

Some Problems of Intensity of Absorption Bands and Chemical Bonding

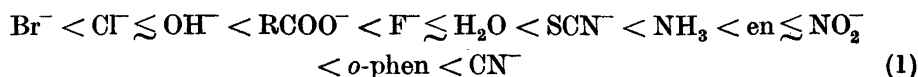
CHR. KLIXBÜLL JØRGENSEN

Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark

The influences of different ligands on the wavenumber and intensity of the absorption bands of a given metal ion are compared. The intensities are connected with the intermixing of about one per cent odd functions in the even wavefunctions $[A]3d^n$. The other types of absorption bands in inorganic salts are classified. The difference between one and more times orbitally degenerate ground states in the cubic fields is shown to be relevant to complexity constants, activation energies and relative displacement of spectra of unsymmetrical complexes towards higher wavenumbers.

The crystal field theory of Bethe¹ has been applied to the absorption spectra of all the ions of the first transition group, first by Hartmann and Ilse^{2,3}, Orgel⁴, and later by J. Bjerrum, Ballhausen and the author⁵⁻¹¹. The agreement with the observed wavenumbers of the absorption band maxima is good, when reasonable values are assumed for the distances within the complex ions and the dipole moments or charges of the ligands. While the energy states are thus determined, the explanation of the transitions between the states has as yet not been fully given (the transition between states of the same electron configuration $[A]3d^n$ is forbidden by Laporte's rule and should have the probability 0). In the following discussion of this problem, some general remarks are first made on the energy states in different complexes of the same metal ion.

Already Fajans¹² developed the "spectrochemical series" of hypsochromic influence of different ligands *inter alia*, and Tsuchida¹³ extended this concept further:



When all six ligands are equal and placed at the same distances in an octahedral complex, the spectrochemical series (1) is easily explained as corresponding to increasing value of $(E_1 - E_2)$ in a crystal field of cubic symmetry, where E_1

is the energy of a γ_3 -electron and E_2 of a γ_5 -electron^{2,3,7}. It might seem curious that anions and neutral molecules all find their fixed places in (1), but it must be remembered that the point-dipoles used in calculations^{2,5,6} are fictitious quantities, only electrical charges occur in reality. In the neutral ligands, the negative part (distributed by polarization) is much nearer to the metal ion than the positive part, which thus has only a very small opposite influence on the crystal field perturbation, since it depends on R^{-5} or R^{-6} in most cases. R is the distance from the centre of the metal ion^{2,6}. The real dipole moments of neutral ligands are undoubtedly somewhat smaller than the crystal field parameter μ caused by the strongly increased effects of the negative end of the dipole. The spectrochemical series (1) is not a direct measure of the affinity to the ligands, since the free energy changes depend on R^{-1} and R^{-2} potentials, which are much less dependent on distance. Therefore, anions, which are not strongly polarizable (as are CN^- and NO_2^-) have an anomalously early position in the series. But a quite paradoxical fact is the lower ($E_1 - E_2$) value of OH^- than of H_2O . Probably, the three lone-pairs of electrons found in OH^- are not so effectively perturbing as the two lone-pairs of H_2O . Analogously, the latter molecule is not as effective as NH_3 with one lone-pair.

If a similar series as (1) is constructed of the intensities of the crystal field spectra, the anions will undoubtedly be placed at very late positions. Chloro- and bromo-complexes of copper(II) complexes have maximum molar extinction coefficients $\epsilon_n = 100$ to 200 at $\sim 10\,000\text{ cm}^{-1}$, while $[\text{Cu}(\text{H}_2\text{O})_6]^{++}$ has maximum at $12\,600\text{ cm}^{-1}$ with $\epsilon_n = 12$. Nitro-complexes of copper(II) measured by Fronæus¹⁵, and cobalt(III) complexes among others by Basolo¹⁶, show relatively very high intensities. In the preceding paper of this series¹⁰, CoCl_4^{--} was shown to have $\epsilon_n \sim 500$ in ordinary and $\epsilon_n \sim 5$ in ΔS -forbidden⁷ bands, while in cobalt(II) complexes with neutral ligands the corresponding values are $\epsilon_n \sim 5$ and $\epsilon_n \sim 0.1$. In a paper to be later published, the dark-coloured bi-nuclear complex of titanium(III) and titanium(IV) in concentrated HCl will be discussed. It deceived Hartmann and Schläfer¹⁴ to assume titanium(III) chloro-complexes alone to be ~ 10 times more absorbing than $[\text{Ti}(\text{H}_2\text{O})_6]^{+++}$, while the real $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}]^{++}$ is sky-blue. Since amine complexes are well known to be more absorbing than aquo ions, the intensity series can be written



