Ligand Field Bands of Hexafluoro Manganate(IV) and Predictions of Band Positions of Transition Group Fluorides

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Ligand field theory describes the energy levels of central ions with partly filled d-shells in octahedral (O_h) complexes in terms of two parameters: the energy difference Δ (also called $(E_1 - E_2)$ or $10\ Dq$) between the two equivalent γ_3-orbitals and the three equivalent γ_5-orbitals; and the ratio β between the interelectronic repulsion parameters in the complex and in the corresponding gaseous ion. Even though these parameters are determined by rather unknown mixtures of electrostatic and covalent bonding [1], they are very useful for an empirical classification of the complexes, and Δ (the spectrochemical series) and β (the nephelauxetic series [2]) as function of central ions and of ligands behave very regularly. It is evident, *e.g.* from the many nickel(II) complexes studied [3,4], that the absorption spectrum of an unknown complex often can be precisely interpolated from other, known spectra, even though the parameters of ligand field theory are not accessible for an *a priori* calculation. The present note will discuss the possibilities of predicting the spectra of fluoride complexes which are interesting for many reasons: they are even less nephelauxetic than aquo ions (corresponding to weaker tendency towards covalent bonding) and they represent high and often unusual oxidation states of the metals involved. Further, the Laporte-forbidden ligand field transitions are not so often masked by Laporte-allowed electron transfer bands as in most other complexes. Unfortunately, these fluoride complexes are generally so reactive with glass and with moisture that no reflection spectra have been published (nor absorption spectra of the gaseous fluorides; solutions are not liable to be made in any solvent). It is hoped that this note will draw attention to the spectra and encourage somebody to surmount the large experimental difficulties. It can be remarked that ligand field theory is not especially applicable to
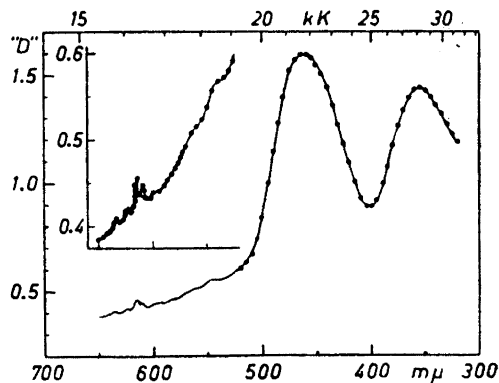
Fig. 1. Reflection spectrum of K_2MnF_6. The optical density "D" is indicated on larger scale for the small bands in the red.

fluoride complexes, because they are the least covalent (and therefore the most "electrostatic") complexes of a given central ion; a similar series of predictions might equally well be given for the relatively more covalent chloride or bromide complexes.

The actual knowledge of ligand field parameters of fluoride complexes is mainly derived from CrF_6^{---}, extensively studied by Dr. Claus Schäffer, and from FeF_6^{---}. The latter ion [2] has $\Delta = 13.9$ kK (1 kK = 1 000 cm^{-1}) and $\beta = 0.79$, as compared with $Fe(H_2O)_6^{+++}$ $\Delta = 14.2$ kK and $\beta = 0.76$. Fig. 1 indicates the reflection spectrum of K_2MnF_6, prepared according to Weinland and Lauenstein [5]. The two spin-allowed bands with maxima at 460 mμ (= 21.75 kK) and 355 mμ (= 28.2 kK) imply $\Delta = 21.75$ kK and the interelectronic repulsion parameter $B = 600$ K. Since $B = 985$ K in [6] gaseous Mn^{+4}, $\beta = 0.61$ for MnF_6^{--}. This is a surprisingly small value for a fluoride complex, showing that Mn(IV) is placed in the nephelauxetic series of metals even after Rh(III) and Co(III). Previously, it has not been possible to determine β of a Mn(IV) complex, because only the first spin-allowed band of the heteropoly molybdate was observed [7] at 21.4 kK. The latter complex has a narrow, spin-forbidden band at 14.3 kK, as also Mn(IV) heteropolywolframate [8] at 14.5 kK. This is nearly the same position as the transitions from $^4\Gamma_2$ to $^2\Gamma_3$ and $^2\Gamma_4$ in chromium(III) complexes. Kröger [9] found narrow phosphorescence lines of Mn(IV),

