

Complexes of the 4d- and 5d-Groups

IV. Electron Transfer Bands with Special Application to M. Delépine's Complexes and a Transition from Iridium(III) to Pyridine, with some Remarks about Intermediate Coupling in Halide Complexes and the Uranyl Ion

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In addition to the narrow pyridine-bands, which are only moderately shifted towards lower wavenumbers in complexes, the twenty iridium(III) pyridine complexes prepared by M. Delépine exhibit a new, broad band in the range 29 000—35 000 K. The qualitative molecular orbital diagrams are related to energy levels of the complexes and it is suggested that the broad band is caused by an electron transfer from iridium(III) to the π^* -orbitals of pyridine. The "redox" bands, caused by electron transfer from reducing halide ions to the central ion are discussed. The doublet structure, which Scheibe and Katzin ascribe to the two possible values of J of a free halogen atom, is related to the energy levels of a single electron in a linear ligand field with intermediate coupling. The influence of non-diagonal elements of energy between two levels with the same Ω is emphasized, *e.g.* of a 5f-electron in a linear dioxo complex. Finally, the absorption spectra of *a,a'*-dipyridyl and *o*-phenanthroline complexes are investigated; the bands at low wavenumbers of complexes with low oxidation state of the central ion seem analogous to the Ir-py band.

The preceding paper¹ of this series considered the iridium(III) complexes, presented by Professor M. Delépine. In addition to the ligand field transitions (singlet \rightarrow triplet bands with $\epsilon \sim 10$ and singlet \rightarrow singlet bands with $\epsilon \sim 100$), and the narrow pyridine bands (which are part of a vibrational structure with $\sigma_c \sim 1\,000$ K and $\epsilon_n \sim 4\,000$ per pyridine molecule), the pyridine complexes exhibit a broad band (with $\epsilon_n \sim 2\,000$ per pyridine molecule) at lower wavenumber than the genuine pyridine bands. Since neither pyridine-free iridium complexes² such as $\text{Ir}(\text{NH}_3)_5\text{Cl}^{++}$ and Ir en_3^{+++} , nor rhodium(III) and platinum(II) pyridine complexes exhibit such a band, it may be denoted by the Ir-py band. Table 1 gives the wavenumbers in Kayser, $\text{K} = \text{cm}^{-1}$, of this band and the vibrational structure py 0, py 1, . . . of the

Table 1. Wavenumbers of the iridium(III) pyridine electron transfer band Ir py and the pyridine bands py 0, py 1, etc. "b" denotes broad maximum without vibrational structure.

	Ir py	py 0	py 1	py 2	py 3
py	—	38 050	38 970	39 890	40 800
Ir py Cl ₅ ⁻	30 400	35 800 b	—	—	—
„ 1 day*	31 000	36 400 b	—	—	—
„ „ +Na ₂ CO ₃	30 000	35 700 b	—	—	—
„ 3 days*	31 700	37 000 b	—	—	—
„ „ +Na ₂ CO ₃	29 400	35 200 b	—	—	—
„ 14 days*	31 900	37 900 b	—	—	—
„ „ +Na ₂ CO ₃	29 300	34 600 b	—	—	—
„ „ +HClO ₄	32 500	39 200 b	—	—	—
Ir py Cl ₄ (H ₂ O) ⁻ (sun)**	31 500	37 000 b	—	—	—
Ir py Cl ₄ OH ⁻ (sun)**	30 000	35 800 b	—	—	—
Ir py Cl ₄ (H ₂ O) ⁻ (warmed)**	31 300	36 900 b	—	—	—
Ir py Cl ₄ OH ⁻ (warmed)**	30 000	36 000 b	—	—	—
<i>cis</i> -Ir py ₂ Cl ₄ ⁻	32 000	37 400	38 000	—	—
<i>trans</i> -Ir py ₂ Cl ₄ ⁻	31 600	36 600	37 400	—	—
1,2,3-Ir py ₃ Cl ₃	30 600	36 200	37 700	—	—
1,2,6-Ir py ₃ Cl ₃	31 400	37 700 b	—	—	—
Ir py ₄ Cl ₂ ⁺	35 200	36 900	37 800	38 900	40 000
<i>cis</i> -Ir py ₂ Cl ₃ (H ₂ O) (sun) ¹	32 800	37 700	38 500	—	—
<i>cis</i> -Ir py ₂ Cl ₃ OH ⁻ (sun) ¹	30 700	36 400	37 400	—	—
<i>cis</i> -Ir py ₂ Cl ₃ (H ₂ O) (autoclave) ¹	32 900	37 800	38 600	—	—
<i>cis</i> -Ir py ₂ Cl ₃ OH ⁻ (autoclave) ¹	31 500	36 300	37 300	—	—
<i>trans</i> -Ir py ₂ Cl ₃ (H ₂ O)	32 600	36 900	37 800	38 500	—
<i>trans</i> -Ir py ₂ Cl ₃ OH ⁻	30 400	35 200 b	—	—	—
Ir py(NH ₃) ₄ Cl ⁺⁺	34 500	36 900	37 800	38 700	39 800
Ir py ₃ (NH ₃) ₃ H ₂ O ⁺³	(35 400)	37 100	38 000	39 000	39 900
Ir py ₃ (NH ₃) ₃ OH ⁺⁺	32 900	36 900	38 000	38 800	—
Ir py ₃ (NH ₃) ₃ Cl ⁺⁺	35 000	37 000	37 900	38 800	—
Ir py ₃ (NH ₃) ₂ Cl ₂ ⁺	33 900	36 800	37 700	38 500	39 400
Ir py ₃ Br ₄ ⁻	31 400	37 000 b	—	—	—
1,2,3-Ir py ₃ Br ₃	29 800	35 200 b	—	—	—
1,2,6-Ir py ₃ Br ₃	31 200	37 200 b	—	—	—

