

Studies of Absorption Spectra

IV. Some New Transition Group Bands of Low Intensity

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A group of bands with low intensities and in some cases with small halfwidths are found in the visible spectra of manganese(II), iron(II), cobalt(II) and other transition group elements. The numbers and positions of the bands are found in agreement with the crystal field theory.

According to the crystal field theory the characteristic absorption spectra of the complex ions of the transition group elements are due to transitions between a small number of discrete energy states. The fields of the nearest other atoms, *i.e.* the ligands of the complex, split the possible levels of the free ion, removing their degeneracy. Fig. 1 gives a qualitative representation of such a splitting. The energy E is given as a function of the effective perturbation strength π (*cf.* Orgel¹). At $\pi = 0$, *i.e.* the unperturbed ion, the terms are 4X , 4Y and 2Z , known from atomic spectroscopy. They exhibit the total spin quantum number $S = \frac{3}{2}$, $\frac{3}{2}$ and $\frac{1}{2}$, respectively, since the multiplicity is equal to $2S + 1$. They are split into respectively three, one and four levels by the crystal field. To a first approximation, this splitting is proportional to π . The number of levels increases generally by increasing L of the original term and by decreasing the symmetry of the field (*cf.* Bethe²). The number arising from a given term cannot exceed $2L + 1$, when comparatively small (L, S) coupling effects are not considered.

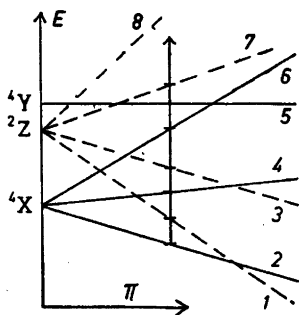


Fig. 1. Orgel diagram. Energy E as function of effective perturbation strength π . Arbitrary choice of terms in the free ion. 4X , 4Y and 2Z . The cross-points between the eight levels and the vertical line represent the possible energy levels of an ion with given π .

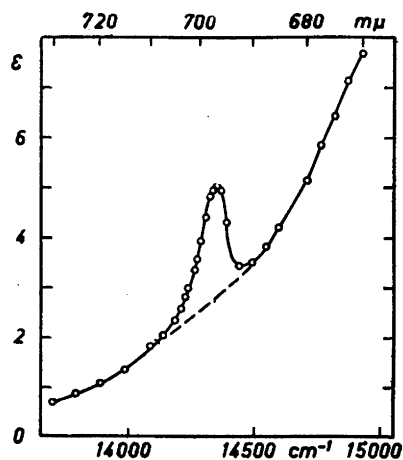


Fig. 2. Small band of tris(oxalato)chromium(III) ions. 0.13 M $K_3[Cr ox_3]$.

The vertical line in Fig. 1 represents the energy levels at a given π . The transitions between the ground-state (line 2) and the other levels with the same multiplicity (lines 4, 5 and 6) correspond to bands of ordinary intensity. As Hartmann and Schläfer³ pointed out, atomic transitions where S changes by 1 correspond to bands having intensities about one percent of the ordinary bands, which occur when S is constant under the transition. The bands mentioned in the present paper are presumably of this type: ions with from two to eight 3d-electrons can exhibit these small bands, since these ions have states of different S .

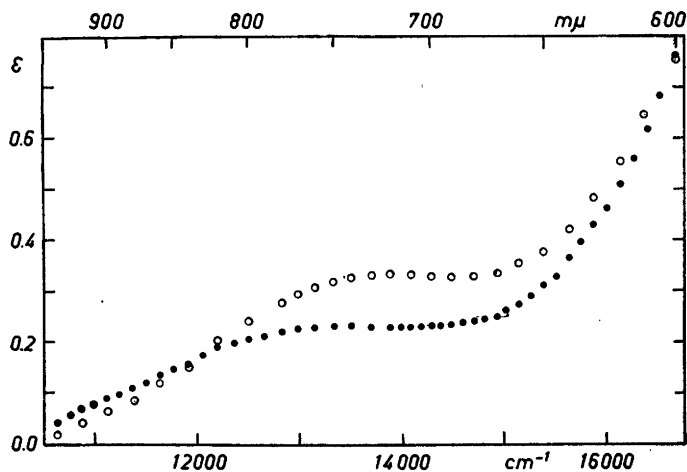


Fig. 3. Small bands of tris(ethylenediamine)cobalt(III) and hexamine cobalt(III) ions. Open circles 0.1 M and 0.8 M $[Co en_3]Cl_3$, filled circles 0.15 M $[Co(NH_3)_6]Cl_3$.

