The Absorption Spectra of Some Complex Ions of Analytical Importance.

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Some characteristic features of the absorption spectra of complex ions are discussed. The bands due to the ligand are modified by the polarising power of the cations and by the part played by the cation in the conjugation of the ligand. The spectra of certain ferrous complexes are due to allowed transitions in which an electron is excited into an orbital which interacts with the ligand; a partial electron transfer from the cation occurs. Some other cation complexes have similar spectra. The absorption spectra of certain ferric complexes are, it is suggested, due to *3d*–*3d* transitions coupled with partial charge transfer to the cation. The intensity and the wavelengths of the absorption of many complexes can be satisfactorily understood on this basis.

In recent years colorimetric methods have been increasingly used for the determination of metal ions in solution. Many of these methods have employed organic reagents which form coloured complexes, ML, with a limited number of cations. Often the absorption spectra of these complexes have been carefully measured but there has been little examination of the electron transitions responsible for the absorption. The following discussion will advance theoretical ideas to account for regularities now apparent in these spectra.

The absorption of light by the complexes ML can arise through transitions of (*a*) non-bonding electrons of the ligand, L, (*b*) non-bonding electrons of the cation, M, or (*c*) bonding electrons between M and L.

Transitions of Non-bonding Electrons of the Ligand.—In ionic complexes there are virtually no bonding electrons and the absorption of the complexes must be the sum of the absorption of M and L separately, but slightly modified by mutual polarisation. The polarisation of the ligand might well be expected to vary inversely with the radii of the cations, provided that the latter have constant charge. An example has been studied by Schwarzenbach, Anderegg, and Sallman (*Helv. Chim. Acta*, 1952, **35**, 1794) who measured the absorption spectra of the complexes, ML^-, formed by the ligand $2:5:1\text{-HO}\cdot C_6H_3(NO_2)\cdot CH_2\cdot N(CH_2\cdot CO_2H)_2$ with zinc, magnesium, calcium, and barium ions.

The spectra are similar to that of the ligand, L^{3-}, and to that of the proton complex, HL^{2-}, but both $\lambda_{max.}$ and $\varepsilon_{max.}$, *fall* slightly with increasing stability of the complexes. The stabilities do not increase with the inverse of the radii, however, but are closely related to the ionisation potentials of the cations, $Zn^{II} > Mg^{II} > Ca^{II} > Ba^{II}$. Apparently the polarisation of the ligand is proportional to the electron affinity of the cation. Anderegg, Flascka, Sallman, and Schwarzenbach (*ibid.*, 1954, **37**, 113) measured the absorption spectra of the complexes of the same series of cations with a second ligand, related to (I), and again found that $\lambda_{max.}$ and $\varepsilon_{max.}$ *fall* parallel with increasing stability of the complexes. In the complexes of these ligands the cation reduces the possibility of quinonoid resonance, as does the proton, and the chelate ring in which it is bound cannot be conjugated with the aromatic ligands.

The relation between the stability of complexes and the positions of the ligand absorption band has also been measured in the series listed in Table 1. In three series, in one of which there is the same chelating bridge –N•C•C•O– as in (I), the value of $\lambda_{max.}$ *increases* with increasing stability of the complex in the order $Cu^{II} > Ni^{II} > Co^{II} \gg Zn^{II}$ (Irving and Williams, *J.*, 1953, 3192). The chelate ring in which the cation is bound is conjugated with the ligand in these cases but, despite the difference in its direction, the shift of the absorption band again follows the electron affinity of the cation. The effect of a cation is not always so simply related to ionisation potentials, for in the absorption spectra of the porphyrin (Table 1) and phthalocyanine complexes (Anderson, Bradbrook, Cook, and Linstead, *J.*, 1938, 1151) the positions of the ligand absorption bands are shifted in the order $Ni^{II} > Co^{II} > Cu^{II} > Zn^{II}$. The complexes of these ligands are covalent, unlike those described above, and 3*d* orbitals are used in the bonding of cobaltous and nickel ions. In all the examples so far studied only small shifts in $\lambda_{max.}$ of the ligand absorption are brought about by complex formation.

