

西-1244

Basic principles of LIGAND FIELD THEORY

H. L. Schläfer
G. Gliemann



Basic Principles of
LIGAND FIELD THEORY

Hans L. Schläfer

and

Günter Gliemann

Translated from the German by

David F. Ilten

WILEY-INTERSCIENCE

a division of John Wiley & Sons Ltd.

LONDON NEW YORK SYDNEY TORONTO

Copyright © 1969 John Wiley & Sons Ltd.
All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical photocopying, recording or otherwise, without the prior written permission of the Copyright owner.

Library of Congress catalog card no. 77-83220

SBN 471 76100 1

Set on Monophoto Filmsetter and
printed by J. W. Arrowsmith Ltd., Bristol, England

Preface

It is not necessary to expand upon the great importance of ligand field theory in the chemistry of transition metal compounds. With the present treatment we have attempted to give an easily-readable introduction to this theory. The necessary concepts are for the most part introduced on the basis of experimental results, and we hope this will prove useful to the experimental chemist.

The book represents a revised and expanded form of lectures and problem sessions held in the physical chemical institute in Frankfurt as well as in the International Summer School in Constance (Lake Constance) in 1962 and in courses on ligand field theory held in Buckow (DDR) in 1964 and in other places.

We wish to thank Dr. G. Herzog and Dr. O. Steinborn, who kindly assisted with the reading of proofs.

Frankfurt am Main, January, 1966.

HANS LUDWIG SCHLÄFER
GÜNTER GLIEMANN

General introduction

During the last ten years a theoretical concept, the so-called crystal field or ligand field theory, has proved of great value in discussions of the properties of transition metal compounds and especially of metal complexes. With the aid of ligand field theoretical concepts it is possible to understand a whole series of physical and chemical properties of transition metal complexes from a unified point of view, and to obtain at least semiquantitative information. On this basis the optical properties of the vast majority of coordination compounds of transition metal ions can be interpreted. Other problems, e.g. the description of magnetic properties, of stereochemical irregularities and questions of kinetic and thermodynamic stability can also be treated effectively.

It is hardly possible today to discuss the chemistry of the transition metals, as offered in general lectures on inorganic chemistry, without employing ligand field theory. It is difficult to find a better example of how useful meaningfully chosen models can be for understanding a large body of exceedingly varied experimental results. Nevertheless, only comparatively few basic concepts are required for a first qualitative understanding of the theory.

In this book an attempt will be made to offer the chemist access to the ligand field theory. We thus intentionally make no attempt to present a complete and self-contained systematic treatment. We refer to the excellent monographs by Ballhausen* and Griffith* as well as to numerous review articles in which those interested in a systematic presentation will find everything necessary. The books by Jørgensen* give a good general survey, especially of the interpretation of absorption spectra of transition metal complexes. Cotton* offers a comparable treatment of group theoretical methods.

According to the impression gained from numerous discussions with colleagues and students, and especially from the experience of introductory lectures held at the Frankfurt institute and elsewhere, understanding ligand field theory presents the chemist with certain difficulties. Not the least cause of these is a lack of familiarity with group and quantum theoretical concepts, often coupled with a lack of the necessary mathematical background. Therefore the emphasis has been placed on didactical

* These references are listed in the bibliography at the end of the book, p. 499 ff.

questions in the following presentation. Prerequisites for understanding this book are simply a basic knowledge of complex chemistry, physical chemistry, physics and mathematics, which the student should have normally obtained by the 'Diplom' examination.

The book consists of two main parts. The first part gives a qualitative introduction to the basic concepts, using selected examples from the field of transition metal complex spectroscopy. These concepts are then used in a study of the magnetic behaviour and thermodynamic stability of complex ions in solutions, the kinetic behaviour in ligand exchange reactions, and other questions from the physical chemistry of coordination compounds. This is done almost completely without the use of mathematical formalism. Rather we have attempted to give a phenomenological presentation on the basis of experimental findings. In doing this it was not possible to avoid making certain compromises, which certainly could be open to much criticism.

