226. *The Absorption Spectra of Some Ferrous and Ferric Complexes.*

By J. C. TOMKINSON and R. J. P. WILLIAMS.

The absorption spectra of a series of complexes of 8-hydroxyquinolines (oxines) with ferrous and ferric ions have been measured. The bands in the visible region of the spectrum are specific to the cations. The changes of intensity and position of the bands are interpreted. The discussion is supported by reference to other measurements in a variety of solvents and to studies of other ligand complexes of the cations.

THE visible absorption spectra of ferric and ferrous complexes have been described by Williams.[1] When the ligand itself had no absorption in the visible region the observed bands were due to the specific properties of these two cations as cations of other metals in the same type of complex did not give rise to similar bands. For a given ligand, *e.g.*, phenanthroline, a change of substituent in it produced opposed shifts in the absorption maxima of the ferrous and the ferric complex. It was concluded that the absorption was due, in part, to charge transfer either from the cation to the ligand (with ferrous ion), or from the ligand to the cation (with ferric ion). Oxinates (8-hydroxyquinoline derivatives) were included in the generalisation although relatively few experimental data were available. In the earlier discussion [1] the change of intensity of the visible absorption in complexes of a number of different cations, *e.g.*, nickel, cobaltous, and ferrous, with unsaturated chelating ligands led to the conclusion that two states of different electron spin, and therefore of different magnetic moment, of the same cation–ligand complex existed in equilibrium.[2] Since then other papers [3, 4, 5] have confirmed the suggestion. Now it will be shown that the existence of such equilibria explains the intensities of the spectra of some further ferrous and ferric complexes.

TABLE 1. *The absorption spectra of ferric oxinates.*

	λ_A (mμ)	λ_B (mμ)	ε_A	ε_B		λ_A (mμ)	λ_B (mμ)	ε_A	ε_B
In 50% dioxan–water					In 75% dioxan–water				
Oxine	460	580	5160	4000	Oxine	462	580	5510	4000
2-Methyl	—	*ca.* 575	—	1120	5-Chloro	475	*ca.* 600	(6490)	(4000)
5-Methyl	479	607	5840	4260	5-Bromo	475	596	(7290)	(4560)
5-Fluoro	477	592	5300	3790	5-Iodo	475	605	(8120)	(5150)
5-CO$_2$Et	450	583	9250	5050	5 : 7-Dichloro	477	614	6280	4450
5-Cyano	453	587	(8650)	(5000)	5 : 7-Di-iodo	480	620	(6830)	(4800)
5-CH:N·OH	487	635	(9550)	(5000)					
5-Formyl	456	595	(12,700)	(6000)	7-Iodo-5-sulphonic acid	460	598	(6000)	(4930)
Xanthurenic acid *	—	625	—	5200	5-Sulphonic acid	452	582	(6540)	(4590)
					5-CO$_2$Et	455	583	10,500	5600

Figures in parentheses are less reliable, and are derived from examination of solutions taken from titration cells after pH-titration experiments. In the other cases specially prepared solutions were used. * 4 : 8-Dihydroxyquinoline-2-carboxylic acid.

TABLE 2. *The absorption spectra of ferrous oxinates* (*room temperature*) (*Solvent*: 50% *aqueous dioxan*).

	$\lambda_{max.}$ (mμ)	ε	Degree of formation		$\lambda_{max.}$ (mμ)	ε	Degree of formation
Oxine	512	1100	2 : 1	5-CH:N·OH	600	2200	3 : 1
	587	2120	3 : 1	5-Cyano	600	2700	3 : 1
2-Methyl	520	400	2 : 1	5-Formyl	608	3300	3 : 1
5-Methyl	595	2060	3 : 1	Xanthurenic acid (aq.)	535	850	2 : 1
5-Fluoro	605	1632	3 : 1				

---

[1] Williams, *J.*, 1955, 137.
[2] Willis and Mellor, *J. Amer. Chem. Soc.*, 1947, **69**, 1237.
[3] Clark and Odell, *J.*, 1955, 3431.
[4] *Idem, ibid.*, 1956, 620.
[5] Sacconi, Paoletti, and Re, *J. Amer. Chem. Soc.*, 1957, **79**, 4062.