FIG. 1. *Comparative plot of* $\lambda_{max.}$ *of some cuprous– and ferrous–phenanthroline complexes. The numbers refer to positions of substitution of methyl groups in phenanthroline.* (*Note the point a for the* 4 : 7-*diphenyl compound*) (I) *Values in the absence of* 3(8)-*methyl groups.* (II) *Values for compounds with one* 3(8)-*methyl group.* (III) *Values for compounds with two* 3 : 8-*methyl groups.*

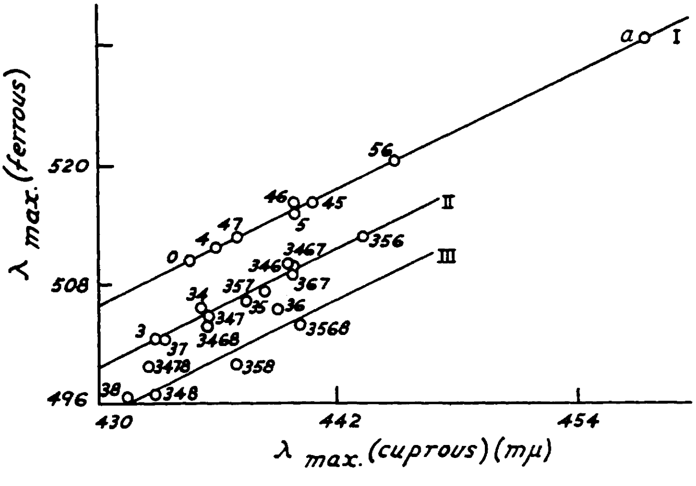


TABLE 1. *Position of the ligand bands in some complexes* ($\lambda_{max.}$ *in* mμ).

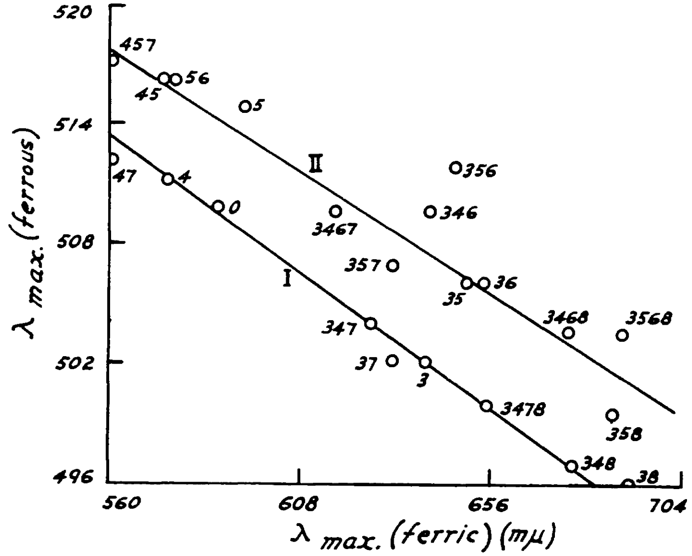
Ligand	Cation Cu^{II}	Ni^{II}	Co^{II}	Zn^{II}	Mn^{II}	H^{I}	Ref.
8-Hydroxyquinoline	412	400(430) *	406	373	396	355	(1)
Acetylacetone	296	294	282	280	—	273	(1)
2-*p*-Dimethylaminophenylazopyridine	570	550	540	538	540	470	(2)
Dipyridyl	298	308—296	305—295	—	280	280	(3)
o-Phenanthroline	—	307	304	270	—	265	(4)
Mesoporphyrin IX dimethyl ester	560	550	—	570	—	570	(5)
	525	515	—	535	—	530	

(1) Sone, *J. Amer. Chem. Soc.*, 1953, **75**, 5207; see also Fernando, Emery, and Phillips, *ibid.*, p. 1983. (2) Klotz and Loh Ming, *ibid.*, p. 4159. (3) Yamasaki, *Bull. Chem. Soc. Japan*, 1937, **12**, 390. (4) Roberts and Field, *J. Amer. Chem. Soc.*, 1950, **72**, 4232. (5) Stern and Dezelic, *Z. phys. Chem.*, 1937, **180**, *A*, 131.

* The anomalous second peak in the nickel–oxine spectrum is discussed on p. 143.

