4-Äthoxycarbonylaminochinuclidin (**1h**) wurde nach *Fischer & Grob* [6] bzw. *Mikhlina et al.* [8] hergestellt. *Hydroperchlorat*: aus Äthanol Nadeln vom Smp. 218–219°.

$C_{10}H_{19}ClN_2O_6$ (298,72) Ber. C 40,21 H 6,41 N 9,38% Gef. C 40,34 H 6,41 N 9,55%

Die pK_a-Messungen wurden, wie in der vorangegangenen Mitteilung beschrieben, durchgeführt und ausgewertet [1] (vgl. Tab. 1).

Die Verbrennungsanalysen verdanken wir Herrn *E. Thommen*, die NMR.-Spektren Herrn *K. Aegerter*.

LITERATURVERZEICHNIS

[1] *E. Ceppi & C. A. Grob*, Helv. *57*, 2332 (1974).

[2] *C. A. Grob, W. Simon & W. D. Treffert*, Angew. Chem. *85*, 310 (1973).

[3] *E. Ceppi, W. Eckhardt & C. A. Grob*, Tetrahedron Letters *1973*, 3627.

[4] *C. A. Grob & P. Brenneisen*, Helv. *41*, 1184 (1958).

[5] *J. Paleček & J. Hlavatý*, Coll. Czechoslov. chem. Commun. *38*, 1985 (1973).

[6] *H. P. Fischer & C. A. Grob*, Helv. *51*, 153 (1968).

[7] *C. A. Grob & K. Kostka*, Helv. *53*, 613 (1970).

[8] *E. E. Mikhlina, N. A. Komarova & M. V. Rubtsov*, Chemistry of Heterocyclic Compounds, Vol. 5, 210 (1969).

---

255. Electron Transfer Spectra of the Hexachloro- and Hexabromoniobate(V) and Tantalate(V) Anions[1]

by **Mario Valloton** and **André E. Merbach**

Institut de chimie minérale et analytique, 3, Place du Château, 1005 Lausanne

(4. IX. 74)

Summary. The electron transfer spectra of the hexachloro- and hexabromoniobate(V), and -tantalate(V) anions are investigated with particular care to avoid hydrolysis products. New interpretations are given, and the optical electronegativities χ of Nb(V) and Ta(V) are recalculated. The difference between both χ values is 0.2, in better agreement with the differences observed for metals of the second and third transition series.

1. Introduction. – During the past few years a series of papers have been published by our group dealing with the NMR. study of the structure, the relative stability and the kinetic behaviour of adducts of niobium(V) and tantalum(V) halides with Lewis bases[2]. Preliminary to a study of the charge transfer spectra of these compounds we consider it necessary to reinvestigate the hexahalides of niobium(V) and tantalum(V). The published data [2–4] for these compounds are not consistent in reason of their great sensitivity to humidity.

For these systems MO theory gives the energy level diagram reproduced in Fig. 1. The relative energies of the ligand π levels has led for a long time to controversy [5–7]. For large internuclear distances the twelve halogen π orbitals remain degenerate; however, in general, the complex is contracted enough so that the degeneracy is lifted. Two reasons account for the splitting of the π levels. Firstly the central atom forms binding molecular orbital with the halides; secondly, the ligand-

---

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

[2] This paper is to be considered as part X of the series. Part IX: see [1].

ligand interactions stabilize the linear combinations of the ligand π orbitals which have the least angular nodal planes [8]. Moreover, one must also take into account the fact that t_{1u} is the only type of symmetry common to the σ and π orbitals. This implies a destabilisation of the $2t_{1u}$ orbitals, which possess a non-negligible σ contribution. Finally, *Henning et al.* [7] have shown by measurements of the *Faraday* effect that in $IrCl_6^{--}$ the order of the energy of the π levels is the following:

$$\pi t_{1g} > (\pi + \sigma)t_{1u} > \pi t_{2u} > \ldots (\sigma + \pi)t_{1u}.$$

In the hexabromides it is necessary to take into account the effects of spin-orbit coupling. The splitting of the twelve halogen π orbitals has been studied in depth by *Jørgensen* [2] [5] [6]. Group theory shows that only the orbitals of t_1 and t_2 symmetry are split by spin-orbit coupling. The question is now to express the energy of the levels resulting from the spin orbit-coupling splitting with respect to unsplit levels as a function of the *Landé* parameters of the ligand and of the metal. We know

