3. *The Absorption Spectra and Stability of Complex Ions.*

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The stability and absorption spectra of complex ions, particularly of transition-metal cations, are discussed with special reference to crystal-field theories. It is maintained that in its present form the theory makes unrealistic assumptions about the strength of the electrostatic field produced by different ligands. The molecular-orbital description of the interaction between ligand and cation does not suffer from the same disadvantages (van Vleck, *J. Chem. Phys.*, 1935, **3**, 807). The stability and absorption spectra of some complex ions are examined from the latter point of view.

Two explanations have been offered for the stability and absorption spectra of complex ions with special reference to the transition-metal complexes. The first depends entirely on considerations of the electrostatic potential energy of the complex in relation to that of its component ligands and cation. Essentially the theory has two parts : (1) the simple interaction of the charge of any cation and the charges or dipoles of the ligands, account being taken as far as possible of mutual polarisation (Van Arkel and de Boer, *Rec. Trav. chim.*, 1928, **47**, 593) ; and (2) the increase in the potential energy of electrons in degenerate states of a cation due to perturbation energy terms which must be included in the wave functions of the electrons when the latter are subjected to an electrostatic field. The second part of this description will be called the crystal-field theory (Bethe, *Ann. Physik*, 1929, **3**, 133) and is only applicable to transition-metal cations. Recently, this theory has been used in an attempt to account for features of the stability and absorption spectra of many complex ions. It is suggested below that the interpretations are unsatisfactory.

The alternative theory used in the discussion of complex ions has three different approaches. They all consider the bonding in complexes as, in part, covalent. The earliest description, that of Pauling (*J. Amer. Chem. Soc.*, 1931, **53**, 1367), lays stress on the available *empty* atomic orbitals of the cation which accept electrons from the full orbitals of the ligand. This valence-bond treatment which will be assumed to be well known, overstressed the importance of certain linear combinations of atomic orbitals (cf. Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332). The second consideration of covalent forces was developed by van Vleck (*loc. cit.*) and used the molecular-orbital method. Whereas in Pauling's treatment empty orbitals of the cation must be available, in the molecular-orbital method any d orbital of a cation together with a σ orbital of the ligand, occupied by two electrons when not bonding, gives a σd bonding and a corresponding σd^* antibonding orbital (p. 10). The electrons are fed into the most stable states one at a time and the bonding that develops will depend upon the number of electrons in these states, amongst other things. The third description of covalent forces in complexes has grown empirically from a study of the stability of complexes of the transition-metal cations in solution. In this work a close correspondence was observed between the ionisation potential of a bivalent transition-metal cation and the stability of its complexes (Irving and Williams, *J.*, 1953, 3192; Williams, *J. Phys. Chem.*, 1954, **58**, 121). The implication here is that the cation acts as an electron acceptor. If this idea is to be put into valence-bond terms, difficulties arise over the choice of the orbitals of the cation which act as the acceptors. Two theories have been given, neither of which is wholly satisfactory. An example makes this clear.

The paramagnetic complexes of bivalent nickel are octahedral. Two valence-bond descriptions of these bonds have been given, one in terms of $4s4p^3$ resonating hybrid orbitals, and the other of $4s4p^34d^2$ orbitals. The bonding is through empty orbitals of the cation only. But the stability of many nickel complexes, as compared with that of other similar cation complexes, is proportional to its ionisation potential (but see p. 12). Atomic spectroscopy has shown that the ionisation of the nickel atom leads to a univalent ion of ground state $3d^9$, so that the second electron is removed from the $3d$ shell (Menzies. *Proc. Roy. Soc.*, 1929, *A*, **122**, 134).* The ionisation potential to the state Ni^{II} is a measure of the stability in part of electrons in $3d$ atomic orbitals. These orbitals must take part in the bonding of ligands if the dependence on ionisation potential is to be explained, but they are not included in the above valence-bond descriptions. The molecular-orbital treatment of the nickel complexes, on the other hand, suggests that part of the bonding is due to $3d\sigma$ bonding orbitals (p. **10**). This description leads to a similar stereochemistry for the transition-metal cations to that given by the crystal-field theory, and on these grounds it is not possible to choose between them (van Vleck, *loc. cit.*). It should be noted that there is no need to involve outer $4d$ orbitals in discussing the octahedral configuration in these complexes.