* 0.0004 M KIrpyCl₅ in aqueous solution kept at ~25°C. After each measurement, the aquated ions were transformed into the hydroxo forms by making the solution 0.1 M in Na₂CO₃. The reversibility of the aquo-hydroxo equilibria were proven by addition of HClO₄, producing 0.2 M free H₃O⁺. After 14 days, this reaction was not completely reversible.

** Recently, M. Delépine has sent me two different isomers of KIr py Cl₄(H₂O), prepared from the action of sun-light and by warming of K₂Ir py Cl₅ in aqueous solution.

iridium(III) complexes and of py itself. In some cases of strong bathochromy, the vibrational structure is blurred out to a broad band, denoted by "b" in the Table.

It might be assumed that the Ir-py band is actually some feature of the absorption spectrum of pyridine itself, which has obtained better possibilities of observation in the complexes. Rush and Sponer³ observed two excited electronic states in gaseous py with 0-vibrational levels at 34 769 K and 38 350 K. Stephenson⁴ assumes that ~90 % of the oscillator strength (0.04) of the pyridine bands in a non-polar solvent such as *iso*-octane is due to the 38 350 K-state, but that ~10 % is concentrated in a weaker band towards lower wavenumbers nearer 34 769 K. The latter band is hidden by the higher band near 38 350 K in solvents such as ethanol⁴. This is also the case in

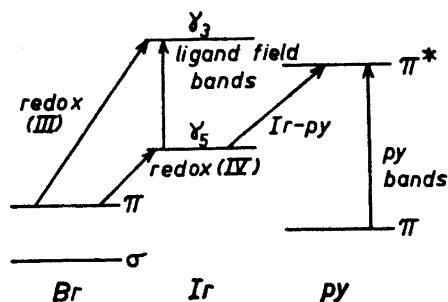


Fig. 1. Relative positions of molecular orbitals in an iridium complex with bromide and pyridine among the ligands. The disagreement of this qualitative picture with the observed energy differences is discussed p. 169. The four types of transitions are indicated:

1. Ligand field transitions within the d-shell (which is, however, intermixed with the orbitals of the ligands by partly covalent bonding).
2. Redox bands, caused by the transfer of an electron from the ligands to the central ion (having smaller wavenumbers in iridium(IV) than in iridium(III) complexes).
3. Ir-py bands, caused by the transfer of an electron from the d-shell to the empty π^* -orbitals of the ligands.
4. py bands, characteristic for the aromatic ligands, caused by internal transitions from π to π^* -orbitals.

aqueous solution¹. The hypsochromic effect of polar solvents is explained by Stephenson⁴ by the interpretation of the weak band as a transfer of a non-bonding electron mainly concentrated on the nitrogen atom, to the anti-bonding π^* orbitals of the heterocyclic ring. When hydrogen bonds stabilize the non-bonding electron, the wavenumber of the transition is increased. The influence of positive central ions will probably be much larger and thus, the Ir-py band can hardly be identified with this transition. Reid⁵ has reported triplet levels of gaseous pyridine at 30 876 K (and also at 31 459 and 32 538 K) corresponding to $\epsilon = 0.10$. The aqueous solution seem less absorbing at these wavenumbers¹. Reid⁵ reported also dubious bands with $\epsilon \sim 10^{-4}$ of liquid py near 25 500, 26 490, and 27 500 K. However, the presence of other heterocyclic compounds*, overtones of infra-red bands etc. may explain this observation. It might be argued that the large extent of intermediate coupling in iridium(III)² ($k_{\zeta_{sd}}^{\zeta} = 2\ 000\ \text{K}$) may explain a high intensity of singlet-triplet transitions in pyridine by intermixing with the orbitals of the central ion. However, the present author believes that the observed effect is too strong for this type of explanation, and that its absence in platinum(II) complexes, where the intensity ratios in PtCl_4^{2-} and PtBr_4^{2-} also imply $k_{\zeta_{sd}}^{\zeta} = 2\ 000\ \text{K}$, is pertinent.

