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Studies on the Coordinate Bond. VII. Ferrous Complexes of α-Iminocarboxylic Acids [1,2].

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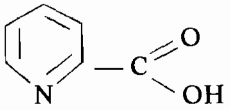
The reaction of ferrous salt with sodium glyoxylate or pyruvate and primary aliphatic or aromatic amines, in aqueous solution and absence of oxygen, has been investigated spectrophotometrically. The spectral characteristics of the colored reaction products are similar to these of picolinato ferrates(II). It is concluded that the products are iron(II) complexes of α-iminocarboxylic acids, R'N=CR.COOH. Spectral evidence is presented for stepwise complex formation leading, eventually, to tris(α-iminocarboxylato)ferrates(II). Formation of mixed tetracyano(α-iminocarboxylato) ferrates(II) is demonstrated. The spectral transitions in the visible are interpreted as «inverse» electron transfer spectra and compared with the corresponding transitions of iron(II)-α-diimine complexes. The origin of the observed band splitting is examined.

Introduction

Heterocyclic acids having a carboxyl group in the α-position to the nitrogen atom, for a long time are known to form deeply colored complexes with iron(II).[3,4] In the case of picolinic acid (1),



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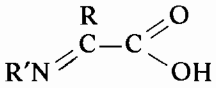

(2)

the successive formation of iron(II) complexes with one, two and three ligand molecules is now well established.[5] With cyanide, these complexes react to form highly colored tetracyano(picolinato)ferrate(II), $[Fe(CN)_4(C_5H_4N.COO)]^{3-}$.[6] Formally, picolinic acid can be considered as a heterocyclic α-iminocarboxylic acid. Eearlier experience with ferrous α-diimine complexes[7] leads one to expect that simple α-iminocarboxylic acids (2), i.e. Schiff bases from α-oxo acids and primary amines, will behave toward iron(II) like their heterocyclic analogues. In fact, it was found that a permanent, brownish red color is produced when a primary aliphatic or aromatic amine is allowed to react, in absence of oxygen, with a solution containing iron(II) and an alkali glyoxylate or pyruvate.[8] Cyanide changes and intensifies the color of the solutions which now became stable toward oxygen. A detailed spectroscopic study was undertaken to ascertain the nature of the colored species.

Experimental Section

Materials. Sodium glyoxylate monohydrate was prepared by neutralizing an aqueous solution of glyoxylic acid (Fluka, purum) with sodium carbonate to pH 7, precipitating with acetone and recrystallizing from acetone-water.[9] Merck sodium pyruvate for biochemical purposes was dried to constant weight *in vacuo* over P_2O_5. Fresh solutions of the sodium salts of the oxo acids in water were prepared daily by weight and kept at 0°. Solutions of sodium picolinate were prepared by neutralizing aqueous solutions of picolinic acid (mp 137°) with sodium hydroxide to pH 7.5. Solutions of methylamine and ethylamine in water, and of freshly distilled aniline in 30% by volume of ethanol in water were de-aerated by bubbling with nitrogen and kept under nitrogen in Schlenk tubes. The solutions of the volatile aliphatic amines were frequently standardized against standard acid. Air-free solutions of reagent grade sodium cyanide were prepared and kept in the same manner and standardized against standard silver nitrate solution. Air-free solutions of reagent grade ferrous sulfate in 0.001 F aqueous sulfuric acid were prepared daily and standardized against standard ceric sulfate solution.

Spectral Measurements. Absorption spectra were measured, from 370 to 650 mμ and at a band width of 0.2 mμ, with a grating instrument previously described[10] and thermostated at 25°. The complex species formed in the iron(II)-oxocarboxylate-amine systems are very sensitive toward oxygen, especially when the amine is aliphatic. Therefore, the reaction mixtures had to be prepared and handled in an inert atmosphere. For measurements at low iron(II) concentrations (0.002 M), the reaction mixtures were prepared directly in the