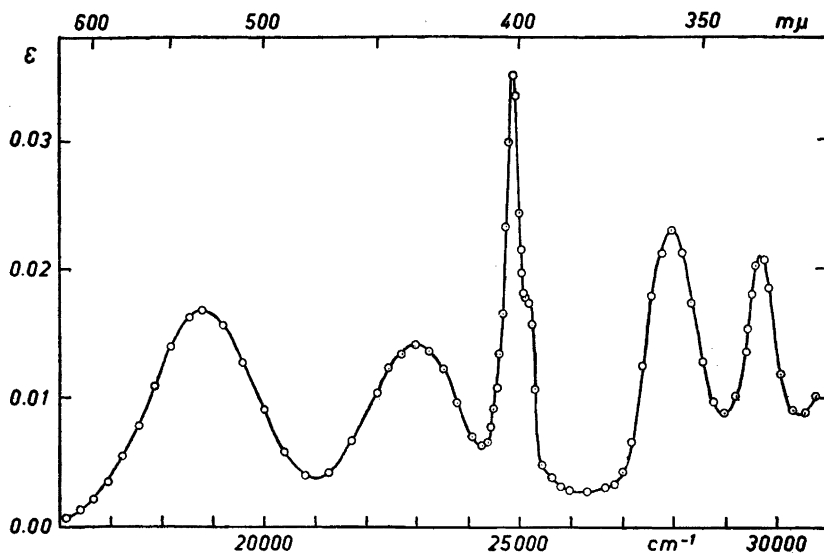


Fig. 4. Absorption spectrum of manganese (II) ions. 2.12 M $MnSO_4$, 0.04 M SO_2 .

Several bands of low intensity, known from the literature or measured here for the first time, are discussed in the first section, arranged according to the different transition group ions:

Chromium (III). It was discovered by Etard⁴ that chromium(III) complexes besides the usual two strong bands have a narrow band in the red. This was later investigated by several physicists: Bois and Elias⁵ for instance studied magnetic and temperature effects. Deutschbein⁶ concluded that the band (which also can be found as narrow lines in the spectrum of the ruby) was due to an atomic transition ${}^4F \rightarrow {}^3G$ in Cr^{+++} .

While the band in $[Cr(H_2O)_6]^{+++}$ can be clearly observed in an ordinary spectroscope, it is not easily measured by a spectrophotometer. Fig. 2 gives the small band of the tris (oxalato) complex $[Cr(ox)_3]^{---}$, which is observable with the resolving power of a Beckman DU. It is seen that it occurs at $697 m\mu$ ($14\,350\text{ cm}^{-1}$) superimposed on the tail of the strong band, and with a halfwidth about $3 m\mu$ or $\sim 60\text{ cm}^{-1}$. This is comparable with the halfwidths of the bands of the rare earth ions (see the review by Stewart⁷).

Cobalt (III). This oxidation state is perhaps only known in one complex with $S = 2$. Grey⁸ studied the light purple K_3CoF_6 , which is hydrolyzed in solution. The reflection spectrum is not known, but it is likely to have one strong band $\sim 540 m\mu$. The high absorption bands of the diamagnetic complexes ($S = 0$) are well known, and it has been found that they also exhibit small bands. Fig. 3 gives the spectra of $[Co(en)_3]^{+++}$ and $[Co(NH_3)_6]^{+++}$ in the red, where each complex has a low and very broad band with maxima at $730 m\mu$ ($13\,700\text{ cm}^{-1}$) and $770 m\mu$ ($13\,000\text{ cm}^{-1}$), respectively, and with halfwidths about $1\,700\text{ cm}^{-1}$. These bands do not seem to be caused by impurities, since the spectrum does not change by recrystallization of $[Co(en)_3]Cl_3 \cdot 3 H_2O$,