Thus, the Ir-py band must rather be ascribed to an electron transfer process. Since pyridine is not so reducing as Br^- , and since the "redox" bands of IrBr_6^{3-} occur at 37 000 and 41 500 K and of IrCl_6^{3-} at 48 500 K (see Table 2), while the Ir-py bands are situated in the range 29 000—35 000 K, it can be concluded

* Recently, Brealey²⁷ has demonstrated that the bands 29 000—33 000 K are caused by one part in 150 000 of pyrazine, and thus, no triplet levels are known of pyridine.

that the electron is transferred from the central ion to the pyridine ligand, the opposite direction of the usual redox bands. This might be visualized in a diagram of the relative energy of molecular orbitals such as Fig. 1. However, this diagram leads to a paradoxical contradiction, if applied to the energy difference between the ground level and the excited level of the Ir-py band. If a complex with pyridine and bromide among the ligands is considered with an energy difference Δ (also called $(E_1 - E_2)$ or $10 Dq$) between the γ_3 - and γ_5 -orbital of the 5d-shell equal to 25 000 K, it is concluded from the redox bands (Table 2) of both IrBr_6^{--} (where the electron is excited to fill the γ_5 -hole) and IrBr_6^{-3} (where the electron is excited to the γ_3 -orbital) that the highest orbital of Br^- is $\sim 15\,000$ K below γ_5 . It is easily recognized that the highest filled π -orbital of py must have an energy at least 15 000 K below Br^- (cf. the redox spectrum¹ of $\text{Rh py}_2\text{Cl}_4^-$). Thus, the excited π^* -orbital of py, which is 38 000 K above the groundlevel, will be only $\sim 8\,000$ K above γ_5 of the central ion, i.e. the Ir-py band should have a wavenumber at least 20 000 K below the observed. This trend of thought leads generally to difficulties for all complexes of ligands, which have empty orbitals not much more than 50 000 K above their highest occupied orbital. While the high ultraviolet absorption⁶ of most *o*-phenanthroline complexes undoubtedly represents a bathochromic shift of the aromatic absorption bands of the free ligand (cf. Table 1) the high band of Fe phen_3^{++} at 19 600 K is perhaps analogous to the Ir-py band, as discussed in the last section. However, these cases do not seem very common; in contrast to $\text{Fe}(\text{CN})_6^{-3}$, which may have redox bands⁷ at 23 900 and 32 900 K, $\text{Fe}(\text{CN})_6^{-4}$ does not exhibit such strong bands below 40 000 K. It may be questioned, if CN^- (which is itself practically non-absorbing⁷ below 50 000 K) actually has π^* -orbitals at much lower energies than CO or N_2 .

The failure of the qualitative diagram of molecular orbitals, Fig. 1, is of course that it does not take into account the change of equilibria positions of the ligands in the excited levels and the reciprocal influence of the energies of the molecular orbitals. Actually, only energy levels of the total system have physical significance; the distribution of the energy on the single orbitals is a matter of choice, if it cannot be assumed that the ionization potentials are a first order approximation to the negative orbital energies, i.e. that the other orbitals re-arrange but slightly during the ionization process. In the case of the Ir-py band, it must not be presumed that the energy of π^* in pyridine is independent of the existence of a hole in the otherwise filled π -orbitals. For this reason, the Ir-py band has higher wavenumber than implied from the energy levels of pyridine.

The former difficulty, the excitation according to the Franck-Condon principle⁸ of vibrations, is probably even more important. Thus, an electron transfer process necessitates often supply of energy in both directions, which act as an activation energy to counteract the unfavourable interatomic distances of the excited system, compared to the vibrational groundstate of the excited system⁹. The reactions

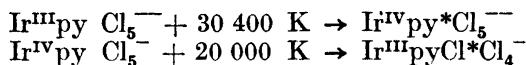


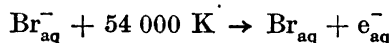
Table 2. "Redox" electron transfer bands of halide complexes. σ_n is the wavenumber in K ($= \text{cm}^{-1}$) and ϵ_n the molar extinction coefficient of each maximum and δ (—) the halfwidth towards smaller wavenumbers.

		σ_n	ϵ_n	δ (—)
I_{aq}^-		44 200	13 100	2 200
$\text{Cr}(\text{NH}_3)_6\text{I}^{++}$	(Ref. 11)	52 000	—	—
$\text{Cr}(\text{NH}_3)_6\text{I}^{++}$	(Ref. 13)	34 400	4 000	—
	"	45 000	10 000	—
$\text{Co}(\text{NH}_3)_6\text{Cl}^{++}$	"	36 500	450	—
	"	43 960	20 500	—
$\text{Co}(\text{NH}_3)_6\text{Br}^{++}$	"	31 800	820	—
	"	39 450	18 500	—
$\text{Co}(\text{NH}_3)_6\text{I}^{++}$	"	26 110	2 700	—
	"	34 930	16 500	—
$\text{Rh}(\text{NH}_3)_6\text{Br}^{++}$	"	40 600	950	—
	"	~50 000	15 000	—
$\text{Rh}(\text{NH}_3)_6\text{I}^{++}$		36 000	3 200	2 500
		44 300	20 000	2 300
RhCl_6^{---}		41 000	21 000	4 000
RhBr_6^{---}		28 600	4 000	1 900
		38 600	18 000	2 900
IrCl_6^{---}		48 500	28 000	4 100
IrBr_6^{---}	(Ref. 1)	37 000	12 000	2 200
	"	41 500	20 000	—
PtCl_6^{--}	(Ref. 7)	38 200	24 500	2 700
PtBr_6^{--}	"	27 500	7 400	2 200
	"	32 200	17 800	2 800
PtI_6^{--}	"	20 250	12 800	1 700
	"	22 400	8 300	—
	"	29 150	17 700	1 600
IrCl_6^{--}	"	17 400	460	1 200
	"	20 450	3 200	900
	"	23 200	2 540	—
	"	24 200	2 480	—
IrBr_6^{--}	"	13 600	1 550	600
	"	14 300	2 050	—
	"	14 800	2 100	—
	"	17 200	3 070	500
	"	18 400	1 500	—
	"	19 600	1 800	800

do not give any immediate evidence on the relative stability of the oxidation states +3 and +4 of iridium. They may suggest Franck-Condon activations of the order of magnitude 10 000 K.