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(1) Part VI: P. Krumholz, *Inorg. Chem.*, *4*, 612 (1965).
(2) Presented in part at the 9th International Conference on Coordination Chemistry, St. Moritz, Sept. 1966, Proceedings p. 136.
(3) Z. H. Skraup, *Monatsh.*, *7*, 210 (1886).
(4) H. Ley, C. Schwartz and O. Münnich, *Ber.*, *57*, 349 (1924).
(5) G. Anderegg, *Helv. Chim. Acta*, *43*, 414 (1960).
(6) A. K. Majumdar and S. P. Bag, *Anal Chim. Acta*, *22*, 549 (1960).
(7) P. Krumholz, *J. Am. Chem. Soc.*, *75*, 2163 (1953).
(8) Pyruvate alone produces a weak color with iron(II) with an intensity about 50 times lower than that produced on further addition of the amine; see W. Franke, *Ann.*, *457*, 37 (1929).
(9) D. E. Metzler, J. Olivard and E. E. Snell, *J. Am. Chem. Soc.*, *76*,
(10) P. Krumholz, *Spectrochim. Acta*, *10*, 274 (1958).
644 (1954).

absorption cell. The glass cell of 5 mm light path had a fused-on cover with two ground 4 mm holes. A ground lucite stopper carrying a polyethylene capillary which served as a gas inlet tube, was inserted in one hole. First, the solution of the oxocarboxylate and sufficient water to bring the final volume to 2.5 ml, was pipetted into the cell and de-aerated by bubbling with nitrogen for 5 min. Next, the solution of ferrous sulfate was added and nitrogen passed for another 5 min. through the solution. Then, the desired amount of the air-free solution of the amine was added by means of a calibrated hypodermic syringe which has been flushed several times with the amine solution. The capillary was now raised above the surface of the liquid, the flow of nitrogen was increased and the second hole in the cover closed with a ground stopper. Finally, a cone-shaped lucite stopper was inserted alongside the capillary and, the latter being quickly withdrawn, pressed into the hole. As shown by the stability of the absorption spectra of the so prepared solutions, uptake of atmospheric oxygen was negligible.

In the systems comprising methylamine and ethylamine, absorbances reached a steady value within 1 min. after mixing, if the concentration of each of the organic reactants was greater than 0.05 M. At 0.02 M, steady readings were reached in about 5 min. At still lower concentration, ferrous hydroxyde was precipitated. When the amine was aniline, color formation was considerably slower. At 0.05 M aniline and oxocarboxylate, steady absorbance readings were obtained in about 20 min. (In the systems comprising aniline, the solvent was 10% by volume of ethanol in water).

In the continuous variation studies, solutions were used which were 0.4 M in sodium glyoxylate or pyruvate and contained iron and methylamine at a total molarity of 0.15. Because of the high concentration of complexed iron(II), it became necessary to use absorption cells with an optical depth of only a few tenth of a mm. The cells were made by cementing, with araldite, two paper strips 3 mm wide and 0.1 to 0.2 mm thick, lengthwise between two glass flats of 20×60 mm. The top and the bottom of the cells was left open. The solutions of the iron(II) complexes were prepared in the manner described before in a cylindrical glass vessel, 25 mm in diameter, closed with a well-fitting polyethylene cap. The cap had two small holes, one for a gas inlet tube and the other for introducing the solutions, and a rectangular slot which the absorption cell fitted tightly. While passing nitrogen over the surface of the solution, the cell was lowered into the liquid and the opening in the cap was closed so that the gas pressure could drive the liquid into the cell. At cell depths of 0.2 to 0.25 mm, the liquid was held by capillarity to a height of 50 to 60 mm, so that the cell could be withdrawn and handled without the danger of spilling the liquid. The small depth of the cells efficiently slows down the diffusion of atmospheric oxygen into the central part of the liquid. Absorbance changes due to oxygen uptake were less than 1% in 20 min. The cells were frequently calibrated with a standard solution of tris(o-phenanthroline)iron(II). If measurements were made within 30 min. after filling and the cells were washed with ethanol and dried before use, optical depths remained constant within about ± 1%.

When the mole fraction of iron, $X_{Fe} = [\text{iron}]/([\text{iron}] + [\text{amine}])$, was smaller than 0.25, solutions were stable for a least 30 min. When X_{Fe} became greater than 0.25, the solutions showed a gradually increasing tendency to become cloudy. Up to $X_{Fe} = 0.4$, absorbance readings could be taken while the solutions were still clear; results were reproducible within about ±2%.

