

Chapter II

Theory of polymer-metal complexes

Previous works and applications

In recent years, the studies of polymer metal complexes have been great interested for several reasons. Thus, polymer-metal complexes may be used as models for metalloenzymes, as electrode coating , as catalysts for dehydrogenation, as catalyst-sensitizers for photodissociation of water, and used for magnetic properties.

Literature studies of polymer-metal complex

Polymethacrylic acid as well as poly(L-glutamic acid) was shown to be complexed with Cu(II) in an aqueous solution and showed UV-VIS absorption spectra with a maximum wavelength of 260 nm. (Leyte, 1968 and Marinsky, 1975).

Polyacrylic acid (PAA) was also found to be complexed with Cu (II) in an aqueous solution and showed maximum absorbance at 260 nm.

(Yokoi, Kawata and Iwaizumi, 1986). The absorption band was suggested to be a coordination complex between the Cu(II) ions and carboxyl groups of the PAA. Complexes of the Cu(II) ions with hydroxyl groups of the PAA were also shown to have a maximum absorption band at 263 nm.

In an aqueous PAA-Ca(II) gel system, formation of a tight crosslinkage in the gel was observed. The crosslinkage was suggested to be the complex formation between Ca(II) ions and carboxyl groups of the PAA. Complexes of Fe(III) ions with carboxyl groups of PAA either in an aqueous solution or in an aqueous gel were also investigated by UV-VIS spectroscopic techniques and showed two absorption bands with maximum wavelength of 472 and 539 nm. The absorption bands were also suggested to be a result of complex formation between Fe(III) ions and carboxyl groups of the PAA (Yokoi and Nishi, 1989).

In case of Fe(II) ions, PAA-Fe(II) complex was shown to have two absorption bands at 218 and 317 nm. However, Fe(II) may be gradually air-oxidized to result a mixture of Fe(II) and Fe(III) ions (Yokoi, Yagishita and Nakanishi, 1990).

Complex of polyvinyl carbazole (PNVC) with CuCl_2 in THF solution was investigated by IR and showed some band shift or broaden upon coordination (Katime and Ochoa, 1987). UV-VIS spectroscopic techniques should be used for investigating the complex, but it is insoluble.

Effect of organic amines upon structure and properties of complexes between Zn(II) salts and ethylene-methacrylic copolymer were studied by thermal analyses and stiffness measurement (Hirisawa, et. al., 1991). It was found that valence, strength of base, rigidity, flexibility and bulkiness of the organic amines affected degree of crystalline order of the ionic crystallites which governed stiffness of the complex ionomers.

Complex forming polymer resulting from substitution of 2,2-bipyridine or 1,10-phenanthroline with a metalating agent and then reacting with a halogenated polystyrene and vinyl benzyl halide was shown to be hydrolytically stable and used as polymeric ligand (Stapersma, 1989).

Complexes of polyvinyl alcohol with Fe(III) as well as Cu(II) ions in an aqueous solution were investigated by NMR (Mori, Yokoi and Fujise, 1995). The complexes were suggested to have a structure of cluster hydroxide.

Complexation

1. Introduction

A complex has been defined as “a species formed by the association of two or more simpler species each of which is capable of independent existence”. When one of the simpler species is a metal ion, the resulting entity is known as a metal complex. A characteristic feature of such a complex is that the metal atom occupies a central position in it, as exemplified by cobalt in hexaamminecobalt (III) ion, platinum in tetrachloroplatinate (II) ion, and copper in bis (glycinato) copper(II).

The metal-centered structure may carry a positive, negative or neutral charge. Complex ions are, of course, always associated with ions of opposite charge and the term metal complex is customarily applied to the compound itself.

Almost every kind of metal atom can serve as a central atom although some kinds do so more readily than others. *Atoms of the transition series, for example, function in this way par excellence but atoms of the alkali metals are rarely found in this role.*

When the central metal atom of a complex is bound to the immediate neighbors by covalent bonds resulting from accepting an electron pair of the metal atom from each nonmetal atom, the bond is customary called a coordinate bond. However, metal atoms themselves



sometimes contribute electrons to the bond as they do in π bonding which is preferable because it avoids any implication about nature of the bond. Negative ion or polar molecule bound to a metal atom is called a ligand (L) and the bond between them is called a metal–ligand bond (M–L).