The crystal-field description of the stereochemistry of transition-metal cations has been summarised recently by Orgel (*J.*, 1952, 4756). In a cubic field which arises in many transition-metal complexes, *e.g.*, those of nickel, the five $3d$ electron states are split into a lower triplet, d_ε states, and an upper doublet, d_γ states. The latter point in the direction of the ligands producing the field, and the former bisect its co-ordinates. The method shows that electrostatic repulsions between the field and the d electrons are reduced to a minimum when the electrons fill the d_ε before the d_γ states. Such is the case in paramagnetic Ni^{II} complexes when the two unpaired electrons are placed in d_γ levels. This division of the electrons stabilises the complex relative to its state in the absence of splitting but in the same field. It also predicts the correct stereochemistry for a number of transition-metal cations, though the splitting of levels varies in complexity. Orgel (*loc. cit.*), in a discussion of the heats of hydration of the cations, rightly pointed out that this stabilisation should be considered when examining the stability of complexes. In order to assess the magnitude of the term he calculated from spectroscopic data the energy difference, Δ, between the state of the cation in the absence of splitting and its state in the field of the water molecules of the hydration sphere. The value, Δ, was then subtracted from the experimental heat of hydration to give the heat of hydration of the cation in the absence of cubic field splitting. These " heats of hydration " of non-degenerated cations are not related to characteristic properties of the isolated ions such as their radii or ionisation potentials. Elsewhere in the Periodic Table when cations with non-degenerate electron configurations are examined there is an empirical relation between heat of hydration and radius and ionisation potential (Williams, *loc. cit.*). This suggests that the correction applied by Orgel to the experimental heats of hydration of degenerate states is of a kind different from that considered by him. Now the difference between the excited and the ground spectroscopic states of complexes, h, can be shown from a molecular-orbital treatment (p. 10) to be related to the overall stability of certain bonding and anti-bonding orbitals of the two states. The difference between the states is represented in terms of the partial covalent bonding between the ligand and the cation. It will be shown, in outline, that this covalency is related to the ionisation potential of the cation so that a relation appears between h, and thence Δ, and ionisation potential. Orgel's corrected " heats of hydration " excluded stabilisation which belonged properly to the state of the cation in the absence of splitting by purely electrostatic fields.

Bjerrum and his collaborators (at least ten papers have been published recently; for references see Jørgensen and Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 180) following Ilse and Hartmann (*Z. Naturforsch.*, 1951, **6a**, 751), who re-introduced the crystal field in discussions on complexes, also omit consideration of covalency. In fact these authors go so far as to describe donor bonds as a "peculiar" hypothesis in co-ordination chemistry. In their account, which is based entirely on electrostatic considerations, the various stabilities of degenerate ionic states in crystal fields of different symmetry have been calculated for a number of cations. In an earlier article it had been indicated that it would be possible to make such calculations but that there was already evidence to show that stereochemistry in

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* It is not generally realised that the ionisation of a transition metal often induces an electronic rearrangement. In the first transition series the states of the atoms are $Cr(3d^54s^1)$, $Mn(3d^54s^2)$, $Fe(3d^64s^2)$, $Co(3d^74s^2)$, $Ni(3d^84s^2)$, $Cu(3d^{10}4s^1)$. Ionisation gives $Cr^+(3d^5)$, $Mn^+(3d^54s^1)$, $Fe^+(3d^64s^1)$, $Co^+(3d^8)$, $Ni^+(3d^9)$, $Cu^+(3d^{10})$. Further ionisation removes all the remaining $4s$ electrons. When comparing the stability of complexes with ionisation potentials it should be noted that the latter do not refer to strictly comparable states. The wave functions of the electrons ionised are mixtures of s, p, and d atomic wave functions, mixtures which change from atom to atom.

the transition-metal cations was in part controlled by covalency even in Pauling's supposedly " ionic " complexes (Williams, Proc. Symp. Co-ordination Chemistry, Danish Chemical Society, Copenhagen, 1954, pp. 56, 68). More recent evidence strongly supports this conclusion.