Position of the Absorption Maxima in Oxinates.—Tables 1 and 2 list the position and the intensity of the absorption maxima in a series of ferrous and ferric oxinates. The stoicheiometry of the complexes is known from their formation functions.[6]

In the ferric spectra there are two bands to be considered, at about 475 and 600 mμ, apart from those of the ligands themselves. As neither of these bands is found for oxine complexes of other tervalent cations they are attributed to the ferric ion. The two bands do not shift in the same way with change of substituent in every case. However, there is a general shift of both bands to longer wavelengths as the electron-donor character of the substituent is increased. This is in keeping with the idea that both bands are, in part, due to charge-transfer transitions to the cation. The interpretation cannot be more detailed while so little is known about the exact order of the effect produced by the individual substituents upon the σ- and π-electron density in the ligand.[7]

The band of the ferrous complexes at about 500—600 mμ is absent for other bivalent metal oxinates and is thus probably due to specific properties of the ferrous cation. It moves but slightly with change of substituent, as with the ferrous phenanthrolines.[1] The interpretation of the band shift is made difficult also by the uncertainty in the band position (±5 mμ) due to the flatness of the absorption peak, but there is little correlation with the shift for the corresponding ferric complexes. There may well be some charge transfer from the ferrous cation to the ligands, as has been postulated for the phenanthroline complexes,[1] but in neither case can charge transfer be such a dominant feature of the spectrum as it is for the ferric complexes.

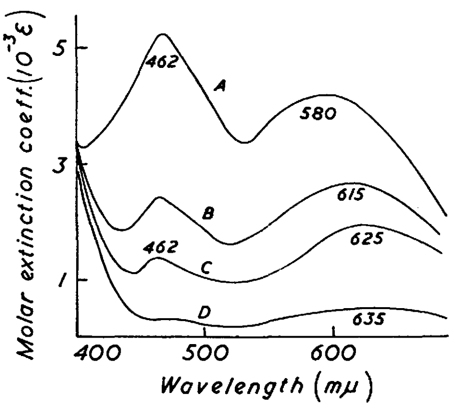

FIG. 1. *The change of absorption spectrum of ferric oxinate solutions as the degree of formation of the complex is increased.*

A, pH 6·0. *B*, pH 2·5
C, pH 2·3. *D*, pH 1·5

Numerals on the curves are mμ.

The Intensity of the Ferric Oxinate Absorption Bands.—As the degree of formation of ferric oxinate is increased the intensity of absorption at 600 mμ rises roughly proportionately and moves *slightly* to shorter wavelengths (Fig. 1). The rise in intensity is similar to that for other ferric complexes, but the shift in band position is smaller in the oxinates than in the other complexes. The band at shorter wavelengths is weaker than that at longer wavelengths at low degrees of formation but increases in intensity as complex formation nears completion (see Fig. 1). It is not possible to say whether this change is common to all ferric complexes although many 3 : 1 ferric chelates have a similar two-band absorption spectra where neither band can be attributed to ligand transitions.[1] In those cases where steric hindrance prevents formation of a 3 : 1 complex, *e.g.*, with 2-methyl- and 2-carboxy-hydroxy-oxines, the short-wavelength absorption band of the ferric chelate is of very low intensity.

Table 3 gives the position and intensity of the absorption spectra of ferric oxinate in many solvents. There is hardly any change in the long-wavelength band from solvent to solvent but the short-wavelength band moves considerably and its intensity also changes

---

[6] Tomkinson and Williams, *J.*, in the press.
[7] Taft, *J. Amer. Chem. Soc.*, 1957, **79**, 1045.

greatly. Similar relatively large variations in intensity of this band have been noted in Table 1. The band movement with solvent shows a rough correlation with change of intensity. Bjerrum, Adamson, and Bostrup[8] have pointed out that charge-transfer bands are sensitive to solvent changes whereas *d–d* transitions are not. The effect of solvent upon the ferric band at short wave-length therefore confirms the description of it as a charge-transfer band but no similar conclusion about the other band appears to be justifiable from this evidence.