with aquo ions being the least coloured complex of a given metal ion. Organic ligands give generally also increasing intensity, *viz.* alcohols and aliphatic amines, compared with H_2O and NH_3 respectively.

The theoretical explanation of intensity can in the author's opinion be found along the lines drawn by Broer, Gorter and Hoogschagen¹⁷, who investigated the weak bands of lanthanide ions. The fundamental difficulty of providing internal d^n - or f^n -transitions with any positive probability is the following: Analogous to departure¹⁸ from Russell-Saunders coupling, which intermix states of different L and S in such a way that only the vector sum J is preserved, the configuration interaction¹⁸ may in the free ion intermix states of different electron configuration, but with the restriction that the

parity is the same. The parity, which thus is one of the most strictly defined quantum numbers of the free ion, is "even" or "odd", according to the sum of the values of l of the individual electrons in the system being even or odd. Laporte's rule for electric dipole radiation is: the transitions shall occur between states of opposite parity. Other radiation types, as electric quadrupole or magnetic dipole, give too small oscillator strengths¹⁷ ($P \sim 10^{-8}$) for most lanthanide and all first-transition group bands, even though they allow transitions between states of the same parity. The oscillator strengths P can be found from the observed absorption spectra¹⁹.

$$P = 4.32 \cdot 10^{-9} \int \epsilon d\nu \simeq 4.6 \cdot 10^{-9} \epsilon_0 [\delta(+)+\delta(-)] \quad (3)$$

ϵ_0 is the maximum extinction coefficient and $\delta(+)$ and $\delta(-)$ the two half-widths towards higher and lower wavenumbers. It is seen that for most normal bands¹⁹ of the first transition group aquo ions, $P \sim 10^{-4}$. For the weak bands, where the total spin quantum number S changes 1 under the transition⁷, $P \sim 10^{-6}$. The factor 10^{-2} is determined from the (L, S) coupling effects with intermixing of states with different S , but the same J as mentioned above.

Now, Broer, Gorter and Hoogschagen¹⁷ pointed out that even the parity can be slightly intermixed by perturbations of crystal fields with no centre of symmetry. Also vibrations of the ligands can provide such an intermixing. In the lanthanides, the statically hemiedric perturbations are presumed¹⁷ to be slightly more important than the vibrational. The intermixing of the wavefunctions can be formally expressed for the groundstate Ψ_1 and the excited state Ψ_2 :

$$\begin{aligned} \Psi_1 &= a_1 \Psi_{\text{even}} + b_1 \Psi_{\text{odd}} & (a_1^2 + b_1^2 &= 1) \\ \Psi_2 &= a_2 \Psi_{\text{even}} + b_2 \Psi_{\text{odd}} & (a_2^2 + b_2^2 &= 1) \end{aligned} \quad (4)$$

In the first transition group Ψ_{even} is represented by $[A]3d^n$ and Ψ_{odd} by $[A]3d^{n-1}4p$, while in the actinide ions the two types of Ψ are $[Em]5f^n$ and $[Em]5f^{n-1}6d$. In the latter case this treatment has given good agreement with the trend of observed intensities of the absorption bands in different actinides.

