrow 2t_{2g}$ [5].

[b]) $\Delta\nu$: energy difference between the first and the second chalcogen-metal transitions.

[c]) In acetonitrile [23].

[d]) In acetonitrile [24].

[e]) Transition too energetic to be measured.

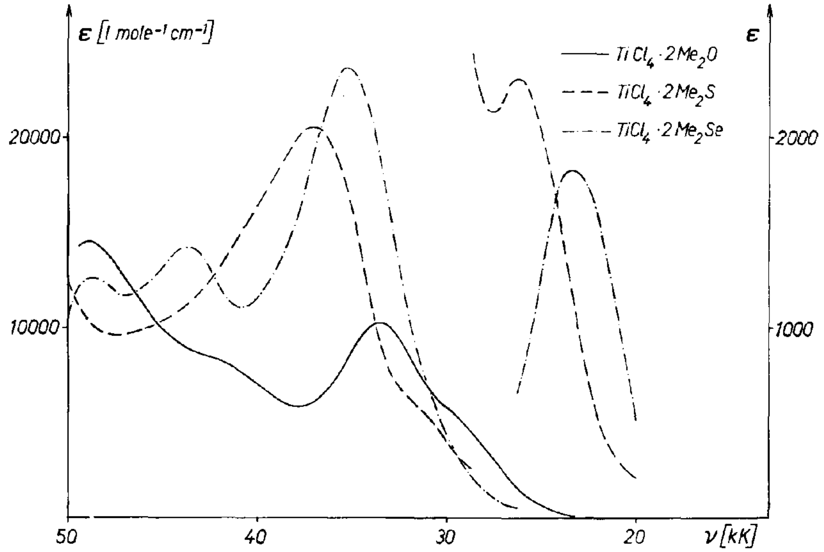

Fig. 4. *Electronic spectra of* $TiCl_4 \cdot 2Me_2O$, $TiCl_4 \cdot 2Me_2S$ *and* $TiCl_4 \cdot 2Me_2Se$ *in* CH_2Cl_2

Me_2Y (Y = O, S, Se, Te) show that in the free ligand the two electron pairs of Y are separated by an energy of around 80 kK [13]. The case a in Fig. 5 may therefore be excluded, and we assume that the two transitions arise from the orbital having essentially p character. The last columns of the Tables 1 to 3 list the observed chalcogen-metal transitions as well as their energy differences $\Delta\nu$ where two bands appear. One sees that these differences are essentially constant for a given metal halide as expected from the case b in Fig. 5. If we interpret the spectra according to this last diagram, the energy difference between the two chalcogen metal transitions is an estimation of 10Dq if one neglects the interelectronic interactions. For $NbCl_6^{2-}$ the d-d transition appears between 15 and 25 kK and for $NbBr_6^{2-}$ between 15 and 20 kK [14]. $TaCl_4 \cdot 2Me_2S$ shows two d-d bands at 15.0 and 21.2 kK [15]. In $TiCl_6^{--}$ the ligand field splitting amounts to 13 kK [16]. These values compare well with our data.

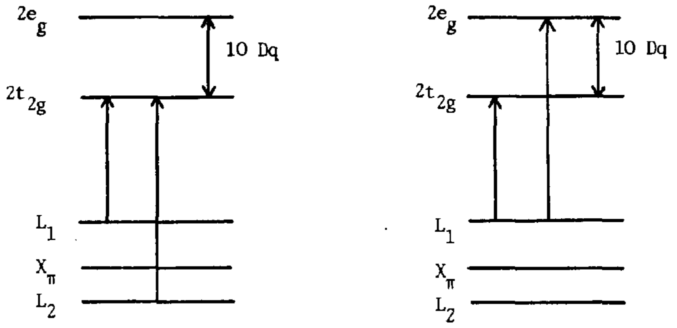

Fig. 5. ***Chalcogen to metal electron transfer in the octahedral adduct of a metal halide with a dialkylchalcogenide: two possible transition diagrams***