The strongest evidence of the unsatisfactory nature of the crystal-field theory is its failure as an absolute method. The usual calculation of the energy states of the *d* electrons in a crystal field (Ilse and Hartmann, *loc. cit.*) leaves one parameter, Q, the strength of the field, undetermined. The parameter is evaluated from the absorption spectra of the complex. It is used as a fitting constant, every complex giving a different value of Q. If the theory were satisfactory it should be possible both to calculate a reasonable value of Q on the basis of a model for any given complex and to correlate empirically determined values of Q generally with the properties of the cations and ligands comprising the complexes. The former approach was made by Kleiner (*J. Chem. Phys.*, 1952, **20**, 1784), who was unable to find a suitable electrostatic model for a cubic field which gave values of Q of the correct size. He showed that one way of obtaining better values would involve covalent terms in the bonding. In the second approach, the experimental determination of Q and its correlation with properties of the ligands and cations, there have been several studies. Owen (*Proc. Roy. Soc.*, 1955, *A*, **227**, 183) summarised the values obtaining in a number of octahedral hydrates and observed that Q was not a simple function of ionic charge or radius of the cation. He also went on to consider covalency in the complexes. Bjerrum (*loc. cit.*) uses a slightly less obvious method of comparing spectra with the ligand field constant Q. The fitting constant in his method is the ligand polarisability, *i.e.*, anomalies in Q are always hidden in chosen values of polarisability. The frequency of the maximum in the absorption spectra of complexes of cobaltic, chromic, cupric, and nickel was found to follow the ligand order $CN^- >$ *o*-phenanthroline $> NO_2^- >$ ethylenediamine $> NH_3 > SCN^- > H_2O > F^- > R{\cdot}CO_2^- > OH^- > Cl^- > Br^-$. By assuming unrealistic values for the polarisability of these ligands it was, of course, possible to conclude that the series came about through the influence of different fields Q. There are peculiar features about this order : unsaturated ligands give the strongest " fields," neutral molecules give stronger " fields " than anions, hydroxide even gives a weaker " field " than water. Moreover, the absorption spectra of other cations, such as ferric and cobaltous, in their complexes show maxima with frequencies in entirely different orders from the above. In order to explain the series of the frequency maxima of the ferric complexes of $CN^- > H_2O > R{\cdot}CO_2^- > Cl^- > SCN^- >$ *o*-phenanthroline, another series of polarisabilities would be required. The different orders do find explanations on the molecular-orbital theory.

The Molecular-orbital Theory.—According to van Vleck (*loc. cit.*) there are bonding and anti-bonding orbitals between combinations of ligand σ orbitals (which will be linear combinations themselves of atomic *s* and *p* orbitals) and d_γ orbitals of the cation which can be written as :

$$\text{Bonding} \qquad \sigma d_\gamma = (1 - \alpha^2)^{\frac{1}{2}} d_\gamma + \alpha \mathrm{f}(\sigma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{Anti-bonding} \qquad \sigma d_\varepsilon^* = \alpha d_\gamma - (1 - \alpha^2)^{\frac{1}{2}} \mathrm{f}(\sigma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

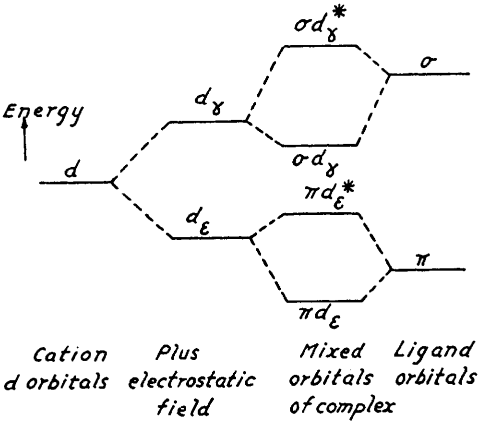
where α is an admixture coefficient and f represents a function of the σ orbitals of the ligands and is also dependent upon the symmetry of their arrangement about the cation. If the d_γ orbitals are not involved in covalent bonding, then α is unity. Apart from these orbitals there will be π orbitals not considered by van Vleck but described by Kimball (*J. Chem. Phys.*, 1940, **8**, 188) for the case where the ligand acts as an acceptor, and by Griffiths and Owen (*Proc. Roy. Soc.*, 1954, *A*, **226**, 96) for the case where the cation acts as an acceptor. They are :

$$\text{Bonding} \qquad \pi d_\varepsilon = \beta d_\varepsilon + (1 - \beta^2)^{\frac{1}{2}} \mathrm{f}'(\pi) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{Anti-bonding} \qquad \pi d_\varepsilon^* = (1 - \beta^2)^{\frac{1}{2}} d_\varepsilon - \beta \mathrm{f}'(\pi) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where β is an admixture coefficient and f′ is a function of the π orbitals of the ligand and their symmetry with regard to the central metal cation. If π bonds are not involved in the complex then β is unity.*

