CONTRIBUTION FROM THE RESEARCH LABORATORY
OF ORQUIMA S.A., SÃO PAULO, BRAZIL

Studies on the Coordinate Bond. V. Ferrous Complexes of 2-Pyridyl Ketoimines[1]

BY P. KRUMHOLZ

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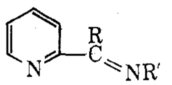
Ferrous complexes of methyl 2-pyridyl and phenyl 2-pyridyl ketoimines have been prepared. Acid hydrolysis of these complexes is considerably slower than that of the corresponding 2-pyridinalimine complexes. The role of steric hindrance to the reaction rate is considered. The visible absorption spectra of the 2-pyridyl ketoimine and 2-pyridinalimine complexes are compared. The spectral effect of phenyl substituents is tentatively correlated with the twisting angle of the phenyl groups with respect to the $X_2C{=}NX$ skeleton of the ligand. Evidence was obtained for the existence of two, probably stereoisomeric, forms of the 2-pyridyl N-arylketimine complexes.

As pointed out by Busch and Bailar,[2] the tris(2-pyridinalimine)iron(II) complexes[2-4] provide a structural link between the complexes of aliphatic α-diimine ligands (*viz.* biacetylbismethylimine[5]) and the iraromatic counterparts, 2,2′-bipyridine and *o*-phenanthroline. The ease of varying the radicals bound to the imino nitrogen makes this class of α-diimine complexes particularly suitable for systematic studies of the influence of substituents on the physical and chemical properties of coordination compounds.[6,7] However, the lability of the 2-pyridinalarylimine complexes imposes some limitations. Attempts to prepare a ferrous complex of the unsubstituted 2-pyridinalimine have so far failed and resulted in the formation of a complex of a tridentate ligand.[8]

We now report on the preparation of iron(II) complexes of 2-pyridyl ketoimines



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where R is methyl or phenyl and R′ is hydrogen or an aliphatic or aromatic radical. These complexes are substantially more stable than the corresponding 2-pyridinalimine complexes (R = H) and offer new possibilities for the study of substitution effects.

The complexes are obtained by allowing methyl 2-pyridyl ketone or phenyl 2-pyridyl ketone to react with a primary amine and ferrous salt in aqueous–ethanolic solution. The reaction proceeds less smoothly than the analogous preparation of the 2-pyridinalimine complexes and in some cases a temperature of 80° must be maintained for several hours to give reasonable yields. The complexes were isolated as sparingly soluble perchlorates of the composition $[Fe(ligand)_3](ClO_4)_2$.

Experimental

Chemicals.—Methyl 2-pyridyl ketone and phenyl 2-pyridyl ketone were obtained from F. Raschig G.m.b.H., Ludwigshafen, and used without further purification. Solutions of ferrous chloride were prepared under nitrogen from reagent grade material and treated with iron powder before using, to reduce any iron(III) present.

Synthesis of Compounds.—Condensations were performed under nitrogen to avoid oxidation of iron(II) and of the organic reactants in the alkaline media. All analyses refer to material dried *in vacuo* over P_2O_5 to constant weight.

(1) **Tris(methyl 2-pyridyl ketimine)iron(II) Perchlorate.**—A mixture of 1.21 g. (10 mmoles) of methyl 2-pyridyl ketone, 4 ml. of ethanol, and 1 ml. of 14 *N* aqueous ammonia (14 mmoles) was kept at 40° in a closed tube for 1 hr.; 7.5 ml. of a 0.4 *M* aqueous solution of ferrous chloride (3 mmoles) was then added and heating continued for 2 hr. The mixture was filtered, sodium perchlorate was added to the filtrate, and the mixture was kept at 5° for 6 hr. The dark brown, microcrystalline precipitate was filtered off and washed with a solution of sodium perchlorate, then with a little cold water; yield, 1.3 g.

Anal. Calcd. for $[Fe(C_7H_8N_2)_3](ClO_4)_2$: Fe, 9.08; N, 13.66. Found: Fe, 9.0; N, 13.75, 13.7.

(2) **Tris[N-1-(2′-pyridyl)ethylidenemethylamine]iron(II) Perchlorate.**—A mixture of 1.21 g. (10 mmoles) of methyl 2-pyridyl ketone, 6 ml. of ethanol, and 1.1 ml. of a 10 *M* aqueous solution of methylamine (11 mmoles) was heated in a closed tube for 1 hr. at 40°. After adding 6.6 ml. of 0.5 *M* ferrous chloride (3.3 mmoles), heating was continued for 30 min. The mixture was then diluted with an equal volume of water and filtered. Addition of sodium perchlorate to the filtered solution produced a dark brown, microcrystalline precipitate which was collected after keeping the mixture at 5° for several hours; yield, 2 g.