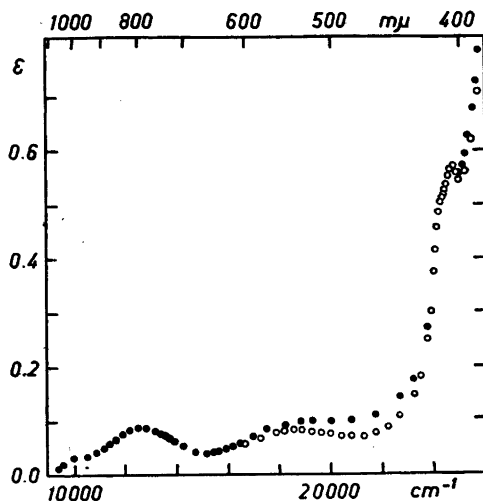


Fig. 5. Absorption spectrum of iron(III) ions. Open circles 0.1 M $Fe(ClO_4)_3$ in 8 M $HClO_4$, filled circles 0.3 M $Fe(ClO_4)_3$ in 2.5 M $HClO_4$.

or to be due to an ion association effect of the type described by Kiss and Czegledy⁹, since Beer's law is obeyed on dilution.

Manganese (II). The ground-state of the free ion,⁶ S , is not split by any crystal field (*cf.* the theory of Bethe²). Since the ion has no other state of $S = \frac{5}{2}$, only bands of small intensity should occur, provided the crystal field does not decrease the energy of one of the states with $S = \frac{3}{2}$ or $S = \frac{1}{2}$ to an extent such that it falls to a lower energy than the original ground-state and thus makes the complex magnetically anomalous (see the cross-point between the lines 1 and 2 in Fig. 1).

Fig. 4 shows the spectrum of 2 M $MnSO_4$ in H_2O and 0.04 M in SO_2 (added in order to suppress hydrolysis and traces of higher oxidation states). The bands, which are so weak that the spectrum had to be measured in 10 cm cells, can be described by the Gaussian parameters¹⁰ ϵ_n and ν_n , which are the extinction coefficient and wavenumber of the maximum of the n 'th band respectively, and $\delta(-)$ and $\delta(+)$, which are the halfwidths toward $\nu < \nu_n$ and $\nu > \nu_n$ for each band. Thus $\epsilon = \frac{\epsilon_n}{2}$ for $\nu = \nu_n - \delta(-)$ and for $\nu = \nu_n + \delta(+)$. The wavelengths λ_n of the maxima are also given (Table 1).

Table 1.

Band No.	ν_n	λ_n	ϵ_n	$\delta(-)$	$\delta(+)$
1	18 800 cm^{-1}	532 $m\mu$	0.017	1 200 cm^{-1}	1 200 cm^{-1}
2	23 000	435	0.014	900	900
3	24 900	402	0.036	200	—
4 (shoulder)	25 150	397.5	~0.018	—	200
5	28 000	357.5	0.023	600	600
6	29 700	337	0.021	400	400

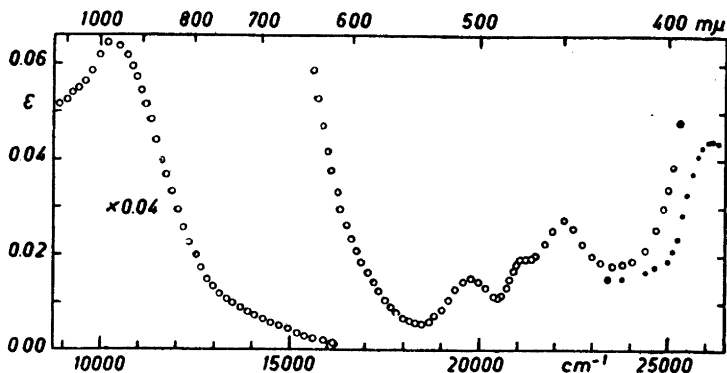


Fig. 6. Absorption spectrum of iron(II) ions. Open circles: 1 M FeSO_4 , 0.1 M SO_2 , 0.9 M H_2SO_4 . The strongest band multiplied by 0.04. Filled circles: 0.5 M FeSO_4 , 2 M H_2SO_4 , measured in the first 10 minutes after dissolution of FeSO_4 , 7 H_2O .

Kato¹¹ photographed bands at 510, 401.5, 358 and 335.5 μm , which correspond fairly well with the bands Nos. 1, 3, 5 and 6 in Table 1. The theoretical interpretation of these and other bands are given in a later section. Dreisch and Kallscheuer¹² showed that there are no bands of lower wavenumbers.

