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The Iron(II)-Methine Chromophore

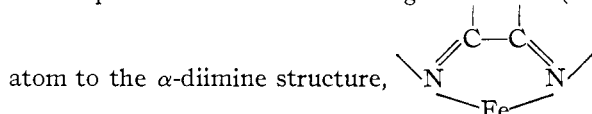
BY DARYLE H. BUSCH AND JOHN C. BAILAR, JR.

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The intensely colored complexes formed by iron(II) with heterocyclic, diamines and triamines and with α -diimines constitute a single class of compounds. A structural link between the complexes of aromatic, heterocyclic diamines and α -diimines is found in the iron(II) derivative of pyridinalmethylimine, which has both structural units and physical properties in common with those of the two extreme types of ligand. Study of the magnetic moments and visible, ultraviolet and infrared spectra of the iron(II) compounds of this class leads to a detailed description of the mode of bonding involved. The behavior and properties of these compounds are best described in terms of six sigma bonds formed between the metal and the six methine nitrogens, the strengths of which depend on the basicity of the ligand, and three π -bonds resulting from interaction of the unhybridized d-electron pairs of the metal atom with the π -system of the ligand. The strength of the π -bonds varies with the degree of conjugation in the chelate ring.

Introduction

The nature of the chromophoric group and of the metal-nitrogen bonds in the iron(II) derivatives of compounds, such as 2,2'-bipyridine, 1,10-phenanthroline and 2,2',2''-terpyridine, have received considerable attention in recent years. In spite of these investigations and of many applications of the color reaction in analytical chemistry, there remain many questions with regard to the exact nature of these complex compounds. The presence of six octahedrally directed sigma bonds between the iron atom and the nitrogen atoms is inferred from the diamagnetism¹ of the complexes and from their resolution into optical isomers.² If the assumption of six d^2sp^3 hybridized sigma bonds were sufficient to describe the interaction of iron(II) with aromatic heterocyclic amines, aliphatic amines would be expected to form similar complexes. However, the ammonia and ethylenediamine complexes of iron(II) are relatively unstable.³ This fact suggests that the presence of an unsaturated group is critical in the formation of this iron(II) chromophore. Krumholz⁴ has shown that an α -diimine group gives the reaction and has suggested that this chromophore involves the linking of an iron(II)



Krumholz also suggested that the unusual stability and characteristic color reaction are the result of π -bonding between the conjugated ligand and the unhybridized d-electron pairs of the iron atom. This explanation seems logical, since any atom or group of atoms adjacent to a π -electron system and possessing electrons in orbitals with π -symmetry may be expected to enter into the conjugation already present,⁵ and in view of the recognized π -symmetry of the d-electron pairs underlying those orbitals involved in the σ -bonded hybrid.⁶ Bonding of this type has been suggested for other complexes exhibiting unusual properties, among which are the

(1) L. Cambi and A. Cagnasso, *Gazz. chim. ital.*, **63**, 767 (1933); **4**, 772 (1935); L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, p. 116.

(2) F. P. Dwyer and E. C. Gyrfas, *THIS JOURNAL*, **74**, 4699 (1952); *J. Proc. Roy. Soc. N. S. Wales*, **83**, 263 (1950); A. Werner, *Ber.*, **45**, 433 (1912).

(3) J. Bjerrum, "Metal Ammine Formation," Copenhagen, 1941.

(4) P. Krumholz, *THIS JOURNAL*, **75**, 2163 (1953).

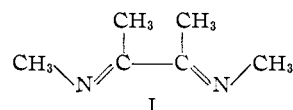
(5) C. A. Coulson, "Valence," Oxford Press, London, 1952, p. 247.

(6) R. S. Nyholm, *Revs. Pure Applied Chem.*, **4**, 32 (1954).

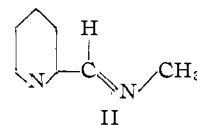
cyanides of the metals of the first transition series,⁷ the carbonyls,⁸ the olefin complexes,⁹ and metal complexes of trivalent phosphorus and arsenic donor compounds.¹⁰ The presence of double bonds among iron(II) compounds of the type in question has been suggested by other investigators.¹¹ Krumholz⁴ based his inclusion of the α -diimine compounds in the same classification with the 2,2'-bipyridine and 1,10-phenanthroline group on their very similar visible spectra. The work reported here provides support for his interpretations, yielding evidence for the presence of π -bonding between the metal and the nitrogen atoms. In order to identify the grouping of atoms which is critical to the formation of this class of compounds, we have chosen to refer to the chromophoric group as the iron(II)-methine chromophore.