Anal. Calcd. for $[Fe(C_8H_{10}N_2)_3](ClO_4)_2$: Fe, 8.50; N, 12.79. Found: Fe, 8.4; N, 12.7.

(3) **Tris[N-1-(2′-pyridyl)ethylideneethylamine]iron(II) Perchlorate.**—This compound was prepared in the same manner as the N-methylimine derivative, using ethylamine in the form of a 12 *M* aqueous solution; yield, 2 g.

Anal. Calcd. for $[Fe(C_9H_{12}N_2)_3](ClO_4)_2$: Fe, 7.98; N, 12.02. Found: Fe, 8.05; N, 11.9.

(4) **Tris[N-1-(2′-pyridyl)ethylideneaniline]iron(II) Perchlorate.**—A mixture of 1.21 g. (10 mmoles) of methyl 2-pyridyl ketone, 6 ml. of ethanol, and 1.21 g. (13 mmoles) of aniline was heated for 2 hr. at 40°; 7.5 ml. of 0.4 *M* ferrous chloride (3 mmoles) was then added and heating continued for 4 hr. The mixture was then diluted with an equal volume of water and filtered. Addition of sodium perchlorate produced a dark, tarry precipitate which was separated by decantation and washed with water. The tarry mass was dissolved in 5 ml. of methanol, an equal volume of ether was added, and the mixture was kept at

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[1] Paper IV: P. Krumholz, *J. Phys. Chem.*, **60**, 87 (1956).

[2] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 1137 (1956).

[3] F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *ibid.*, **75**, 3834 (1953).

[4] G. Bähr and H. Thämlitz, *Z. anorg. allgem. Chem.*, **282**, 3 (1955); G. Bähr and H. G. Doge, *ibid.*, **292**, 119 (1957).

[5] P. Krumholz, *J. Am. Chem. Soc.*, **75**, 2163 (1953).

[6] R. K. Murmann and E. A. Healy, *J. Am. Chem. Soc.*, **83**, 2002 (1961).

[7] P. Krumholz, "Theory and Structure of Complex Compounds," B. Jeżowska-Trzebiatowska, Ed., Pergamon Press, Warszawa, 1964, p. 217.

[8] P. Krumholz, *Inorg. Chem.*, **4**, 757 (1965).

−5° for 2 hr. The crude product (1.7 g) was recrystallized twice from 60 ml. of a 1:1 methanol–water mixture, yielding 1 g. of very dark violet crystals.

Anal. Calcd. for $[Fe(C_{13}H_{12}N_2)_3](ClO_4)_2$: Fe, 6.62; N, 9.96. Found: Fe, 6.8; N, 9.85.

From the collected filtrates, diluted with twice their volume of water, sodium perchlorate precipitated 0.4 g. of a product with slightly different spectral properties.

(5) **Tris[N-1-(2′-pyridyl)ethylidene-*p*-phenylenediamine]-iron(II) Perchlorate.**—Methyl 2-pyridyl ketone (0.6 g., 5 mmoles) was added to a solution of 0.65 g. (6 mmoles) of *p*-phenylenediamine in 4 ml. of ethanol and the mixture heated at 40° for 1 hr.; 4 ml. of 0.4 *M* ferrous chloride (1.6 mmoles) was then added and heating continued for 2 hr. After diluting with an equal volume of water and filtering, the complex was precipitated by slow addition of sodium perchlorate. The crude product (1.4 g.) was recrystallized from 40 ml. of a 1:1 methanol–water mixture; yield, 1 g. of a violet powder.

Anal. Calcd. for $[Fe(C_{13}H_{13}N_3)_3](ClO_4)_2$: Fe, 6.28; N, 14.19. Found: Fe, 6.25; N, 14.15.

(6) **Tris(phenyl 2-pyridyl ketimine)iron(II) Perchlorate.**—Aqueous ammonia (28 mmoles) was added to a solution of 1 g. (5.5 mmoles) of phenyl 2-pyridyl ketone in 3 ml. of ethanol and the mixture kept at 25° in a closed tube for 24 hr. After adding 3 ml. of 0.6 *M* ferrous chloride (1.8 mmoles), the mixture was heated for 12 hr. at 40° and then kept at 25° for 24 hr. Excess ammonia was removed by passing a stream of nitrogen through the reaction mixture which was then diluted with an equal volume of water and filtered. Sodium perchlorate precipitated a dark tarry mass which was separated and washed with water. The tar became solid when treated with 5 ml. of methanol. After cooling at −5° for 2 hr., the mixture was filtered, and the residue was washed with a little cold methanol and finally with ether; yield, 0.25 g. of a violet powder.