If there are no σd_γ^* anti-bonding electrons then expression (1) is of the same form as in valence-bond treatments, and likewise if there are no πd_ε^* anti-bonding electrons then the set of πd_ε bonding orbitals are the same as those described by Pauling as double bonds in carbonyls and cyanides (" Nature of the Chemical Bond," Cornell Univ. Press, New York, 1939, p. 250). It should be observed that the d_γ and d_ε orbitals in equations (1)—(4) are the perturbed wave functions used in crystal-field calculations. The effect of covalency upon the energy of these states is shown in the accompanying Figure, due to Owen (*loc. cit.*). No quantitative applications of this type of diagram can be made as yet but several qualitative observations are of interest.



Schematic representation of the formation of mixed orbitals of a complex ion from the component orbitals of the cation and the ligand. (Particular attention is directed to the footnote on this page with regard to this diagram.)

It is self-evident that the bonding orbitals in expressions (1) and (3) are of greater potential energy than the anti-bonding orbitals. As electrons are supplied to the molecular orbitals, those that are bonding are occupied first. On filling of the bonding orbitals, electrons are added to the anti-bonding orbitals until the full complement of electrons of the cation and ligand is reached. Whereas the filling of bonding orbitals stabilises the complex relative to its components in the absence of covalency, yet filling anti-bonding orbitals destabilises it (see Figure). If the anti-bonding orbitals contain as many electrons as the bonding orbitals, then the total potential energy of the electrons is highest when α and β are close to unity; there is no covalency involving *d* electrons. The coefficients α and β are evaluated, of course, so that the total potential energy is a maximum in this and other cases where the anti-bonding orbitals are not filled. It is obvious that the admixture coefficients decrease as the number of anti-bonding electrons decreases, and maximum covalency is reached when there are no anti-bonding electrons. The situation is extremely complicated in these complexes and exact expressions have not yet been derived but the overall picture is comparable with the extent of covalent bonding in He_2 and He_2^+. In the latter ion, covalency stabilises the bond, there is but one anti-bonding electron, but the neutral molecule is not stable (cf. Coulson, " Valence," Oxford, 1952, p. 94). The covalency decreases with the number of anti-bonding electrons. A comparable case is that of the bonding in the zinc complexes compared with that in the complexes of transition-metal cations immediately preceding zinc. In zinc the $3d\sigma^*$ anti-bonding orbitals will contain as many electrons as the corresponding bonding orbitals, with a result that α is close to unity. In the transition cation complexes α will be less than unity, as there are fewer anti-bonding than bonding electrons. Relatively to their ionisation potentials even, the zinc complexes

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* This representation of the molecular orbitals formed from *d* cation atomic orbitals and other atomic orbitals of the ligand is a gross over-simplification. Linear combinations of *s* and *p* cation atomic orbitals with the former group can also be written and will add to the stability of the complex. The purpose of the present argument is to indicate the part played by the *d* orbitals, and for this reason more correct but more complicated expressions have been omitted. The qualitative conclusions drawn are not likely to be affected by the simplification.

are less stable than those of the transition-metal cations, illustrating the better bonding potentialities of *d* orbitals than of *s* and *p* orbitals.