Compounds of the Iron(II)-Methine Class.—

In order to understand the chemical nature of the compounds of this class, a number of new complexes were designed and prepared. Their properties were compared with the well-known 2,2'-bipyridine and 1,10-phenanthroline complexes and with biacetylismethylimine



which is representative of the compounds reported by Krumholz.⁴ Pyridinalmethylimine was prepared in the form of its iron(II) complex to provide



a structural link between the aromatic ligands which enter into the iron(II)-methine chromophore and the relatively simple α -diimines of Krumholz. This new ligand is composed of two structural units: the pyridine ring, corresponding to one-half of the aromatic grouping in 2,2'-bipyridine, and the side-chain imine group, corresponding to half of

(7) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944.

(8) Ref. 7, pp. 251-254.

(9) J. Chatt, "Cationic Polymerization," Ed. P. H. Plesch, Heffer and Sons, Ltd., Cambridge, 1953, p. 40.

(10) A. Kabesh and R. S. Nyholm, *J. Chem. Soc.*, 3245 (1951).

(11) W. A. Brandt, F. P. Dwyer and E. C. Gyrfas, *Chem. Revs.*, **54**, 959 (1954).

a glyoxalbismethylimine molecule. The striking similarity of the iron(II) complex containing this ligand with both those of 2,2'-bipyridine and of the α -diimine type confirms the presence of a single chromophoric group throughout the series.

Bis-(pyridinal)-ethylenediimine (see Table II), contains, within a single molecule, four unsaturated nitrogen atoms which presumably may act as donors to a single iron(II) atom. (Scale models indicate that such behavior is sterically favored if the four nitrogen atoms are coplanar with the central metal atom.) This compound and its iron(II) derivative were prepared to test the hypothesis that six unsaturated nitrogen atoms are required in the formation of the iron(II)-methine chromophore.

Attempts to prepare iron(II) derivatives of biacetylbisbenzylimine and biacetylbisethylimine were unsuccessful. Similarly, Krumholz found that biacetylbisaniil does not form a compound of this type.

An iron(II) compound of biacetyldihydrazone (Table II) was also prepared in order to provide a further test on the structural features of this color reaction. The steric requirements and location of double bonds in this ligand are very similar to those in biacetylismethylimine.

Magnetic moments, and visible, ultraviolet and infrared spectra lead to the conclusion that the iron(II)-methine chromophore is associated with six iron(II)-nitrogen links involving d^2sp^3 hybridized sigma bonds and π -bonding between the unhybridized d -electron pairs of the iron(II) and the π -electron cloud of the ligand.

Experimental

Materials.—Samples of 2,2'-bipyridine and tris-(2,2'-bipyridine)-iron(II) perchlorate were provided by Professor G. Frederick Smith, for which kindness the authors are genuinely grateful. Tris-(biacetylismethylimine)-iron(II) iodide was prepared by the method of Krumholz.⁴ *Anal.* Calcd. for $[\text{Fe}(\text{C}_8\text{H}_{12}\text{N}_2)_3]\text{I}_2$: C, 33.42; H, 5.61; N, 12.97. Found: C, 33.02; H, 5.57; N, 12.61.

Tris-(pyridinalmethylimine)-Iron(II) Iodide.—Ten and seven-tenths grams of pyridinaldehyde (0.1 mole) in 75 ml. of ethanol was added to 10 ml. of 7.5 *N* aqueous methylamine and the mixture was allowed to stand at room temperature for 15 minutes. When 20 ml. of a one molar solution of iron(II) chloride (0.02 mole) was added, a deep rose-red color formed immediately. The solution was stirred for ten minutes and allowed to stand for 30 minutes. The solution was then concentrated to 40 ml. under reduced pressure at 60°. Twenty-five grams of potassium iodide was added and the solution was cooled. Very dark crystals with a metallic luster precipitated. They were recrystallized by dissolving in a small amount of water, adding potassium iodide, and cooling. *Anal.* Calcd. for $[\text{Fe}(\text{C}_7\text{H}_8\text{N}_2)_3]\text{I}_2 \cdot 2\text{H}_2\text{O}$: Fe, 8.04; C, 36.18; H, 3.88; N, 12.04. Found: Fe, 8.06; C, 36.06; H, 4.12; N, 11.70.