Some ligands are attached to the metal atom by more than one donor atom in such a manner as to form a heterocyclic ring. An example of such a ring is the one formed by the glycinate ion.

2. Fundamental concepts

2.1. The central metal atom

As might be expected, properties of a metal complex are influenced to a considerable extent by the nature and oxidation state of the central metal atom. One method of studying this influence is to compare the compounds formed by a series of different metal atoms in a given oxidation state with a particular chelating agent. The central metal atom sometimes endows a metal chelate with an individuality which is quite striking.

2.2. The metal–ligand bond

The strength and stability of this bond will, of course, depend on the nature of M and L on their size and electronegativity; more specifically on their electronic structure. The ligand atom, L, may have

other atoms attached to it, number and nature of which will also influence the stability of the M-L bond.

Lewis (1916) and Langmuir (1919) were the first who identified a covalent bond with a pair of electrons, one from each atom, and both held in common.

2.3. The nature of donor atom

Influence of nature of the donor atom on stability is a complicated one since the donor atom must also be considered in relation to the acceptor atom. The relative affinities of ligand atoms for acceptor ions have been discussed in detail by Ahrland and his associates (1958).

2.4. Influence of the central metal atom

This may be studied by comparing stabilities of the complexes formed by a particular molecule with a series of metal atoms in a given oxidation state. The order of stability in such a series may be independent with nature of the chelating agent (Dwyer and Mellor, 1964).

3. Molecular complexes in organic chemistry

The term molecular complex is used to describe a variety of types of association products of two or more molecules. It has different

significance for different investigators and is not subjected to brief all encompassing definition. In the past, extensive experimental attention has been given to a large group of complexes formed by the weak interaction of certain classes of organic substances, functioning as electron donors, with other substances which act as electron acceptors. These kinds of coordination products are of particular interest to organic chemists in large part because of their possible function as intermediates in reactions leading to stable products, that this discussion will be primarily concerned.

The donor-acceptor complexes, the compositions of which can be represented by integral mole ratios of the components, are in many instances so unstable that they cannot be isolated in the pure state at ordinary temperatures but exist only in solutions in equilibrium with their components. they can, however, usually be detected readily because of differences in their physical properties(e.g., absorption spectra) from those of the pure components. The rates of formation of complexes in solution are generally so rapid that kinetic studies of the reactions cannot be made, at least by ordinary procedures. The heats of interaction are generally small, and there is abundant evidence that the forces of coordination are much more feeble than those established in the formation of covalent bonds. That is, the degree to which electron transfer from the donor to the acceptor component takes place is much less than ordinarily occurs when new compounds are formed (Andrews and Keefer, 1964).

3.1. Types of donors

The substances which serve as donor components can be grouped in two general categories. The first category includes alkenes, alkynes, aromatic hydrocarbons, and their substitution products (Dewar, 1946). These are donors having electrons available for sharing. The second major class of donors encompasses a large group of substances in which there are non-bonded electrons available for coordination. Typical examples of these groups are alcohols, organic sulfides, organic iodides, and nitrogen bases.

3.2. Types of acceptors

Complexes of a wide variety of inorganic acceptors have been reported. Interactions of the halogens, particularly with aromatic substances, have been studied intensively in recent years (Andrews and Keefer, 1961). The fact that color of solutions of iodine changes from deep violet to reddish violet, or even to brown, as the solvent is changed from carbon tetrachloride, or an aliphatic hydrocarbon, or an atomic substance, or an alcohol, ether, or alkyl iodide is familiar to most chemists. There is an abundance of experimental evidence which indicates that in the 'brown solvents' interaction of the form 1:1 iodine-solvent adducts takes place. For example, the freezing point depression which results when a small amount of a 'brown solvent' is added to a bromoform solution of iodine is less, because of iodine complex formation, than that observed when an equimolar quantity of a 'violet solvent' is added (Hildebrand and Glascock, 1909). Recently a solid 1:1

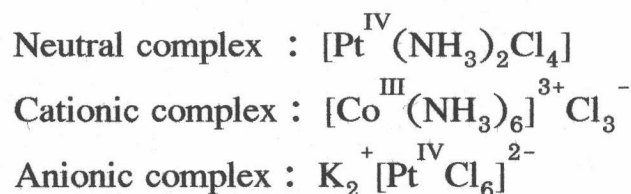
benzene-bromine complex with a melting point of -14° C actually has been isolated (Hassel and Stromme, 1958). The marked changes in near-ultraviolet absorption spectra which result when donor type solvents interact with the halogens (Cl_2 , Br_2 , ICl as well as I_2) have served as the experimental basis for many studies of halogen complex equilibria. Spectrophotometric evidence has been presented that iodine atoms, as well as the elemental halogen, interact with aromatic substances, and there is good evidence to be discussed that chlorine atoms can also serve as acceptors (Strong and Perano, 1961; Russel, 1957).