REDOX BANDS OF METAL HALIDE COMPLEXES

Scheibe^{10,11} assumed that the strong absorption bands in the far ultra-violet of Cl^- , Br^- , and I^- in aqueous solution is due to the photochemical reaction *e.g.*



where the solvated electron of course is unstable towards formation of molecular hydrogen etc. Since the corresponding reaction *in vacuo* necessitates¹²

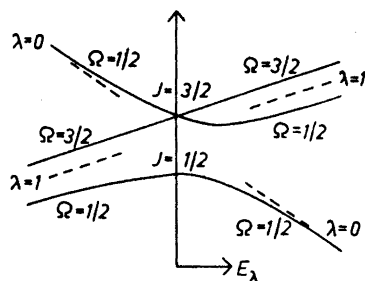


Fig. 2. The energy levels of a p-electron in a linear ligand field as function of the parameter E_λ . The intermediate coupling splits the levels with definite values of λ into two (for $\lambda > 0$) with different values of Ω (analogous to J of the gaseous ion). Levels with the same Ω interact, forming hyperbolic curves in the diagram.

only 3.56 eV, *i.e.* 27 700 K, Br^- must be stabilized considerably better by solvation than e^- .

If the halide ion is near a metal ion with larger electron affinity than water, it is natural to assume a smaller energy necessary for the transfer of an electron to the metal ion. Thus, the strong absorption will be shifted more towards lower wavenumbers, the more oxidizing the metal ion. This assumption was applied by Linhard and Weigel^{13,14} to the halide pentammine cobalt(III) and chromium(III) complexes. If the electron shall penetrate the first coordination sphere, then the bathochromic shift of the electron transfer band will be smaller, as found for the ion pairs¹⁵ of halide and $\text{Co}(\text{NH}_3)_6^{+++}$, even though the effect is stronger¹⁶ in solid $\text{Co}(\text{NH}_3)_6\text{I}_3$, where the second ligand field band is masked.

Scheibe^{10,11} found further that the absorption band of $\bar{\text{I}}_{\text{aq}}^-$ is double with maxima at 44 500 K and 52 000 K, while the splitting is smaller in Br_{aq}^- and not detectable in Cl_{aq}^- . This was ascribed to the two possible states ${}^2P_{1/2}$ of lowest and ${}^2P_{3/2}$ of higher energy of the free halogen atom with the outer electron configuration s^2p^5 . This energy difference is for the gaseous atoms 881 K for Cl, 3 685 K for Br and 7 603 K for I, corresponding to increasing values of $3/2 \zeta_{np}$ for $n = 3, 4, 5$. Katzin¹⁷ has recently continued this study and found that a large number of iodide complexes have two absorption bands in the near ultraviolet with a wavenumber difference 6 000—8 000 K, while the similar values for bromide complexes are 3 000—7 000 K.

The present author does not doubt that most of these splitting effects* are caused by intermediate coupling. However, it is not very probable that the excited levels resemble the states with $J = 3/2$ and $1/2$ of the atomic spectroscopy very much. It is seen from Table 2 that only one broad redox band is observed of IrCl_6^{-3} and PtCl_6^{-2} , while two bands are observed of IrBr_6^{-3} and PtBr_6^{-2} with the intensity ratio $\sim 1:2$, arranged according to increasing wavenumber. This is not quite expected in Scheibe's theory, since the de-

* However, most crystalline alkali metal halides¹⁸ have from four to six absorption bands in the range 45—90 000 K and hence, the nature of the electronic states is not easily recognized.

generacy numbers of the levels are 4 and 2. Generally, the first band of bromide and iodide complexes is often remarkably weak.

However, it can be theoretically justified that the degeneracy numbers of the two first levels may be 2 and 2, while a third level, also with 2, may give rise to an even stronger absorption band at higher wavenumbers than usually observed. If the six halide ions are not very strongly perturbed by the central ion, they can be treated as independent of each other, placed in a linear ligand field from the positive central ion. If the ligand contains an electron with the angular momentum quantum number l , and if the effects of intermediate coupling are neglected, $l+1$ equidistant energy levels occur with the quantum number $\lambda = l, l-1, l-2, \dots, 0$. The first-order effect of intermediate coupling will be to split all the levels with $\lambda > 0$ in two with the quantum number $\Omega = \lambda + \frac{1}{2}$ and $\lambda - \frac{1}{2}$ and with the energy difference $\lambda \zeta_{nl}$.