Biacetyldihydrazone.—To a boiling solution of 39.7 g. of 54% aqueous hydrazine (0.67 mole) in 300 ml. of ethanol was added 25 ml. of biacetyl (0.291 mole) over a period of 90 minutes. Refluxing was continued for an additional 30 minutes. Two hundred and fifty milliliters of water was then added and the ethanol was removed by distillation. When the resulting aqueous solution was cooled in an ice-bath, white crystals formed. These were filtered, washed with a little water, recrystallized from 150 ml. of hot absolute ethanol and dried *in vacuo*; m.p. 158–159° (reported 158°); yield 10.5 g. (32%). *Anal.* Calcd. for $\text{C}_8\text{H}_{10}\text{N}_4$: C, 42.2; H, 8.78; N, 49.1. Found: C, 42.71; H, 8.92; N, 47.91.

Tris-(biacetyldihydrazone)-Iron(II) Tetrachloroferrate(II).—Two grams of biacetyldihydrazone (0.0175 mole) was dissolved in 100 ml. of hot absolute ethanol and added to a

solution of 1.75 g. of iron(II) chloride 4-hydrate (0.0088 mole) in 30 ml. of absolute ethanol. On cooling, rust colored crystals separated from the deep red-brown solution. The substance melted without decomposition at 202–205°, but long heating, even at 110°, resulted in decomposition. *Anal.* Calcd. for $[\text{Fe}(\text{C}_8\text{H}_{10}\text{N}_4)_3]\text{FeCl}_4$: Fe, 18.79; C, 24.16; H, 5.04; N, 28.20. Found: Fe, 18.95; C, 24.22; H, 4.82; N, 26.79.

Bis-(pyridinal)-ethylenediimine.—Thirty grams of pyridinaldehyde (0.28 mole) dissolved in 50 ml. of absolute ethanol was mixed with 8.5 g. of anhydrous ethylenediimine (0.14 mole), whereupon a considerable amount of heat was evolved. After standing for 30 minutes, the solvent was removed by warming to about 60° under vacuum. As the last of the solvent was removed, the product solidified as a tan wax-like cake. It was recovered by extracting into several 150 to 200-ml. portions of hot, low boiling petroleum ether, from which it crystallized on cooling. Recrystallization from petroleum ether gave a product melting at 67 to 68°. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{14}\text{N}_4$: C, 70.59; H, 5.89; N, 23.65. Found: C, 69.74; H, 5.61; N, 22.98. Treatment of alcoholic solutions of this Schiff base with equivalent amounts of iron(II) chloride 4-hydrate, cobalt(II) chloride 6-hydrate and copper(II) chloride 2-hydrate, dissolved in alcohol, resulted in the separation of solid products. However, it was found that they were generally contaminated by excess metal salt. The insolubility of these substances in ethanol and their instability toward water made it impractical to purify them. However, several qualitative observations are of significance. The iron(II) compound has a deep purple color, similar to that observed for other iron(II) complexes; however, the compound is rapidly hydrolyzed in water. The reaction of copper(II) chloride is rather remarkable. Upon first mixing, a green powder separated. Then, upon standing, blue crystals slowly formed. The nitrogen content of the blue product corresponds closely to that demanded by the formula $[\text{Cu}(\text{C}_{14}\text{H}_{14}\text{N}_4)]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. *Anal.* Calcd.: N, 13.73. Found: N, 13.70.

Magnetic Measurements.—The magnetic moments of the iron(II) compounds were determined with a modified Curie-Cheveneau magnetic balance.¹² The instrument was calibrated for each series of readings with Mohr's salt and air. Tris-(biacetylismethylimine)-iron(II) iodide and tris-(pyridinalmethylimine)-iron(II) iodide were found to be diamagnetic. This supports the suggestion that the iron atoms in these species, like those in the 2,2'-bipyridine and 1,10-phenanthroline complexes, utilize d^2sp^3 hybridized bond orbitals.

The magnetic moment of biacetyldihydrazone (BH) complex is 5.32 Bohr magnetons, calculated for the formula $[\text{Fe}(\text{BH})_3]\text{FeCl}_4$. This may be explained on the assumption that the iron atom in the cation is diamagnetic while that of the anion is paramagnetic, showing a normal moment for iron(II). Confirmation of the assumption that the cation is $[\text{Fe}(\text{BH})_3]^{+2}$, is found in recent investigations of the complexes of biacetyldihydrazone.¹³

The product from the reaction of bis-(pyridinal)-ethylenediimine with iron(II) chloride was also found to be paramagnetic.