It must be remarked that the intermixing coefficients b_1^2 and b_2^2 are very small in most transition group complexes and that the meaning of "even" and "odd" is weakened, if this is not the case. Only the part $(a_1 b_2 + a_2 b_1)^2 \simeq (b_1 + b_2)^2$ will contribute to the oscillator strength of electric dipole radiation:

$$P \simeq \frac{1}{30} (b_1 + b_2)^2 \quad (5)$$

The proportionality factor between 10^{-1} and 10^{-2} consists of the following factors: The wavenumber ν divided by the Rydberg constant $109\,740 \text{ cm}^{-1}$; the "strength" of the transition, as defined by Condon and Shortley¹⁸, divided by $e^2 a_0^2$ (e is the electronic charge and a_0 the Bohr radius), and finally some statistical weights.

Since $P \sim 10^{-4}$, either the groundstate or the excited state or both (which is more reasonable) must be intermixed with odd functions to the extent of

$\sim 10^{-3}$. In the chloro- or ethylenediamine-complexes (see the series (2)), P has mostly increased to $\sim 10^{-3}$, and in the special case of CoCl_4^{--} (where the tetrahedral configuration perhaps provides a stronger hemiedric perturbation than in octahedral complexes), $P \sim 10^{-2}$.

The intermixing of about one per cent odd functions in the complex ion states $[\text{A}]3d^n$ cannot be directly connected with the electron overlap from the ligands, which according to calculations of Craig, Maccoll, Nyholm, Orgel and Sutton²⁰ is recognized also to be $\sim 10^{-2}$. However, the assumption of one per cent covalency* may very well result in the same effects on intensity as the more atomic-spectroscopical picture given above. The most divergent point between the current theories of covalency in coordination chemistry and the crystal field theory is the assumption of the magnetic criterion. It seems unreasonable from the latter point of view to assume discontinuous appearance of considerable covalency in cobalt(III) complexes, whose two ordinary bands have $P \sim 10^{-3}$ as do magnetically normal complexes. Below, another criterion, the "robustness" of the complexes is discussed on the basis of the crystal field theory.

Empirically, it can be shown that the intensities of different bands of the same metal ion develop in slightly different ways. Let us consider¹⁹ $\text{Ni}(\text{H}_2\text{O})_6^{++}$ and Ni en_3^{++} . They give values of $(E_1 - E_2) = 7\,600\text{ cm}^{-1}$ and $10\,500\text{ cm}^{-1}$ respectively, and their second and third bands have the transition probabilities:

	$\text{Ni}(\text{H}_2\text{O})_6^{++}$	Ni en_3^{++}
${}^3\Gamma_2 \rightarrow {}^3\Gamma_4(F)$	** $P = 3.5 \cdot 10^{-5}$	$P = 10.2 \cdot 10^{-5}$
${}^3\Gamma_2 \rightarrow {}^3\Gamma_4(P)$	$P = 7.2 \cdot 10^{-5}$	$P = 14.3 \cdot 10^{-5}$

If a similar calculation is performed with $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ and *** Cr en_3^{+++} which have respectively $(E_1 - E_2) = 17\,400\text{ cm}^{-1}$ and $21\,600\text{ cm}^{-1}$, one obtains:

	$\text{Cr}(\text{H}_2\text{O})_6^{+++}$	Cr en_3^{+++}
${}^4\Gamma_2 \rightarrow {}^4\Gamma_5(F)$	$P = 2.0 \cdot 10^{-4}$	$P = 11.1 \cdot 10^{-4}$
${}^4\Gamma_2 \rightarrow {}^4\Gamma_4(F)$	$P = 3.0 \cdot 10^{-4}$	$P = 11.5 \cdot 10^{-4}$

Just as the series (1) is quantitatively expressed with the ratio between $(E_1 - E_2)$ in the considered complex and in the aquo ion ($(E_1 - E_2)_{\text{cm}} / (E_1 - E_2)_{\text{aq}} = 1.38$ in nickel(II) and 1.24 in chromium(III) systems), the intensity series (2) seems to determine the intensity changes of the individual absorption band by change of ligand. For example in the two cases cited above P of the first band increases more than P of the second band. Generally, all chromium(III) complexes with relatively intense absorption have their first band highest contrary to the aquo ion.