In carbon tetrachloride solution, the alkylbenzenes interact with sulfur dioxide to form 1:1 complexes which, like the aromatic halogen complexes, have relatively high intensity absorption maxima in the near-ultraviolet (Andrews and Keefer, 1964). Several low-melting solid sulfur dioxide adducts of alkylbenzenes and aromatic amines have actually been isolated or detected in connection with freezing point-composition studies.

4. Molecular complex in inorganic chemistry

4.1. Transition metal complexes

The expression 'transition metal complex' has frequently been used. A metal complex consists of a central metal atom or ion which is surrounded by a cluster of other ions or neutral molecules. The overall charge which resides on the complex may be positive or negative (in which case it is present in the complex compound together with the appropriate number of counter ions) or zero. It is customary notation to write the complex within square brackets:



The complex unit tends to retain its identity in solutions and through mild reactions, particularly those involving the exchange of counter ions (in the case of charge complex), without being disrupted. Thus, aqueous solutions of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ are resistant to hot concentrated HCl and exchange all Cl^- with AgNO_3 , neither chloride nor nitrate becoming involved in the complex part. The ions or molecules bound to the metal are called *ligands*; the metal–ligand bond often being called the coordinate bond. The nature of this bond will not be discussed; it is predominantly covalent, but we shall see that many of the spectroscopic properties of complexes may be easily interpreted if the bond is assumed to be ionic. The number of ligands or ligand atoms co-

transmittance (the sample being pressed into a thin, transparent disc) or by a technique involving diffuse reflection of light from the surface of the finely powdered solid. This makes a comparison of solution and solid species possible. It even widens considerably the definition of a complex unit to embrace also simple neutral compounds such as transition metal halides, oxides, etc. For example, the spectrum of the complex ion $[\text{CrCl}_6]^{3-}$ is entirely consistent with its structure which consists of a chromium (III) ion octahedrally co-ordinated by chloride ions; similarly, in the crystal of anhydrous CrCl_3 each chromium(III) ion is again octahedrally surrounded by six chloride ions, so that here again each Cr (III) can be considered to have its own environment of six ligands, even though these may be shared with neighbouring chromium ions. For spectroscopic, magnetic, and some other purposes it is entirely legitimate, and useful, to include such ionic arrangements within the scope of 'complexes'. Alternatively, it may be preferable to speak of the ' CrCl_6 ' chromophore existing in both cases. This idea can be extended since, for a given metal ion, say Cr(III), it is frequently found that the spectra of a number of complexes and simple compounds, which are alike in having both identical geometry (e.g., octahedral) and the same coordinating atom (e.g., oxygen) all turn out to be very similar in the number and the positions of the d-d absorption bands. Thus, in this example, the chromophore is written as $\text{Cr}^{\text{III}}\text{O}_6$, thereby drawing attention to the common features exhibited by all chromium(III) ions which are octahedrally coordinated by oxygen ligands.

ordinated to metal is called the *coordination number* which is six in examples illustrated above. Finally the *oxidation number* of the metal (in roman numerals in the above examples) gives the formal charge on the metal ion from which the actual charge on the complex is derived.

Properties of the complex are usually quite distinct from those of the free metal ion (which is usually, in aqueous solution, strictly the hexa-aquo complex ion $[M(H_2O)_6]^{n+}$ and from those of the free ligand. Again using the quoted examples, the NH_3 ligand in $[Co(NH_3)_6]^{3+}$ resists acid, and the chloride in $[Pt(NH_3)_2Cl_4]$ is not precipitated by Ag^+ in cold aqueous solution.