surrounded octahedrally by six oxygen atoms, at 15.26 and 15.32 kK. This effect corresponds to the opposite influence on the interelectronic repulsion parameters of increasing ionic charge and increasing covalency, which nearly cancel each other in Mn(II) and Fe(III) complexes [2,10]. Actually, Fig. 1 shows four weak, narrow bands * at 610, 614.5, 622 and 632 mμ. The wavenumbers 15.8 — 16.4 kK are some 8 % larger than in the oxo complexes of Mn(IV) (corresponding to the larger nephelauxetic effect of O^{--} than of F^-) and indicates a value of $\beta \sim 0.8$. In the molecular orbital theory [11] the wavenumber of $^4\Gamma_2 \rightarrow {}^2\Gamma_3$ is $3K(4,5)$, representing the interaction between two γ_5-electrons, while the energy difference between $^4\Gamma_5$ and $^4\Gamma_4$ is $J(3,4) - J(1,4) - K(3,4) + K(1,4)$, representing interactions between a γ_5- and a γ_3-electron. If the γ_3-electrons are delocalized more by σ-bonding than the γ_5-electrons are by π-bonding, this difference is intelligible. However, configuration interaction in the complex may disturb this description rather much.

In Table 1 are indicated the positions of ligand field bands of octahedral fluoride complexes, predicted from the general behaviour of Δ and β as function of oxidation state. A few such predicted values have previously been given [12]. Wheeler, Perros and Naeser [14] indicate that PtF_6^{--} has bands at 31.4 and 36.4 kK. Dr. Perros, George Washington University, Wash. D.C., has kindly informed me that these two bands have $\varepsilon = 33$ and 24, respectively, while two weak bands are observed at 22.5 and 24.5 kK with $\varepsilon \sim 4$ and 5. Thus, the spectrum resembles very much that [16] of $IrCl_6^{-3}$, and the excited levels can be

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* When K_2MnF_6 is dissolved in saturated aqueous NH_4F, relatively broad bands are observed in the red at 600, 660, and 702 mμ. Since these bands do not have the same positions as the narrow bands of the solid compound, it must be concluded that it decomposes to hydroxo- or perhaps polymeric oxo-complexes, and a slow evolution of the spectrum is also seen in some ten minutes, before the solution is too opaque of precipitated MnO_2. That hydrolysis products of halide complexes of d³-systems often have the narrow, spin-forbidden bands highly broadened and somewhat intensified, is known from rhenium(IV)[13]. The bridged compound $W_2Cl_9^{-3}$ has also anomalously high, broad bands in the red at 13.2 and 16.3 kK[12].

Table 1. Predicted positions of ligand field bands of fluoro complexes in kK (= 1 000 cm⁻¹).

d³-systems	$^4\Gamma_2 \rightarrow {}^2\Gamma_{3,4}$	$^2\Gamma_5$	$^4\Gamma_5$	$^4\Gamma_4$
MnF₆⁻⁻ obs.	16.2	—	21.75	28.2
MoF₆⁻⁻⁻	11	16	24.5	30
TcF₆⁻⁻	10.5	15	28	34
RuF₆⁻	10	14.5	31	36.5
RhF₆	9.5	14	33	38
ReF₆⁻⁻	10	15, 16.5	32	38
OsF₆⁻	9.5	14.5, 16.5	35	40
IrF₆	9.5	14, 16	37	41.5

d⁶-systems	$^1\Gamma_1 \rightarrow {}^1\Gamma_4$	$^1\Gamma_5$
NiF₆⁻⁻	20	28
RhF₆⁻⁻⁻	24.5	32
PdF₆⁻⁻	27	34
IrF₆⁻⁻⁻	28	34
PtF₆⁻⁻ obs.	31.5	36.4
(CoF₆⁻⁻⁻	$^5\Gamma_5 \rightarrow {}^5\Gamma_3$ 17)	