Iron(III) is isoelectronic with Mn^{++} , having the configuration $[\text{A}]3d^5$. Since the hexaquo ion is a fairly strong acid, and $[\text{Fe}(\text{H}_2\text{O})_6\text{OH}]^{++}$ is very highly absorbing, especially in the ultraviolet, the spectrum is not easily obtained pure. Fig. 5 gives the spectrum of $\text{Fe}(\text{ClO}_4)_3$ in 2.5 M and 8 M HClO_4 . Even the strongest possible acid concentration cannot totally suppress the hydroxy-complexes. The bands are given in Table 2.

Table 2.

Band No.	ν_n	λ_n	ϵ_n	$\delta (-)$	$\delta (+)$
1	12 600 cm^{-1}	794 μm	0.1	1 600 cm^{-1}	1 700 cm^{-1}
2	18 500	~ 540	0.1	$\sim 2 300$	—
3 (shoulder)	24 300	411	0.4	500	—
4	24 600	406	0.5	—	—

The narrow band discovered by Rabinowitch and Stockmayer¹³ has a fine structure (bands Nos. 3 and 4) similar to bands Nos. 3 and 4 of manganese(II). The intense molecular spectra of iron(III) complexes are due to transfer of electrons from the ligands to the central ion. They are more pronounced in "oxidizing" cations such as $\text{Fe}(\text{III})$, $\text{Cu}(\text{II})$ or $\text{Ir}(\text{IV})$ compared with ions of lower electron affinity, e.g., $\text{Mn}(\text{II})$ or $\text{Co}(\text{II})$. The wavenumbers of these bands are determined by the electron affinity of the central ion and the ionization potential of the ligands, which of course are strongly altered in the polarizing field of the central ion. For this type of band, the explanation of Linhard and Weigel¹⁴ of the $\text{Co}(\text{III})$ bands in the far ultraviolet with $\epsilon \sim 10\,000$ applies very well.

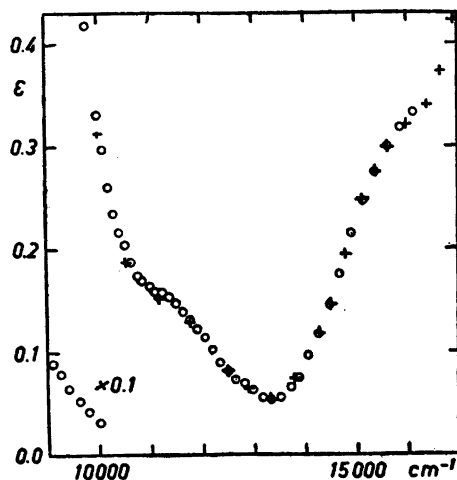


Fig. 7. Small bands of hexaquo cobalt(II) ions. Open circles 0.9 M CoSO_4 , 0.2 M H_2SO_4 , measured by the author. Cross-points 0.1 M and 0.5 M $\text{Co}(\text{NO}_3)_2$, measured by Miss Lene Rasmussen, M. Sc.

Iron(II) has six 3d-electrons. Fig. 6 gives the spectrum, which is described in Table 3.

Table 3.

Band No.	ν_n	λ_n	ϵ_n	$\delta (-)$	$\delta (+)$
1	10 400 cm^{-1}	960 $\text{m}\mu$	1.6	—	1 700 cm^{-1}
2	19 800	505	0.014	700 cm^{-1}	—
3	21 100	474	~ 0.01	~ 200	—
4	22 200	450	0.025	~ 600	~ 600
5	25 900	386	~ 0.04	~ 800	—

The first band corresponds to a transition between the two levels of the groundstate 5D , which is split up by a cubic crystal field. No evidence has been found for the vibrational structure reported by Dreisch and Trommer¹⁵ for the first band, but it is flattened somewhat as in the analogous band of copper(II) complexes¹⁶. Kato¹¹ has photographed the spectrum of an iron(II) solution with so low a metal concentration that the wavelengths 520 and 498 $\text{m}\mu$ given by Kato cannot be very certain.

Cobalt(II). This 3d⁷ system also has small bands. Fig. 7 shows the spectrum of $[\text{Co}(\text{H}_2\text{O})_6]^{++}$ in the range 9—17 000 cm^{-1} . At least two bands are found:

ν_n	λ_n	ϵ_n	$\delta (-)$	$\delta (+)$
11 300 cm^{-1}	880 $\text{m}\mu$	~ 0.1	—	1 200 cm^{-1}
16 000	625	~ 0.2	1 200 cm^{-1}	—

Dreisch and Trommer¹⁵ measured a stronger band in the infra-red at $\sim 8 000 \text{ cm}^{-1}$, which corresponds to a transition between two levels of the 4F groundstate. The tail of this band can also be seen in Fig. 7.