Turning now to the spectroscopic properties of metal complexes, it will be recalled that the d-d spectrum is a feature of the whole complex and not just the metal atom, and that the type of spectrum observed is significantly related to the geometry of complex. The majority of spectra are measured for solutions: very often aqueous solutions. Most solvents for metal complexes are also potential ligands in themselves (particularly water) and many compete with the other ligands for places in the coordination sphere of the metal. For this reason, the question of the actual metal complex species existing in the solution must always be kept in mind. It is very dangerous indeed to deduce properties of a solid complex from measurements on its solution without performing additional tests.

As well as making measurements on solutions it is also possible to record the spectra of solid substances directly, either by

4.2. Crystal field theory

So far, it has been possible, just by the use of very simple symmetry arguments, to deduce a lot of valuable information on the extent to which splitting of atomic orbitals or terms will occur for metal ions in complexes. At this stage, it is possible to account for the single visible absorption band of the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ which was mentioned in elementary of d-d spectra as the transition of the solitary d-electron from one of the levels (t_{2g} or e_g) arising from the splitting of the d-levels in octahedral environment to the other, of higher energy. At the moment, provided this is indeed the correct interpretation (which we must be very careful not to imply too strongly without a good deal more evidence), then this transition may be represented either as $e_g \rightarrow t_{2g}$ or as $t_{2g} \rightarrow e_g$. In other words, although symmetry tells us that, the t_{2g} and e_g levels are not of equal energy, it cannot supply us with the answer as to which of these is in fact lower in energy. To find this out it is necessary for us to make one assertion about the nature of the interaction between the metal ion and the ligands. Using these as a basis, it should then be possible by using only quite simple arguments, to see in what order this place the t_{2g} and e_g levels. Clearly, the metal-ligand bonding might be considered as (a) purely electrostatic or (b) purely covalent. Historically, the electrostatic model was, by just a few years, the first to be applied. In 1929, Bethe used symmetry arguments in order to qualitatively determine the nature of the orbital splitting, and followed this up in the same paper with an electrostatic model by which he deduced the energy sequence of the resulting levels. The development of this model in the early 'thirties

was mainly due to the work of Van Vleck and his collaborators, principally in rationalizing some of the magnetic properties of transition metal complexes, particularly those of the 3d row. This early application of the electrostatic model to crystalline complexes resulted in its being given the name *crystal field* theory, since the principal feature of the theory is just the behaviour of the central metal ion under the influence of the electrostatic field generated by the surrounding environment of negative ligands. A little later, in 1935, Van Vleck wrote down the ideas behind the molecular orbital approach to metal-ligand bonding. Each approach has developed enormously up to the present time, but whereas the crystal field approach has been widely used as a basis for the interpretation of electronic spectra, the similar use of the molecular-orbital theory is only recently becoming the fashion, largely due to the work of Ballhausen, Liehr, and Gray.

There is a wealth of evidence, nowadays, which demonstrates that co-valency is the important factor in metal-ligand bond, in which case the crystal field approach must be viewed as a rather crude approximation. These has been the preferred model for so many publications on spectra of complexes because both extreme models give qualitatively the same result as to energy sequence of the split levels; the choice between them therefore must be made on quantitative grounds. Calculation of the splitting of d-orbitals using crystal field theory provides a fit with experiment which, even for favourable complexes (e.g., those for which π -bonding is important — which an electrostatic theory cannot account for at all) is very poor indeed. The fault clearly lies to



some extent in the total neglect of metal–ligand orbital overlaps. The saving grace of the crystal field model is that calculations are really relatively easy to make using it, and because it is so mathematically manageable that it has been looked upon so favourably. The simple electrostatic model accounts for the broad features of the spectra of a large number of complexes (e.g., number of bands observed), and it correctly reproduces the splitting pattern for d-orbitals and terms. Without further modification, however, the energies of the transitions and therefore the positions of the bands are usually not satisfactorily accounted for, but agreement with experiment can be improved, by slight modifications of the theory, to take account of the probable effects of covalency, within the relatively simple framework of the crystal field model. It is to this modified form that the term *ligand field theory* is usually applied.

According to crystal field theory, complex units are described as being composed of a positively charged central metal atom, which is surrounded by ligands, which may be either negatively charged or neutral. Even in the case of neutral ligands, these will be polyatomic, and by virtue of dipolar charge separation will frequently have a finite dipole moment. Such a ligand will be expected to orient itself so that the negative end of the dipole approaches the metal atom most closely, so that electrostatic bonding to the metal can be visualized even in these cases. For water and ammonia this will be the oxygen and nitrogen atoms respectively.