If we denote the energy difference between the levels $\lambda+1$ and λ by E_λ , E_λ will be positive when the linear field is caused by a positive charge and negative, when the linear field is supplied by negative ligands. For a p-electron with $l = 1$, this has a simple physical explanation: If the charge is placed on the z-axis of a Cartesian co-ordinate system, $\lambda = 0$ is represented by the p_z orbital (of which the potential energy is decreased by a positive charge) and $\lambda = 1$ is represented by the two equivalent orbitals p_x and p_y , concentrated in the plane perpendicular to the linear field. In a ligand field of tetragonal symmetry, supplied by four square-planar ligands, the opposite behaviour of p_z will occur.

If E_λ is not much larger than ζ_{nl} , the two levels with equal values of Ω (if less than $l + \frac{1}{2}$) will interact, forming a hyperbola in the energy diagram as function of E_λ . Fig. 2 gives the result for a p-electron and Fig. 3 for a f-electron. In the former case, the diagonal elements of energy, corresponding to the asymptotes of the hyperbolae, are:

$$\begin{aligned} \lambda = 1, \Omega = 3/2: & \quad 1/3 E_\lambda + 1/2 \zeta_{np} \\ \lambda = 1, \Omega = 1/2: & \quad 1/3 E_\lambda - 1/2 \zeta_{np} \\ \lambda = 0, \Omega = 1/2: & \quad -2/3 E_\lambda \end{aligned} \quad (1)$$

while the square of the non-diagonal element between the two latter levels is $1/2 \zeta_{np}^2$. Thus the two levels with $\Omega = \frac{1}{2}$ cannot have a smaller distance than two times the non-diagonal element, viz. $\sqrt{2} \zeta_{np}$. In the general case, the diagonal elements of energy will be

$$\begin{aligned} \Omega = \lambda + \frac{1}{2}: & \quad \left(\lambda - \frac{l(l+1)}{2l+1} \right) E_\lambda + \frac{\lambda}{2} \zeta_{nl} \\ \Omega = \lambda - \frac{1}{2}: & \quad \left(\lambda - \frac{l(l+1)}{2l+1} \right) E_\lambda - \frac{\lambda}{2} \zeta_{nl} \end{aligned} \quad (2)$$

while the square of the non-diagonal element between two levels with the same Ω will be

$$\frac{1}{4} (l + \frac{1}{2} + \Omega) (l + \frac{1}{2} - \Omega) \zeta_{nl}^2 \quad (3)$$

The slopes of the lines in the energy diagram (Figs. 2 and 3) for $E_\lambda \rightarrow 0$ are a linear function of Ω . For the upper level with $J = l + \frac{1}{2}$ are the first-order splittings

$$E = \frac{2l}{2l+1} \left(\Omega - \frac{l+1}{2} \right) E_\lambda + \frac{l}{2} \zeta_{nl} \quad (4)$$

while for the lower atomic level with $J = l - \frac{1}{2}$, the first-order energies are

$$E = \frac{2l+2}{2l+1} \left(\Omega - \frac{l}{2} \right) E_\lambda - \frac{l+1}{2} \zeta_{nl} \quad (5)$$

In the case of an electron transfer, where a hole is created in a p-shell, and only one significant energy level occurs in the system which has accepted the electron, one would thus expect three absorption bands, arranged according to increasing wavenumbers:

$$(\lambda = 1, \Omega = 3/2) \quad (\lambda = 1, \Omega = \frac{1}{2}) \quad (\lambda = 0, \Omega = \frac{1}{2}).$$

The distance between the two first bands will be somewhat less than ζ_{nl} , while the distance between the two last bands will be slightly larger than $E_\lambda - \frac{1}{2}\zeta_{nl}$. The two first bands are due to transfer of π -electrons ($\lambda = 1$), if the intermixing of the two levels with $\Omega = \frac{1}{2}$ is neglected, and the last band is due to transfer of a σ -electron ($\lambda = 0$).

Orgel⁹ assumes that the two bands, observed of halide pentammine cobalt(III) complexes^{13,14}, which have highly different intensities (*cf.* Table 2) are due to transfer of π - and σ -electrons, respectively. These bands are also observed of $\text{Rh}(\text{NH}_3)_5\text{Br}^{++}$ and $\text{Rh}(\text{NH}_3)_5\text{I}^{++}$ by the present author, but are perhaps a special feature of d^6 -systems, since they seem to be absent in halide chromium(III) pentammines. The weak bands might be introduced by intermixing with ligand field bands by vibrational interaction with odd electron transfer states*. However, it is also possible that they actually represent the $\Omega = 3/2$ bands with accidentally low intensity. The similar problem has been treated by Mulliken^{18,19} for halogen compounds and the halogen molecules²⁰. Mulliken¹⁹ found the distance between the two bands ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ (highest) equal to 5 570 K in HI, 4 915 K in CH_3I , 4 650 K in $\text{C}_2\text{H}_5\text{I}$, 3 457 K in HBr, and 3 070 K in CH_3Br . The intensity ratios were > 10 in the chlorides, ~ 4 in the bromides and ~ 2 in the iodides in favour of the second band, resembling the behaviour of halide pentammine- d^6 -complexes. The partly σ -character of the second band might have been used as an argument for increased intensity, if it was higher for iodide than for chloride complexes.