Visible and Ultraviolet Spectra.—The spectra reported here were obtained with the Carey Recording Spectrophotometer with a one-cm. cell, using water as the blank. The concentrations of the aqueous solutions varied from 10^{-3} to 2×10^{-5} molar, depending on the extinction coefficients of the compounds being studied. The wave lengths and extinction coefficients of major bands are reported in Table I. Where possible, the ultraviolet spectra of the complexes are compared with those of the free ligands.

Infrared Spectra.—The infrared spectra were obtained over the range from 600 to 4000 cm^{-1} with a Perkin-Elmer model 21 recording spectrophotometer, using sodium chloride prisms and, in most cases, a Nujol suspension of the compound in question, the only exceptions being 2,2'-bipyridine and bis-(pyridinal)-ethylenediimine. The spectra of these two were obtained on melts of the pure compounds. The results are recorded in Table II.

The substances examined were of analytical purity except the complexes of bis-(pyridinal)-ethylenediimine which

(12) F. H. Driggs and B. S. Hopkins, *THIS JOURNAL*, **47**, 363 (1925).

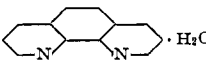
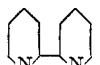
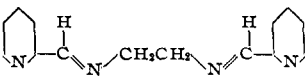
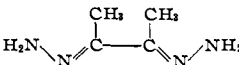
(13) Melvin Noland, Carl Stouffer and Daryle H. Busch, unpublished results.

TABLE I
 VISIBLE AND ULTRAVIOLET ABSORPTIONS OF IRON(II) COMPLEXES AND FREE LIGANDS

Compound ^a	λ_{\max}	Bands of the complex ^b		Bands of ligand ^b		
		Visible	Ultraviolet	Visible	Ultraviolet	
	λ_{\max}	E_{\max}	λ_{\max}	E_{\max}	λ_{\max}	E_{\max}
[Fe(C ₁₂ H ₈ N ₂) ₃]Cl ₂	510	11,500	320	4,500	322	3,000
			[290	26,500	[310	3,000
			267	88,000	263	41,300
			225	79,250	226	>44,000
[Fe(C ₁₀ H ₈ N ₂) ₃](ClO ₄) ₂	522	8,700	348	6,500	[262	18,100
			[298	62,500	[225	12,000
			290	55,000	215	13,900
			246	27,750		
[Fe(C ₈ H ₁₂ N ₂) ₃]I ₂	568	10,700	345	1,214		
			227	38,100		
[Fe(C ₇ H ₈ N ₂) ₃]I ₂	551	11,150	346	6,750	[280	9,400 ^c
			[285	31,000	272	11,400
			276	31,000	266	11,500
			227	51,000	260	10,400
					235	16,550
[Fe(C ₄ H ₁₀ N ₄) ₃]FeCl ₄	444	7,000	283	19,600		
			215	17,900		

^a See names and structures in columns 1 and 2 of Table II. ^b The bracket indicates that the peaks are fused together, those of lower intensity appearing as shoulders. ^c The ligand compared with this complex is the structurally similar bis-(pyridinal)-ethylenediimine.