4.2.1. Octahedral complexes

With the dipolar character of some neutral ligands in mind, the general features of octahedral complex are the same whether the ligand is negative or neutral. Crystal field theory is concerned that six negative nearest-neighbour ligand atoms or dipoles are octahedrally situated about the positive central metal atom. Note that the arrangement which has adopted here, namely that of situating the ligands on the rectangular axes is purely a matter of convenience, in that it preserves the accepted convention for orienting the x , y , z axes through the six vertices of the octahedron in setting up the transformation properties of x , y , z , $x^2 - y^2$, xy , etc., in O_h symmetry.

First, it is mentioned qualitatively at the way in which the proximity of these ligands influences the energy of the electrons on the metal atom for such an octahedral complex. Recall that the earlier symmetry arguments require $d_{x^2-y^2}$ and d_{z^2} to constitute one degenerate set and d_{xy} , d_{yz} , d_{zx} the other. The angular distribution plots for these orbitals clearly indicate how these orbitals differ in their angular distribution with respect to the ligand positions. For d_{xy} , the ligands lie in the direction in which the distribution function is a minimum, whereas for $d_{x^2-y^2}$ the same directions correspond to the maximum value. The influence of these ligands upon the d -electron may be pictured as having two related parts. In the first place, the potential energy of an electron in either d_{xy} or $d_{x^2-y^2}$ must increase over the free ion value purely as a result of the repulsion which it experiences from the surrounding ligands. In addition, the different actual spatial arrangement of the ligands towards

these two orbitals will mean that, since an electron in $d_{x^2-y^2}$ approaches the ligand positions more closely, it must as a result have a greater potential energy than when in d_{xy} . For all five d-orbitals in the octahedral complex the total effect can similarly be broken down as (a) an increase of their energy by some general amount, and (b) a splitting of the orbitals according to energy, with $e_g(d_{x^2-y^2}, d_{z^2})$ somewhat higher in energy than $t_{2g}(d_{xy}, d_{yz}, d_{zx})$.

The subtle relation between the two molecules may be seen more clearly if it uses a slightly alternative approach. Consider some hypothetical situation where it has the central metal cation surrounded by a concentric spherical shell which has a radius equal to the actual metal-ligand distance, and which consists of uniformly distributed negative charge. Also let the total charge distributed be just equal to the total charge of the six ligands. A full set of ten d-electrons on the metal (which together must have spherical symmetry) will have, as a result, their total energy raised from the free ion value by some amount which is called Δ_s . Imagine now the charge to be collected equally into the six ligand positions, moving only on the surface of the sphere. This operation does not change the energy of these ten electrons as a whole but clearly those electrons in e_g orbitals now become further increased in energy as a result of the charge being gathered into axial positions whilst the energy of electrons in t_{2g} orbitals becomes lowered on account of the removal of charge from positions off the axes. The energy gap between e_g and t_{2g} is called Δ_o .

So much for this outline of the crystal field model of octahedral complexes. On the basis of the theory, the electronic spectrum of a d^1 complex must now be accounted for as the excitation of the solitary d-electron from the t_{2g} to the e_g level over the energy gap Δ_o .

4.2.2. Tetrahedral complexes

As in the octahedral case, it is known from previous symmetry considerations that for this geometry the d-orbitals are also splitted into a doubly and a triply degenerate set, being $e(d_{x^2-y^2}, d_{z^2})$ and $t_2(d_{xy}, d_{yz}, d_{zx})$. Using the special relationship of the tetrahedron to the cube, and to the rectangular coordinates, it will be noted that, in this case, none of the d-orbitals has maximum angular distribution in the direction of ligands. For the same reasons as before, the $d_{x^2-y^2}$ orbital has maximum distribution along the rectangular axes, towards the centres of four cube faces, whereas the four lobes of d_{xy} point towards the mid-points of four cube edges. This places an electron in d_{xy} somewhat closer in proximity to the ligands than is the case for $d_{x^2-y^2}$, although clearly the distinction is less drastic than in octahedral case. The energy gap between the lower energy level e , and the upper one t_2 is labeled as Δ_t for this tetrahedral geometry.