Absorption due primarily to the Cation.—In the spectra of ferric, cuprous, and diamagnetic ferrous complexes with aromatic di-imines, such as *o*-phenanthroline and dipyridyl, there are intense bands in the visible region which can be readily distinguished from the ligand bands around 270 mμ (Table 1). The bands in the visible region are not present in other similar cation complexes of the same ligands, *e.g.*, of nickel, cobaltous, or zinc ions (Roberts and Field, *loc. cit.*; Yamasaki, *loc. cit.*) and must be due therefore to electron transitions of the specific cations. The absorption spectra of these ferrous and cuprous complexes are very similar. Their extinction coefficients are invariably around 10^4, implying allowed electron transitions, and there is a linear 1 : 1 relation between $\lambda_{\text{max.}}(\text{Fe}^{\text{II}})$ and $\lambda_{\text{max.}}(\text{Cu}^{\text{I}})$ in the methyl-substituted phenanthroline complexes (Fig. 1; data from Brandt and Smith, *Analyt. Chem.*, 1949, **21**, 1313; McCurdy and Smith, *Analyst*, 1952, **77**, 846). Such a relation indicates that the electron transitions involved in the complexes are also similar. Intense absorption bands in the visible region are not found in other series of cuprous or ferrous complexes, *e.g.*, with chloride or cyanide, even if the latter are diamagnetic (Fromherz and Menschick, *Z. phys. Chem.*, 1929, *B*, **3**, 1; Samuel, Zamen, and Zubairy, *Indian J. Physics*, 1936, **9**, 491). The appearance of the bands requires both a conjugating and chelating di-imine and that the ferrous ion should be in the diamagnetic state with an electron configuration in which the 3*d* levels are filled, as in the cuprous ion, with either atomic or bonding electrons. An electron transition which accords with these features is the excitation of a 3*d* electron into a higher quantum level, such as the 5*p*, which can be coupled with the empty π levels of the ligand. The excitation suggested is a partial electron transfer *to the ligand*, which explains the shift to longer $\lambda_{\text{max.}}$ as the acceptor character of the ligand increases (Table 2). In other transition series the ruthenous and osmous cation complexes of phenanthroline and dipyridyl have similar absorption spectra (Brandt and Smith, *loc. cit.*; Burstall, Dwyer, and Gyarfas, *J.*, 1950, 953) and the electron transition involved is presumably similar too.

FIG. 2. *A comparative plot of* $\lambda_{\text{max.}}$ *of some ferric– and ferrous–methylphenanthroline complexes. (The numbers refer to the positions of the methyl substituents in the phenanthroline molecule.) (I) Values in the absence of* 5*-methyl groups. (II) Values for compounds containing one* 5(6)*-methyl group.*



(Values for compounds containing two 5 : 6-methyl groups lie above line II.)

A comparison between the absorption spectra of the ferrous and ferric complexes of methylphenanthrolines (Fig. 2; Brandt and Smith, *loc. cit.*) shows that the sensitivity of the values of $\lambda_{\text{max.}}(\text{Fe}^{\text{III}})$ to changes in the substituents is greater than that of $\lambda_{\text{max.}}(\text{Fe}^{\text{II}})$ and that the shifts in $\lambda_{\text{max.}}$ are in opposite directions. The intensity of the ferric spectra is one-tenth of that of the ferrous. This low intensity suggests that the electron transition is not an allowed one. A large number of other ferric complexes has been examined (Table 3). The position of maximum absorption in these complexes is also sensitive to substituents in the ligand. Examples amongst phenanthroline (Brandt and Gullstrom, *J. Amer. Chem. Soc.*, 1952, **74**, 3532), 8-hydroxyquinoline (Molland, *Tidsskr. Kjemi*, 1941, **3**, 50), fatty acid (Kiss, Abraham, and Hegedius, *Z. anorg. Chem.*, **1940**, **244**, 98), and phenol (Brode and Wesp, *J. Amer. Chem. Soc.*, 1934, **56**, 1037) complexes show that increase in the electron-donor properties, by such groups as methyl as opposed to nitro- or carboxyl, shifts the absorption to longer wave-lengths. The intensity ranges from that typical of forbidden transitions $\varepsilon_{\text{max.}} \ll 10^2$, to that of allowed transitions $\varepsilon_{\text{max.}} \simeq 10^4$ (Table 3 and Fig. 3). The weak absorption found in some of these ferric complexes arises from a 3*d*–3*d* transition (Bowen, *Quart. Reviews*, 1950, **4**, 243). This has been put beyond reasonable doubt in the case of ferric thiosulphate (Page, *Trans. Faraday Soc.*, 1953, **49**, 635), and the similarity between the absorption of this complex and many other ferric complexes (Fig. 3) allows the argument to be extended to them. The usual 3*d*–3*d* transition, as found in the complexes of chromic and diamagnetic cobaltic, changes slightly in wave-length on the change of the ligand but the shifts are accompanied by little change in intensity (contrast Table 3; Kiss and Czegledy, *Z. anorg. Chem.*, 1938, **235**, 407; Linhard and Weigel, *Z. anorg. Chem.*, 1952, **271**, 101). The maximum absorption in these complexes has an extinction, $\varepsilon_{\text{max.}}$, of about 10^2. Now the cobaltic and chromic ions in their normal states have two unoccupied 3*d* levels which are used in the formation of covalent, inner-orbital, complexes and there is no possibility of increase in covalency by electron rearrangement. In the majority of ferric complexes

TABLE 2. *Absorption maxima of some ferrous phenanthrolines.*

o-Phenanthroline	$\lambda_{\text{max.}}$	Ref.
Unsubstituted	510	(1)
4 : 7-Diphenyl-	533	(1)
4-Hydroxy-	544	(2)
3-Ethoxycarbonyl-4-hydroxy-	561	(2)
Several 4 : 7-diamino-	530—560	(3)
8-Ethoxycarbonyl-7-hydroxy-4-methyl-2-aza-	605	(4)

(1) McCurdy and Smith, *loc. cit.* (2) Hale and Mellon, *J. Amer. Chem. Soc.*, 1950, **72**, 3217. (3) Wilkins, McCurdy, and Smith, *Analyt. Chim. Acta*, 1953, **8**, 46. (4) Irving and Williams, *Analyst*, 1952, **77**, 813.