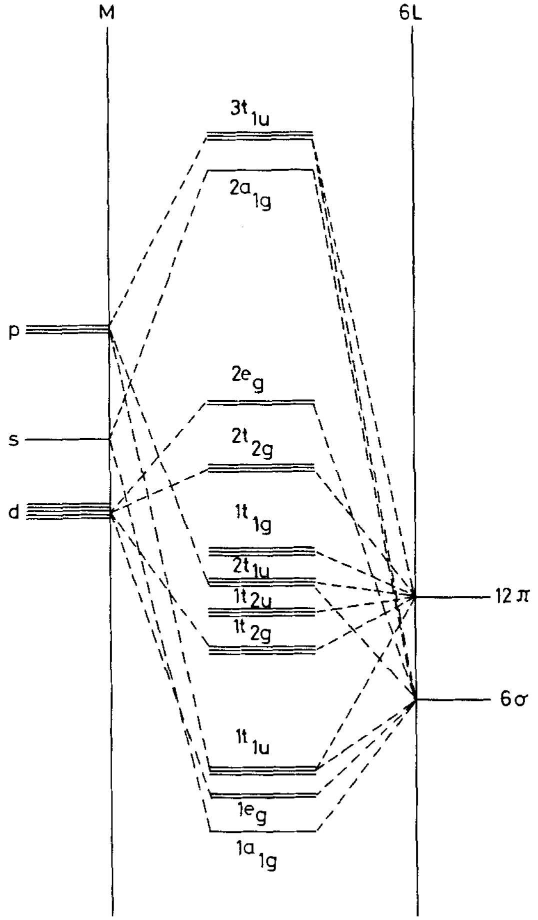


Fig. 1. *Molecular orbital diagram for an octahedral* MCl_6 *complex*

that for the metal $2t_{2g}$ level, a $t_{2g}{}^{q}$ configuration behaves as a function of ζ_{nd} in the same way that p^{6-q} varies as a function of ζ_{np} [10]. Thus $2t_{2g}$ is split into $3u'_g$ at $-{}^1/_2\zeta_{nd}$ and $2e''_g$ at $+\zeta_{nd}$. In a general way by reason of the nephelauxetic effect ζ_{nd} is smaller in a complex than in the corresponding free ion. The $2t_{2g}$ molecular orbital comes from a linear combination of the metal atomic and the halide orbitals. The spin-orbit coupling of the latter must therefore influence that of $2t_{2g}$ and it is expected that this spin-orbit splitting will be more pronounced in the hexabromides of Nb(V) and Ta(V) than in the corresponding hexachlorides.

The splitting of the $1t_{2g}$, $1t_{2u}$, $2t_{1u}$ and $1t_{1g}$ levels is principally due to the contribution of the ligand's spin-orbit coupling. The *Landé* parameters for the neutral gaseous atoms are:

$$\text{Cl: } \zeta_{3p} = 0.59\ \text{kK} \quad \text{Br: } \zeta_{4p} = 2.46\ \text{kK}. \tag{1}$$

The spectrum of $NbCl_6^-$ shows that the energy difference between the $1t_{1u}$ and $2t_{1u}$ levels is of the order of 10 kK. This difference is clearly greater than the *Landé* parameters for chlorine and bromine. For this case *Jørgensen* [11] has shown the following splitting of the levels in the hexahalide complexes

$$\begin{array}{llll} & u' \text{ at } +{}^1/_4\zeta_{np} & & e'' \text{ at } +{}^1/_2\zeta_{np} \\ t_1: & & t_2: & \\ & e' \text{ at } -{}^1/_2\zeta_{np} & & u' \text{ at } -{}^1/_4\zeta_{np}. \end{array} \tag{2}$$

The effective value of ζ_{np} has to be estimated for each split level. For $1t_{1g}$ and $1t_{2u}$ which are not bonding, ζ will be close to the value given in (1). For $1t_{2g}$ there will be a contribution from the metal d orbitals of corresponding symmetry. For $2t_{1u}$, the metal p orbitals may theoretically have an influence. However, in reason of the great energy difference between the components of the molecular orbital, this influence will be small[3]. The σ contribution in $2t_{1u}$ $(\pi + \sigma)$ diminishes the spin-orbit coupling of this level, because the σ orbitals are not split [12].

The splitting of the ligand π levels in $IrBr_6^{--}$ has been determined from the electronic spectrum of this compound measured at 4 K [9]. The energy difference between the two levels arising from spin-orbit coupling is 1.78 kK for $1t_{1g}$ and 1.08 kK for $2t_{1u}$. We can see that for non-bonding levels, ζ_{np} is close to the value given in (1). The smaller value in $2t_{1u}$ is due to a σ contribution.

2. Results and discussion. – 2.1 *The hexachlorides.* Et_4NNbCl_6 and Et_4NTaCl_6 were first prepared by *Adams et al.* [13], and their IR. and *Raman* spectra are well known [14] [15]. The existence of $NbCl_6^-$ in acetonitrile has been shown by conductivity [12], and the UV. spectra of $NbCl_6^-$ and $TaCl_6^-$ was studied by different authors in the same solvent [2–4]. The UV. spectrum of $CsNbCl_6$ was also known [16]. We prepared $NbCl_6^-$ and $TaCl_6^-$ by reaction of the pentachloride with Et_4NCl in acetonitrile. The energies and the assignment of the electron transfer bands are compared in Table 1 and our spectra are given in Fig. 2.

---

[3] Recent high resolution MCD work by *Schatz et al.* [24] suggests that in several hexahalides the $2t_{1u}$ orbital may be split more than was previously thought, probably as a result of mixing in $(n + 1)p$ on the central metal.

Table 1. *Electronic absorption spectra and assignements of the hexachloroniobate (V) and -tantalate (V) anions in acetonitrile* (energies in kK, and $\varepsilon_{max} \cdot 10^{-3}$ in parentheses)

		$1t_{1g} \rightarrow 2t_{2g}$	$2t_{1u} \rightarrow 2t_{2g}$	$1t_{2u} \rightarrow 2t_{2g}$	$1t_{1u} \rightarrow 2t_{2g}$	Unassigned
$NbCl_6^-$	*Jørgensen*[a] [2]	31.5 sh	43.5	35.5		
	Jørgensen[a] [6]	31.5 sh	35.5	43.5		
	Furlani[b] *et al.* [3]	28.2 sh (4.0)	31.6 sh (15.5)	34.3 (39.8)	41.5 (10.0)	48.8 (12.0)
	Brisdon et al. [4]	28.7 sh (<2.0)	31.7sh (<15.0)	34.2 (37.5)	41.7 (8.8)[c]	
	Our values	28.9 sh (<2.0)	31.8 sh (11.4)	34.5 (28.9)	41.4 (6.4)	
$TaCl_6^-$	*Brisdon et al.* [4]	29.9 sh (vw); 31.8 (<2.0)	34.9 (<9.0)	38.0 (40.0)		41.3 (50.0)
	Our values	34.8 (5.8)	38.0 (23.8)	41.5 (38.0)	49.5 (11.0)	

[a] Same experimental data, assigned before and after *Henning et al.* work on $IrCl_6^{2-}$ [7].