* The effective value E_{af} of the non-diagonal element of energy between even and odd levels, to which the forbidden (with the oscillator strength P_f and wavenumber σ_f) and allowed (P_a, σ_a) transitions occur, can be defined:

$$\frac{P_f}{P_a} = \frac{\sigma_f}{\sigma_a} \cdot \frac{E_{af}^2}{(\sigma_f - \sigma_a)^2}.$$

For a large number of $3d^n$, $4d^n$, $5d^n$, and $5f^n$ -transitions, E_{af} is remarkably invariant in the range 1 500—2 500 K. The physical significance of E_{af} is the product of the amplitude of the odd vibrations in atomic units (~ 0.1) and an electrostatic interaction energy of the order of magnitude 20 000 K, as discussed for the case of benzene by Murrell and Pople²⁶.

The present author is not inclined to believe that the σ -band can occur at lower wavenumbers than the absorption band of the free halide ion in aqueous solution. Even though the strongest band of $\text{Rh}(\text{NH}_3)_5\text{I}^{++}$ has nearly the same wavenumber as the first band of I^- (Table 2), it cannot simply be argued that the transfer of electrons will occur to the solvent, if the metal ion has no larger electron affinity than water. The iodide ion must be stabilized by its bonding to the rhodium ion (even though the partial contribution to the ligand field strength is remarkably negative¹) while the excited state, the free I, hardly can be so much stabilized. Thus, the anti-bonding character of the excited state will tend to increase the wavenumber of the σ -band in all cases.

From group-theoretical reasons, it is difficult to understand, why the redox spectra of hexahalide complexes do not contain much more than two bands. The 36 states of the resonance structure of five halide ions and one halogen atom (s^2p^5) might give 18 levels, if only one state is possible of the central ion + the added electron. If q states are possible in the latter system, 18 q levels are expected, if the Kramers' degeneracy does not allow 36 q levels (as is the case, if an even number of electrons occur in totality). Even though ReCl_6^{--} exhibits^{21,22} three bands and ReBr_6^{--} six bands, such a complicated behaviour has never been reported. However, the "one-ligand excitation" model of the linear ligand field above seems to develop splittings for very large electron affinities of the central ion, e.g. the visible redox spectra of IrCl_6^{--} and IrBr_6^{--} , which exhibit, respectively, four and six bands (Table 2) while in this case, $q = 1$ for the excited central ion configuration γ_5^2 . If the symmetry of the complex is restricted to the cubic O_h , only four π -levels and three σ -levels are predicted². If the Laporte-forbidden transitions to even levels are neglected, only two π - and one σ -absorption bands are expected of a d^5 -system, while a d^6 -system with $q = 4$ ($\gamma_5^2\gamma_3$) should exhibit the double number each of singlet and triplet levels. However, when intermediate coupling is considered, more bands are predicted. Thus, eight odd levels ($2\Gamma_6$, $2\Gamma_7$ and $4\Gamma_8$, of which the last four may be split by ligand fields of lower symmetry) occur, when a π -electron is transferred to the empty γ_3 -shell of a d^6 -system. It may be reasonable to conclude that the "one-ligand excitation" model seems satisfactory for redox spectra at not too low wavenumbers, e.g. of IrBr_6^{--3} or PtBr_6^{--} , while systems with a large tendency of the electron transfer, e.g. PtI_6^{--} , may begin to exhibit some of the many bands predicted from group theory, i.e. the exchange integrals between different halide ligands begin to be important.

Table 3. The vibrational structures of the two weak uranyl band groups. Absorption spectra of 0.2 M down to 0.002 M $\text{UO}_2(\text{ClO}_4)_2$ in 0.1 M HClO_4 .

Tentative Δv	λ_n $m\mu$	σ_n K	ϵ_n	Tentative Δv	λ_n $m\mu$	σ_n K	ϵ_n
-1	486.5	20 550	0.3	-1	(350.5)	28 530	4
0	468.5	21 340	1.1	0	342	29 240	8
1	454	22 030	1.6	1	335	29 850	16
2	440	22 730	3.2	2	326	30 670	32
3	425	23 530	5.9	3	318	31 450	43
4	413.5	24 180	7.2	4	(311)	32 150	50
5	403	24 810	6.4				
6	(390)	25 640	4.6				
7	(380)	26 320	2.7				

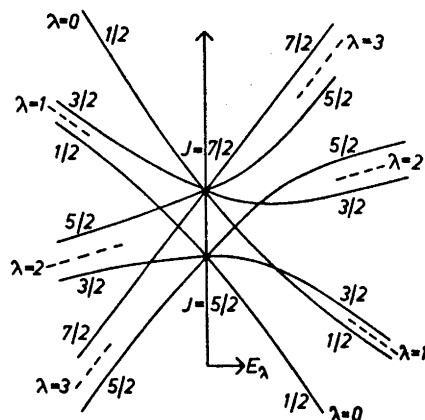


Fig. 3. The energy levels of a f-electron in a linear ligand field as function of the parameter E_λ . The numbers indicate the value of Ω for the individual levels. The oxygen atoms in dioxo actinide ions produce a negative value of E_λ .