TABLE 3. *Absorption spectra of some ferric complexes.*

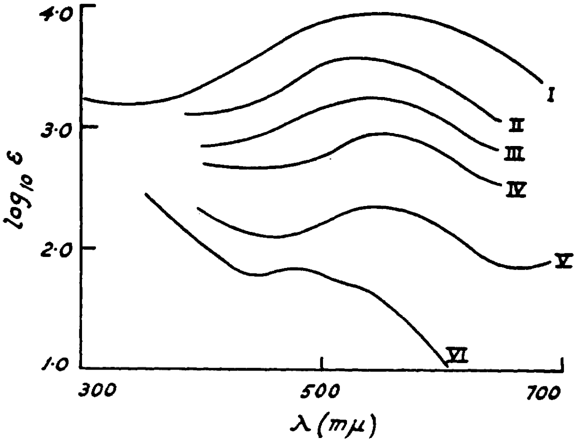
Ligand (salt or complex)	Formula of complex	$\lambda_{\text{max.}}$	$\varepsilon_{\text{max.}}$	Ref.
Citrate	1 : 1	450 *	10^2 *	(1)
Acetate (maximum co-ordination)	—	465	50	(2)
m-Nitrophenoxide	1 : 1	510	50	(3)
p-Nitrophenoxide	1 : 1	515	30	(3)
Resorcinol complex	1 : 1	550	50	(3)
Ethyl acetoacetate	1 : 1	500	50	(3) (4)
Salicylaldehyde complex	1 : 1	530	800	(3) (4)
Salicylate	1 : 1	530	10^3	(3)
Phenanthroline complex	3 : 1	590	10^3	(5)
Acetylacetone complex	3 : 1	—	$10^{3\cdot5}$	(6)
8-Hydroxyquinoline complex	3 : 1	600	$10^{3\cdot7}$	(6)
Thiocyanate	3 : 1 (?)	525	$10^{4\cdot0}$	(7)
Thioglycollate	?	530	$10^{4\cdot0}$	(8)
3-Sulphosalicylate	1 : 1	510	$10^{3\cdot3}$	(9)
,,	2 : 1	460	$10^{3\cdot6}$	(9)
,,	3 : 1	425	$10^{3\cdot8}$	(9)

* There is no maximum in the spectrum as recorded, and the band at about these wave-lengths appears to have merged with the general absorption at shorter wave-lengths (1). This is also apparent in the formate and trichloroacetate complexes (Kiss, Abraham, and Hegedius, *loc. cit.*).

(1) Lanford and Quinan, *J. Amer. Chem. Soc.*, 1948, **70**, 2900. (2) Reiss, Hazel, and McNabb, *Analyt. Chem.*, 1952, **24**, 1646. (3) Broumand and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 1013. (4) Herbst, Close, Mazzacua, and Dwyer, *ibid.*, p. 269. (5) Brandt and Smith, *loc. cit.* (6) Sone, *loc. cit.*; Henecka, *Ber.*, 1948, **81**, 179. (7) Ovenston and Parker, *Analyt. Chim. Acta*, 1949, **3**, 277. (8) Swank and Mellon, *Analyt. Chem.*, 1938, **10**, 7. (9) Agren, *Acta Chem. Scand.*, 1954, **8**, 266.