The material of this first part is intended to give the reader an impression of the underlying model and of its capabilities of interpreting the properties of transition metal complexes. Among other things it is shown what concrete information can be obtained in special cases, e.g. in the identification of *cis-trans* isomers of $[MA_4B_2]$ complexes ($M = Cr^{3+}, Co^{3+}$) on the basis of absorption spectra, the question of the appearance of low-spin complex ions, the connection between stereochemistry and the orbital moment contribution to the magnetic moment for Co^{2+} and Ni^{2+} compounds, the problem of the pronounced stability of Co^{3+} and Cr^{3+} complexes in ligand exchange reactions, and so on.

In the second part an introduction to the mathematical treatment is offered to those who are interested in a deeper understanding. Here we have utilized experience gained in holding seminars and problem sessions. The material of this more demanding part requires rather intensive concentration, especially from the chemist not fully acquainted with the thinking patterns of the theoretical physicist. Also, the knowledge of certain mathematical principles is essential. As an aid we have collected in an appendix important elements of matrix and determinant theory, as well as explanations of the terms operator, eigenvalue, normalization, orthogonality, etc. in condensed form.

It is recommended that the reader not familiar with the elementary basis of quantum theory should study the appropriate sections in one of the introductory texts cited before beginning the material of part B. A presentation of these additional points would have produced a book of unmanageable length. The derivation of the necessary quantum mechanical relations and group theoretical theorems is not given; neither is the pertinent literature. The second part rather attempts to explain the necessary

calculatory methods by using selected examples. The chapter on the theory of the states of free atoms and ions is followed by a section on the basic principles of group theory, in so far as these are necessary for application in ligand field theory. After the treatment of the splitting of the one-electron d states in ligand fields of various symmetries, a presentation of the methods of determining the term systems of complex ions whose central ions contain several d electrons follows. The molecular orbital method is also treated (and in the appendix the valence bond method). Sections on spin-orbit coupling as well as magnetic susceptibility follow. In all cases the problems are explained on the basis of typical examples, for which the method of calculation is presented.

Finally a collection of important original literature, arranged in order of topics, is given, which is intended to make it easier for the reader to study particular questions in more detail.

The following book was arranged so as to give the chemist an easily-readable introduction to the ligand field theory. After studying the first part he should be in a position to understand the important concepts of the theory and to have an idea of their applicability. After completing the second part the reader should be capable of grasping the quantitative side as well, at least in its elementary form, so that he can treat simple problems and can read the original literature. The material given in the review articles and monographs cited in the bibliography should then offer no further difficulties.

For the majority of the symmetries which usually appear for complex ions, especially for the cubic microsymmetry realized at least approximately in the largest number of cases, (symmetry groups O_h or T_d), the term systems for the complexes with central ion having 1 to 9 d electrons have been calculated and the matrix elements are given in the original papers (cf. bibliography). Generally, therefore the chemist today fortunately does not need to carry out calculations himself. He will, using term diagrams or tabulated matrix elements, simply obtain the parameters characterizing the ligand field, e.g. from the absorption spectra, and assign the observed bands to specific electronic transitions. Also in those cases where spin-orbit coupling plays an important rôle, e.g. in magnetic susceptibility or the g factor, the theory is so far developed that for many problems one can refer to original papers in which the needed matrix elements are given.

Contents

General introduction	ix
PART A	
1 Optical properties of transition metal complexes	
1.1 Historical survey and description of the problem	2
1.2 Survey of the experimental findings; absorption spectra of selected metal complexes	4
1.3 The complex models of Kossel-Magnus and of Pauling	13
1.4 The extended ionic model: The ligand field	15
1.5 Term splitting under cubic symmetry	24
1.6 Analysis of absorption spectra	28
1.7 The strong- and weak-field methods	51
1.8 Term diagrams	70
1.9 Dq values, Racah parameter B, spectrochemical and nephelauxetic series	76
1.10 Relative intensities and half widths	84
1.11 Spin-orbit coupling	93
1.12 Treatment of complexes by the molecular orbital theory	97
1.13 Charge-transfer spectra	109
2 Magnetic properties of transition metal complexes	
2.1 General introduction. Survey of experimental findings	118
2.2 Interpretation of low-spin complexes according to Pauling	120
2.3 Interpretation of the appearance of low-spin complexes on the basis of the ligand field theory	126
2.4 Orbital moment contribution and stereochemistry	131
2.5 The refined theory of the paramagnetic susceptibility of transition metal complexes; consideration of spin-orbit coupling	137
3 Stabilization of ions	
3.1 Ligand field stabilization of cubic complexes	142
3.2 Stabilization and tendency of formation of low-spin complexes	147
3.3 Influence of ligand field stabilization on the thermodynamic properties of transition metal complexes	150
3.4 The relative stability of tetrahedral and octahedral high-spin complexes	158
3.5 Ionic radii of transition metals of the iron group	160