3.2. *Ligand ionisation potential and ligand-metal charge transfer energy.* In a molecule having the energy levels i, j and k, the differences between the i → j and j → k transitions are linked to the vertical ionisation potentials I of i and j by the relation (1), assuming the validity of *Koopmans'* theorem [17]. Neglecting

$$[\Delta E(j \rightarrow k) - \Delta E(i \rightarrow k)] - [I(i) - I(j)] = J_{ik} - J_{jk} + 2(K_{jk} - K_{ik}) \qquad (1)$$

the *Coulomb* and exchange integrals, J and K, we obtain the relation (2) which can be used, in a first approximation, to assign

$$\Delta E(j \rightarrow k) - \Delta E(i \rightarrow k) = I(j) - I(i) \qquad (2)$$

or estimate the ligand-metal charge transfer energy. In the two complexes $MX_5 \cdot R_2Y_i$ and $MX_5 \cdot R_2Y_j$, I(i) and I(j) are the ionisation potentials of the higher energy free electron pair of R_2Y_i and R_2Y_j. $\Delta E(i \rightarrow k)$ and $\Delta E(j \rightarrow k)$ represent the energy of the transitions $R_2Y_i \rightarrow 2t_{2g}$ (or $2e_g$) and $R_2Y_j \rightarrow 2t_{2g}$ (or $2e_g$). For a given metal halide, if the energy of $2t_{2g}$ (or $2e_g$) is independent of the nature of R_2Y and if the stabilization of the free electron pair of R_2Y by the chalcogen-metal bond is only slightly dependent on R_2Y, relation (2) is valid. In Fig. 6 we report vertical ionisation potential of the free bonding pair of Me_2Y as a function of the chalcogen to metal charge transfer energy. The straight line portions link the representative points of the adducts of the same metal halide. Their slope, close to one, shows that relation (2) applies. Similar diagrams have been described by *Perkampus* [18] for the adducts of $TiCl_4$, $NbCl_5$, and $TaCl_5$ with olefins and aromatic compounds.

Fig. 6 allows us to predict the energy of bands difficult to observe, and it may be used to confirm the interpretation of some spectra. For example, by extrapolating the line corresponding to the adducts of $TaCl_5$ to intersection with the horizontal line representing the ionisation potential of the free electron pair of Me_2O, we obtain an energy of the order of 41 kK for the transition $Me_2O \rightarrow 2t_{2g}$; this explains the appearance of a shoulder at 43.1 kK in the spectrum of $TaCl_5 \cdot Me_2O$. In $TaCl_5 \cdot Et_2O$

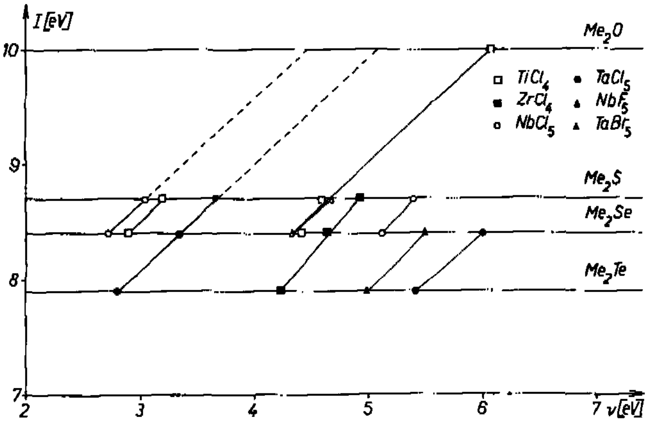

Fig. 6. *Vertical ionisation potential I of Me_2Y (Y = O, S, Se, Te) as a function of the chalcogen to metal charge transfer energy ν in a series of metal halide adducts*