Ferric Porphyrin Complexes.—The above discussion of ferric oxinate spectra leads to a new assignment of the bands in ferric porphyrins. The band positions and intensities for some ferric hæmoglobin complexes are given in Table 4, together with the magnetic moments of the complexes.[9,10,11] The Soret band (410 mμ) moves to longer wavelengths as the magnetic moment falls. There is no difficulty in locating this band. The band at long wavelengths around 625—650 mμ is also readily located: it is not due to the ligand, and is absent from other metal porphyrins, and its general behaviour suggests that it is a charge-transfer band similar to that in oxinates at 600 mμ. It falls in intensity as the magnetic moment of the complex falls. Now, in general, metal complexes of porphyrins have α- and β-bands separated by 20—30 mμ in the 520—580 mμ region of the spectrum: these bands are due to the ligands. In ferriporphyrins, *e.g.*, hæmoglobin, bands in this region are not found easily although there is usually a weak band near 570 mμ and an inflection near 540 mμ: we consider these to be the (weak) α- and β-bands. In addition

TABLE 3. *The spectrum of ferric oxinate in different solvents.*

Solvent *	λ_A (mμ)	λ_B (mμ)	ε_A	ε_B	Solvent *	λ_A (mμ)	λ_B (mμ)	ε_A	ε_B
Water	454	580	4355	4000	γ-Collidine	467	577	6780	4000
MeOH	459	578	5380	4045	Dioxan	466	572	6770	4070
EtOH	461	582	5325	3950	75% H_2O–dioxan	462	580	5560	4000
Pr^nOH	463	582	5280	3900	50% H_2O–dioxan	460	580	5160	4000
Pr^iOH	465	582	5450	3980	25% H_2O–dioxan	457	580	4770	4000
Bu^nOH	462	580	5420	3950	Nitromethane	461	577	5420	3860
Bu^iOH	462	582	5200	3840	Acetonitrile	463	575	5870	4070
Bu^sOH	463	582	5675	4050	Acetone	463	573	6450	3960
Bu^tOH	463	580	5690	3950	MeCOEt	465	576	6390	3780
*cyclo*Hexanol	464	580	5520	4000	Benzene	469	577	6500	4035
Nonan-1-ol	463	582	5760	4000	Chloroform	468	585	5730	3890
Pyridine	468	580	6440	4070	CCl_4	473	585	6260	3510

* The order of solvents is chosen so as to bring out obvious relations.

TABLE 4. *The absorption spectra of ferric hæmoglobin complexes*[11] ($\lambda_{max.}$ in mμ).

Ligand	Soret band	α-Band	β-Band	Other bands		Magnetic moment
Water	404	(575)	—	500	631	5·65
Fluoride	403	(565)?	(530)?	482	605	5·76
Formate	404	573	(535)	497	620	5·44
Acetate	404	573	(535)	497	620	5·44
Cyanate	407	573	—	501	625	5·40
Thiocyanate	410	—	—	—	630	5·06
Hydroxide	409	575	540	—	(595)	4·66
Nitro	412	576	538	—	(624)	4·13
Glyoxaline	411	560	534	—	—	2·87
Cyanide	419	(575)	540	—	—	2·50
Azide	417	575	540	—	(630)	2·35

The bands at 500 and 625 mμ fall in intensity as those at 575 and 535 mμ rise and the magnetic moment falls. Similar results have been obtained for other ferric porphyrin complexes, *e.g.*, for a series of myoglobins.[11] Weak bands are given in parentheses.

---

[8] Bjerrum, Adamson, and Bostrup, *Acta Chem. Scand.*, 1956, **10**, 329.

[9] Keilin and Hartree, *Biochem. J.*, 1951, **49**, 88.

[10] Hartree, *Ann. Reports*, 1946, **43**, 295.

[11] Scheler, Schoffa, and Jung, *Biochem. Z.*, 1957, **329**, 232.

there is a band at 490 mμ not common to other metal porphyrins: this shifts in a similar manner to that at 625 mμ when the protein is combined with fluoride, acetate, or formate (cf. Table 4). The bands at 490 and 625 mμ disappear when covalent ferric complexes are formed with cyanide and the usual α- and β-bands in the region of 530—570 mμ appear. Now charge-transfer bands are found only for the ionic ferric complexes. We suggest that the 480—500 mμ band is the second charge-transfer band and is similar to that in other ionic ferric chelates (oxinates) described in this paper.