* Intermixing with electron transfer states is supported by the higher intensities⁷ of d^n -transitions in iron(III) compared to the isoelectronic manganese(II), or by copper(II) compared to nickel(II). The high intensity in anion complexes may be connected with the relatively low energy of the excited states with an extra electron in the metal ion.

** This band of the nickel(II)hexaquo ion is presumably double, because the two states with $J = 2$ in 3F and 1D give an extraordinarily large intermediate coupling effect¹⁸. This causes intermixing of the state ${}^1\Gamma_3(D)$ predicted¹¹ at about $17\,000\text{ cm}^{-1}$.

*** Measurements by Mr. F. Woldbye in this laboratory.

These features cannot support the unfortunate distinction between the origin of the first and the second band, which confused Tsuchida's otherwise very useful classification¹³. Rather, Rabinowitch²¹, Lindhard and Weigel²² are correct in distinguishing between bands with $\epsilon_n \sim 10$ due to energy states of the metal ion and bands with $\epsilon_n \sim 10\,000$ due to electron transfer from the ligands to the metal ion. According to the modern theories, all the absorption bands of inorganic salts in the range between the vibrational bands in the infra-red and the ionization bands in the far ultraviolet can be classified according to increasing perturbations of the environment:

f^n -transitions with nearly no chemical influence

($P \sim 10^{-6}$ in lanthanides and $\sim 10^{-4}$ in actinides)

$f^n \rightarrow f^{n-1}d$, broad bands with $P \sim 10^{-1}$ (see ref. 23, 24, 25)

d^n -transitions with strong influence of crystal fields

($P \sim 10^{-4}$ for $\Delta S = 0$, $P \sim 10^{-6}$ for $\Delta S = 1$ in the first transition group)

electron transfer spectra ($P \sim 10^{-1}$)

Electron transfer from ligands to metal ion or between different metal ions (*e. g.* some element in different oxidation states or with metallic bonding).

But the value $P \sim 10^{-4}$ assigned in this table to internal d^n -transitions is no absolute upper limit. In metal ions, strongly perturbed by the environments, it is possible to have $P \sim 10^{-1}$. Thus, it can be difficult to distinguish such bands from the electron transfer spectrum, as in the tris(*o*-phenanthroline) and tris(α, α' -dipyridyl) iron(II) complexes. The electron transfer spectrum may also have structure due to crystal fields, *e. g.* the tetrahedral CrO_4^{--} or MnO_4^{--} show two extremely strong bands. The groundstate contains only a very little of a 3d-electron wavefunction (perhaps causing the temperature-independent paramagnetism) while the excited state contains one 3d-electron, captured from the oxygen atoms, which can be either in the state γ_3 or γ_5 . Recently, these ions were investigated by Wolfsberg and Helmholtz²⁶ by the method of molecular orbitals. Empirically, it is known²⁷ that tetrahedral configurations give spectra with much more vibrational fine structure than complexes with octahedral configuration. The rare case of a weak electron transfer spectrum ($P \sim 10^{-4}$) is found in the bands of UO_2^{++} at $22\,000\text{ cm}^{-1}$, where the hexavalent uranium takes up a 5f-electron²⁵, while the strong ($P \sim 10^{-1}$) bands $\sim 40\,000\text{ cm}^{-1}$ are due to formation of $[\text{Em}]6d$.

In the theory of chemical bonding, covalency has often been connected with the criterion of robustness, *i. e.* high activation energy (or extraordinarily low frequency factor). In the crystal field theory the standard state of reactivity is represented by ions with closed shells (Ca^{++} , Zn^{++}) whose 1S -states are not influenced by crystal field perturbations. Magnetically normal d^5 -systems (Mn^{++} , Fe^{+++}) have similar properties in their 6S -states. Of the other d^n -systems in octahedral complexes, some have groundstates, which in crystal fields of cubic symmetry would be several times orbitally degenerate, *viz.* magnetically normal d^2 , d^4 , d^6 , d^7 and d^9 -systems, while the others have non-degenerate cubic groundstates, *viz.* d^3 , d^8 and diamagnetic d^6 -systems. It was