Formation of mixed cyano complexes was studied in solutions 0.015 M in ferrous sulfate, 0.1 to 0.2 M in sodium glyoxylate or pyruvate and methylamine, and 0.1 to 0.8 M in sodium cyanide. First ferrous sulfate, oxocarboxylate and amine were allowed to react in the manner described before. The mixture was allowed to stand for 2 min. and then an air-free 3 M aqueous solution of sodium cyanide was injected, by means of a hypodermic syringe, within about 1/2 sec. During the addition of the cyanide, a rapid stream of nitrogen was passed through the solution. Spectra were measured, after 15 min., in capillary cells of about 0.25 mm optical depth. In the system comprising glyoxylate, spectral intensities became considerably lower when, under otherwise identical conditions, cyanide was added at a slower rate.[11]

The spectrum of tri(picolinato)ferrate(II) was measured in solutions 0.0015 M in ferrous sulfate and 0.1 to 0.2 M in sodium picolinate, at an optical depth of 5 mm. From Anderegg's[5] formation constant data it can be concluded that under these conditions more than 99% of the iron is present in form of the tris(picolinato) complex. The spectrum of a solution 0.005 M in sodium picolinate and 0.1 M in ferrous sulfate, provided a rough estimate of the spectrum of the mono(picolinato) iron(II) complex.

The mixed cyano complex formed when the iron(II) picolinato complexes are allowed to react with excess cyanide, was shown by Majumdar and Bag[6] to contain iron and picolinate in the ratio of 1 : 1 and was formulated as tetracyano(picolinato)ferrate(II). This assumption was now confirmed by a mole ratio study made in solutions 0.015 M in ferrous sulfate and 0.1 M in sodium picolinate, to which varying amounts of sodium cyanide had been added. At wave lengths between 430 and 450 mμ, plots of absorbancies versus the mole ratio [cyanide]/[iron], were nearly straight lines which broke to an almost constant value at a mole ratio 4.1 ± 0.1. The spectrum of the mixed cyano complex was measured in solutions containing twice the theoretical amount of cyanide.

Absorbance readings were always referred to a blank containing all reaction components, but iron. The reported wave lengths of the absoprtion maxima are believed to be correct to within ± 1 mμ, molar absorptivities to within ± 3%, except when obtained by extrapolation (see later).

Results

Observation of the absorption spectra of a series of solutions containing iron(II), oxocarboxylate and amine in varying proportions, provided some insight into the course of the reaction. The results obtained in the

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[11] The low value of ε_{max} reported earlier[2] for the mixed cyano complex derived from N-glyoxylidenemethylamine, resulted from the ignorance of this fact.

system iron(II)-pyruvate-methylamine proved particularely simple and will be discussed first.

When, at constant metal concentration (0.002 M) and a molar ratio of pyruvate to amine of 1 : 1, the concentration of the organic reactants was gradually increased from 0.02 to 0.1 M, the single absorption maximum in the visible shifted gradually from about 460 to 472 mμ. At the same time, the intensity of the absorption band increased by a factor of about two. A further increase of the concentration of each of the organic reactants or of pyruvate alone, up to 0.3 M, did not produce any significant change of the spectrum. Thus a single complex species, the spectrum of which is shown in Figure 1, curve B, seems to be present, or at least to predominate at ligand concentrations of, or in excess of 0.1 M. In order to obtain information on the composition of this species, a continuous variation study was made in which, at a total molarityy of iron plus amine of 0.15, the mole fraction $X_{Fe} = [\text{iron}]/([\text{iron}] + [\text{amine}])$ was varied while the concentration of pyruvate was held at a high and constant level (0.4 M). Figure 2 shows plots of absorbancies at several wave lengths, *vs.* X_{Fe}. These plots clearly indicate the formation of a compound in which amine and metal are combined in the ratio of 3 : 1. The instability of solutions containing a large excess of amine over pyruvate, made it impossible to determine the ratio of pyruvate to iron in this compound.

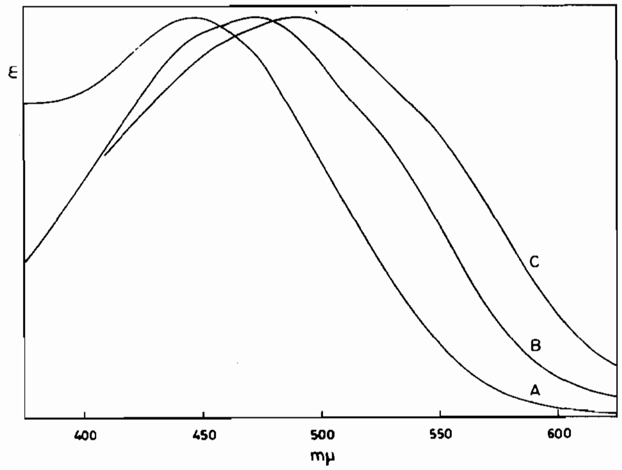

Figure 1. Absorption spectra of tris(α-iminocarboxylato) ferrates(II). Ligands: A, picolinic acid; B, N-pyruvylidene-methylamine; C, N-pyruvylideneaniline. Curves are drawn to equal height at the absorption maximum. Numerical values of the molar absorbancy indices are given in Table I.