the ferric ion has five 3*d* electrons all unpaired, so that these complexes are " ionic," outer-orbital complexes, with no 3*d* binding. The increase of $\lambda_{max.}$ of the ferric complexes with increasing electron donation from the ligand indicates that the electron-acceptor properties of the ferric ion are increased in the excited state. This can come about if the transition involved, which is now assumed to be forbidden 3*d*–3*d*, is such as to vacate a 3*d* level, making it available for bonding. Such a transition would be associated with a change in permanent dipole in the cation–ligand bond and could be considered as a partial electron transfer *from the ligand* to the cation, *i.e.*, in the opposite direction from that which adequately explained features of the spectra of ferrous complexes. It is now more apparent why changes in substituents in phenanthroline produced opposed shifts in the absorption spectra of the ferric and ferrous complexes of this ligand (Fig. 2). The intensity of the spectra of the ferric complexes is thus linked with the size of the change in the permanent dipole on excitation. In the extreme case the transition could go over to a full electron transfer to the ferric ion, and an intensity of 10^4 would be expected as for an allowed transition. This case, it is suggested, is realised in ferric thiocyanate and in a number of other complexes in which ferric is co-ordinated through sulphur atoms, *e.g.*, thioglycollate (Swank and Mellon, *loc. cit.*). The suggestion that the spectra of the latter complexes are true charge-transfer spectra is strengthened by the relative instability of the complexes to light and by the fact that the absorption moves to longer wave-lengths as the number of ligands bound to the cation is increased (Rabinowitch, *Rev. Mod. Physics*, 1942, **14**, 112). On the other hand, many ferric complexes have absorption of much lower intensity and are stable to light, and increase in co-ordination to them shifts the absorption maxima to shorter wave-lengths (Agren, *loc. cit.*; Harvey and Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488; Swank and Mellon, *Analyt. Chem.*, 1937, **9**, 406). The shift to shorter wave-lengths with increasing co-ordination may well be due to increasing symmetry altering the splitting of the 3*d* energy levels in the ferric ion, in accord with the idea that this weaker absorption is due to a 3*d*–3*d* transition.

FIG. 3. *The absorption spectra of some ferric complexes. (I) Thiocyanate,* 3 : 1 *complex. (II) Catechol-*3 : 5-*disulphonate,* 3 : 1 *complex. (III)* 3-*Sulphosalicylate,* 1 : 1 *complex. (IV) Salicylaldehyde,* 1 : 1 *complex. (V) Thiosulphate,* 1 : 1 *complex. (VI) Acetate, maximum complex formation. References are in the text and in Table* 3.



(*Note :* Due allowance has been made for the formation of different complexes, and the extinctions given all refer to a single complex. Similarly data for other complexes can be obtained by reference to Table 3.)

The argument furthermore predicts that bands of varying intensity from 10 to 10^4 should be found in certain other transition-metal ion complexes. The following absorption spectra appear of particular interest, since alternative explanations are lacking for their characteristics: the ruthenium(III) and osmium(III) complexes of sulphur-containing ligands (Ayres and Wells, *Analyt. Chem.*, 1950, **22**, 317) which differ from the other

Group VIII metal complexes excepting only ferric; the osmium(III) complex of dipyridyl (Dwyer and Gyarfas, *J. Amer. Chem. Soc.*, 1951, **73**, 2322); the octahedral complexes of manganese(III) with three molecules of oxalate or pentanedione (Cartledge, *ibid.*, 1952, **74**, 6015).

Details of the Spectra of Complexes of Di-imines.—A methyl substituent in an aromatic base such as phenanthroline or pyridine increases the basicity of the nitrogen (Herrington, *Discuss. Faraday Soc.*, 1950, **9**, 26; Irving, Cabell, and Mellor, *J.*, 1953, 3417; Brandt and Gullstrom, *loc. cit.*). Bjerrum (*Chem. Reviews*, 1950, **46**, 381) has shown that in a series of complexes of a given metal and a number of ligands derived by substitution from one parent compound the stability of the complexes is closely related to ligand basicity. The complexes of methylphenanthrolines would all be expected to be more stable than that of the parent compound, and the generalisation has been confirmed in some cases (Brandt and Gullstrom, *loc. cit.*; Irving, Cabell, and Mellor, *loc. cit.*) and is borne out by the values of oxidation–reduction potentials (Brandt and Smith, *loc. cit.*). It might have been expected therefore that all methyl groups would have shifted the absorption spectra of the phenanthroline complex of a given cation in the same direction. The following discussion of the absorption spectra of the ferrous and cuprous complexes will indicate why this expectation is not fulfilled.

It is not possible to compare the spectra of all the methylphenanthroline complexes of these two cations, as the formation of the 2(9)-methyl ferrous complexes is sterically hindered to such an extent that the complexes do not give the absorption characteristic of the ferrous diamagnetic complexes (see Table 4). The cuprous complexes are normal, however. Fig. 1, a comparative plot of $\lambda_{\text{max.}}(\text{Fe}^{\text{II}})$ against $\lambda_{\text{max.}}(\text{Cu}^{\text{I}})$ for methyl-substituted complexes, 2(9)-substituents being omitted, is a 1 : 1 linear relation in the absence of 3(8)-methyl groups, the continuation of line going through the point for the 4 : 7-diphenylphenanthroline complexes. It also shows that in contrast with 4- or 5-methyl groups a 3-substituent reduces rather than increases $\lambda_{\text{max.}}$ in both cation complexes, and that two such groups have about twice the effect of one. The reduction in $\lambda_{\text{max.}}$ is greater in the ferrous complexes than in those of cuprous, leading to three parallel relationships between $\lambda_{\text{max.}}(\text{Fe}^{\text{II}})$ and $\lambda_{\text{max.}}(\text{Cu}^{\text{I}})$ (see Fig. 1). A comparative plot of the extinction coefficients of these complexes shows that 3-methyl substituents decrease $\varepsilon_{\text{max.}}$ in the ferrous complexes but increase it in the cuprous complexes.