A final group of ferric complexes to which we would like to refer are those of dimethylglyoxime(DMG).[12] In the complex $Fe(DMG)_3$ there are no absorption maxima above 320 mμ. In the complex $Fe(DMG)_2OH(H_2O)$, on the other hand, there is a weak band at 675 mμ and a stronger band at 460 mμ. We consider that these two bands are the charge-transfer bands expected for ionic ferric chelates. It is predicted that $Fe(DMG)_3$ will be covalent on the grounds that it does not show these bands.

The Intensity of Absorption in Ferrous Oxinates.—The absorption spectra of ferrous oxinates are given in Table 2. The intensity of absorption in the $Fe^{II}(Ox)^-_3$ complexes rises along the series of 5-substituents, fluoro < methyl < H < CH:N·OH < cyano < formyl, which is the series of substituents of increasing π-electrophilic character.[7] Now it has been suggested that the intensity of the band at 500—600 mμ in ferrous complexes, a band absent from spectra of other cation complexes, is related to the amount of the cation which is in the diamagnetic state.[1] The existence of this type of equilibrium has been established by the study of several other transition-metal cation complexes (not oxinates) which have absorption bands at very different wavelengths.[3, 4, 5] We consider that there is an increase in the proportion of the ferrous ion in the diamagnetic state in the order of the above series of substituents. The substituents, in the same order as the intensity of the absorption in the ferrous complexes, are in the order which would be expected to stabilise the diamagnetic state as they are arranged according to their ability to act as π (in this case d_ϵ)-electron acceptors. There is a second line of evidence which leads to the same conclusion as to the importance of these properties.

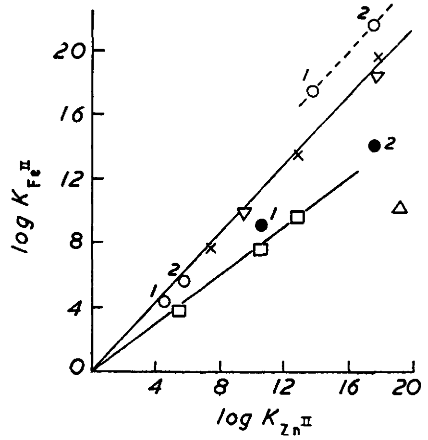

FIG. 2. *A comparison of the stability constants of a number of ferrous and zinc complexes.*

○, *Dipyridyl* (1) *and* o-*phenanthroline* (2).
●, *Nitrilotriacetate* (1) *and ethylenediaminetetra-acetate* (2).
×, 5-*Formyloxinate.*
□, *Ethylenediamine.*
▽, *Acetylacetone.*
△, *Cysteine.*

The larger values refer to higher degrees of formation in each case. Note that the stronger the electron-donor the more stable the zinc complex, and the stronger the π-electron acceptor the stronger the ferrous complex (cf. Irving and Rossotti, *Acta Chem. Scand.*, 1956, **10**, 72).

The Relative Stability of Bivalent Cation Complexes of Oxines.—The Irving–Williams series for the stability of complexes of bivalent cations of the first transition series is $Mn^{II} < Fe^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$. This order is broken by the intensely coloured diamagnetic ferrous complexes of phenanthroline and dipyridyl. In the much more weakly absorbing chelate compounds of ferrous iron, *e.g.,* the parent oxinate, although the stability series is not broken, the stability of the ferrous chelate is greater than expected when compared with, for example, the zinc complex, but it does not

---

[12] Jillot and Williams, *J.*, 1958, 462.

exceed it in stability. This is a general observation concerning all ligands which are conjugated and form strongly coloured ferrous complexes. The only ferrous chelates known for which the stability order is $Fe^{II} > Zn^{II}$, however, are those which form diamagnetic complexes and break the stability series. Amongst substituted 8-hydroxyquinolines we have determined the stability order for 2 : 1 complexes of 5-formyloxine (Fig. 2; Tables 5 and 6). It is Mn^{II}, $Zn^{II} < Fe^{II} < Ni^{II}$. The ferrous chelate is stabilised relatively to zinc, but not markedly so with respect to nickel. The stabilisation can be interpreted as a stabilisation of the d_ϵ-electrons by π-bond formation which, as indicated, would also stabilise the diamagnetic form of ferrous ion. For some other oxinates substituted with π-electron-acceptor groups, and particularly in pteridine complexes, Albert and Hampton [13] observed an anomalously high stability of ferrous complexes, which we take to arise in the same manner.