[b] Spectrum unassigned by *Furlani et al.*

[c] Band unassigned by *Brisdon et al.*

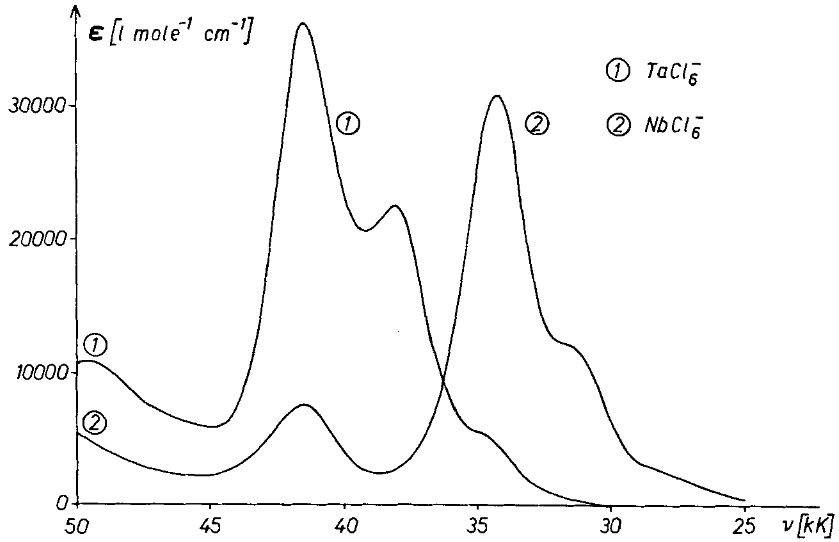


Fig. 2. *Absorption spectra of* $NbCl_6^-$ *and* $TaCl_6^-$ *in acetonitrile*

In the hexachlorides the ligand-ligand interaction is not the only possible reason for the multiplicity of the $\pi \rightarrow t_{2g}$ transitions. The excited configurations give rise to several states, but only the transition towards the $^1T_{1u}$ state are symmetry and spin allowed [3–5]. Moreover since the two unpaired electrons lie on two different atoms, the states coming from a same excited configuration will have almost the same energy [6]. In the case of $NbCl_6^-$ our results agree well with those of *Furlani et al.* [3] and *Brisdon et al.* [4]; the band measured at 48.8 kK in [3] is due to the partial hydrolysis of the complex [18].

In the case of $TaCl_6^-$ we made the same observation as *Brisdon et al.* [4], except for two transitions of low energies and intensities ($\varepsilon < 2000$) described by these authors, which did not appear in our spectra. Our assignments are different: the most intense band of the spectra is assigned to $1t_{2u} \rightarrow 2t_{2g}$ by analogy with $NbCl_6^-$; *Brisdon et al.* left this band unassigned.

Until now the most energetic band of the spectra of $NbCl_6^-$ and $TaCl_6^-$ has not been discussed. One can think of the transfer of a ligand π electron to $2e_g$, or to the transition $1t_{1u} \rightarrow 2t_{2g}$. In the first alternative the energy difference between the transitions $\pi \rightarrow 2t_{2g}$ and $\pi \rightarrow 2e_g$ is equal to 10 Dq, if one assumes that the *Coulomb* integrals $J(\pi, 2t_{2g})$ and $J(\pi, 2e_g)$ are equivalent and if the exchange integrals are neglected. To evaluate 10 Dq one must also know from which ligand π level the electron is excited in the $\pi \rightarrow 2e_g$ charge transfer. The transfer $1t_{1g} \rightarrow 2e_g$ can be excluded on the basis that the $\pi \rightarrow 2e_g$ transitions are less intense than $\pi \rightarrow 2t_{2g}$ [12]. The intensity of $2t_{1u}(\pi + \sigma) \rightarrow 2e_g$ is difficult to predict, the σ and π contribution calling respectively for an increase and a decrease of intensity with respect to $2t_{1u}(\pi + \sigma) \rightarrow 2t_{2g}$. If we assign the most energetic band of Fig. 2 to $2t_{1u} \rightarrow 2e_g$ we obtain 10 Dq values of 9.6 kK for $NbCl_6^-$ and 10.4 kK for $TaCl_6^-$. These are too small in comparison with the d–d transitions in the hexachloroniobate(IV) which appears around 20 kK [19]. The assignment of this band to $1t_{2u} \rightarrow 2e_g$ would give still smaller values for 10 Dq. Moreover we have shown that in the octahedral adduct of $NbCl_5$ and $TaCl_5$ the ligand field splitting is of the order of 20 kK [22].

The second alternative, $1t_{1u} \rightarrow 2t_{2g}$, seems more plausible. An energy difference between the ligand σ and π orbitals of 10 to 15 kK is generally observed from the electron transfer spectra [6]. On the other hand, the band intensity agrees with the fact that $\sigma \rightarrow 2t_{2g}$ is less intense than $\pi \rightarrow 2t_{2g}$ [12]. The experiment confirms the predicted order of intensities:

$$1t_{2u} \rightarrow 2t_{2g} > 2t_{1u}(\pi + \sigma) \rightarrow 2t_{2g} > 1t_{1u}(\sigma + \pi) \rightarrow 2t_{2g}.$$

Table 2. *Electronic absorption spectra of the hexabromoniobate (V) and -tantalate (V) anions in acetonitrile* (energies in kK, and $\varepsilon_{max} \cdot 10^{-3}$ in parentheses)