4 Consequences of the Jahn–Teller theorem for transition metal complexes	164
5 The kinetic stability of transition metal complexes	176
6 Bonding	186

PART B

1 The theory of free atoms and ions.

1.1 One-electron systems	207
1.1.1 The energy	207
1.1.2 The orbital angular momentum	215
1.1.3 The electron spin	220
1.2 Many-electron systems	222
1.2.1 The Schrödinger equation	222
1.2.2 The central-field approximation	223
1.2.3 Electron configurations	226
1.2.4 Total angular momentum and total spin	232
1.2.5 The states ^{2S+1}L	235
1.2.6 The functions $\psi(L, M_L, S, M_S)$	238
1.2.7 Electron interaction	243
1.2.8 The matrix elements (ψ, H_1, ψ)	247

2 Group theory

2.1 Symmetry operations and symmetry groups	255
2.1.1 Definition of a symmetry operation and of a group	255
2.1.2 Classes and subgroups	260
2.1.3 Special symmetry groups	261
2.2 Representations	270
2.2.1 Definition of a representation	270
2.2.2 Equivalent representations: similarity transformations	276
2.2.3 Characters	277
2.2.4 Reduction of representations	278
2.3 Coordinate transformations	286
2.4 Group theory and quantum mechanics	293
2.4.1 The symmetry group of the Hamiltonian	293
2.4.2 Degenerate systems	296
2.4.3 Perturbation theory	309
2.5 Product representations	312
2.6 Double groups	317

3 Ligand field theory	
3.1 The model	321
3.2 Ligand fields	324
3.3 d^1 systems	333
3.3.1 <i>Ligand fields of O_h symmetry</i>	336
3.3.2 <i>Ligand fields of symmetry T_d</i>	342
3.3.3 <i>Ligand fields of symmetry D_{4h}</i>	343
3.4 d^N systems	347
3.4.1 <i>The weak-field case</i>	348
3.4.2 <i>Strong-field case</i>	362
3.4.3 <i>Rigorous treatment</i>	386
4 The molecular orbital theory as an extension of the ionic ligand field theory	
4.1 The method	407
4.2 Symmetry-adapted functions	410
4.3 Energies	419
5 Spin-orbit coupling and magnetic properties	
5.1 Spin-orbit coupling in free atoms and atomic ions	429
5.2 Spin-orbit coupling of d^1 ions in ligand fields of octahedral symmetry	438
5.3 Zeeman effect in free atoms and atomic ions	448
5.4 Zeeman effect on octahedrally bound d^1 ions	453
5.5 Magnetic susceptibility	459
PART C	
Appendix	
1 Mathematical terms and aids	465
2 Character tables of the point groups of most importance for the ligand field theory	479
3 The most important symmetries of complex ions	481
4 Hybridization of central ion orbitals in the valence bond theory	484
5 Selection rules	494
6 Atomic units	498
Bibliography	499
Subject Index	521

PART A

1. Optical properties of transition metal complexes

In the following it is planned to present the underlying concepts of the ligand field theory on the basis of a discussion of selected absorption spectra of transition metal ions in the visible and ultraviolet regions. We have chosen this method because the interpretation of spectra represents an especially impressive example of the application of the theory. Also, such a phenomenological treatment is well suited to the experimental background of the chemist. Certainly it would have been simpler to introduce the principles of the ligand field theory by considering the magnetic moments of the transition metal complex ions. In that case one is generally interested in only the energetically lowest-lying (most stable) state of a compound—the ground state. On the other hand, a treatment of the optical properties requires the consideration of the energetically higher-lying (excited) states because the maxima of the absorption bands are to the first approximation associated with transitions from the ground state to the respective excited states. It is well known that in most cases it is possible to explain magnetic properties—at least in so far as is necessary to rationalize the existence of low-spin complexes—with the help of *Pauling's valence bond theory*. This theory is of course familiar to the chemist. However, the valence bond theory does not provide a suitable interpretation of absorption spectra, whereas the crystal field or ligand field theory* does. When considering magnetic properties one is concerned with comparing only a single value with experiment, namely the multiplicity of the ground state and thereby the effective magnetic moment at room temperature of the compound in question. However, when one is interested in interpreting absorption spectra, the theory must provide the number and relative location of all the various absorption bands (e.g. the $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ion has eight bands). Certain effects such as the splitting of energy levels accompanying a descent in symmetry are sometimes reflected directly in the visible absorption spectrum. Therefore, the range

* Concerning the use of the terms crystal field or ligand field, cf. p. 17 (footnote).

of phenomena embraced by the theory is greater than for the case of magnetic moments.