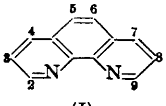
Unlike the 4- and the 5-position which are strongly conjugated to the nitrogen atoms in phenanthroline (I), the 3-position is *meta* to the nitrogen but *para* to the bond joining the two nitrogen-containing rings. A 3-methyl group will shorten this bond by increasing its double-bond character, whilst a 4- or a 5-methyl group will mostly alter the donor properties of the nitrogen. The shortening of the distance between the nitrogen atoms would be expected to have a greater effect on the ferrous spectra as the bonding orbitals here are d^2sp^3, which are very sensitive to bond-angle changes, whereas in the cuprous complexes the bonding is through the less sensitive sp^3 orbitals. Assuming then that it is the difference in directive power that largely affects the shifts in $\lambda_{\text{max.}}$, a 2-methyl group should behave, in the absence of steric hindrance, *e.g.*, in cuprous complexes, in the same way as a 4-methyl substituent. The values obtained by McCurdy and Smith (*loc. cit.*) confirm this : both $\lambda_{\text{max.}}$ and $\varepsilon_{\text{max.}}$ are increased, *e.g.*,

	$\lambda_{\text{max.}}$	$\varepsilon_{\text{max.}}$
Cuprous *o*-phenanthroline	435	7040
Cuprous 2 : 9-dimethyl-*o*-phenanthroline	455	7890

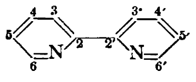
An examination of the absorption spectra of the cuprous and ferrous complexes of other aromatic bases again demonstrates the importance of the different directive influences of differently substituted methyl groups. In complexes with dipyridyl (II) (Cagle and Smith, *J. Amer. Chem. Soc.*, 1947, **69**, 1860; Hoste, *Analyt. Chem.*, 1950, **4**, 23), the values of $\lambda_{\text{max.}}$ and $\varepsilon_{\text{max.}}$ are as follows ($\varepsilon_{\text{max.}}$ in parentheses) :

	Ferrous		Cuprous
Unsubstituted	522 (8650)	Unsubstituted	435 (4550)
3 : 3′-Dimethyl	526 (1770)	6 : 6′-Dimethyl	455 (6570)
4 : 4′-Dimethyl	529 (8470)		
5 : 5′-Dimethyl	510 (8310)		

The 4 : 4′- and 6 : 6′-methyl groups, of which the 6 : 6′-groups have the expected greater effect on $\lambda_{\max.}$ (the ferrous and cuprous complexes being assumed to behave similarly), increase $\lambda_{\max.}$ and are *ortho* and *para* respectively to the nitrogen atoms of dipyridyl. The 5 : 5-methyl groups, *para* to the 2 : 2′-bond, decrease $\lambda_{\max.}$, also much as expected, but the 3 : 3′-methyl groups, which would have been expected to induce a similar effect to that of the 5 : 5-groups, in fact increase $\lambda_{\max.}$. The anomaly arises through the steric hindrance between these two 3 : 3′-methyl groups preventing the two pyridyl rings from lying in the same plane, and hence instead of decreasing the length of the 2 : 2′-bond, these groups increase it. For the same steric reasons the value of $\varepsilon_{\max.}$ is very low in these compounds. That such steric hindrance is present in the dipyridyls can be demonstrated by analogy with the effect of methyl substituents in diphenyl (O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906), for it has been shown that 3 : 3′- but not 4 : 4′- or 5 : 5′-methyl groups eliminate the absorption band of diphenyl which is characteristic of the interaction between the two rings. This work also proves that the shift observed in the 5 : 5′-dimethyldipyridyl ferrous complex is intimately concerned with the co-ordination to the cation, for it is in the opposite direction to the shift produced by methyl groups in the same positions in diphenyl. In 3-methyldiphenyl (Braude, Sondheimer, and Forbes, *Nature*, 1954, **117**, 173) steric hindrance is very slight. Hoste (*loc. cit.*), and Irving and Williams (*Analyst, loc. cit.*), quote examples of the formation of cuprous and ferrous complexes of dipyridyl derivatives in which single 3-substituents do not prevent the formation of complexes with high extinction coefficients. In diquinolyl complexes of cuprous, where 4 : 4′-substituents [see (III)] behave as in dipyridyl and phenanthroline, a single 3-substituent does not lower the extinction coefficient very greatly, and it is noteworthy that $\lambda_{\max.}$ decreases as expected from the presumed shortening of the 2 : 2′-bond produced by such groups in the absence of steric hindrance (Smith and Wilkins, *Analyt. Chim. Acta*, 1954, **10**, 139).