d⁸-systems	$^3\Gamma_2 \rightarrow {}^1\Gamma_3$	$^3\Gamma_5$	$^3\Gamma_4$(F)	$^3\Gamma_4$(P)
CuF₆⁻⁻⁻	13	15	22	35

identified as $^3\Gamma_4$, $^3\Gamma_5$, $^1\Gamma_4$, and $^1\Gamma_5$. Hepworth, Robinson, and Westland [15] give a band at 31.6 kK of IrF_6^{--}. Since it is known from the chloro complexes of 4d⁵ Ru(III) and 4d⁶ Rh(III) [16] that the first spin-allowed ligand field band occurs nearly at the same wavenumber, a similar analogy may exist between Ir(IV) and Pt(IV). Thus, RhF_6^{--} is expected to have a band ~ 350 mμ. The d⁴-systems with $S = 3/2$ might be studied as fluoro complexes for finding the ligand field bands, which are as yet not known [16]. OsF_6^{--} has a band [15] at 32.5 kK, which is expected to be found in IrF_6^- at 36 and in RuF_6^{--} at 29 kK.

There is no doubt that the quinque- and sexavalent metals have very late places in the nephelauxetic series, corresponding to a certain principle of electroneutrality [10]. The parameters of interelectronic repulsion will probably have the same magnitude as in gaseous ions with charges $+1$ or $+2$. Further, the orbital energy differences such as Δ assume large values, corresponding to the diamagnetism of NiF_6^{--} and low-spin behaviour of all the 4dⁿ- and 5dⁿ-fluorides. Nevertheless, a confirmation by measurements would be very valuable, and especially the numerical values of the nephelauxetic effect very interesting. Finally, an interesting stereochemical problem exists by comparison of the green gas RuF_5 with RuF_6^-. If the former is not a double-bridged dimer Ru_2F_{10}, it is one

of the very rare cases [12] of a d^3-system deviating from octahedral symmetry, and any information about its absorption spectrum will be highly desirable.

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Some Observations on Betaine-Homocysteine-Methyl-Transferases

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Experiments carried out in our laboratory suggest that enzymes capable of synthesizing methionine by means of a transfer of a methyl group from betaine (carboxymethyl-trimethyl-ammonium chloride) to homocysteine, are present in appreciable amounts only in the livers of vertebrate animals. Attempts to find such enzymes in microorganisms, plants or invertebrates have so far failed [1]. The apparent pH-optima of the betaine-homocysteine-methyl-transferases of all the vertebrate livers tested occur between 7.0 and 7.8. These transferases are strongly inhibited by dimethylglycine, which besides methionine is a product of the enzymic reaction [1,2]. Choline can not replace betaine as the methyl donor with purified enzyme preparations nor does choline act as an inhibitor of the transferases.

In order to study the characteristics of this type of methyl group transfer in more detail, a procedure for the purification of the betaine-homocysteine-methyl-transferase of pig liver was worked out. It comprises the following steps:

1. One part of fresh pig liver is homogenized in three parts of water in a Waring blender. The pH of the homogenate is adjusted to 5.1 at 0°C and the thick "brei" obtained immediately centrifuged at 44 000 $\times$ g for 30 min.

2. The supernatant fluid is adjusted to a pH-value of 7.7 and poured into a series of test tubes which are then placed in a water bath at 80°C for 90 sec. An inactive precipitate is formed and is removed by centrifuging at 44 000 $\times$ g for 30 min.

3. The enzyme which is contained in the supernatant fluid from step 2, is adsorbed on calcium phosphate gel prepared according to Keilin and Hartree [3]. The enzyme is eluted from the gel by means of 0.15 M orthophosphate and 0.1 M pyrophosphate.

4. The eluates from step 3 are pooled and the pH adjusted to 7.2. Acetone is added to a final concentration of 50 %. The precipitate that forms is collected by centrifuging at 5 000 $\times$ g for 10 min, dissolved in water and dialysed against water at pH 8.5.