1.1 Historical survey and description of the problem

A collection of brilliantly coloured, beautifully crystallized salts of metal complexes is aesthetically pleasing to the casual observer; for the spectroscopist it presents an immediate challenge. The prefixes such as violeo-, praseo-, luteo-, purpureo-, roseo-,* refer to the most variegated visual impressions given by such compounds. When one considers their underlying chemical structures, the remarkable colour changes which accompany a change of ligand or of steric arrangement are brought to mind. The transition metal complexes are especially well suited for investigations on the relationship between colour and composition. They show an amazing variety of colours and at the same time variations of the basic chemical structure are easily obtained. It is therefore not surprising that directly after the introduction of the coordination theory by Alfred Werner¹ several of his students began to study the absorption spectra of solution complexes. The results of these early investigations conducted in Werner's laboratory in Zürich are to be found only in doctoral dissertations.

Starting about 1915 spectroscopic studies were undertaken by such Japanese investigators as Shibata and co-workers² and later by Tsushida

* These notations, which were introduced by Fremy (*Ann. Chim. Phys.*, **35**, 257 (1852)), give the colours of the appropriate complexes, e.g. $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ is also called bromopurpureo-cobalt (III) ion. Today one occasionally uses these notations to describe classes of compounds.

Colour	Name	Structure
green	praseo-	$\text{trans-}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
violet	violeo-	$\text{cis-}[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
purple red	purpureo-	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
rose	roseo-	$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$
yellow	luteo-	$[\text{Cr}(\text{NH}_3)_6]^{3+}$ bzw. $[\text{Co en}_3]^{3+}$
yellow	croceo-	$\text{trans-}[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$
brown	flavo-	$\text{cis-}[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$

1. Cf. A. Werner: *Ber. dt. chem. Ges.*, **40**, 15 (1907) A Werner: *Neuere Anschauungen auf dem Gebiet der anorganischen Chemie*, revised by P. Pfeiffer, Friedr. Vieweg und Sohn, Braunschweig, 1923. R. Weinland: *Einführung in die Chemie der Komplexverbindungen*, 2nd edn, Ferdinand Enke Verlag, Stuttgart, 1924.
2. Y. Shibata: cf. contribution in *J. Coll. Sci. imp. Univ., Tokyo*, 1915 to 1921, also *J. chem. Soc. Japan*, 1915; *Compt. Rend.*, 1913.

*et al.*³. Also, von Kiss and co-workers⁴ and Samuel *et al.*⁵ have measured numerous absorption spectra of complexes in solution. On the basis of these findings the authors attempted to derive phenomenological rules, for example, relating the number of bands to the nature of the central ion, or describing the position of the bands as a function of the nature of the ligands for complexes having similar structures. Joos and Deutschbein⁶ and Bose and Datta⁷ attempted to give interpretations using the theory of electrons. It was soon recognized that *d* electrons are important in determining the colour of transition metal ion complexes. Further, concepts of polarization as introduced by Fajans proved to be useful⁸.

None of these efforts, however, led to a satisfactory solution of the problem cited. Certainly not the least cause of this failure was the fact that the published spectra could not stand up to a critical examination. First of all in the years before 1940 the technique and apparatus for measuring absorption spectra had not been developed far enough to give results of the quality which can be obtained today almost effortlessly using commercial spectrophotometers. Secondly, far too little attention was paid to the state of the solution for the majority of the spectral studies on solutions. Frequently, depending upon the conditions of concentration and acidity, the most diverse ionic species can appear (consecutive equilibria between various complex species, hydrolysed ions, etc.). These species can all contribute to the absorption. That is, one cannot assume that the absorbing ion in the solution is the same ion which exists in the solid salt. Furthermore, in many cases the substances studied were not sufficiently pure; they can seldom be prepared without chemically-similar side products being present.