Anal. Calcd. for $[Fe(C_{12}H_{10}N_2)_3](ClO_4)_2$: Fe, 6.97; N, 10.49. Found: Fe, 6.95; N, 10.4.

(7) **Tris[N-(2′-pyridyl)benzylidenemethylamine]iron(II) Perchlorate.**—A mixture of 1 g. (5.5 mmoles) of phenyl 2-pyridyl ketone, 6 ml. of ethanol, and 0.8 ml. of a 10 *M* aqueous solution of methylamine (8 mmoles) was heated in a closed tube at 40° for 2 hr. After adding 4.5 ml. of 0.4 *M* ferrous chloride (1.8 mmoles) heating was continued for 2 hr. The mixture was diluted with an equal volume of water and filtered and sodium perchlorate was added, thereby producing a tarry precipitate. On being treated with 5 ml. of methanol the tar became crystalline. After adding 5 ml. of ether, the mixture was kept at −5° for 6 hr., and the dark violet precipitate was filtered off and washed with ether; yield, 0.6 g.

Anal. Calcd. for $[Fe(C_{13}H_{12}N_2)_3](ClO_4)_2$: Fe, 6.62; N, 9.96. Found: Fe, 6.55; N, 9.85.

(8) **Tris[N-(2′-pyridyl)benzylideneaniline]iron(II) Perchlorate.**—A mixture of 1 g. (5.5 mmoles) of phenyl pyridyl ketone, 6 ml. of ethanol, and 0.93 g. (10 mmoles) of aniline was heated at 80° for 2 hr.; 4.5 ml. of 0.4 *M* ferrous chloride (1.8 mmoles) was then added and heating continued for 2 hr. The reaction mixture was worked up as described for the analogous N-methyl derivative. The crude product (0.8 g.) was recrystallized from 50 ml. of a 1:1 methanol–water mixture, yielding 0.4 g. of a very dark violet microcrystalline powder (product I). From the filtrate, diluted with an equal volume of water, sodium perchlorate precipitated an additional 0.12 g. (product II) with slightly different spectral properties.

Anal. Calcd. for $[Fe(C_{18}H_{14}N_2)_3](ClO_4)_2$: Fe, 5.42; N, 8.16. Found for I: Fe, 5.5; N, 8.1. Found for II: Fe, 5.65; N, 8.1.

(9) **Tris[N-(2′-pyridyl)benzylidene-*m*-phenylenediamine]iron-(II) Perchlorate.**—This compound was prepared according to the procedure for the unsubstituted N-phenyl derivative using an excess of 80% of *m*-phenylenediamine. From the filtered reaction mixture sodium perchlorate precipitated a solid product which was filtered off and washed with a 1:1 methanol–ether mixture to remove brown by-products. Recrystallization of the crude product (1.05 g.) from 100 ml. of a 2:1 methanol–water mixture yielded 0.6 g. of a dark violet powder.

Anal. Calcd. for $[Fe(C_{18}H_{15}N_3)_3](ClO_4)_2$: Fe, 5.20; N, 11.73. Found: Fe, 5.2; N, 11.7.

(10) **Tris[N-(2′-pyridyl)benzylidene-*p*-phenylenediamine]iron-(II) Perchlorate.**—This compound was prepared in exactly the same manner as the analogous 3-aminophenyl derivative. Recrystallization of the crude product (1 g.) from 50 ml. of a 1:1 methanol–water mixture yielded 0.65 g. of a dark violet powder.

Anal. Calcd. for $[Fe(C_{18}H_{15}N_3)_3](ClO_4)_2$: Fe, 5.20; N, 11.73. Found: Fe, 5.35; N, 11.65.

Kinetic Measurements.—The acid hydrolysis of the tris(2-pyridyl ketoimine)iron(II) complexes was studied with the main purpose of detecting the presence of isomeric species and obtaining a rough measure of their relative percentage. The rate studies were carried out spectrophotometrically at wave lengths close to the respective absorption maxima. Figure 1 shows typical kinetic curves for the acid hydrolysis of two different preparations of the same complex, consisting of one species only (curve 1) and of a mixture of two species (curve 2). Since close to the absorption maxima the molar absorptivities of the two species are not very different, extrapolation of the linear part of the kinetic curves to zero time provides a rough measure of the relative amounts of the two forms.