Nickel(II). The $3d^8$ system in $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$ does not give observable small bands. The absorption minimum at $502 \text{ m}\mu$ has $\epsilon = 0.04$, while the minimum at $895 \text{ m}\mu$ has $\epsilon = 0.29$, which can be explained by superposition of the strong bands alone¹⁰. $[\text{Ni en}_3]^{++}$ has flatter minima at $405\text{--}430 \text{ m}\mu$ ($\epsilon = 0.28$) and $\sim 670 \text{ m}\mu$ with $\epsilon = 0.7$. The strong bands are discussed in the following section.

THEORETICAL DISCUSSION

In cubic crystal fields such as originate from six octahedrally placed ligands the energy of the central ion can be expressed by

$$E = E(\text{free ion}) + NE_1 + (n-N)E_2 \quad (1)$$

where E (free ion) is the energy of the corresponding state in the free ion *in vacuo*, while E_1 and E_2 are complicated perturbation energy expressions (see, e.g., Ref.¹⁷) and $(E_1 - E_2)$ is the energy difference between the two states in a cubic field of a one-electron system. n is the number of $3d$ -electrons in the ion, and N a characteristic constant for each of the levels into which a given term in the free ion is split by the crystal field. This is a first-order approximation; for increasing values of $E_1 - E_2$ second-order contributions to the energy must also be taken into consideration.

The slopes of the lines in the Orgel diagram (*vide* Fig. 1) are given by

$$\frac{dE}{d\pi} = k\left(N - \frac{2n}{5}\right) \quad (2)$$

where k is a universal constant for all complexes of regular octahedral configuration. In the one-electron system, the upper doubly degenerate state has $N = 1$ and the lower triply degenerate state $N = 0$. As Santen and Wieringen¹⁸ pointed out, it is also formally possible in systems with more than one effective electron to consider N as the number of γ_3 -electrons and $(n-N)$ as the number of γ_5 -electrons (γ_3 and γ_5 are the two possible states of one electron in a cubic field in Bethe's notation²). The numbers N are the best first-order approximation at small perturbation strengths π .

In chromium(III) and cobalt(III) complexes the crystal field is so strong that in some cases it changes the numbers N from their first-order values. The two bands of normal intensity arise from the transitions $\gamma_5^3 \rightarrow \gamma_5^2\gamma_3$ ($S = \frac{3}{2}$) in Cr^{+++} and $\gamma_5^6 \rightarrow \gamma_5^5\gamma_3$ ($S = 0$) in Co^{+++} . As shown by Orgel¹ each of the excited states mentioned here is a doublet whose internal energy difference is $\sim 8\,000 \text{ cm}^{-1}$. In the following, energy differences will for convenience be given in the wavenumber unit, cm^{-1} , corresponding to $\frac{1}{hc}$ erg.

Manganese(II) has in the free ion *in vacuo* the following terms¹⁹ when small multiplet splittings (some hundred cm^{-1}) due to (L,S) -coupling are disregarded.

$[\text{A}]3d^5:$	6S	0 cm^{-1}
	4G	26 800
	4P	29 200
	4D	32 300
	4F	43 600

According to a theorem of Bethe², the centre of gravity of a term in the free ion cannot be displaced except by a constant amount for all terms. In the calculation of the centre of gravity the energy of each level is multiplied by its degeneracy number (*e.g.*, 1, 1, 2, 3 and 3 for Γ_1 , Γ_2 , Γ_3 , Γ_4 and Γ_5 in a cubic field²). Thus 6S and 4P , which do not split up in a cubic crystal field, must both have $N = 2$ in eq. 1, and their energy difference in the manganese (II) complex must be nearly the 29 200 cm^{-1} of the free ion. The narrow band No. 6 with $\nu_6 = 29\,700\ \text{cm}^{-1}$ is thus identified. The other bands are due to the split levels of 4G and 4D which in some cases must have N less than 2, while others have higher N corresponding to bands with wavenumbers higher than the transition in the free ion. In the eighth paper of this series, it will be shown that the deviations of N from 2 are due to second-order effects.