$NbBr_6^-$:	*Furlani et al.*[a]) [2]	21.5 sh (0.4) $[3u'_g \rightarrow t_{2g}]$; 23.8 sh (1.6) $[3u'_u \rightarrow 2t_{2g}]$; 26.7 (10.0) $[e''_u \rightarrow 2t_{2g}]$; 29.0 (20.0 $[2u'_u \rightarrow 2t_{2g}]$; 37.6 (20.0) $[3u'_u \rightarrow 2e_g]$; 45.8 (50.1) $[2u'_u \rightarrow 2e_g]$
	Brisdon et al.[b]) [3]	17.1 sh ($\gtrsim$0.1) and 20.0 sh (<1.0) $[3u'_g \rightarrow 2t_{2g}]$; 23.0 (3.1) $[3u'_u \rightarrow 2t_{2g}]$; 27.0 sh (<7.0) $[e''_u \rightarrow 2t_{2g}]$; 28.8 (10.0) $[2u'_u \rightarrow 2t_{2g}]$; 32.9 (4.1); 36.2 (5.3)
	Brisdon et al.[c]) [3]	17.0 (vw); 21.0 sh (<7.0); 22.6 (11.8); 26.9 (30.0); 35.3 (10.5); 43.7 (23.6)
	Our values[d])	17.0 (0.3); 21.3 (3.8); 22.8 (6.3); 27.2 (29.4); 35.7 (6.5)
$TaBr_6^-$:	*Brisdon et al.*[b]) [3]	22.2 (<0.45) $[3u'_g \rightarrow 2t_{2g}]$; 26.1 (8.2) $[3u'_u \rightarrow 2t_{2g}]$; 29.8 sh (20.0) $[e''_u \rightarrow 2t_{2g}]$; 31.9 (43.0) $[2u'_u \rightarrow 2t_{2g}]$; 33.6 (38.0); 36.9 (vw)
	Brisdon et al.[c]) [3]	22.2 (<3.0); 25.8 (8.0); 30.0 sh (<18.0); 31.7 (36.0); 33.0 (32.0)
	Our values[d])	22.7 (0.7); 26.0 (7.9); 29.8 sh (15.0); 32.0 (34.7); 33.6 (32.5); 41.7 (6.8)

[a]) Assignements of *Jørgensen* [6].
[b]) With excess bromide.
[c]) Without excess bromide.
[d]) Assignements: see text and Fig. 3.

The fact that the second allowed transition is more intense than the first one indicates that $2t_{1u}$ is more energetic than $1t_{2u}$. The order of the ligand energy levels is the same as found by *Henning et al.* [7] for $IrCl_6^{--}$.

2.2 *The hexabromides.* Et_4NNbBr_6 and Et_4NTaBr_6 were prepared [4] [20] and the IR. and *Raman* spectra studied [14]. Their electron transfer spectra were measured in acetonitrile [3] [4]. Our experimental results are compared with the latter in Table 2, and our spectra are given in Fig. 3. The assignments will be discussed later.

In the case of $NbBr_6^-$ only the spectra of *Brisdon et al.* measured without excess of bromide are comparable to ours. *Furlani et al.* recognize that Et_4NNbBr_6 is especially air sensitive and that $NbOBr_5^{--}$ is often present in solution; according to these authors the spectra of fresh solutions of $NbBr_6^-$ in CH_3CN distilled several times over P_2O_5 and Na_2CO_3 are reproducible and change slowly towards $NbOBr_5^{--}$ which has the following bands:

ν [kK]	26.7	29.8	32.8	45.8
ε [l mol^{-1} cm^{-1}]	1600	5000	9000	3200

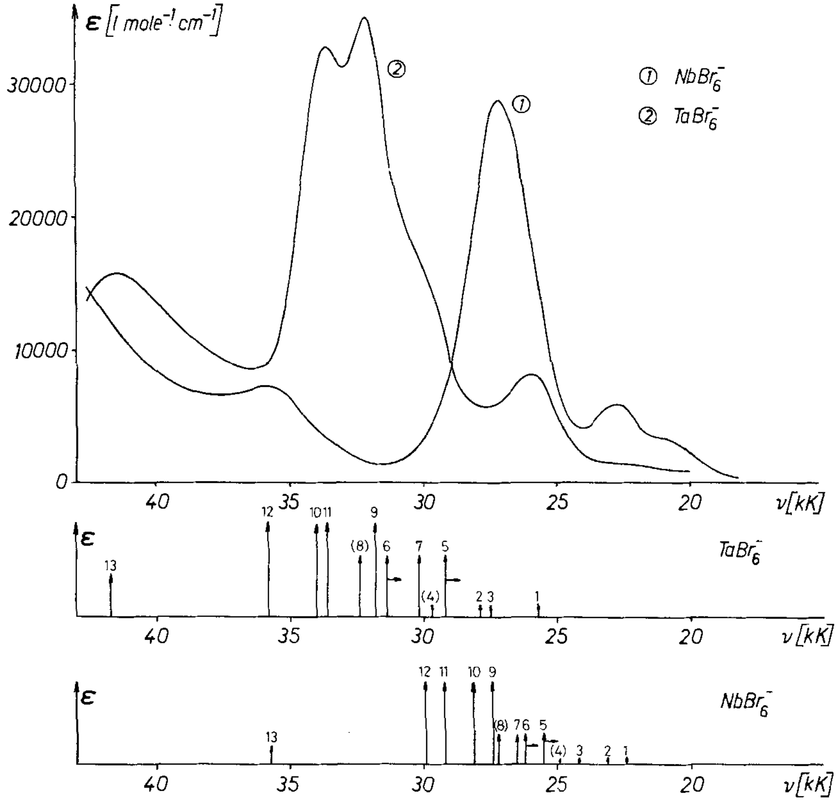


Fig. 3. *Absorption spectra of $NbBr_6^-$ and $TaBr_6^-$ in acetonitrile.* At the bottom: predicted transitions from the semi-quantitative diagram of Fig. 5

Brisdon et al.'s results differ whether or not there is an excess of bromide. They discarded the values without excess bromide thinking that there was a reaction with the solvent in this case. Our spectra with or without excess of bromide are identical to that obtained by *Brisdon et al.* without excess of bromide. As a function of time our spectra change: the large band at 27.1 kK diminishes in intensity, when the band observed by *Furlani* & *Brisdon* at 29.0 kK appears and increases (Fig. 4). The band at 35.6 kK diminishes and those at 38.2 and 33.0 kK appear. The entire spectrum changes towards those supposed by these authors to be the spectrum of $NbBr_6^-$; in other words it is changing towards that of $NbOBr_5^{--}$. The older assignments of Table 2 lose their interest because they concern spectra of partially decomposed $NbBr_6^-$. Unfortunately *Brisdon et al.* did not use the spectrum measured without excess bromide which was less decomposed than the spectrum retained for interpretation.