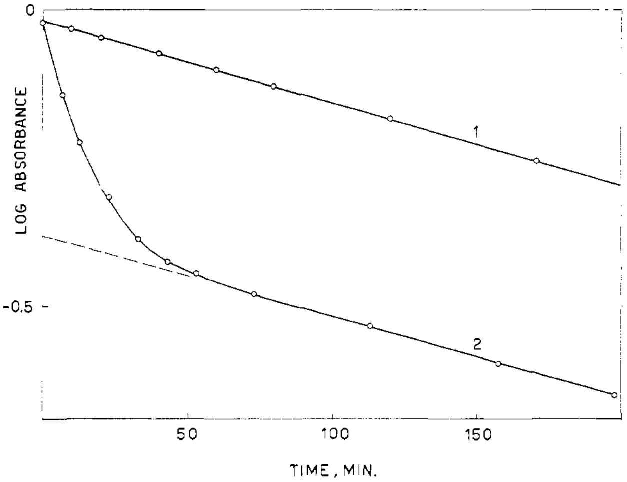

Figure 1.—Rate of acid hydrolysis of tris[N-(2′-pyridyl)-benzylideneaniline]iron(II) in 0.1 *M* hydrochloric acid at 45°: (1) recrystallized product (8-I); (2) soluble fraction (8-II). Substrate concentration 6×10^{-5} *M*; cell path length 13.5 mm.

Spectrophotometric Measurements.—Absorption spectra were measured with a grating instrument previously described[9] at a band width of 0.2 mμ. When preparations were found to consist of a mixture of two species (*vide supra*), the spectrum of the more stable form was measured after most of the labile form had been destroyed by acid treatment. Sodium acetate was added when the complex decomposed too quickly in acid solution or when spectra were subjected to changes at high acidities (*viz.* N-aminophenyl derivatives). Absorption spectra of the labile forms were estimated from the experimental spectra of preparations in which the labile form was the major component.

The reported wave lengths of the absorption maxima of the stable forms of the complexes are believed to be correct to within ±1 mμ, molar absorptivities to within ±3%.

Results and Discussion

Isomeric Forms.—While the absorption spectra of different preparations of the iron(II) complexes of the free 2-pyridyl ketimines (R′ = H) and of their N-alkyl derivatives were practically identical, small but distinct

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(9) P. Krumholz, *Spectrochim. Acta*, **10**, 274 (1958).

TABLE I

ABSORPTION MAXIMA (IN mμ) AND SPECTRAL SHIFTS (xx) IN THE SERIES OF TRIS(2-PYRIDINALIMINE)- AND TRIS(2-PYRIDYL KETOIMINE)IRON(II) COMPLEXES. STABLE FORMS OF THE N-PHENYLKETIMINE COMPLEXES ARE CONSIDERED. SOLVENT, WATER; 23 ± 2°

	R′			
R	H	CH_3		C_6H_5
H	...	551	(23)	574
		(7)		(−6)
CH_3	572	558	(10)	568
	(18)	(7)		(11)
C_6H_5	590	565	(14)	579

variations were observed in the case of the N-aryl derivatives. The presence of isomeric species was suspected, particularly as Murmann and Healy[6] have presented kinetic evidence for isomerization of the tris(2-pyridinal-α-phenylethylimine)iron(II) complex.

An analysis of the rate of acid hydrolysis of the N-arylketimine complexes revealed the presence of two kinetically different species which differed in their reaction rates by a factor of about 20 (see Figure 1). In general, the more stable form was found to predominate in the crude preparations of the phenyl 2-pyridyl N-arylketimine complexes and the labile in the complexes of the methyl 2-pyridyl N-arylketimines.

On recrystallizing the crude perchlorates of the iron(II)–N-arylketimine complexes from mixtures of methanol and water, the stable form becomes enriched in the less soluble fraction. In the case of the phenyl 2-pyridyl N-arylketimine complexes, the stable form was obtained in a practically pure state after one recrystallization (see Figure 1, curve 1). The soluble fraction consisted of at least 50% of the labile form. Separation was more difficult in the case of the methyl 2-pyridyl N-arylketimine complexes. Two recrystallizations of a preparation of the N-phenyl derivative which consisted of roughly equal parts of the two forms gave a product which still contained about 20% of the labile form.