The absorption maxima of the reaction mixtures used in the continuous variation study moved, with increasing mole fraction of the metal, from 472 mμ at $X_{Fe} \leqslant 0.15$, to about 440 mμ at $X_{Fe} = 0.39$. This, and the spectral shifts noted before, indicate the formation of complex species in which amine and metal are combined in a ratio smaller than 3 : 1 and which absorb at shorter wave lengths.

The spectral behaviour of the system iron(II)-pyruvate-ethylamine was very similar to the behaviour of the corresponding methylamine system, except that the absorption spectrum became stationary at a somewhat higher ligand concentration (approx. 0.15 M). When the amine was aniline, the highest ligand concentration used (0.3 M) was not quite sufficient to make the spectrum stationary. Therefore, the experimental spectral data were extrapolated to infinite ligand concentration. The extrapolated spectrum (curve C in Figure 1) differed very little from the experimental spectrum obtained at a ligand concentration of 0.3 M.

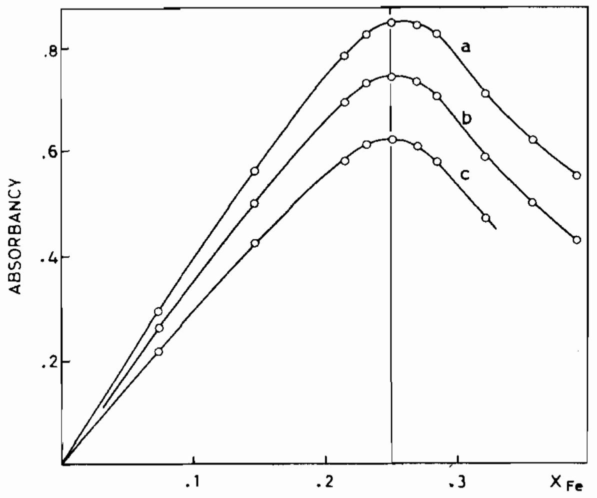

Figure 2. Continuous variation study of the system iron(II) pyruvate-methylamine at 475 (a), 500 (b) and 520 mμ (c). Solutions are 0.4 M in pyruvate and 0.15 M in iron plus amine. $X_{Fe} = [\text{iron}]/([\text{iron}] + [\text{amine}])$. Optical depth, 0.245 mm.

The behaviour of the iron(II)-glyoxylate-amine systems was, in general, quite similar to that of the corresponding pyruvate systems. However, careful measurements revealed some minor and hitherto unexplained anomalies which became more pronounced when glyoxylate was present in a large excess over the amine. At 0.002 M iron(II) and equimolecular concentration of glyoxylate and methylamine, the molar absorptivity at the absorption maximum became practically stationary when the molarity of each of the organic reactants reached the value of 0.1. However, the absorption maximum still shifted slightly (approx. 1 mμ) toward the red when the ligand concentration was increased from 0.1 to 0.3 M. When the experiments were repeated using a moderate excess (25%) of methylamine over glyoxylate, this shift became yet smaller and was barely detectable. When, on the other hand, an excess of glyoxylate over the amine was used, spectral changes became quite distinct. At 0.1 M methylamine and 0.4 M glyoxylate, the absorption maximum had shifted by 6 mμ toward the red and the molar absorptivity had decreased by about 8%, as compared with a solution 0.1 M in amine and glyoxylate. The shape of the absorption band remained essentially unchanged and was actually very similar to that of the corresponding pyruvate species shown in Figure 1. Apparently, the spectral effects produced by a large excess of glyoxylate are due to secondary reactions rather than to a further displacement of the primary equilibrium which in the analogous pyruvate system, has led to a single complex species with a perfectly stationary spectrum. It seems also that no great error will be committed if the spectrum of a solution 0.1 M in glyoxylate and methylamine is taken as that of the «normal» species resulting from the primary equilibrium.