the oxygen-metal electron transfer must be displaced by about 0.5 eV towards lower energy according to the photoelectron spectra of Me_2O and Et_2O [19]. This displacement accounts for the disappearance of the shoulder observed in $TaCl_5 \cdot Me_2O$. For $NbCl_5 \cdot Me_2O$ the $Me_2O \rightarrow 2t_{2g}$ charge transfer should appear around 36.3 kK which is manifested by a broadening, at the high energy side, of the $Cl \rightarrow 2t_{2g}$ transition (Fig. 2), while for $NbCl_5 \cdot Et_2O$, the displacement of the charge transfer transition towards lower energy makes a shoulder appear at 31.3 kK, on the other side of the maximum. In the same way, we predict that the $Me_2O \rightarrow 2e_g$ transition in $TiCl_4 \cdot 2Me_2O$ should be found at about 48 kK, which is confirmed by experiment. It is more difficult to make predictions for the case of the phosphoryl ligands whose photoelectron spectra are more complicated. Based on the difference in the ionization potential between the 5e orbitals of $POCl_3$ and $PSCl_3$ [20], one predicts an energy difference of 14.4 kK between the phosphoryl- and thiophosphoryl-metal transitions; the experimental difference in the case of the adducts $NbCl_5 \cdot OP(NMe_2)_3$ and $NbCl_5 \cdot SP(NMe_2)_3$ being 15.6 kK. In acetonitrile, the first ionization potential associated with the π electrons of the cyano group is 12.12 eV, and the second, due to the lone pair on the nitrogen, amounts to 13.11 eV [21]; we therefore predict an acetonitrile to niobium (V) electron transfer at an energy of the order of 50 kK, and even higher for tantalum (V).

3.3. *Optical electronegativities of the ligands.* In the adducts described the concept of optical electronegativity χ is at the limit of usefulness. For example, we obtain different values for $\chi(Me_2S)$ in the adducts of different metal chlorides with dimethylsulfide: 2.67 (Nb^V), 2.61 (Ta^V), 2.81 (Ti^{IV})[4], 2.93 (Zr^{IV})[4]. Similarly the value of the transitions for the two series of complexes of $NbCl_5 \cdot L$ and $NbF_5 \cdot L$ should be aligned on the same line in Fig. 6, which is far from being the case. The important displacement of the $L \rightarrow M$ transitions towards higher energies in passing from the chloride to the fluoride adducts may be explained if we use relation (3) given in [22]. In this relation the exchange

$$E(L,2t_{2g}) - E(L,L) = E(2t_{2g}) - E(L) + J(L,2t_{2g}) - J(L,L) \qquad (3)$$

integrals have been neglected. For a given ligand L the *Coulomb* integral J(L, L) remains constant whatever the nature of the metal halide. It is possible that E(L) is more stabilized in $NbF_5 \cdot L$ than in $NbCl_5 \cdot L$, the metal-ligand bond being more likely shorter and allowing a better orbital overlap. If the metal halide π bonds are stronger in the pentafluorides than in the pentachlorides, the $2t_{2g}$ acceptor orbital will be higher in $NbF_5 \cdot L$. Finally, if the metal-ligand bond is shortened, $J(L,2t_{2g})$ would have to be larger. It is the sum of these three contributions which may cause the important displacement of the $L \rightarrow M$ transitions towards higher energies in passing from $MCl_5 \cdot L$ to $MF_5 \cdot L$.

With the limitation just discussed in mind we give in Table 4 a series of ligand optical electronegativities calculated from the adducts of niobium (V) and tantalum (V) pentachlorides.

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[4] Calculated with $\chi(Ti^{IV}) = 1.94$ and $\chi(Zr^{IV}) = 1.61$ as obtained from the $1t_{2u} \rightarrow 2t_{2g}$ transition in Table 3, with $\chi(Cl^-) = 3.0$.

Table 4. *Optical electronegativities of a series of ligand L in the adducts $MCl_5 \cdot L$ of niobium(V) and tantalum(V) chlorides*

L	χ(L) in $NbCl_5 \cdot L$	χ(L) in $TaCl_5 \cdot L$
Cl_3PO	3.10	
$(MeO)_3PO$	3.09	
$(Me_2N)_3PO$	3.06	
$(Me_2N)_3PS$	2.54	2.53
$(i\text{-}Pr)_3P$		2.46
Me_2O [a]	3.06	2.99
Et_2O [a]	2.93	2.86
Me_2S	2.67 [b]	2,61
Et_2S	2.65	2.58
Me_2Se	2.58 [b]	2.52
Me_2Te		2.35

[a] See text for the estimation of the $R_2O \rightarrow 2t_{2g}$ transition.