The principal additional factor which determines the size of the covalency coefficients is the relative electron affinity of the atomic orbitals which form the molecular orbitals; the more equal these two affinities, the more covalent the bond. Now, in general, σ orbitals of the ligand have a greater electron affinity than d_γ orbitals of the cation. It is not surprising, then, that, as the ionisation potential of the cation increases and that of the ligand decreases, the complexes become more covalent. These relations are confirmed, not only by a study of the stability of complex ions, but also by an analysis of their paramagnetic absorption spectra. Owen (*loc. cit.*) showed that the values of α are smaller in tervalent than in bivalent hydrates. Comparison of the values of α in cupric and nickel hydrates with van Wieringen's data (*Discuss. Faraday Soc.*, 1955, **19**, in the press) shows that these hydrates are more covalent than that of manganous. The latter cation has the lowest ionisation potential. It should be noted that the values, $\alpha = 0{\cdot}83$, for nickel hydrate and 0·84 for cupric hydrate invalidate the comparison of α with ionisation potential, for the cupric ion has the greater ionisation potential. As Owen pointed out, however, nickel forms an octahedral hydrate with six equal bonds of 3% covalent character, whereas the cupric ion forms only four covalent bonds involving *d* orbitals each of which has 4% covalent character. The study of the stability of the cupric complexes shows the first four ligands are added in equivalent steps which involve a larger free-energy change than in the corresponding nickel series of complexes. The position is reversed during the addition of two further ligands (Davies, Singer, and Staveley, *J.*, 1954, 2304), and nickel forms the more stable octahedral complexes. The paramagnetic resonance measurements agree in indicating that there are individually more covalent bonds in cupric complexes but that the overall covalency is greater in nickel complexes. Despite the general applicability of the Irving–Williams stability sequence to the formation constants of complexes involving the addition of four co-ordinating groups, it is not applicable to six-co-ordination, and in the latter complexes the parallel with ionisation potential is broken. The reasons for the failure of the correlation are apparent from equations (1) and (2). The cupric complexes are reduced in stability by the additional electron in the anti-bonding orbitals—a reduction which is not compensated by the greater stability of the bonding orbitals and has little influence until the addition of the fifth ligand because of the stereochemistry of the d_γ orbitals. The ionisation potential is not a proper measure of the overall stability of a complex, for the latter includes two unrelated energy terms, the splitting of the *d* levels by an electrostatic field (cf. Orgel, *loc. cit.*) and the directional character of $d_\gamma\sigma$ and $d_\gamma\sigma^*$ orbitals which increases or restricts covalency. Usually, however, changes in ionisation potential have sufficiently large influence to mask other factors.

Measurements by van Wieringen (*loc. cit.*) have shown also that covalency involving *d* orbitals increases along the series of manganous salts, oxide, sulphide, selenide, telluride, which is the order of ease of ionisation of the anions. The paramagnetic absorption method has also shown that ammines are more covalent, *i.e.*, have smaller α, than hydrates (Owen, *loc. cit.*).

So far, the discussion has centred about the size of the α coefficients. Unlike the values of α, those of β can be small through electron-donor as well as -acceptor properties of the ligand. Unsaturated ligands accept electrons from the d_ε orbitals (see, *e.g.*, the work of Calvin and Wilson, *J. Amer. Chem. Soc.*, 1945, **67**, 2003). Now, in such complexes the molecular orbitals spread over the entire complex, and stability should increase with the number of ligands in a complex. Data in the literature (cf. Irving and Williams, *loc. cit.*) show that, in accordance with this idea, the differences between the step stability constants are smaller for chelating aromatic ligands than for similar aliphatic compounds; *e.g.*, compare the values for complexes of glycine with those of 8-hydroxyquinoline, or ethylenediamine complexes with those of phenanthroline. Other aspects of this type of πd_ε bonding have been considered by Craig, Maccoll, Nyholm, Orgel, and Sutton (*loc. cit.*). It may well have a decisive influence on the preferred stereochemistry of complexes even outside a transition series. For example, the aliphatic ammines of zinc are generally tetrahedral, but the aromatic ammines show no tendency to remain four co-ordinated and the cation has octahedral complexes in these cases.

The ligand may also act as a π electron donor. As the ionisation potentials of neutral ligands, such as water, are relatively higher than those of anions, it is to be expected that π-electron donation will only be strong in anionic complexes. The paramagnetic absorption spectra of a number of complexes indicate that this type of covalency is weak even in tervalent hydrates but that it is strong in many halide complexes. The following interpretation of the absorption spectra of some complex ions would strongly favour these suggestions.

The Absorption Spectra of Some Complex Ions.—The theory that will be given here has already been outlined in a discussion of the absorption spectra of ferric complexes (Williams, *J.*, 1955, 137). It considers the difference in covalency between the ground and the excited spectroscopic states brought about by the changed occupation of the orbitals given in equations (1)—(4). All the transitions to be examined arise from the splitting of the *d* states. The absorption bands are often, but not always, weak, therefore, because the transitions are formally forbidden. It is useful to divide the transitions into two kinds, those involving a change of multiplicity and those involving no such change. The former are the more strongly forbidden by selection rules. The latter will be discussed first by taking a typical example, the cupric complexes.