Analytical and spectral data strongly suggest that the two forms of the iron(II)–N-arylketimine complexes represent the two possible geometrical isomers of octahedral complexes of unsymmetrical bidentate ligands.

Rates of Dissociation.—The rates of dissociation (or hydrolysis) of the tris(2-pyridyl ketoimine)iron(II) complexes are always lower than the rate of the 2-pyridinalimine complex derived from the same amine. Differences in reaction rates are particularly large in the case of the N-aryl derivatives. At 24° and in 0.1 *N* HCl containing 20% of methanol, the first-order rate constants of acid hydrolysis of the 2-pyridyl N-phenylketimine complexes (stable forms) are approximately 2.7×10^{-6} and 1.7×10^{-6} sec.$^{-1}$ where R is methyl and phenyl, respectively. Under the same experimental conditions the rate constant of the 2-pyridinalphenylimine complex amounts to approximately 1×10^{-1} sec.$^{-1}$!

In the series of related N-alkyl derivatives, variations in the rate of hydrolysis are still considerable, though less spectacular than in the series of N-aryl compounds. At 50° and in the same solvent as before, the rate constants of the N-methylimine complexes are approximately 3.5×10^{-4}, 2.5×10^{-5}, and 4×10^{-6} sec.$^{-1}$, where R is H, methyl, and phenyl, respectively.

It is suggested that steric effects are an important factor affecting the rate of dissociation of the abovementioned octahedral iron(II)–α-diimine complexes. There is evidence that the dissociation of such complexes involves the "one-ended" detachment of one ligand.[1,10] Ellis and Wilkins[11] assume that the transition state approximates to a combined square pyramid of nitrogen around the central metal plus two additional groups at a further distance, namely, one nitrogen of the outgoing ligand and one incoming water molecule. Acid catalysis seems to depend on sufficient flexibility of the ligand to permit addition of a proton to the free nitrogen atom of the "half-bonded" intermediate.[10] Considering this mechanism one should expect that bulky substituents such as R and R′ in I will tend to retard the rate of dissociation by restricting the freedom of motion of the ligands and hindering the approach of a reagent toward the reaction centers.[12] When R and R′ are methyl and phenyl or *vice versa*, or when both are phenyl, steric hindrance to the reaction rate should be particularly large, since mutual spatial interference of the substituents will force the phenyl groups out of the plane defined by the $X_2C{=}NX$ skeleton and make them project into the interstices of the coordination sphere.

Steric effects of the kind just discussed might well explain the general trend of the reaction rates within each of the two series (R′ = CH_3 and C_6H_5, respectively) of α-diimine complexes considered before. However, cross comparisons and interpretations of finer details would evidently require many other effects to be taken into account, which is outside the scope of the present study.

Absorption Spectra.—The visible absorption spectra of the tris(2-pyridyl ketoimine)iron(II) complexes are very similar to the spectra of the iron(II) complexes of other α-diimine ligands and in particular to the spectra of the 2-pyridinalimine complexes.[7] The absorption maxima of the complexes listed in Table I depend on the substituents R and R′ in a seemingly quite irregular manner. This is due in part to the rather anomalous position of the absorption maxima of the complexes derived from the free ketimines (R′ = H). In all other respects the data in Table I can be rationalized, admitting that the bathochromic effect of an aromatic substituent depends on the twisting angle of the phenyl group with respect to the plane defined by the $X_2C{=}NX$ skeleton (*vide supra*).

Twisting angles of the phenyl groups in phenyl- and methyl-substituted ethylenes have recently been

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[10] (a) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **75**, 5102 (1953); (b) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 152–157.

[11] P. Ellis and R. G. Wilkins, *J. Chem. Soc.*, 299 (1959).

[12] See A. Jensen, F. Basolo, and H. M. Neumann, *J. Am. Chem. Soc.*, **80**, 2354 (1958).

TABLE II

MOLAR ABSORPTIVITIES ($\times 10^{-3}$) OF TRIS(2-PYRIDINALIMINE)- AND TRIS(2-PYRIDYL KETOIMINE)IRON(II) COMPLEXES IN DEPENDENCE UPON R AND R′ IN I. SOLVENT, 20% BY VOLUME OF METHANOL IN WATER; 23 ± 2°