[b] From $NbF_5 \cdot L$ we obtain: $\chi(Me_2S) = 3.10$ and $\chi(Me_2Se) = 3.01$.

4. Preparations. – The purification of $NbCl_5$ and $TaCl_5$ [2], $NbBr_5$ and $TaBr_5$ [4] have been described previously. NbF_5 (*Ozark-Mahoning*) (80°/10^{-1} Torr) and $ZrCl_4$ (*Fluka*) (220°/10^{-5} Torr) were sublimed and kept a few weeks in sealed Pyrex tubes under vacuum. $TiCl_4$, trimethylphosphate and hexamethylphosphoramide (*Fluka*) were distilled twice under vacuum. The ethers, the thioethers and phosphorus oxychloride (*Fluka*) were distilled over sodium. Dimethylselenide and -telluride (*Strem Chemicals Inc.*), tri-isopropylphosphine were used as received. Thiohexamethylphosphoramide was prepared from Me_2NH and PCl_3 to obtain $(Me_2N)_3P$ [25], which was next treated by sulfur [26]. The procedure for the preparation of the solutions of adducts and for recording the spectra, with particular care to avoid hydrolysis products are described in [5].

We are indebted to Dr. *P. Day* and Dr. *W. Ludwig* for helpful discussions. Mr. *D. Zbinden* is thanked for his technical assistance. We acknowledge the support of the *Fonds National Suisse de la Recherche Scientifique* for this work by means of grant 2.218-0.74.

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247. Templat-Reaktionen II. Herstellung von tricyclischen und tetracyclischen Metallkomplexen aus aliphatischen Diaminen und Phenylazo-malondialdehyd-Derivaten

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(6. X. 75)

Template-Reactions II. Syntheses of tricyclic and tetracyclic metal complexes from aliphatic diamines and phenylazo-malondialdehyde-derivatives. *Summary.* A template synthesis of metal complexes with 14- and 16-membered macrocycles **6** resp. **10** has been devised. These compounds are obtained in high yield by the condensation of aliphatic 1,2- or 1,3-diamines with phenylazo-malon- dialdehydes in the presence of divalent metal ions such as Cu(II) and Ni(II). This is the first reported one-step synthesis of tetraaza-annulenes with aliphatic diamines. The formation of the intermediate tricyclic complexes **5** and **9**, obtained either by a template or a nontemplate synthesis, is also described. Ring closure with diamines leads again to **6** and **10** or to asymmetric tetraaza-macrocyclic systems such as **7** or **11**.

Schon 1940 haben *Schwarzenbach & Lutz* [1] gezeigt, dass aus Äthylendiamin und Acetylaceton je nach Versuchsbedingungen anstelle von 1,4-Diazepinen Bis-Enamine bzw. Bis-Azomethine entstehen können, da der intramolekulare Ringschluss zum Siebenring weniger bevorzugt ist als bei den aromatischen 1,2-Diaminen. Aufgrund von früheren Beobachtungen [2] war ferner zu erwarten, dass die Templat-Reaktion zur Bildung von Tetraaza-[14]-annulenen des Typus **6** (*Schema 1*, $R^1 = R^3 = CH_3$; $R^2 = H$) aus Äthylendiamin, Acetylaceton und einem zweiwertigen Metallkation leicht verlaufen sollte. Bekanntlich bleibt aber diese Reaktion auf der Stufe des Tricyclus Bis-(acetylaceton)-äthylendiiminmetal(II) stehen [3], sogar das Kochen in Äthylendiamin als Lösungsmittel führt nicht zum Ziel [4]. Bisher waren solche Macrocyclen (**6**, $R^1 = R^2 = CH_3$, $R^3 = H$) nur über eine mehrstufige Nichttemplat-Synthese zugänglich [4]. Einige Autoren haben aber gezeigt [5–7], dass Metallchelate von verschiedenen β-Ketoaldiminen mit aliphatischen Diaminen wie Äthylendiamin und