The step stability constants for the formation of the 1 : 1, 2 : 1, and 3 : 1 oxine complexes of these cations give further evidence. They are listed in Table 5. For 5-formyloxine the third constant is close to the other two in magnitude, which is not the case for other substituted oxinates except the 5-cyano-compound. In fact the oxinate which forms one of the least stable 1 : 1 complexes, 5-cyano, has the greatest third-step stability constant. We are unable to offer an alternative explanation to that given above, that the d_ϵ-electrons are stabilised by the electron-withdrawing substituents $^-$CN and $^-$CHO.

The change in intensity of the absorption spectra of ferrous oxinates with the degree of formation of the complex is also interesting when compared with results for ferric oxinates. In the latter the intensity rises almost proportionately to the degree of formation. In ferrous chelates the intensity rises rapidly on going from the 2 : 1 to the 3 : 1 complex (Table 1). There is a parallel with the behaviour of the *o*-phenanthroline–ferrous complex. The extinction coefficient of the 1 : 1 ferrous–phenanthroline complex is approximately one-tenth of that of the 3 : 1 complex. It is not possible to determine the extinction coefficient of the 2 : 1 phenanthroline chelate. Another parallel between the two series is the effect of steric hindrance. The 2-methylphenanthroline–ferrous

TABLE 5. *The stability constants of ferrous oxinates.* (50% Aqueous dioxan, 0·3M-sodium chloride, 25°.)

	log K_1	log K_2	log K_1K_2	log K_3	pk_{NH}	pk_{OH}
Oxine	8·71	8·12	16·83	5·3	4·08	10·82
5-Methyl	—	—	16·90	6·0	4·24	11·25
2-Methyl	8·75	8·35	17·10	v. small	5·05	11·45
5-Fluoro	—	—	15·9	5·4	2·76	10·55
5-Sulphonic acid	—	—	15·7	6·0	3·40	9·68
5-CH:N·OH	—	—	14·9	5·3	3·52	9·22
7-Iodo-5-sulphonic acid	—	—	13·8	5·0	1·75	8·13
5-CO_2Et	—	—	16·2	5·5	2·88	8·73
5-Cyano	7·10	7·15	14·25	6·0	2·02	7·85
5-Formyl	6·90	6·85	13·75	5·8	2·51	7·43

The acid dissociation constants are " practical constants " and the stability constants are stoicheiometric constants.[14] A discussion of the change in stability of the complexes with the acid dissociation constant is given elsewhere.[15]

TABLE 6. *The step stability constants for the formation of* 5-*formyloxinates in* 50% *aqueous dioxan.*

Metal	Ni	Fe^{II}	Zn	Mn	Fe^{III}
Log K_1	8·27	6·90	6·45	5·73	11·7
Log K_2	7·56	6·85	6·23	4·97	10·0
Log K_3	6·70	5·70	4·95	4·58	8·3

---

[13] Albert and Hampton, *J.*, 1954, 505.

[14] Irving and Rossotti, *J.*, 1954, 2910.

[15] Jones, Poole, Tomkinson, and Williams, *J.*, in the press.

complex is paramagnetic and has a low extinction coefficient despite the fact that it is a tris-chelate. It has been shown that steric hindrance effectively prevents the formation of the diamagnetic complex. Amongst oxinates the extinction coefficient of the 2-methyloxine–ferrous complex is noticeably much lower than that of the other derivatives. All these facts indicate that the field due to an oxine is sufficiently strong to set up an equilibrium between diamagnetic and paramagnetic ferrous ions in which the two forms are present in similar concentrations.

Experimental.—The method used in the determination of stability constants has been described elsewhere.[14] Oxygen was excluded during the measurements on the ferrous complexes.[6] Absorption spectra were measured in a conventional manner with matched cells and appropriate blanks.

We thank Professors A. Albert and G. R. Clemo, Mr. R. G. Hollingshead, and Messrs. Reid Ltd. (Barking, England) for gifts of oxines; also the Royal Society for the loan of a Unicam S.P. 600 spectrophotometer. One of us is indebted to the Gas Council for a Research Fellowship. We had many helpful discussions with Dr. D. F. Evans. The Referees are thanked for much helpful comment.

THE UNIVERSITY, OXFORD.

[*Received, September* 30*th*, 1957.]