Only after about 1940 did systematic investigations of the absorption spectra of dissolved complexes take all necessary factors into account.

3. R. Tsuchida: *Bull. chem. Soc. Japan*, **13**, 388, 436, 471 (1938); **15**, 427 (1940); and other works.
4. A. v. Kiss and others: *Acta chem. mineralog. physica (Szeged)*, **7**, 119 (1939); *Z. phys. Chem.* **A 180**, 117 (1937); **A 186**, 239 (1940); *Z. anorg. allg. Chem.* **235**, 407 (1937); **244**, 98 (1940); **245**, 355 (1940); **246**, 28 (1941); other works, e.g. *Acta chim. hung.*
5. R. Samuel and others: *Trans. Faraday Soc.*, **31**, 423 (1935); *Z. phys. Chem.*, **B 22**, 424 (1933); *Z. Phys.*, **80**, 395 (1933); and other works.
6. G. Joos: *Ann. Phys.*, **81**, 1076 (1926); **85**, 641 (1928); *Ergebn. exakt. Naturw.*, **18**, 78 (1939); *Z. phys. Chem.*, **B 20**, 1 (1933); *Phys. Z.*, **29**, 117 (1928); and other works. O. Deutschbein: *Z. Phys.*, **77**, 489 (1932); *Ann. Phys.*, **14**, 753 (1932); **20**, 828 (1934); and other works.
7. D. M. Bose and S. Datta: *Z. Phys.*, **80**, 376 (1932).
8. K. Fajans: *Z. Kristallogr. Mineralogr. Petrogr.*, **A 61**, 18 (1925); **A 66**, 321 (1928); *Naturwiss.*, **11**, 165 (1923). K. Fajans and G. Joos: *Z. Phys.*, **23**, 1 (1924).

Of these, the work of Linhard and co-workers⁹ on Co^{3+} and Cr^{3+} complexes stands out as an example of utmost precision. With this work the necessary material for a theoretical investigation became available. Because many compounds are stable only in the solid state, the spectroscopy of crystalline compounds, especially the determination of reflectance spectra of finely pulverized salts, as has been made possible by the critical and pioneering work of Kortüm¹⁰, has developed into a very important tool of the complex spectroscopist.

1.2. Survey of the experimental findings; absorption spectra of selected metal complexes

The absorption spectra of complexes of transition metals, with the exception of certain examples which will be treated later, have in general an appearance such as is schematically indicated in Figure A.1. In the

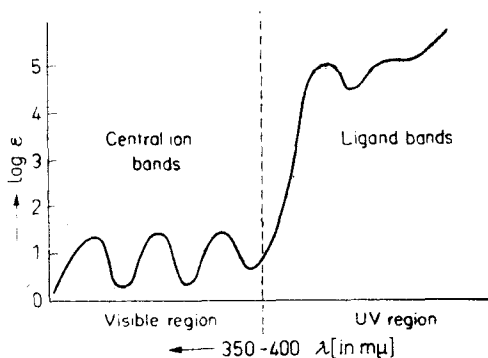


Figure A.1. Absorption spectrum of a transition metal ion complex (schematic). $\lambda < \text{ca. } 350\text{--}400 \text{ m}\mu$ ligand bands. (a) Charge transfer bands (Transitions: I Central ion \rightarrow ligand; II ligand \rightarrow central ion). (b) Transitions between states of the ligands. Inner-ligand transitions. e.g. $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$; $\lambda > \text{about } 350\text{--}400 \text{ m}\mu$ central ion bands ($d \rightarrow d$ bands).

9. M. Linhard and others: *Z. Electrochem.*, **50**, 224 (1944); *Z. anorg. allg. Chem.*, **262**, 328 (1950); **264**, 321 (1951); **266**, 49, 73 (1951); **267**, 113, 121 (1951); **271**, 101, 131 (1952); **278**, 287 (1955); *Z. phys. Chem. (Frankfurt)*, **5**, 20 (1955); **11**, 308 (1957); and additional works.
10. G. Kortüm and J. Vogel: *Z. phys. Chem. (Frankfurt)*, **18**, 110, 230 (1958). G. Kortüm and G. Schreyer: *Angew. Chem.*, **67**, 694 (1955); *Z. Naturf.*, **11a**, 1018 (1956). G. Kortüm: *Spectrochim. Acta. Coll. spectrosc. internat.* VI, 534 (1957). G. Kortüm and D. Oelkrug: *Naturwiss.*, **23**, 600 (1966).