THE DIOXO ACTINIDE IONS AND 5f-ELECTRONS IN LINEAR LIGAND FIELDS

The uranyl ion UO_2^{++} has no partly filled shell, and thus all electronic absorption bands must be due to electron transfer. Besides the well known group of bands in the range 20 500—26 300 K, a similar group with vibrational structure is observed in the range 28 500—32 200 K (see Table 3). The molar extinction coefficients ϵ_n of these bands are remarkably low, ~ 6 and ~ 10 (when corrected for the raising background). Besides the two band groups, there is only a monotonously increasing absorption in the ultraviolet ($\epsilon = 60$ at 300, 135 at 280, 300 at 260, 720 at 240 and 1 300 at 220 $m\mu$).

The two band-groups are undoubtedly Laporte-forbidden and can be ascribed²³ to the transfer of an odd electron (e.g. with $\lambda = 1$, which is not σ -bonding as those with $\lambda = 0$) from the ligands to the empty 5f-shell of the central ion. Eisenstein and Pryce²⁴ investigate the dioxo actinide ions with one 5f-electron, viz. UO_2^+ and NpO_2^{++} , and assume a large value of $E_\lambda \sim -15\,000$ K of eqn. 2. These authors did not discuss the influence of the non-diagonal elements of intermediate coupling (eqn. 3), which is rather conspicuous (cf. Fig. 3). While ζ_{5f} in trivalent and quadrivalent uranium²³ is $\sim 1\,600$ K, it cannot easily be decided, if ζ_{5f} of UO_2^{++} has the value $\sim 3\,000$ K expected²⁵ for gaseous U^{6+} , or if the partly covalent bonding²⁶ has decreased the value much.* Generally, it cannot be expected that the intermixing with the orbitals of the ligands conserves the equidistant splitting of the λ -levels, as expressed in eqn. 2. Rather, the distance between $\lambda = 0$ and $\lambda = 1$ may be much lar-

* Professor B. Weinstock, Argonne, has kindly informed me that NpF_6 exhibits a group of bands at 7 300—9 500 K and hence the ligand field splittings are small compared to $\zeta_{5f} \approx 2\,400$ K. Weinstock will later discuss the absorption spectrum of PuF_6 , which has a sub-level $\Gamma_J = \Gamma_1$ as a rather isolated groundstate²⁷, corresponding to 3H_4 as weak field asymptote and γ_3^2 as strong field asymptote.

ger than between $\lambda = 2$ and $\lambda = 3$. In the latter case, Fig. 3 will be distorted (the left-hand side with negative E_λ applies to UO_2^{++}) such that the three lowest levels would have $\Omega = 5/2, 3/2$, and $7/2$, with the subsequent distances $\sim 1/2$ and $\sim 5/2 \zeta_{5f}$.

Since neither E_λ nor ζ_{5f} is known *a priori* for UO_2^{++} , Fig. 3 allows many possible explanations of the existence of the two electronic states with a distance $\sim 7\,900$ K (Table 3). If E_λ is small, then the observed distance is simply the atomic splitting $\frac{7}{2} \zeta_{5f}$. This cannot be excluded, if 5f-electrons actually do not take any part in the covalent bonding.* However, it is more probable that E_λ is larger, and that the lowest level (which is fluorescent) is that with $\Omega = 5/2$. Then, the next electronic level might either have $\Omega = 7/2$ (with less than $3 \zeta_{5f}$ higher energy) or $\Omega = 3/2$ (the energy difference then mainly being composed of E_λ).

Eisenstein and Pryce²⁴ assume that the weak bands of NpO_2^{++} with vibrational structure in the range 15 400—23 800 K are caused by an internal 5f-transition from $\Omega = 5/2$ to the two levels of $\lambda = 2$. However, the present author assumes as an alternative possibility that the weak vibrational bands of UO_2^{++} , NpO_2^{++} , PuO_2^{++} , and AmO_2^{++} (which must not be confused with the high, extremely narrow bands occurring in systems with at least two 5f-electrons in the groundstate²³) have a common cause, *viz.* the transfer of an electron to the 5f-shell of the central ion. The wavenumbers decrease with increasing electron affinity of the central ion, analogous to the ordinary redox bands, and seem very high in the species MO_2^+ .

ABSORPTION SPECTRA OF α, α' -DIPYRIDYL AND *o*-PHENANTHROLINE COMPLEXES

The complexes of α, α' -dipyridyl and *o*-phenanthroline have much more complicated absorption spectra than the pyridine iridium(III) complexes discussed above. Especially, low oxidation states of metals seem stabilized and form strongly coloured complexes with the heterocyclic diimines: red iron(II), red ruthenium(II), brown copper(I)²⁸, black vanadium(—I)²⁹, blue vanadium(0)³⁰, purple vanadium(I)³⁰, green vanadium(II)³⁰, blue chromium(I)³¹ and purple chromium(II)³¹.