(I)



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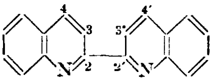

(III)

The absorption spectra of some terpyridyl ferrous complexes have been studied (Wilkins and Smith, *ibid.*, 1953, **9**, 338). 4-Methyl and 4-phenyl substituents have the expected effects, increasing both $\lambda_{\max.}$ and $\varepsilon_{\max.}$.

Spectra of Some Further Ferrous Complexes.—The classification of the intense spectra of the above diamagnetic complexes of ferrous as allowed transitions from the filled 3*d* shell (see p. 139) suggests that the similar, though much less intense, absorption of a large number of other ferrous complexes might well arise from the same transition, especially as the ligands with which ferrous shows such spectra are all conjugating and chelating imines (Table 4). It is clear from the Table, too, that as the number of these ligands which are co-ordinated to the cation is increased, the intensity of the absorption increases rapidly until it is equal to that of the diamagnetic complexes on six-fold co-ordination. Very similar rapid changes in absorption concomitant with change in paramagnetic moment of ferrous complexes have been frequently observed on further co-ordination of ferroporphyrins (Williams, *Biol. Review*, 1953, **28**, 381), but there is no absorption in the ferrous complexes of glycine, ethylenediamine, or *o*-aminobenzoic acid. Furthermore, it is known that ferrous complexes are abnormally stabilised when co-ordinated directly to an aromatic ring with ligands such as 8-hydroxyquinoline (Irving and Williams, *loc. cit.*; Albert and Hampton, *loc. cit.*). It appears probable that the absorption is due to the presence of a small proportion of the diamagnetic form of the ferrous complexes, the intensity of absorption around 400—600 mμ increasing as this proportion increases (see Table 4).

Nickel and Cobaltous Complexes.—Nickel perchlorate, when dissolved in water, has two weak absorption bands at $\lambda_{\max.}$ 400 and 600 mμ and of $\varepsilon_{\max.}$ 10—100. In many nickel complexes the absorption around 400 mμ is greatly increased without a corresponding effect near 600 mμ (Kiss and Szabo, *Z. anorg. Chem.*, 1943, **252**, 172). In some of the paramagnetic complexes, *e.g.*, those of oxine, the extinction at these wave-lengths which cannot be attributed to the ligand (see Table 1) is of the order 10^3—10^4. Such extinction is too great to be attributed to a simple $3d$–$3d$ transition (McKenzie, Mellor, Mills, and Short, *J. Proc. Roy. Soc. N.S.W.*, 1944, **78**, 70; Sone, *loc. cit.*). Elsewhere (Williams, *J. Phys. Chem.*, 1954, **58**, 121) it has been pointed out that nickel complexes, such as that with oxine, are adversely affected in stability if the ligand forces the cation out of either a planar or an octahedral arrangement despite the fact that the complexes are paramagnetic. Furthermore, the rates of exchange of nickelous ions from many paramagnetic complexes are low as compared with the corresponding exchange rates for cupric, cobaltous, and zinc ions (West, *J.*, 1954, 395). Low rate of exchange of an ion has been frequently correlated with covalent, and in the case of nickel, diamagnetic, forms of complexes (Taube, *Chem. Review*, 1952, **50**, 69). An absorption band, differing only in intensity from that at 400 mμ described above, is also found in diamagnetic nickel complexes. It has a maximum extinction coefficient greater than 10^4, implying that it must arise from an allowed transition. These lines of evidence suggest that there is a contribution to the properties of the (mostly) paramagnetic nickel complexes from their diamagnetic forms.