In iron(III) complexes the values of N are identical to those in the iso-electronic Mn^{++} . The observed states of the free ion¹⁹ when 6S is put at 0 cm^{-1} include 4G at 32 000 cm^{-1} and higher excited states. The perturbation in $[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$ must be essentially stronger than in the corresponding $[\text{Mn}(\text{H}_2\text{O})_6]^{++}$, since $(E_1 - E_2)$ is increased for the same values of N . The first four bands in each of the two spectra presumably correspond to the same transitions. The low wavenumber 12 600 cm^{-1} of the first iron(III) band shows that the magnetically anomalous state with $S = \frac{3}{2}$ is not far from crossing the ground-state (see the vertical line in Fig. 1 slightly before the cross-point of lines 1 and 2). The case where increasing perturbation decreases the wavenumber in contrast to most bands is also exemplified by the chloro- and ethylenediaminetetraacetate-complexes of Mn(II), which displace the band at 532 $\text{m}\mu$ to 524 and 540 $\text{m}\mu$, respectively, while the band at 402 $\text{m}\mu$ in the case of the ethylenediaminetetraacetate complex is displaced to 416 $\text{m}\mu$. For comparison can be stated that in nickel(II) complexes the bands are displaced in opposite directions as in most other cases — bathochromic effects in the chloro- and hypsochromic effects in the ethylenediaminetetraacetate-complexes.

The identification of the four small bands in Fe^{++} is hindered by the crowding in the free ion of the energies of 3P , 3H and 3F between 19 400 and 21 800 cm^{-1} .

In cobalt(II) the states of the free ion are¹⁹:

[A]3d ⁷ :	4F	0 cm^{-1}
	4P	15 400
	2G	17 300
	2H	23 000

It may appear anomalous that small bands are observed at wavenumbers as low as 11 300 cm^{-1} and 16 000 cm^{-1} when the excited states of $S = \frac{1}{2}$ are so high in the free ion. But the ground-state 4F is split into three levels, the lowest having $N = \frac{11}{5}$ and the others having $N = 3$ and 4^{18} . The strong band in the infrared at 8 000 cm^{-1} thus corresponds to $(3 - \frac{11}{5})(E_1 - E_2)$ in the case of $[\text{Co}(\text{H}_2\text{O})_6]^{++}$, giving $E_1 - E_2 = 10\,000\ \text{cm}^{-1}$. Since the excited states can assume considerably lower values of N (minimally 1, since at most six γ_5 -electrons can occur in the system), a perturbation energy of $(1 - \frac{11}{5})(E_1 - E_2) = -12\,000\ \text{cm}^{-1}$ is possible, thus explaining the low wavenumbers of the observed small bands.

The observed energy differences in nickel(II) complexes are explained very well by the crystal field theory, as expressed in eq. 1. In the free ion ¹⁹ ³P is situated 16 900 cm⁻¹ over the ground-state ³F. If ($E_1 - E_2$) = 7 600 cm⁻¹ in [Ni(H₂O)₆]⁺⁺ and 10 500 cm⁻¹ in [Ni en₃]⁺⁺, remarkable agreement with the experimental data is obtained (Table 4).

Table 4.

Transition	Energy difference	[Ni(H ₂ O) ₆] ⁺⁺		[Ni en ₃] ⁺⁺	
		calc.	obs.	calc.	obs.
³ F(Γ_3) - ³ F(Γ_5)	1($E_1 - E_2$)	7 600 cm ⁻¹	~ 8 000 cm ⁻¹	10 500 cm ⁻¹	11 200 cm ⁻¹
³ F(Γ_2) - ³ F(Γ_4)	$\frac{9}{5}(E_1 - E_2)$	13 700	~14 000	18 900	18 350
³ F(Γ_2) - ³ P(Γ_4)	$\frac{6}{5}(E_1 - E_2) + 16 900$ cm ⁻¹	26 000	25 300	29 500	29 000

The crystal field quantum numbers of the levels are given in parentheses, using the notation of Bethe ². The conclusion drawn by Roberts and Fields ²⁰ that the term scheme of nickel(II) complexes disagrees with the crystal field theory does not seem to be justified. Recently Griffiths and Owen ²¹ identified the two first bands of the aquo nickel(II) ion with the internal transitions of ³F.