	R′		
R	H	CH_3	C_6H_5
H	...	11	8
CH_3	13	11.5	9.5
C_6H_5	17	14	12.5

discussed by Favini and Simonetta.[13] For the corresponding aza analogs[14] presently considered, twisting angles are likely to follow the same order, *viz.*, $\mathrm{H},\mathit{C_6H_5} < \mathit{C_6H_5},\mathrm{H} < \mathrm{C_6H_5},\mathit{C_6H_5} < \mathit{C_6H_5},\mathrm{C_6H_5} < \mathrm{CH_3},\mathit{C_6H_5} < \mathit{C_6H_5},\mathrm{CH_3}$ where substituents are listed in the order R,R′ and $\mathit{C_6H_5}$ is the phenyl group whose twisting angle is considered. Inspection of Table I shows that the bathochromic effect of replacing methyl by phenyl decreases exactly in the order of increasing twisting angles of the phenyl groups concerned (the corresponding order of the spectral shifts is 23-18-14-11-10-7 mμ). This correlation between twisting angles and the spectral effect of phenyl substituents also provides an easy explanation for the hypsochromic effect of replacing hydrogen by methyl in the $\mathrm{H,C_6H_5}$ complex, as compared with the opposite effect of the same substitution in the $\mathrm{H,CH_3}$ derivative (see Table I).

The spectral effect of amino substituents in the 2-pyridyl N-arylketimine complexes depends on the position of the free amino group. Absorption maxima of the iron(II) complexes of the 3-aminophenylketimines and of the unsubstituted phenylketimines are practically the same. 4-Amino substituents produce a bathochromic shift of about 10 mμ. The 2-aminophenyl derivatives behave as tridentate ligands[15] and are thus not directly comparable with the other isomers.

The molar absorptivities of the complexes at their respective absorption maxima, listed in Table I, are summarized in Table II. Absorptivities increase on passing from the 2-pyridinalimine complexes to the complexes of the methyl 2-pyridyl and particularly the phenyl 2-pyridyl ketoimines. Curiously, changing the substituents on the imino nitrogen affects intensities in just the opposite direction.

The absorption spectra of the two forms of the 2-pyridyl N-arylketimine complexes are substantially alike, except for the position of the absorption maxima. When R is methyl, the absorption maximum of the labile form is shifted by approximately 3 mμ toward longer wave lengths, as compared with the maximum of the stable form. When R is phenyl, the difference amounts to approximately 10 mμ.

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[13] G. Favini and M. Simonetta, *Theoret. Chim. Acta*, **1**, 294 (1963).

[14] 2-Pyridinalphenylimine is compared to *trans*-stilbene, phenyl 2-pyridyl ketimine to 1,1 diphenylethylene, etc.

[15] P. Krumholz, *Inorg. Chem.*, **4**, 612 (1965).

CONTRIBUTION FROM THE RESEARCH LABORATORY
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Studies on the Coordinate Bond. VI. The Nature of the Chromophoric Group in Iron(II) Complexes of Tridentate Imine Ligands[1]

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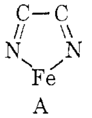
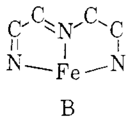
The visible absorption spectra of iron(II) complexes of a series of "terpyridine-like" tridentate imine ligands containing the functional grouping $N{=}C{-}C{=}N{-}C{\cdot}C{\cdot}N$ have been recorded. Independently of the nature of bonding in the C·C·N chain, these complexes belong to a single chromophoric class. The specific spectral pattern which characterizes this class is correlated with the fusing of a second chelate loop on the iron(II)–α-diimine ring. The resulting spatial structure and mutual orientation of metal and ligand orbitals may cause a significant distortion of the ligand field from cubic symmetry. Splitting of the metal t_{2g} orbitals by noncubic field components is held responsible for the appearance of a new transition in the spectra of the tridentate imine complexes.

Introduction

It is well established[2,3] that the octahedral iron(II) complexes of bidentate α-diimine ligands such as 2,2′-bipyridine, 2-pyridinalmethylimine, and glyoxalbismethylimine constitute a single class of compounds with very similar spectral properties. The cyclic iron(II)–α-diimine grouping A can be considered as the common structural element or "chromophore."[4]


A


B

In the iron(II) complexes of the related tridentate imine ligands such as terpyridine,[5] a second chelate ring is fused on the iron(II)–α-diimine ring, as pictured in B. It is the object of this study to investigate the

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[1] Part V: P. Krumholz, *Inorg. Chem.*, **4**, 609 (1965).

[2] P. Krumholz, *J. Am. Chem. Soc.*, **75**, 2163 (1953).

[3] D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 1137 (1956).

[4] It is tacitly assumed that three of these "chromophores" are actually present and linked through the common central metal.

[5] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 20 (1932).