In the case of $TaBr_6^-$ we observed no decomposition and our results are the same as those of these authors independent of the excess of bromide.

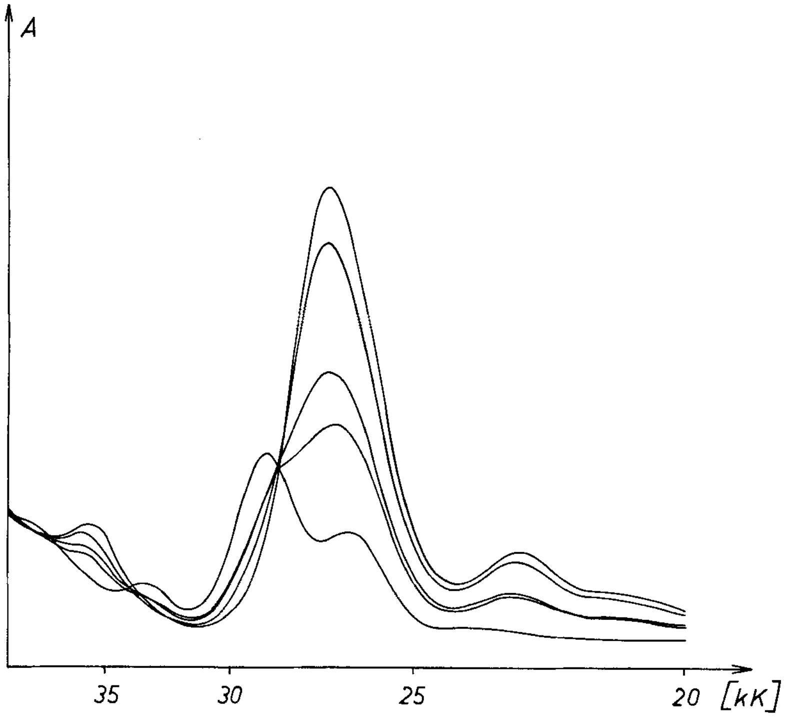


Fig. 4. *Evolution of the* $NbBr_6^-$ *spectrum as a function of time*

The interpretation of the spectra of $NbBr_6^-$ and $TaBr_6^-$ is complicated by splitting of the levels due to spin-orbit coupling. In Fig. 5 we have built up a semi-quantitative energy level diagram for these complexes. As a first step we have determined the shift of the ligand levels with respect to the metal level when passing from the hexa-