4.3. Ligand field theory

Having just stated that the electrostatic model gives poor results when quantitative calculations of Δ are attempted, the impression may have been conveyed that good agreement is, however, found using a simple covalent model. Unfortunately, this is not the case, using the straightforward molecular orbital approach, even though the first calculation of this sort appeared to give such agreement. Very recently, efforts to make the molecular orbital calculation using more realistic equations seem to worsen the agreement, but the inclusion of very sophisticated reasoning about the actual nature of the covalent metal-ligand interaction is now enabling much better results to be achieved. It is now becoming clear that there are several factors contributing to the splitting parameter, but as no single completely satisfactory theory of the magnitude of this parameter has emerged yet.

For the interpretation of the d-d spectra, in particular the evaluation of Δ , ligand field theory has been found to give very satisfactory results where the simple crystal field theory is quite inadequate. It is, in fact, merely a modification of crystal field theory, and there is a certain amount of basis for believing that the modifications that distinguish ligand field from crystal field theory are in the nature of allowances for covalent effects. For example, allowance might be made for the polarization of the ligand electron cloud by the positively charged metal ion. This would result in the metal d-electrons overlapping with the ligand electrons, with the result that the d-orbitals would expand in view

of the increased repulsions, thereby lessening the mutual repulsions of the d-electrons themselves. The result of these will be revealed by the rather B and C values appropriate to the free ion actually being too large when applied to the complexes. Similarly, the value of the spin orbital coupling parameter ζ should be likewise reduced from the free ion value. In the ligand field theory, therefore, it is able to calculate, from first principles, the appropriate values of the various parameters Δ , B, and C; instead, the theory is used only semiempirically, retaining the broad significance attached to these quantities but leaving them to be obtained experimentally from an analysis of the spectra. The importance of this approach is that it enables the energies of the electronic levels in complex to be calculated, in terms of Δ , using mathematically simpler crystal field theory, these then being adjusted to fit the experimentally determined levels using appropriate values of B, C, and perhaps ζ .

4.4. Selection rules

The majority of transition metal complexes are coloured; that is, they possess the property of absorbing certain wavelengths in the visible region of the spectrum. This is accompanied by absorption in the adjacent near-infrared and near-ultraviolet regions, so that the expression 'visible absorption spectrum' is usually interpreted somewhat loosely to include these closely neighbouring regions. The considerable attention which has centred on the chemistry of transition metal complexes in recent years can be traced largely to the development of successful theories for interpreting those properties, which are peculiarly

associated with compounds of metals having an incompletely filled d-subshell. Such theories needed, in the first place, to account particularly for the colour and magnetism of complexes. These same properties now provide a stringent basis for testing fine points of theory in connection with a wide range of transition metal compounds having markedly differing properties. As a consequence, visible absorption spectra are now known for a vast number of complexes, and at the present time the measurement of the visible spectrum is considered to be an essential part of the characterization of any new complex.

Absorption in this region may arise through a variety of processes which are alike in that they all involve the excitation of an electron from one energy level to a second level, which is somewhat higher in energy. These processes are different from each other only in the way choosed to describe and to categorize the initial and final levels. This necessarily leads to the result that the borderlines between catagories are somewhat hazy. Principally, however, so far as transition metal complexes are concerned, visible absorption arises when an electron is excited between two energy levels, both of which are d-orbitals of the metal. This is therefore called the d-d transition. The particular spectrum exhibited by any one compound is dependent upon the energy of the d-orbitals, in which degeneracy, and the number of electrons distributed. These features in turn are controlled by the oxidation state of metal, the number and kind of ligands (the term ligand refers to the atom, molecule or ion which is bound directly to the transition metal ion in a complex.) and the geometry of the complex. It is quite clear from these remarks that, once the general principles have been laid down, the correct interpretation

of a spectrum can yield a significant amount of information about a new complex, with the result that the technique figures prominently in the study of the structure and bonding of transition metal complexes.

Absorption bands may vary considerably, so far as the actual values of their intensities are concerned. This is true, both spectra of different compounds, and when comparing different bands in the spectrum of a given sample. In the case of really intense bands, values for ϵ_{\max} may reach 10^4 or 10^5 ; yet other be so weak as to have ϵ_{\max} of only 10^{-1} or 10^{-2} . In term of oscillator strengths, these are 10^{-1} or 1 for the intense bands, and 10^{-7} or 10^{-6} for the very weak ones. It is possible to make some general correlations beteewn the nature of an electronic transition and the magnitude of the absorption intensity. These are usually expressed in the form of '*selection rules*' which predict whether a transition will be 'allowed' or 'forbidden', and therefore whether the absorption band will be intense or rather weak.