 TABLE II
 INFRARED ABSORPTIONS OF COMPLEX COMPOUNDS INVOLVING A CARBON-NITROGEN DOUBLE BOND

Compound	Name	Assignments (cm. ⁻¹)								
		H ₂ O	OH	NH	(aryl) C=N	(alkyl) C=N	C=C	NH ₂	CH ₃ - N	CH
[Fe(C ₁₂ H ₈ N ₂) ₃]Cl ₂ ·6H ₂ O	Tris-(1,10-phenanthroline)-iron(II) chloride 6-hydrate	3350	1635	..	1605	723
							1584	782
							1517	
 ·H ₂ O	1,10-Phenanthroline 1-hydrate	3400	1623	..	1592	761
							1567	733
							1511	708
[Fe(C ₁₀ H ₈ N ₂) ₃](ClO ₄) ₂	Tris-(2,2'-bipyridine)-iron(II) perchlorate	1611	..	1575	762
							1472	
	2,2'-Bipyridine	1585	..	1565	756
							1540	
[Fe(C ₈ H ₁₂ N ₂) ₃]I ₂	Tris-(biacetylbismethylimine)-iron(II) iodide	?	1450
								1333
[Fe(C ₇ H ₈ N ₂) ₃]I ₂ ·H ₂ O	Tris-(pyridinalmethylimine)-iron(II) iodide 1-hydrate	3450	1616	1560(?)	1600	1440
								1370
[Fe(C ₁₄ H ₁₄ N ₄)]Cl ₂ ·xH ₂ O	Bis-(pyridinal)-ethylenediimine-iron(II) chloride	3400	1602	1642	1572	767
	Bis-(pyridinal)-ethylenediimine	1595	1655	1577	797
α -[Cu(C ₁₄ H ₁₄ N ₄)]Cl ₂ ·xH ₂ O	Bis-(pyridinal)-ethylenediimine-copper(II) chloride	3400	1607	1651	1577	785
β -[Cu(C ₁₄ H ₁₄ N ₄)]Cl ₂ ·2H ₂ O	Bis-(pyridinal)-ethylenediimine-copper(II) chloride 2-hydrate	..	3390	3260	1611	..	1580	780
[Co(C ₁₄ H ₁₄ N ₄)]Cl ₂ ·xH ₂ O	Bis-(pyridinal)-ethylenediimine-cobalt(II) chloride	3400	1604	1643	1575	775
[Fe(C ₄ H ₁₀ N ₄) ₃]FeCl ₄	Tris-(biacetyldihydrazone)-iron(II) tetrachloroferrate(II)	3370	..	1590	..	1622
				3270						
				3190						
	Biacetyldihydrazone	3330	..	1580	..	1615
				3180						

were contaminated with slight excess of metal salts; however, the ratio of nitrogen to carbon in these substances indicated the presence of the desired ligand, and the characteristics of their spectra are of considerable interest.

Tentative assignments are offered for nine different vibrations found in the spectra of these related compounds. The proposed assignments are in accord with correlations appearing in the literature,¹⁴ which report ranges of occur-

rence of the bands shown by these particular types of atomic groupings. Anomalies are reported in lines 5 and 6 of Table II. These anomalies and the shifts observed in the other spectra are discussed below.

Results

Visible Spectra.—In their visible absorption characteristics, the iron(II) complexes with 1,10-D. Van Nostrand Co., New York, 1952; F. Miller, "Organic Chemistry, an Advanced Treatise," Ed. Gilman, Vol. 3, p. 122, John Wiley and Sons, New York, 1953.

(14) R. B. Barnes, U. Liddell and Z. F. Williams, *Ind. Eng. Chem., Anal. Ed.*, **15**, 659 (1943); A. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangle, "Infrared Determinations of Organic Structures,"

phenanthroline, 2,2'-bipyridine, biacetylismethylimine and pyridinalmethylimine constitute a single class. The visible spectra of these complexes exhibit single maxima of high extinction coefficient (8,700 to 11,500, Table I) and having a shoulder on the violet side of the point of maximum absorption. The range of maxima is from 510 to 568 m μ . The iron(II) complex of biacetyldihydrazone does not conform to this class, having a single symmetrical peak of somewhat lower extinction coefficient at 444 m μ . The characteristic shape of the visible absorption spectrum of the iron(II)-methine chromophore may be seen for a number of these compounds in the paper by Krumholz.⁴ The data reported in Table I emphasize the fact that compounds having the iron atom linked to six aromatic or imine nitrogen atoms belong to a single chromophoric class.

It is probably significant that the wave length of maximum absorption of the complex in the visible range shifts toward the violet as the number of aromatic rings in the free ligand increases (Table III).

TABLE III

VARIATION OF WAVE LENGTH OF MAXIMUM ABSORPTION IN THE VISIBLE SPECTRA OF COMPOUNDS OF THE IRON(II)-METHINE CHROMOPHORE WITH NUMBER OF AROMATIC RINGS IN THE FREE LIGAND