Presumably, these strong absorption bands in the visible are caused by electron transfer from the central ion to the ligand, analogous to the Ir-py band studied here. The ground-state of the purplish red Fe dip_3^{++} and red-orange Fe phen_3^{++} has been described³² in terms of Pauling's directed valence bonds as a resonance of three π -bonds (in the direction towards the ligands) besides the usual d^2sp^3 -hybridization. As discussed by Orgel⁹, this is more adequately described by the molecular orbital theory, assuming increased

* Recently, Coulson and Lester³³ proposed that 6f-rather than 5f-electrons are involved in the partly covalent bonding of actinide complexes. Generally, the group-theoretical requirements of molecular orbitals (given for f-electrons by Eisenstein³³) refer to the angular part of the wavefunction only, while the radial function can be chosen rather arbitrarily. Hence, the partly covalent bonding can often be described by a complicated intermixing of empty and filled orbitals from the central ion and the ligands, resulting in the current reconciliation of ligand field and molecular orbital theory⁴⁰.

energy of the empty γ_3 -sub-shell by formation of π -antibonding linear combinations with the empty orbitals of the ligands. Recently, Schläfer³³ has applied an electrostatic perturbation calculation to the energy levels of α, α' -dipyridyl, analogous to the considerations of Belford³⁴ for acetylacetonate. Even though it is interesting to note that a certain group of bands are identically shifted for all mono- and tris-dipyridyl complexes of divalent metal ions, Schläfer's theory³³ appears somewhat too simplified in the case of *o*-phenanthroline. These compounds have a very irregular vibrational structure of the bands, indicating strong coupling between electronic and vibrational states. Furthermore, while the pyridine complexes have only one conspicuous σ_c , several of the 60 characteristic frequencies seem to occur in *o*-phenanthroline, since no equidistant band groups can be observed.

The following bands are observed of some representative complexes in the range 12 500—50 000 K, with approximative values of ϵ_n , and shoulders in parenthesis.

dip		dip H ⁺		Fe dip ₃ ⁺⁺		Ni dip ₃ ⁺⁺	
(31 100)	1 000	33 200	15 700	19 100	8 600	24—30 000 increase	
35 600	12 800	(37 000)	4 000	(20 200)	7 800	32 400	40 000
42 900	10 700	41 600	8 000	(24 100)	2 400	33 800	42 000
				(25 800)	3 700	40 800	32 000
				28 500	6 500		
				33 500	70 000		
				(34 500)	60 000		
				40 500	32 000		
phen		phen H ⁺		Fe phen ₃ ⁺⁺		Ni phen ₃ ⁺⁺	
30 900	750	(33 300)	7 000	19 600	11 200	24—28 000 increase	
(32 300)	1 200	36 200	29 000	(21 000)	9 500	29 100	1 500
(34 600)	9 200	36 800	31 000	(22 800)	7 300	30 600	2 400]
37 800	28 000	45 500	36 000	31 200	3 300	(32 000)	3 300
44 000	40 000	48 700	38 000	(34 400)	20 000	34 000	28 000
				37 600	67 000	37 100	78 000
				44 400	64 000	44 000	93 000

The first five bands * of Fe dip₃⁺⁺ and at least the three first bands of Fe phen₃⁺⁺ can thus be ascribed to a Laporte-allowed electron transfer from the γ_5 -orbitals of iron(II) to the heterocyclic π^* -orbitals. They are very far removed from being internal dⁿ-transitions in the central ion, as also contradicted by the highly different band structure of the dip and the phen complex. The other bands can mainly be identified as bands of the free ligand, which are shifted and partly split during the influence of H⁺, Fe⁺⁺, and Ni⁺⁺. However, many remarkable features are still unexplained: the slowly increasing absorption in the near ultraviolet of the nickel(II) complexes may be interpreted as a similar electron transfer or as a shift of the first shoulder of dip, not mentioned by Schläfer³³. The narrow bands of moderate intensity of Ni phen₃⁺⁺ were found by Roberts and Field⁶, who reported too many bands, because the absorption of an aqueous solution of 3 phen was subtracted from

* Busch and Bailar³² prepared the diamagnetic tris (biacetylbiethylimine)iron(II) iodide Fe(C₆H₁₃N₂)₃I₂, which contains no heterocyclic rings. The bands reported at 17 600 K ($\epsilon=10 700$) and 29 000 K ($\epsilon=1 200$) are undoubtedly of the Ir-py type, while the band at 44 000 K ($E=38 100$) is under suspicion for being simply the iodide band.

that of Ni phen_3^{++} . They seem to be a general feature of all phen-complexes, comparable to the first, weak band of benzene³⁵. The higher oxidation state iron(III) has in the blue Fe phen_3^{++} (a band at 16 800 K, $\epsilon = 750$) and Fe dip_3^{++} (16 300 K) much less colour. The broad band may be due to electron transfer from the ligands to the central ion, and may be compared to the relatively weak first band⁷ of IrCl_6^{--} .

Acknowledgements. I am very much indebted to Professor Marcel Delépine of Collège de France for the valuable samples of iridium(III) and rhodium(III) complexes, which have made the observation of the Ir-py band possible. Further, I thank Professor Jannik Bjerrum for his kind interest in the work.

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Received October 12, 1956.