In cupric hydrate the 3*d* electrons of the cupric ion and the electrons of the σ and π orbitals of the water molecules are divided amongst the molecular orbitals shown in the figure. The πd_ε and $\pi d_\varepsilon{}^*$ orbitals, which are lowest, are fully occupied and there are then three electrons remaining for each pair of σd_γ and $\sigma d_\gamma{}^*$ orbitals. The latter are of the greater energy and are only half filled. In the ground state of the cupric ion, then, β will will be close to unity, $\pi d_\varepsilon{}^*$ will be filled, but α will be considerably less than unity (p. 11). On excitation by the absorption of light, an electron of the anti-bonding $\pi d_\varepsilon{}^*$ orbitals is excited into one of the $\sigma d_\gamma{}^*$ orbitals. It follows from the discussion on p. 11 that the value of α must rise to nearly unity, for the anti-bonding orbital $\sigma d_\gamma{}^*$ is now full. There is a loss of covalency and a concomitant change in polarity in the complex on excitation. The transition which is related to a forbidden atomic transition will become, in terms of the mixed orbitals, less strongly forbidden because of its association with a polarity change. In this way an apparent breakdown of selection rules is observed. The fact that β will have become less than unity in the excited state, the $\pi d_\varepsilon{}^*$ orbitals not being fully occupied, has so far been ignored. The concomitant change in πd_ε covalency will produce a polarity change in the opposite direction from that given by the change in σd_γ covalency. However, the change in β is believed to be small in cations of the first transition series when they are bound to neutral ligands, and it is probably the case that the change in α represents the major change in polarity. Now the probability of a given transition is related to the change in polarity which it brings about and to the area under the maxima of the absorption spectrum curve with which it has been identified. In a series of similar complexes the areas under absorption peaks can be roughly obtained from the maximum extinction coefficients. This extinction coefficient should be found to increase with increasing covalency in the ground state in a series of cupric complexes : it should increase with the σ donor properties of the ligand. Experiment strongly supports this conclusion. For example, changing the ligand attached to the cupric ion from water to ammonia, or along the series of substituted amines, ammonia, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine (Irving and Griffiths, *J.*, 1954, 213) or from chloride to bromide, increases the intensity of the cupric absorption band at long wavelength, a *d–d* transition, which follows the donor character of the ligands. Very similar observations have been made on the absorption spectra of complexes of nickel, cobaltic, and chromic. In each case the absorption maximum increases in intensity from water to ammonia to ethylenediamine complexes. In titanous and vanadous complexes the intensity of absorption increases along the series water, alcohol, ether, or along the series methanol, ethanol (Hartmann and Schläfer, *Z. phys. Chem.*, 1951, **197**, 116; *Z. Naturforsch.*, 1951, **6a**, 754, 760). If a series of cations are compared in their complexes with one ligand, then according to the above discussion the intensity of the absorption should increase with the ionisation potential of the cation. In the bivalent series of hydrates and ammines $\mathrm{Cu^{II}} > \mathrm{Ni^{II}} > \mathrm{Co^{II}} > \mathrm{Fe^{II}}$ this parallel is found. Elsewhere (Williams, *loc. cit.*) the change in intensity in other series of complexes follows the ionisation potential of the cation rather than any function of the radius and charge which might have indicated that polarisation by electrostatic forces was important.

The positions of the absorption maxima in many complexes can also be interpreted with the aid of equations (1)—(4) and the Figure. A transition from a πd_ε^* orbital to σd_γ^* will involve a greater energy change the greater the covalency, σd_γ bonds, in the complex. This covalency gives an increase in the splitting of the d_γ and d_ε electronic states which must be added to the effects produced by the electrostatic field of the ligands alone. As the intensity of the electrostatic field due to a given ligand is unlikely to parallel its ability to form co-ordinate covalent bonds, the total splitting cannot be calculated at all readily. This complication, which is absent from considerations of the intensities, makes all discussion more difficult. In those complexes where β is expected to be close to unity in both the ground and the excited spectroscopic states, increasing covalency in a complex should move a given transition to shorter wavelengths as the splitting between σd_γ^* and πd_ε^* is increased. This is observed in the movement of the weak bands of chromic, cobaltic, cupric, nickelous, and cobaltous on replacement of the water molecules of the hydrate by ammonia or, to a greater extent, by ethylenediamine. Moreover, the shift in the individual cation complexes follows the change in covalency in the complex. During the addition of the first four ligands, the largest shift occurs in the order $\mathrm{Cu^{II}} > \mathrm{Ni^{II}} > \mathrm{Co^{II}}$; as pointed out earlier, this is the order of the ionisation potentials of these cations. Now, on p. 12, it was shown that the nickel complexes exceed the cupric complexes in covalency on the addition of the last two ligands, making a hexaco-ordinate complex, despite the order of the ionisation potentials. This is also reflected in the absorption spectra, the shift from the hydrate to the hexammine being greatest in the order $\mathrm{Ni^{II}} > \mathrm{Cu^{II}} > \mathrm{Co^{II}}$. Such observations as these can only be explained on crystal-field theory by assuming a different relative polarisability for water and ammonia in each cation complex, and sometimes different relative polarisabilities for the different steps of the complex formation (cf. Bjerrum *et al.*, *loc. cit.*, who list the relevant absorption spectra).