No. of rings	0	1	2	3
λ_{\max} , m μ	568	551	522	510

A tentative explanation of this phenomenon may be based on the observations of Mellor and his co-workers¹⁵ and on the concept of crossed resonance. It has been observed that when a conjugated donor group donates electrons to a metal ion, a shift toward the red occurs. This implies that lower excited states have been produced for the electrons. Mellor suggested that participation of these electrons in resonating rings, as a result of double bonding by the metal atom, should release restraint on the electrons further and cause a still greater shift toward the red. In accord with the concept of crossed resonance, the presence of a second resonating system coupled to the one in question will result in a decrease in the resonance of both systems. That is, a given conjugated system will involve a greater degree of resonance when coupled to no other aromatic or similar groups. From this, it would be expected that the iron(II) atom of the iron(II)-methine chromophore would show its greatest tendency to contribute its d-electron pairs to a π -bonded, resonating chelate ring in combination with those ligands having no aromatic residues. The condition leading to the highest degree of resonance in the chelate ring should, according to the preceding discussion, lead to a maximum shift toward the red. Also, as the amount of crossed resonance is increased (or the number of residual aromatic rings is increased), the absorption band should shift toward the violet. These expectations are borne out by the data of Table III.

Ultraviolet Spectra.—Comparison of the ultraviolet spectra of the diamagnetic iron(II) com-

plexes also reveals a number of pertinent correlations. Those complexes, the ligands of which contain at least one aromatic ring, show three distinct regions of absorption, the second involving a combination of two peaks. Tris-(biacetylismethylimine)-iron(II) ion, where no aromatic group is present, exhibits only the first and third bands. The second (double) band also shows an extinction coefficient roughly proportional to the number of aromatic rings present in one molecule of ligand (compare 31,000, 62,500, 88,000, as shown in Table I). This is consistent with the assumption that a transition involving electrons of the C=C groups is involved, since the probability of the transition and, hence, the extinction coefficient of the band should increase with the number of such groups present. The occurrence of the first and third bands in the spectra of all the complexes indicates that electronic transitions within the conjugated nitrogen-carbon chain give rise to these absorptions.

Infrared Spectra.—Comparison of the effect of complexing with iron(II) on the vibrational spectra of the C=N groups of the ligands reveals divergent behavior in the case of the aromatic and the α -diimine ligands. Lines 1-4, Table II, show that complexing of the nitrogen atoms of the aromatic compound leads to a shift of the C=N band to higher frequencies. This behavior is interpreted as an indication that the bond order of the carbon-nitrogen link is increased. In these same compounds, the bands attributable to the unsaturated carbon-carbon bonds are also shifted to higher frequencies. These shifts are both compatible with the assumption that complexing has led to increased localization of the electrons in the aromatic ligand. Such an effect is to be anticipated if the chelate ring constitutes an additional resonating ring coupled in crossed resonance with the aromatic rings of the ligand. (Compare bond orders of 1,2-bonds in naphthalene and anthracene.)¹⁶ Substitution of electron donor groups (*i.e.*, methyl groups) for the hydrogen atoms in these aromatic ligands also produces shifts of the unsaturated bands to higher frequencies.¹⁷

The over-all effect of complexing may then be summarized as a localization of electrons with a probability of an increase of electron density in the π -system of the ligand. π -Bonding of the unhybridized d-electron pairs of the iron(II) would account for an increase in the electron density in the ligand, while the formation of six sigma bonds by donation of electrons to the metal atom should lead to a decrease in the electron density of the ligand.

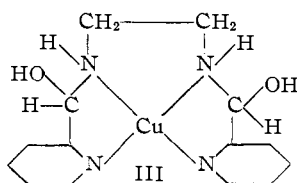
In the case of the α -diimine complex, tris-(biacetylismethylimine)-iron(II), a more striking behavior is found. The spectrum (line 5, Table II) of this complex does not exhibit a band which can be assigned with any certainty to the stretching vibration of the C=N groups. No absorption occurs at frequencies greater than 1450 cm.⁻¹ (except the C-H stretching vibration at a much higher frequency) and the bands which occur at 1450 and

(15) H. A. McKenzie, D. P. Mellor, J. E. Mills and L. N. Short, *J. Proc. Roy. Soc., N.S. Wales*, **78**, 70 (1944).

(16) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, p. 250.

(17) G. Frederick Smith, private communication, 1954.