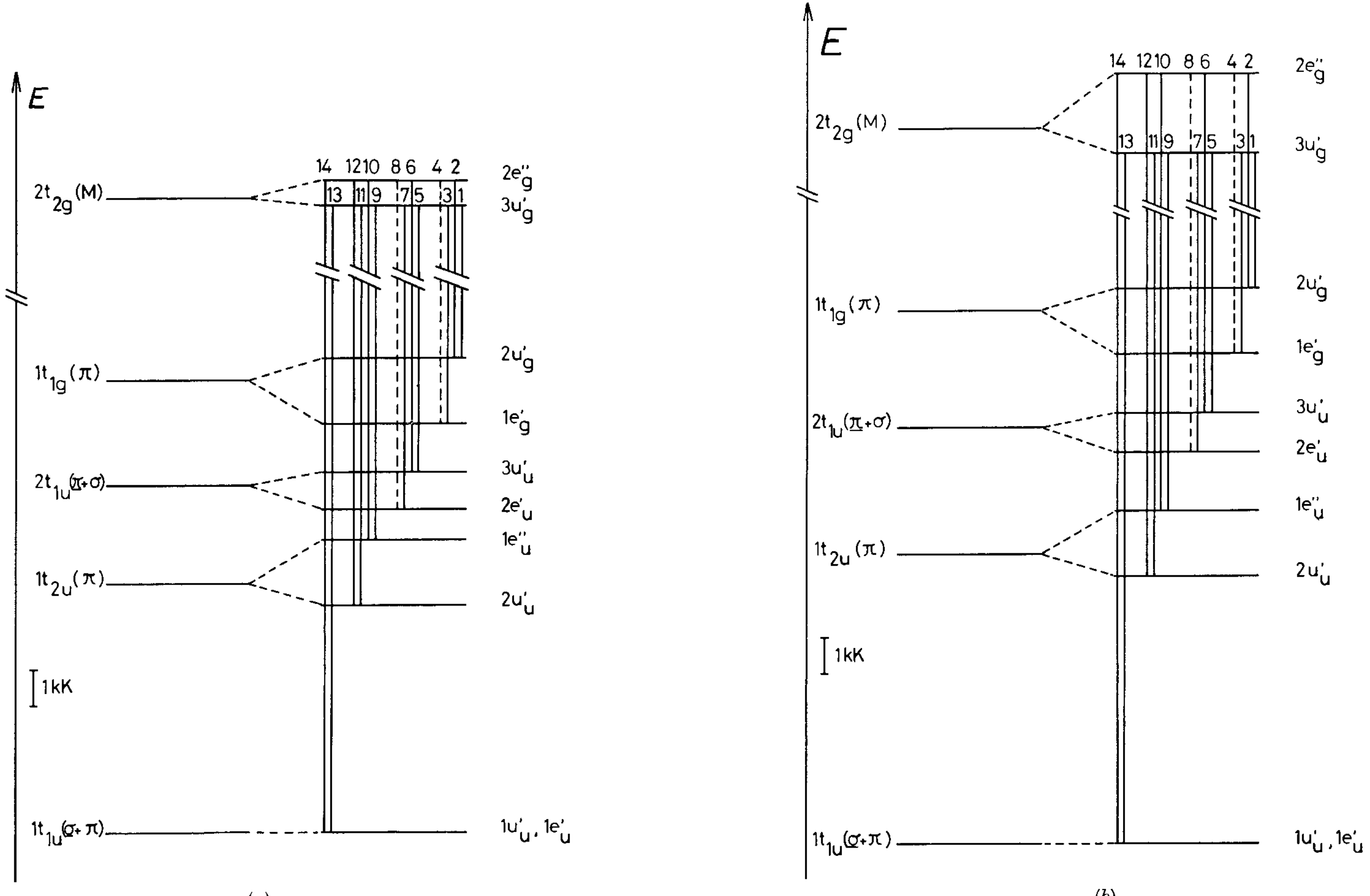


Fig. 5. *Semi-quantitative description of the electron transfer transitions in* $NbBr_6^-$ *(a) and* $TaBr_6^-$ *(b).* Transitions 4 and 8 are symmetry forbidden

chloride to the hexabromide. This shift can be obtained from the optical electronegativities of Cl^- and Br^-. But we prefered to use the experimental energy difference between the transition $1t_{1u} \rightarrow 2t_{2g}$ in MCl_6^- and MBr_6^- (M = Nb, Ta), for a given metal. Moreover the $1t_{1u}$ level, essentially σ bonding, is not split by spin-orbit coupling and can be considered as non-bonding owing to the great energy of the metal p orbitals. The energy shift amounts to 5.7 kK for Nb and to 8.0 kK for Ta, in good agreement with the difference in optical electronegativities for Cl^- and Br^-. For the ligand π levels it is known that the ligand-ligand interactions are equivalent in the hexachloride and hexabromide complexes [5]. Moreover we assume that the stabilisation of $1t_{1u}$, $2t_{1u}$ and $1t_{2g}$ is similar in both compounds and that the same is true for the destabilisation of $2t_{2g}$. All the ligand levels are therefore shifted by the same amount on going from MCl_6^- to MBr_6^-.

The spin-orbit coupling must now be considered. In the ground state no level is split for these d° complexes: the levels are either filled or empty. In the excited state however one electron is lacking in a ligand level and an electron is present in $2t_{2g}$. Hence these two levels are split by spin-orbit-coupling, which gives rise to four possible transitions. The amount of splitting of the $1t_{2g}$, $1t_{2u}$ and $2t_{1u}$ levels was obtained from the expressions (2) and from the results of *Bird et al.* [9]. The empirical *Landé* equation [10] gives for ζ_{nd} of the Nb^{4+} and Ta^{4+} isolated ions: 0.84 kK and 2.38 kK respectively. Experimentally one obtains 0.5 kK for the free Nb^{4+} ion [23]. As a first approximation we use this latter value to estimate the splitting of $2t_{2g}$ in $NbBr_6^-$. We recall that ζ_{nd} should be smaller in the complex than in the free ion and that in the case of $2t_{2g}$, this parameter is influenced by the spin-orbit coupling of the ligand. Due to the lack of an experimental value of ζ_{5d} for Ta^{5+}, we have used the empirical *Landé* value multiplied by the ratio ζ_{4d} (measured)/ζ(calculated) for Nb^{4+}.

The transition energies predicted according to the discussed assumptions are reported at the bottom of Fig. 3 in order to be compared with the experimental spectra. The reported intensities are similar to those observed for the same transitions in the hexachlorides. The great number of theoretically possible transitions show that it is illusory to propose too precise assignments. The first shoulder and the first peak of $NbBr_6^-$ arise from the transitions $1t_{1g} \rightarrow 2t_{2g}$ and $2t_{1u} \rightarrow 2t_{2g}$ respectively. The overlap of these two types of transitions is greater than expected. It is probably due to a destabilisation of $3u'_u$ through interaction with $2u'_u$ of the same symmetry which induces a shift of bands 5 and 6 towards lower energies. The most intense band is assigned to $1t_{2u} \rightarrow 2t_{2g}$. In the case of $TaBr_6^-$, the first peak is attributed to $1t_{1g} \rightarrow 2t_{2g}$ with probably some contribution of $2t_{1u} \rightarrow 2t_{2g}$. The large shoulder comes mainly from the latter transition, when the two intense peaks have essentially $1t_{2u} \rightarrow 2t_{2g}$ for origin. The fact that the predicted energies are a little too high may come from possible stronger ligand-ligand interactions in the hexabromides than in the hexachlorides.

The general aspect of these spectra shows that the spin-orbit coupling is less important in $NbBr_6^-$ than in $TaBr_6^-$. In fact, surprisingly, the spectra of $NbBr_6^-$ is not more complicated than that of $NbCl_6^-$. By looking to the spin-orbit coupling for each level separately we have assumed that the transitions with spin change were allowed; this is particularly true when the coupling is important. It may be possible that in the hexabromides, especially in $NbBr_6^-$, these transitions remain partially forbidden which simplifies the spectrum[4]).