region between 200 and 1000 $m\mu$ ($50,000$ – $10,000\text{ cm}^{-1}$) bands of varying intensity are found. In the long wavelength spectral region, that is, with $\lambda > 350$ – $400\text{ m}\mu$, one finds one or more bands with values of the logarithm of the molar decadic extinction coefficient ($\log \epsilon$) for the band maxima which lie between roughly 0 and 2. In the short wavelength portion of the spectrum, that is, for wavelengths < 350 – $400\text{ m}\mu$, intense absorption bands with $\log \epsilon$ values of the order of 4–5 appear. They are approximately as intense as similar bands in organic dyes.

For the case of metal complexes where the central ion is not a transition metal ion, e.g. Al^{3+} or Zn^{2+} , the weak bands at long wavelengths do not appear. However, the intense absorption bands at long wavelengths remain. (Compare Figures A.2 and A.3, the spectra of $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$ and

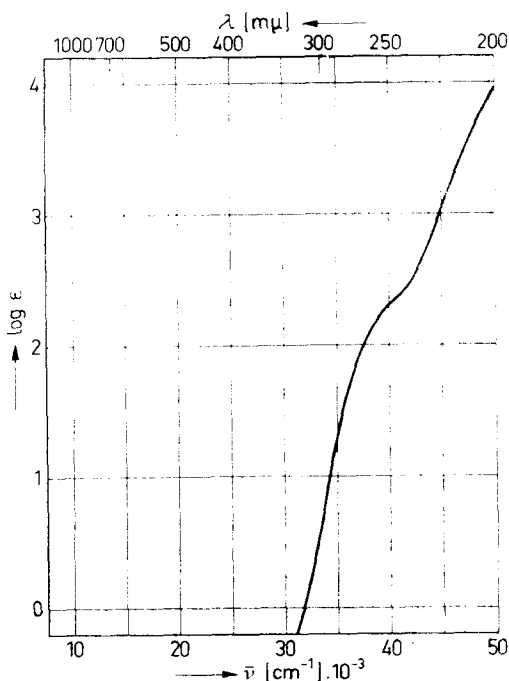


Figure A.2. Absorption spectrum of $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$.

$[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$). The weak bands in the long wavelength region were already assigned to the d electrons of the central ion by Shibata. They originate from transitions within the d shell, so-called $d \rightarrow d$ transitions. We shall refer to them summarily as *central ion bands* ($d \rightarrow d$ bands).

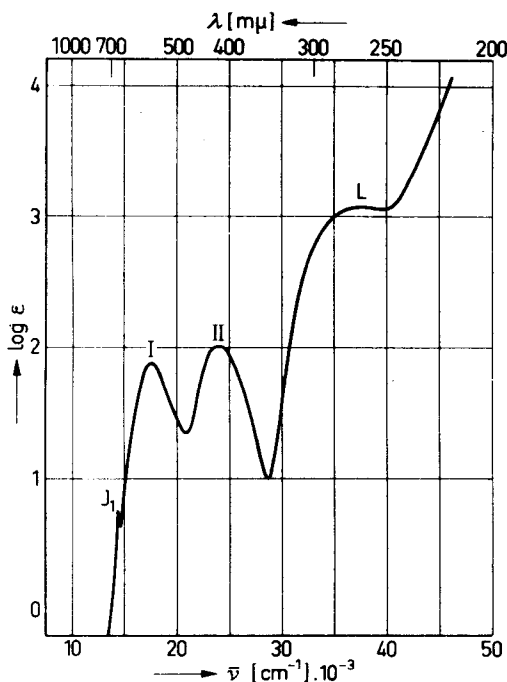


Figure A.3. Absorption spectrum of $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$.