4.4.1. Spin selection rule

For a transition to be allowed, the number of unpaired electrons in the initial state must be identical with the number in the final state. Where these are concerned with a single electron under going a transition, the spin of the electron must be identical with the initial and the final orbitals.

4.4.2. Laporte selection rule

This rule, formulated by Laporte, may be stated in a number of alternative but complementary ways. One definition is that a transition is forbidden if it simply involves a redistribution of electrons within the same type of orbital, in a single quantum shell. This way of expressing the selection rule is particularly relevant to the spectra of transition metal complexes. Many the transitions are d-d type, involving only the d-orbitals in a given quantum shell, and as such are strictly Laporte forbidden.

In order to try to obtain some grasp of the theoretical basis of these selection rules it is necessary, first of all, to inquire just what goes on when electromagnetic radiation of the correct wave number interacts with a molecule which is potentially capable of undergoing an electronic transition corresponding to a matching energy change.

(a) The important feature of the radiation is the oscillating electronic vector.

(b) The absorption of energy from the radiation arises from the ability of this oscillating electric component to induce a transition in the molecule, which itself corresponds to a displacement of electronic charge in the same sense. Thus, if these are somehow able to be fixed the direction of the electric vector as, say the z direction, then only transitions which involve a resultant distribution of electronic charge

in the z direction are able to become activated. A quantity which expresses the magnitude of this charge displacement is called the dipole strength of the transition. the transition is said to be an electric-dipole type.

(c) Only the electronic transitions, which correspond to the charge displacement requirements of the electric-dipole radiation will be excited by the incident radiation(i.e., will be 'allowed'); all other transitions will be 'forbidden'. This is the basis of the Laporte rule. Whether or not a transition is allowed, is directly determined by the symmetry properties of the orbitals concerned. A transition between two orbitals of the same kind(e.g., two d-orbitals) does not satisfy these requirements and so is forbidden. In other words the dipole strength is zero.

(d) In the case of an allowed transition, it can be shown that the oscillator strength (f) of the transition is proportional to the wavenumber, and to the value of the dipole strength. The latter will depend on the particular transition involved. Whilst it is generally true to say that an 'allowed' transition usually gives rise to high oscillator strengths, it is nevertheless entirely feasible for some allowed transitions to occur with only a meagre dipole strength, and so give rise to bands which have abnormally low intensity. In this respect intensity must be looked upon as a rough, but not infallible, guide to the nature of transitions.

(e) The dipole strength is itself closely related to the wave functions of the initial and final orbitals for the excited electron. For many purposes, it may be assumed that the space and spin parts of the wave functions may be factorized out, in which case the dipole strength then becomes related to the product of two terms, one involving space wave functions, the other the spin part.

Under certain conditions, when there is considerable interaction between the magnetic effects arising out of the spin of the electron and those from its orbital motion. This is called spin-orbital interaction. It is then possible for the spin to change as a result of the transition without the expression for the dipole strength automatically becoming identically zero. This corresponds to a partial breakdown of the spin selection rule, leading to enhance intensity for formally spin-forbidden transitions. This phenomenon is not very important for lighter elements, e.g., complexes of 3d metals, but becomes very important in the case of heavier elements, e.g., those of the 4d and 5d series.

4.5. Spectra of transition metal complexes

Because of the large number of known transition metal complexes, and the many factors which have to be taken into account, it is not possible to give a general description of the kind of spectrum these compounds exhibit which holds good in each and every example. The best that can be done is to say that the visible and near infrared region contains rather weak absorption bands for which ϵ_{\max} values fall in the range 1-

10^2 , and that toward the ultraviolet much stronger absorption sets in, with reaching 10^3 or 10^4 . A typical example is the spectrum of an aqueous solution of chloropentaamminecobalt (III)chloride. In this example, the whole of the spectrum is associated with complex ion $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. The spectrum of $[\text{CoCl}_4]^{2-}$ is shown in two regions of absorption falling within the range of most spectrophotometers, and there is some evidence for an additional weaker band farther into the infrared region (i.e., $\approx 3200 \text{ cm}^{-1}$).