TABLE 4. *Absorption spectra of some ferrous complexes.*

Ligand	$\lambda_{\text{max.}}$	$\varepsilon_{\text{max.}}$	Magnetic moment, B.M.	Ref.
Picolinic acid, 2 : 1 complex	440	3×10^2	5·2	(1) (2)
,, plus cyanide	440	10^4	—	(1)
Pyrazine-2 : 3-dicarboxylic acid	495	3×10^2	—	(3)
Pyridine-2 : 5-dicarboxylic acid	415	2×10^2	—	(4)
Quinaldinic acid, 2 : 1 complex	515	3×10^2	5·2	(1) (2)
,, plus cyanide	515	10^4	—	(1)
5 : 6-Diphenylquinaldinic acid, 2 : 1 complex	515	4×10^2	—	(1)
,, ,, plus cyanide	515	10^4	—	(1)
Quinoxaline-2 : 3-dicarboxylic acid	520	3×10^2	—	(3)
Dipyridyl, 1 : 1 complex	435	2×10^2	5·2	(5) (6)
o-Phenanthroline, 1 : 1 complex	400—450	2×10^2	5·2	(7) (6)
2-Methylphenanthroline, 2 : 1 complex	440	10^3	5·2 (?)	(8) (6)
2-Chlorophenanthroline, 2 : 1 complex (?)	510	Weak	—	(8)
Dipyridyl, 3 : 1 complex	523	10^4	0·0	(9)
o-Phenanthroline, 3 : 1 complex	510	10^4	0·0	(9)
*cyclo*Hexanedione dioxime, 2 : 1 complex	464	3×10^3	—	(10)
,, ,, plus pyridine	531	10^4	—	(11)
,, ,, plus ammonia	541	10^4	—	(11)
Diacetyl dianil, 2 : 1 complex	600	Weak	—	(12)
Diacetyl di-*N*-methylimine, 3 : 1 complex	510	10^4	—	(12)

N.B. Many derivatives of 8-hydroxyquinoline also give red-yellow ferrous complexes (Albert and Hampton, *J.*, 1954, 505).

(1) Majumbar and Sen, *Analyt. Chim. Acta*, 1953, **8**, 369; 1953, **9**, 529; *J. Indian Chem. Soc.*, 1950, **27**, 245. (2) Cambi and Cagnasso, *Gazzetta*, 1933, **63**, 767. (3) Ley, Schwarte, and Munnish, *Ber.*, 1924, **57**, 349. (4) Chang and Reddick, *Analyt. Chem.*, 1954, **26**, 536. (5) Krumholtz, *J. Amer. Chem. Soc.*, 1949, **71**, 3654. (6) Basolo and Dwyer, *ibid.*, 1954, **76**, 1454. (7) Kolthoff, Leussing, and Lee, *ibid.*, 1950, **72**, 2173. (8) Irving, Cabell, and Mellor, *loc. cit.* (9) Brandt and Smith, *loc. cit.* (10) Banks and Byrd, *Analyt. Chim. Acta*, 1954, **10**, 129. (11) Griffing and Mellon, *Analyt. Chem.*, 1947, **19**, 1017. (12) Krumholtz, *J. Amer. Chem. Soc.*, 1953, **75**, 2163; see also Walter and Freiser, *Analyt. Chem.*, 1954, **26**, 217, for further examples of the absorption spectra of ferrous di-imine complexes.

As ready excitation of a $3d$ electron from a full $3d$ shell seemed to be common to three series of cation complexes, *viz.*, ferrous, cuprous, and nickelous, it was sought in others. Most cobaltous complexes show weak absorption between 450 and 600 mμ, $\varepsilon_{\text{max.}}$ 10. The band persists almost unchanged in the phenanthroline and dipyridyl complexes (Field and Roberts, *loc. cit.*), but in the cobaltous terpyridyl complex there is strong absorption over the range 400—500 mμ of extinction coefficient greater than 10^3 (Wilkins and Smith, *Analyt. Chim. Acta*, 1953, **9**, 338). The effect of substituents in terpyridyl upon the absorption closely parallels that in the corresponding ferrous complexes (*idem, ibid.*). Now, although in dipyridyl and *o*-phenanthroline complexes the cobaltous ion exchanges very rapidly, yet in terpyridyl complexes the exchange is slow, suggesting that a change to a covalent complex has taken place, *i.e.*, a cobaltous complex involving 3*d* orbitals (West, *J.*, 1954, 578). The evidence indicates that the absorption observed in this cobaltous complex is similar to that discussed in the covalent ferrous complexes. In this connection, the cobaltous complexes of *NN'*-disalicylidene-ethylenediamine and *o*-phenylenediamine are covalent and intensely coloured, and the exchange of the cobaltous ion in them is slow (West, *J.*, 1954, 395).

Transitions of Bonding Electrons.—From the above discussion it is clear that the distinction between a bonding and a non-bonding electron will frequently be artificial. An electron not involved in bonding in the normal or ground state of the complex may become so in the excited state. Such cases have been considered under non-bonding electrons. In certain charge-transfer spectra the excited state is the only state in which a bond is formed, the normal state being a " no-bond " structure. A full discussion of these molecules and their spectra has been given by Mulliken (*J. Phys. Chem.*, 1952, **56**, 801). It is also possible in charge transfer for the excited state to be the no-bond structure, but as Bowen (*loc. cit.*) has pointed out, there will be very many other cases in which excitation will produce a modification of bonding and it is doubtful if any purpose is served by labelling all these spectra as charge-transfer bands.

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