For complex ions with the usual ionic, dipolar- or dipolar-ionic ligands such as F^- , Cl^- , Br^- , I^- , NO_3^- , NO_2^- , SO_4^{2-} , SO_3^{2-} , NH_3 , $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (en), $\text{CO}(\text{NH}_2)_2$, CH_3CO_2^- , $\text{C}_2\text{O}_4^{2-}$ (ox), H_2O and ROH, the intense bands at short wavelengths are usually *charge transfer bands*, as has been indicated by Rabinowitsch¹¹, Linhard¹² and others. One usually is able to observe only the general sharp rise of these bands (and not the fine structure). Absorption of light in this spectral region is accompanied by an electron transfer from the central ion to the ligand, an idea first applied by Franck and Scheibe¹³ to the interpretation of the absorption spectra of free halogens in aqueous solutions. For the case of the free halogens Cl^- , Br^- , and I^- the electron transfer probably takes

11. E. Rabinowitsch: *Rev. mod. Phys.*, **14**, 112 (1942); cf. also L. E. Orgel: *Q. Rev. chem. Soc.*, **8**, 422 (1954).
12. M. Linhard and others: *Z. anorg. allg. Chem.*, **262**, 328 (1950); **266**, 49 (1951); and additional works.
13. J. Franck and G. Scheibe: *Z. phys. Chem.*, **A 139**, 22 (1928). J. Franck and F. Haber: *Sitz. Ber. preuss. Akad. Wiss., phys.-math. Kl.*, 1931, 250.

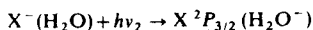
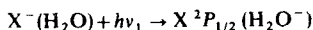
place from the halogen ion to a water molecule of the hydrate sphere*.

For chloro-, bromo-, and iodo-complexes, the most intense absorption bands of the inner complex halogen ions appear in the short wavelength spectral region. These bands generally have a form similar to that of free halogen ions, but have undergone a red shift. Similar facts are true for the complex ions formed with the other ligands which were discussed earlier. For the case of chromium(III) trisethylenediamine molecules one finds in the u.v. the band of the inner-complex ethylenediamine molecule. This, however, appears at longer wavelengths as compared to the band of the free ethylenediamine molecule. It is in general observed that the absorption of the free ligand, after it has been complexed, undergoes a small red shift†.

In Figure A.4 the absorption bands of various free ions and molecules which frequently function as complex ligands are presented. (Compare the band of the free oxalate ion with the u.v. absorption of $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ or $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$, Figures A.2 and A.3.)

We shall refer to the intense u.v. absorption bands as ligand bands. Besides the charge-transfer bands of the ligand, other bands, such as those of complexes with organic ligands having π -electron systems, can appear. When studying pyridine complexes, one observes the u.v. absorption band of the inner complex of pyridine, which has undergone only a slight shift to longer wavelengths in comparison to that of free pyridine (Figure A.5). Frequently traces of the vibrational fine structure of the pyridine band are found in the spectra of pyridine complexes (Figure A.9). This is a case of $\pi \rightarrow \pi^*$ transitions (*inner ligand transitions*) of the pyridine molecule which are modified slightly by the polarizing influence of the central ion as the complex is formed. In certain cases it is also to be expected that electron transfers between essentially ligand states can appear.

* Interpretation of the spectra of dissolved halogen ions X^- as charge-transfer spectra is supported by the fact that in these spectra in general two intense bands are found. Their difference in wave-number $\Delta\bar{\nu}$ corresponds approximately to that of the ground doublet $^2P_{3/2} - ^2P_{1/2}$ of the free halogen atoms equation



$\Delta\bar{\nu}$ for the free halogen atoms I, Br, and Cl is 7600, 3600 and 880 cm^{-1} respectively. Schiebe, Fromherz and Menschick (Z. Phys. Chem., Haber Band, 22(1928); Z. Elektrochem., **34**, 497 (1928); Z. Phys. Chem., **B5**, 355 (1929); Z. Phys. Chem., **B7**, 439 (1930); **B3** 1 (1929) found the following separations of the band maxima for aqueous alkali halogenide solutions: for I^- 7300 cm^{-1} , for Br^- 2000 cm^{-1} , for Cl^- only one band which can be interpreted as being the superposition of two maxima of the same height lying close to one another. In recent years these suggestions have been refined. (R. Platzman and J. Franck, *Farkas Memorial Volume*, Weizman Press, Jerusalem 1952; Z. Physik, **138**, 411 (1954)).

† Complexes having central ions of lower valence are an exception, e.g. the tris-dipyridyl compounds described by Herzog and coworkers. $[\text{Vdip}]^+$, $[\text{Vdip}_3]$, $[\text{Vdip}_3]^-$ (dip = α, α' dipyridyl).