Jørgensen [6] suggested assigning the transitions of the $NbBr_6^-$ spectrum with energies higher than 30 kK to transfer of electrons from ligand π levels to $2e_g$. This assignment which implies a 10 Dq value of about 12 kK can be excluded. Indeed the d–d transitions appear between 15 and 20 kK in $NbBr_6^{--}$ [19] and the spectrum of the octahedral adduct $NbBr_5 \cdot Me_2Se$ shows a 10 Dq of the order of 17 kK [22]. One expects therefore to find the $2t_{1u} \rightarrow 2e_g$ transition between 40 and 50 kK for $NbBr_6^-$ and $TaBr_6^-$. A band is effectively observed around 48 kK for $NbBr_6^-$. The exact location cannot be known precisely, the bromide absorbing in this region. This transition is intense ($\varepsilon > 10^4$), which indicate the importance of the σ contribution in $2t_{1u}$.

2.3 *Optical electronegativities.* The optical electronegativities χ of niobium(V) and tantalum(V) can be calculated from the spectra of their hexachlorides [6] [17]. Before the measurements of *Henning et al.* [7] the first parity allowed transition was used for the calculation. Knowing now that $2t_{1u}$ is higher in energy than the nonbonding $1t_{2u}$, it is better to use the second parity allowed transition[5]) for the calculation. There are two reasons for the discrepancies between ours and the published χ values (Table 3). Firstly the previous calculations used the first allowed transition, secondly some assignments and experimental results are questionable. The characteristic of our values is a greater difference between the optical electronegativities of niobium and tantalum. This difference of about 0.2 is more consistent with that usually observed when passing from the second to the third series of transition elements. In the octahedral 1:1 adduct of $NbCl_5$ and $TaCl_5$ with dimethylsulfide and -selenide, the chalcogen-metal charge-transfer is shifted by 5 kK from Nb(V) to Ta(V). This implies a difference of 0.17 in χ values [22]. *Knox & Brown* [19] observed in the spectra of $Nb(NCS)_6^-$ and $Ta(NCS)_6^-$ a shift of 4.7 kK by changing the metal, which corresponds to a $\Delta\chi$ of 0.16.

Table 3. *Optical electronegativities of niobium (V) and tantalum (V)*

	Jørgensen [6]	*Brisdon et al.* [4]	Our values
Niobium (V)	1.85	1.94	1.85
Tantalum (V)	1.80	1.84	1.62

Although it is difficult to locate precisely the $1t_{2u} \rightarrow 2t_{2g}$ transition in the hexabromides it is interesting to estimate the $\chi(M^{+5})$ values using $\chi(Br^-)$ equal to 2.8.

---

[4]) One can predict that in MCl_6^- only the symmetry allowed transitions $^1A_{1g} \rightarrow T_{1u}$ will be intense. If the spin-orbit coupling is small in the complex, only $^1A_{1g} \rightarrow {}^1T_{1u}$ will be important, $^1A_{1g} \rightarrow {}^3T_{1u}$ being spin forbidden. The state $^1T_{1u}$ being unsplit ($S = 0$), the spectrum is simple. If the spin-orbit coupling becomes more important then the intensity of $^1A_{1g} \rightarrow {}^3T_{1u}$ increases, $^3T_{1u}$ being split ($S = 1$), the spectrum is more complex.

[5]) Strictly speaking, the optical electronegativity should be calculated for each ligand orbital separately and referred to the baricentre of each excited configuration.

Taking 27.2 kK and 33 kK for the energy of the $1t_{2u} \rightarrow 2t_{2g}$ transition in the hexabromides we obtain respectively: $\chi(Nb^{+5}) = 1.89$ and $\chi(Ta^{+5}) = 1.70$.

The transition $1t_{1u} \rightarrow 2t_{2g}$, visible in the four spectra, allows us to calculate χ_σ for the chloride and bromide:

$\chi_\sigma(Cl^-)$:	3.23 (Nb)	3.27 (Ta)
$\chi_\sigma(Br^-)$:	3.04 (Nb)	3.01 (Ta)

In these last calculations we used the $\chi(M^{5+})$ values obtained in the chlorides which are more precisely known.

Experimental Part

The work in dry atmosphere, the preparation of the solutions, the purification of $NbCl_5$, $TaCl_5$ and acetonitrile are described in [21]. The purification of $NbBr_5$ and $TaBr_5$ is given in [1]. $Et_4NCl \cdot 5H_2O$ and Et_4NBr (*Fluka*, purum) were dried over $MgSO_4 \cdot 2H_2O$ in chloroform, and recrystallised in the same solvent. Microcells UV-O2 of *Research and Instruments* Co. provided with teflon UV-OTA spacers of 7.10^{-4} to 10^{-1} cm thickness were used. To exclude decomposition due to unavoidable traces of impurities (especially water) in the solvent, the concentration of the complexes were higher than 10^{-2} M. Before each measurement, the cells were dried one hour under 10^{-2} mmHg and introduced under vacuum in the dry box. The spectrometers *Beckmann* DB-G, DB-GT and ACTA V were used.

We are indepted to Dr. *W. Ludwig* for discussions and helpful advice on the interpretation of the spectra. We thank Mr. *D. Zbinden* for technical assistance. We acknowledge the generous support of the *Fonds national suisse de la recherche scientifique* through grant 2.0490.73.