1333 cm.^{-1} are probably due to the absorption by the N-CH₃ groups. Three possible explanations for the absence of the expected band in the "double-bond region" have been considered: (a) reduction of the double bond; (b) partial hydrolysis of the double bond; and (c) enhanced conjugation of the double bond as a result of participation of the metal atom in double bonding. Although unsaturated linkages are sometimes rendered infrared inactive by molecular symmetry (*e.g.*, the N=N vibration of azobenzene), such an effect could hardly arise in the octahedral complexes under consideration. The possibility of saturation of the C=N groups in these iron(II) complexes seems unlikely on the basis of infrared evidence alone, although other evidence is cited below to bolster this argument. The addition of water to the methine double bond should either result in production of an α -hydroxy secondary amine, or else complete reversal of the Schiff base reaction leading to liberation of the primary amine and the aldehyde or ketone. No bands appear in this spectrum which might be attributed to the -NH₂, -OH, or >C=O groups. The absence of N-H stretching vibrations also is in disagreement with the possibility of reduction of the unsaturated group. A very good case for comparison is found in the two copper(II) derivatives of bis-(pyridinal)-ethylenediimine (lines 9 and 10, Table II). The α -form exhibits all the major spectral characteristics of the free ligand (line 8, Table II) and the observed shifts are compatible with those observed in the analogous products with other metals (lines 7 and 11, Table II). However, the β -form shows two sharp bands (3390 and 3260 cm.^{-1}) in the region where -N-H and -O-H stretching vibrations normally occur; a second broad band which may be assigned to the presence of an alcoholic OH group is found at 1225 cm.^{-1} . Coincident with these effects, it is observed that the band attributed to the side-chain C=N disappears in the spectrum of the β -form. The structure of the β -form is probably



Thus, it would seem that saturation of the C=N group would be apparent from the infrared spectra of compounds of this type.

The spectrum of the iron(II) complex of the mixed type of ligand, pyridinalmethyimine, provides a link between the two types of shifts discussed above. In this complex both types of methine groups are present, and each type follows the behavior observed in complexes containing only the single kind of methine group. Because of the structural similarity in the ligand, the spectrum of tris-(pyridinalmethyimine)-iron(II) may be compared with that of bis-(pyridinal)-ethylenediimine (lines 6 and 8, Table II). On this basis, it is observed that the C=N and C=C bands of the pyridine ring are shifted to higher frequencies, follow-

ing complexation; an observation in accord with the effect of complexing on 1,10-phenanthroline and 2,2'-bipyridine. Again, complexing results in a great change in the absorption due to the side chain methine group. Only the relatively weak band at 1560 cm.^{-1} remains as a possible manifestation of the absorption due to this C=N group. The slight intensity of this band is quite unusual if it be due to the C=N stretching vibration. This anomalous behavior is consistent with that observed for the complex of biacetyl-bismethylimine.

In the case of the tetradentate donor, bis-(pyridinal)-ethylenediimine, the spectrum of the iron(II) derivative does not differ greatly from that of the free ligand, the side-chain C=N band being shifted only slightly toward a lower frequency. Thus infrared data, as well as magnetic measurements and general stability, separate this species from the general class of compounds which is of primary interest here. Examination of the data presented for the major infrared absorptions of other metal complexes of this ligand (lines 9, 10, and 11, Table II) reveals that the C=N bands of the aromatic groups are generally shifted to higher frequencies while the absorptions due to the side chain methine groups are shifted slightly toward lower frequencies. Although the direction of the effects is the same, the magnitude is somewhat less than is the case with compounds involving the iron(II)-methine chromophore.

The effect of complexing on the infrared absorption bands of biacetyldihydrazone is quite different. The C=N band is shifted to a higher frequency upon complexing.

Discussion

From the considerations presented above, it is evident that those complexes containing six aromatic or conjugated imine nitrogen atoms bonded to a single iron(II) ion belong to a characteristic class of compounds. This class of compounds may be characterized by the presence of diamagnetic iron(II) atoms, by distinct visible and ultraviolet spectral features, and by great stability of the complex and of the dipositive oxidation state for iron(II).

A number of observations support the presence of methine groups in compounds derived from the reaction of aldehydes or ketones with amines and iron(II) salts despite the absence of the predicted C=N vibration in their infrared spectra. The alternate structures (hydrolysis or reduction products of the imines) are *less tenable* on the basis of the infrared data. Analytical data for tris-(biacetyl-bismethylimine)-iron(II) iodide obtained in two different laboratories indicate that the complex contains no oxygen, thus eliminating the possibility of hydrolysis. Iron(II) complexes of saturated amines are generally recognized to be very weakly colored, unstable in aqueous media and paramagnetic, thus eliminating the possibility of reduction of the methine groups in the cases in question. The visible and ultraviolet spectra and magnetic moments definitely show that the electronic states in these compounds correspond to those in iron(II) complexes of heterocyclic amines.