The omission of effects due to changes in β in the discussion of the position of the absorption spectra of complexes is probably only justifiable where the ligands are saturated uncharged compounds such as ammonia and water (p. 13). The effect of mixing d_ε orbitals of the cation with ligand π orbitals can produce two additional effects. If the ligand is unsaturated, then the mixing with empty orbitals lowers the d_ε states of the cation. But there are now no anti-bonding electrons so that it is these highly stabilised πd_ε bonding electrons which are excited to the σd_γ^* anti-bonding states. The absorption maxima are shifted to short wavelengths by unsaturated ligands. In fact, the absorption bands of the cations, nickel, cobaltous, chromic, cobaltic, and cupric move to shortest wavelengths with cyanide and phenanthroline. However, the stabilisation of the d_ε electrons is observed even in the pyridine complexes of cupric. Despite the fact that pyridine is a much weaker base than ammonia, the bands in the cupric complexes of the former are at the shorter wavelength (Bjerrum and Nielsen, *Acta Chem. Scand.*, 1948, **2**, 297). On the other hand, if a ligand acts as a π electron donor, then the d_ε electrons of the cation are accommodated in elevated πd_ε^* orbitals, with the result that the excitation to σd_γ orbitals is energetically easier—the absorption band moves to longer wavelengths. It has already been mentioned that paramagnetic absorption spectra indicate that anions such as chloride seem able to act as better π electron donors than neutral molecules. Part of this effect may arise from the fact that the neutral molecules so far used as ligands are derived from first-period elements, oxygen and nitrogen, whereas the anions examined include chloride and bromide. In general, the directional characteristics of orbitals of higher principal quantum number are better than those of earlier shells. Be this as it may, the position of the absorption bands of anions is generally at much longer wavelengths, in agreement with predictions that can be made from the paramagnetic measurements. The order of the position of the absorption band maxima for different ligands with one cation, *i.e.*, unsaturated ligands, saturated neutral molecules, anions, is now seen to be a result of the variety of bonding that can arise in a complex and cannot be directly related to one of the factors in the bonding, namely, the electrostatic field.

When the ground state of the complex is non-degenerate, as in ferric complexes, transitions require a change of spin multiplicity which is strongly forbidden by the selection rules. Absorption in the simple hydrates of such ions is extremely weak. In the ferric complexes, for example, the ground state is ^6S and the first excited state ^4G. An analysis of the very weak absorption bands which result from transitions between these states has been made by Schläfer [*Z. phys. Chem.* (*Frankfurt*), 1955, **4**, 116]. When the ferric ion is bound to any ligand that can act as a π electron donor, however, the intensity of the absorption rises, sometimes even reaching values comparable with those of fully allowed transitions (Williams, *loc. cit.*). Here it is the excited state which is the better acceptor, for the excitation of an electron from the ground state leaves an empty orbital, probably a πd_ε orbital. Further, the absorption bands in the ferric complexes move to longer wavelengths the better the donor properties of the ligand. This shift is in the opposite direction from that found in the complexes described earlier, *e.g.*, of Cu^{II}, where the transitions took the cation to a bonding state of lower potential covalency than the ground state. It appears difficult to explain these different observations in terms of the crystal-field theory.

Finally, it is clear that if the covalency described becomes sufficiently strong, the antibonding orbitals may be destabilised to such an extent that they are of higher energy than another state of lower multiplicity. In such a case a change of magnetic moment is observed in the ground state (van Vleck, *loc. cit.*).

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