No cubic crystal field alone can make a nickel(II) complex diamagnetic ($S = 0$), since the ground-state ³F(Γ_2) has $N = 2$, which is the lowest number of γ_3 -electrons any d⁸-system can have. But tetragonal fields of sufficient strength can give one of the states with $S = 0$ lower energy than the original state with $S = 1$, as predicted by Orgel ¹. Calculations of C. J. Ballhausen, to be published later, show that it is one of the three states which in a cubic field degenerate to the level ¹G(Γ_4) that has strongly decreased energy in the square-planar nickel(II) complexes. Second-order effects in strong crystal fields of tetragonal symmetry can also decrease the energy of one of the two states, forming the cubic level ¹D(Γ_3).

The copper(II) aquo ion was discussed by J. Bjerrum *et al.*¹⁶ and found to be a distorted octahedral complex [Cu(H₂O)₆]⁺⁺, the absorption spectrum consequently being greatly influenced by tetragonal fields. Another proof of the non-regularity of the coordination sphere of copper(II) is the decreasing value of ($E_1 - E_2$) found in divalent aquo ions of the first transition group except in Cu⁺⁺:

V ⁺⁺	~13 000 cm ⁻¹
Cr ⁺⁺	~12 000
Fe ⁺⁺	10 400
Co ⁺⁺	~10 000
Ni ⁺⁺	7 600
Cu ⁺⁺	13 600

showing that the quantity ($E_1 - E_2$) is not determined by a pure cubic field¹ in the last ion. The values of ($E_1 - E_2$) for trivalent hexaaquo ions are of the order of magnitude 20 000 cm⁻¹, because the ionic radii are smaller and the perturbation effects thus larger.

The first-order approximations of the crystal field theory thus accommodate all observed features of the absorption spectra. In particular the narrow bands

are placed at nearly the same wavenumbers as with the free ions *in vacuo*, because the perturbation energies of the excited and the ground-states are nearly equal (*i.e.* the two lines in the Orgel diagram have equal slopes as the lines 2 and 3 in Fig. 1). In these cases the suggestions of Deutschbein⁶ and Kato¹¹ are thus correct. The distinction between weak and strong crystal fields is only significant in the systems with more effective electrons, *i.e.* from d^2 to d^8 , which are also the configurations presenting more values of S .

EXPERIMENTAL DETAILS

The spectra were measured in 10 cm cylindrical or 1 cm rectangular absorption cells at 25° C in a Beckman DU spectrophotometer. The solutions were rendered dust-free by filtration through the new Frisenette filters No. 651. These seem to produce slight absorption in the ultraviolet, but were nevertheless very useful for the measurements made here.

The salts used for the measurements were Merck and AnalaR reagents, selected with special regard to avoiding traces of other coloured materials (*e.g.* Fe in manganese(II) or Ni in cobalt(II) salts).

While most interest in absorption spectra has been concentrated on the maxima of the bands, the minima studied here (in 1 M solutions using 10 cm cells) may also have some analytical interest. Thus coloured impurities at 10^{-4} M concentration can often be directly determined. None of the new bands found are situated where strong bands of other transition group ions might be expected.

In iron(II) solutions containing high excess of SO_2 and only a little H_2SO_4 , a straw-yellow colour is observed, presumably from sulphito-complexes. These have a steeply increasing absorption from the blue and outwards into the ultraviolet, due to molecular spectra with high extinction coefficients. But the small quantity of SO_2 added to FeSO_4 in addition to the H_2SO_4 had no influence on the small bands. For stoichiometrical reasons, MnSO_4 cannot have been disturbed by the addition of SO_2 . 6 M HCl alters the spectrum considerably, due to formation of chloro-complexes. A solution of MnSO_4 and excess of tetrasodium ethylenediaminetetraacetate was also measured. It is not oxidizable by the air. The difficulties in preparing pure $[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$ from $\text{Fe}(\text{OH})_3 + \text{HClO}_4$ have been mentioned above. As comparison solutions sulphuric acid and perchloric acid were used at the same concentrations as the total content of sulphates and perchlorates in the measured solutions. This is important in the infra-red, where water is strongly absorbing.

The small bands of $[\text{Co}(\text{H}_2\text{O})_6]^{++}$ must not be confused with the bands in the orange of chloro-cobalt(II) complexes and other acido complexes. Miss Lene Rasmussen, M. Sc., of this laboratory, has shown that the spectrum of 0.5 M CoCl_2 in water does not differ from the usual aquo ion spectrum.

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