A necessary consequence of the interpretations

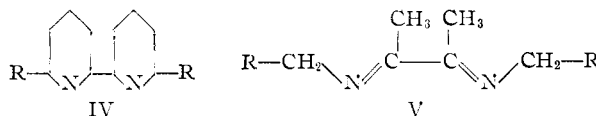
given to the infrared spectra of the complexes of the iron(II)-methine class is that the chelate ring constitutes a resonating system which involves contributions of d-electron pairs by the iron to the π -electron interaction. This assumption also serves to explain the shift in wave length of absorption in the visible region of the spectrum of the series of complexes. On the basis of this concept of the bond type in compounds of the iron(II)-methine chromophore, it is also possible to correlate a number of isolated observations reported by other investigators.

Observations on the effect of substitution on the reactions of 1,10-phenanthroline and 2,2'-bipyridine with iron(II) provide support for the bond-type proposed here. It was observed¹⁸ that substitution of electron donor groups in the 4- and 7-positions of 1,10-phenanthroline led to an increase in the wave length of maximum absorption in the visible spectra and an increase in the molecular extinction coefficient of the complex. Since substitution in these positions leads to an increase in the electron density on the nitrogen atoms, it might be expected that increased stability of the complexes would also be a result of substitution. (The strength of the sigma bonds should increase with the basicity.) This has been verified experimentally.¹⁹ It is, however, significant that the wave length of absorption in the visible region shifts in the opposite direction to that which would be predicted if the sigma bonded electrons were responsible for the absorption since in that case increased strength of bonding should lead to increased restraint on the bonding electrons and higher frequencies. The explanation applied to correlate wave lengths of absorption in the visible spectra of the compounds studied in the work reported here provides a clue to this apparent anomaly. Substitution of electron donor groups in the aromatic ligand tends to localize the electrons in that system or to decrease the resonance of the system. This in turn reduces the effect of crossed resonance on the highly conjugated chelate ring, thereby allowing an increase in the aromatic nature of its associated π -electron system. As was pointed out above, this behavior is accompanied by a decrease in the restraint on the π -electrons and a consequent shift of the absorption band toward lower frequencies. Similar effects have also been reported in the case of 4,4'-disubstituted 2,2'-bipyridine.¹⁸

A second generalization by Smith and his co-workers¹⁸ is especially cogent to the argument in favor of a dependence of the chromophore in question of the formation of resonating chelate rings. They found that the intensity of these color reactions decreases upon 3-substitution of the ligand, 2,2'-bipyridine (and 2,2'-diquinoline, in the case of

copper(I)),^{20,21} even though the electron density on the nitrogen atom increases. This behavior is most easily explained on the assumption that 3-substitution interrupts the necessary coplanarity of the resonating chelate ring.

The 2,9-substituted 1,10-phenanthrolines and 6,6'-substituted 2,2'-bipyridines do not form iron(II) complexes as a result of steric interferences between adjacent substituent groups in the octahedron of the iron atom; however, they give very intense color reactions with copper(I) and are among the best ligands of the related cuproine class.¹⁸ This same type of steric interference is probably responsible for the failure of benzylamine and ethylamine to react with biacetyl and iron(II) in the same manner as does methylamine. Structures IV and V indicated the similarity of the expected diimines to the analogous 6,6'-disubstituted 2,2'-bipyridines.



The implication that chelation of iron(II) to these aromatic groups leads to increased localization of the π -electrons of the ligand and to an increase in the electron density on the ligand leads to the conclusion that the ligand should become more reactive as a result of complexing. An indication that this is indeed the case is found in the report by Kuznetsov²² that tris-(1,10-phenanthroline)-iron(II) ion will couple with diazonium salts while the free ligand will not. Such a behavior is certainly not to be expected if complexing leads only to a removal of electrons from the organic molecule.

The behavior of the bis-(pyridinal)-ethylenedimine complex of iron(II) is quite significant, since this species differs structurally from the other compounds in that only four nitrogen atoms are attached to the iron. Not only is this complex different in spectral characteristics but it alone is paramagnetic and relatively unstable, hydrolyzing readily in dilute solutions. The paramagnetic character of this complex is consistent with the fact that the iron(II) atoms in heme²³ and in ferrous phthalocyanine²⁴ are paramagnetic. Conversely, dipyrindine ferrohemochromogen is diamagnetic.

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