REFERENCES

[1] *R. Good & A. E. Merbach*, Helv. *57*, 1192 (1974).
[2] *C. K. Jørgensen*, Halogen Chemistry *1*, 265 (1967).
[3] *C. Furlani & E. Zinato*, Z. anorg. allgem. Chem. *351*, 210 (1967).
[4] *B. J. Brisdon, G. W. A. Fowles, D. J. Tidmarsh & R. A. Walton*, Spectrochim. Acta *25A*, 999 (1969).
[5] *C. K. Jørgensen & W. Preetz*, Z. Naturforsch. *22a*, 945 (1967).
[6] *C. K. Jørgensen*, Progress inorg. Chemistry *12*, 101 (1970).
[7] *G. N. Henning, A. J. McCaffery, P. N. Schatz & P. J. Stephens*, J. chem. Physics *48*, 5656 (1968).
[8] *D. S. McClure*, Solid State Physics *9*, 399 (1959).
[9] *B. D. Bird, P. Day & E. A. Grant*, J. chem. Soc. A *1970*, 100.
[10] *C. K. Jørgensen*, Orbitals in Atoms and Molecules, Academic Press London 1962.
[11] *C. K. Jørgensen*, Structure and Bonding *1*, 3 (1966).
[12] *C. K. Jørgensen*, Mol. Physics *2*, 309 (1969).
[13] *D. M. Adams, J. Chatt, J. M. Davidson & J. Geratt*, J. chem. Soc. *1963*, 2189.
[14] *I. R. Beattie, T. R. Gilson & G. A. Ozin*, J. chem. Soc. A *1968*, 2765.
[15] *W. van Bronswyck, R. J. H. Clark & L. Maresca*, Inorg. Chemistry *8*, 1395 (1969); *T. L. Brown, W. G. NcDugle & L. G. Kent*, J. Amer. chem. Soc. *92*, 3645 (1970); *J. E. D. Davies, D. A. Long*, J. chem. Soc. A *1971*, 1273.
[16] *S. M. Horner & S. Y. Tyree*, Inorg. nuclear Chemistry Letters *1*, 43 (1965); *S. M. Horner, R. J. H. Clark, B. Crociani, D. B. Copley, W. W. Horner, F. N. Collier & S. Y. Tyree*, Inorg. Chemistry *7*, 1859 (1968).
[17] *A. B. P. Lever*, Inorganic Electronic Spectroscopy, Elsevier Publishing Company, Amsterdam 1968.
[18] *C. Miranda, M. da Silveira & J. Vernois*, J. Inorg. nucl. Chemistry *32*, 839 (1970).
[19] *G. W. A. Fowles, D. J. Tidmarsh & R. A. Walton*, Inorg. Chemistry *8*, 631 (1969).
[20] *D. Brown, G. W. A. Fowles & R. A. Walton*, Inorg. Syn. *12*, 225 (1970).

[21] *A. Merbach & J. C. Bünzli,* Helv. *54,* 2543 (1971).
[22] *A. Merbach, R. Good & M. Valloton,* Proceedings of the XVth International Conference on Coordination Chemistry, June 25–30 *1973,* Vol. II, p. 478; *M. Valloton, E. Turin & A. E. Merbach,* Part XI of this series to be submitted to this journal.
[23] Gmelins Handbuch der anorganischen Chemie No 49, Verlag Chemie, Weinheim 1970.
[24] *W. H. Inskeep, R. W. Schwartz & P. N. Schatz,* Mol. Phys. *25,* 804 (1973); *J. C. Collingwood, R. W. Schwartz & P. N. Schatz,* Mol. Physics *27,* 1291 (1974).

---

256. Synthese von Pyrimido[1,2-*a*]benzimidazolen durch Umsetzung von 2-Aminobenzimidazol mit Acetylendicarbonsäure-dimethylester und ihre Überführung in Imidazo[1,2-*a*]benzimidazole

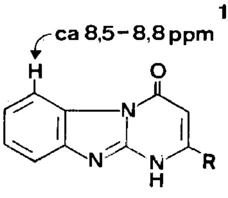
von **Franz Troxler** und **Hans Peter Weber**

Sandoz AG, Pharma-Departement, Chemische Forschung, Basel, Schweiz

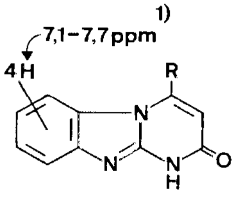
(23. VIII. 74)

Summary. The main product of the reaction between 2-aminobenzimidazole and dimethyl acetylenedicarboxylate is shown to be methyl 1,2-dihydro-2-oxo-pyrimido[1,2-*a*]benzimidazole-4-carboxylate (**6**), which can be methylated at position 1 to give **7**. Catalytic hydrogenation of **7** leads to the 1,2,3,4-tetrahydro derivative **8**, whereas $NaBH_4$ reduces the ester and, to some extent, the double bond to yield a mixture of **9** and **10**. When a 1-substituted 1,2-dihydro-4-hydroxymethyl-pyrimido[1,2-*a*]benzimidazol-2-one (for example **11**) is catalytically hydrogenated, the double bond is unaffected, but hydrogenolysis of the alcohol group occurs instead to give **13**. The lactam group is less stable in the tetrahydro series than in the dihydro compounds. For example, the lactam is cleaved when **8** is treated with amines containing a small amount of water, and the monoamides **16** and **17** are formed. Similarly, sodium hydroxyde cleaves the lactam under mild conditions to the dicarboxylic acid **19**, which can be converted to 2,3-dihydro-1-methyl-2-oxo[1*H*]imidazo[1,2-*a*]benzimidazole-3-acetic acid (4-methyl)piperazide (**20**) with thionyl chloride and N-methylpiperazine. However, when **7** is treated with methylamine at low temperature, the amide **22** is formed, whilst at room temperature the amine attacks both the ester and the double bond to give **23**. The structure of **8** was confirmed by X-ray analysis.

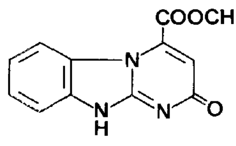
Pyrimido[1,2-*a*]benzimidazole waren bisher zugänglich durch Kondensation von 2-Aminobenzimidazolen mit Malonestern [1] [2], *β*-Diketonen [2] [3], *β*-Ketoestern oder funktionellen Derivaten davon [2] [4] [5], *α,β*-ungesättigten Carbonsäurederivaten [6] [7] oder Acetylencarbonsäureestern [4] [6] [7]. In den Fällen, wo die Kondensation zu zwei isomeren Tricyclen, z.B. **1** und **2**, führen kann, erfolgte die Struk-



1



2



5

---

1) In $CDCl_3$ [7].