pointed out by Van Vleck²⁸ that the former type of complex with six equal ligands is not stable with cubic symmetry, but due to the Jahn-Teller effect must distort to a field of tetragonal (d^4 , d^9) or even rhombic symmetry (d^1 can show "compressed" tetragonality¹¹ in the place of rhombic symmetry, having¹⁰ $\Sigma(x) = \Sigma(y) < \Sigma(z)$). The two types of complex ion are referred to here as "distorted" and "regular" octahedral complexes.

The distorted complexes are seen to have low activation energies²⁹, sometimes even lower than the closed shell-configurations. In these cases, the distortion during the chemical exchange reaction is promoted by the tetragonal or rhombic splitting of the groundstate. However, in the regular complexes, the crystal field energy decrease is weakened during the distortion, because five (or seven loosely bound) ligands cannot produce as much perturbation as six ligands. The robust complexes with activation energy over 20 kcal/mole are all found in the regular group (*e. g.* nickel(II), cobalt(III), rhodium(III) and platinum(IV) complexes). Homogeneous reaction rates with cobalt(III) amines and neutral ligands have as yet not been determined, but they probably all correspond to activation energies over 30 kcal/mole, while the cubic crystal field energy decrease¹¹ is $\sim 60\,000\text{ cm}^{-1} = 85\text{ kcal/mole}$. Electron transfer agents as carbon or palladium³⁰ catalyze the cobalt(III) reactions, probably because the labile cobalt(II) complexes are intermediately formed.

The consecutive formation constants of complexes $MA_{6-n}B_n$ and their absorption spectra are also widely different in the "distorted" and "regular" octahedral group. In the former group, characteristic³⁰ coordination numbers 2 and 4 can occur. While the latter is quantitatively supported³⁰ by copper(II) amines, and qualitatively observed for chromium(II) complexes, evidence for the characteristic coordination number 2 is also indicated in the irregular behaviour of cobalt(II) amines, where the existence range of the tri-amine complex is anomalously narrow (Ref.³⁰, p. 287). In the regular group, the rest effects³⁰ are small except due to steric influences. Here, the absorption spectra are linear combinations¹¹ of $(1 - \frac{n}{6}) [MA_6] + \frac{n}{6} [MB_6]$, when the centre of gravity of tetragonal and rhombic split bands are considered. Contrary to this, the distorted group exhibits tetragonal splitting also of the groundstate and thus shows systematic displacement of the absorption spectrum towards higher wavenumbers by decreasing symmetry of the complex. This is exemplified in $[Cu(NH_3)_5(H_2O)]^{++}$, which is less pronounced tetragonal than $[Cu(NH_3)_4(H_2O)_2]^{++}$ and thus gives rise to the pentammine effect⁵.

Hellwege³¹ has investigated the selection rules in crystal fields and concluded that for octahedral complexes the transitions from Γ_4 to Γ_1 , Γ_3 , Γ_4 and Γ_5 and from Γ_5 to Γ_2 , Γ_3 , Γ_4 and Γ_5 and the reverse are the only possible ones for dipole radiation. Hellwege agrees with the present author that Laporte's rule is exactly valid in crystal fields, having a centre of symmetry (as have octahedral (O_h), but not tetrahedral (T_d) complexes). These selection rules are not entirely fulfilled by the relative intensities of different transitions arising from the hemiedric potential. Thus, transitions from Γ_1 in diamagnetic cobalt(III) and from Γ_2 in nickel(II) and chromium(III) to both Γ_4 and Γ_5 have nearly the same probability. Therefore, only a rough proportionality to the orbital degeneracy number can be expected. Since the transi-

tion probabilities in fields of lower symmetry are not much higher than in the octahedral complexes, these cannot alone be important in determining the intensity of the bands. However, an increased intensity in tetrahedral and *cis*-MA₄B₂ complexes, due to hemiedric potentials, is observed in some cases.

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