A continuous variation study made in solutions which were 0.15 M in iron plus methylamine and 0.4 M in glyoxylate, revealed again the presence of a complex in which amine and metal are combined in the ratio of 3: 1 (see Figure 3). Surprisingly, the spectra af solutions in which the mole ratio X_{Fe} was between 0.06 and 0.12, seemed to belong to the «normal» species although glyoxylate was present in a large excess over the amine.

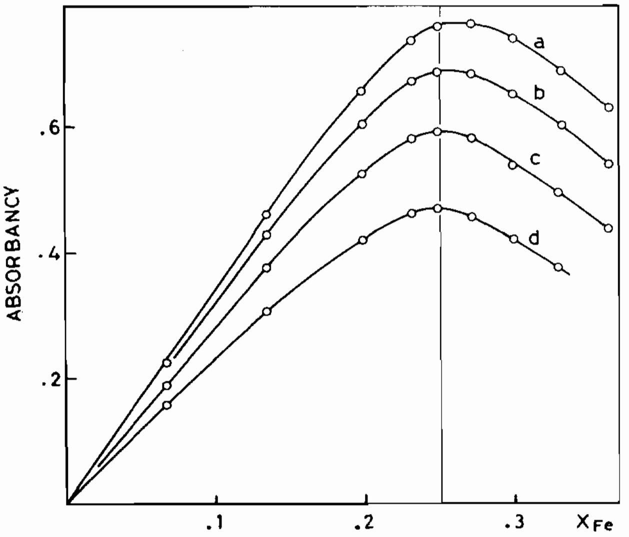

Figure 3. Continuous variation study of the system iron(II) glyoxylate-methylamine at 480 (a), 500 (b), 520 (c) and 540 mμ(d). Solutions are 0.4 M in glyoxylate and 0.15 M in iron plus amine. X_{Fe} = [iron]/[iron]+[amine]). Optical depth, 0.245 mm.

Spectral anomalies of the type discussed before were also discovered in the iron(II)-glyoxylate-ethylamine system. Since molar absorptivities at the band maximum became stationary at 0.15 M amine and glyoxylate, the spectrum of such solution was considered as the spectrum of the «normal» species. When the amine was aniline, this spectrum had to be obtained by extrapolation, just like in the corresponding pyruvate system. The observed spectral anomalies make this extrapolation in the glyoxylate system less reliable.

The absorption maxima (λ_{max}), the corresponding molar absorbancy indices (ε_{max}) and the half widths toward smaller wave numbers (δ(-)) of the complex iron(II) species discussed in this section and believed to contain amine and metal in the ratio of 3: 1, are listed in Table I. In the case of the complexes derived from glyoxylic acid, spectra of the «normal» species are considered.

When solutions of the afore-said iron(II) complexes, derived from aliphatic amines were allowed to react with cyanide, pronounced spectral changes were observed which indicated the formation of mixed-ligand complexes. When cyanide was used in a large excess, the reaction seemed to lead to a single, spectrally well defined species. The spectrum of a solution 0.015 M in iron(II), 0.15 M in pyruvate and methylamine, and 0.4 M in cyanide is shown in Figure 4 (curve B). An increase of the cyanide concentration to 0.8 M left the spectrum practically unchanged. At 0.2 M cyanide, the molar absorptivity at the band maximum had decreased by about 5% and minor qualitative changes of the spectrum were observed. At still lower cyanide concentrations both effects became more pronounced. In the analogous glyoxylate system, a cyanide concentration of about 0.6 M was required to make the spectrum (curve C in Figure 4) stationary. Spectral data for the afore—mentioned mixed cyano complexes are listed in Table I.

Table I. Spectral data for iron(II) complexes of α-iminocarboxylic acids R′N=CR.COOH[a]

Ligand substituents R′	R	λ_{max} mμ	ε_{max} $\times 10^{-2}$	δ(-) cm^{-1} $\times 10^{-3}$
	Tris(α-iminocarboxylato)ferrates(II)			
CH_3	H[b]	477	9.6	3.05
C_2H_5	H[b]	479	8.9	3.1
C_6H_5	H[c, d]	508	7	3.0
CH_3	CH_3	472	10.7	3.0
C_2H_5	CH_3	479	10.3	2.95
C_6H_5	CH_3[c, d]	490	7.6	3.0
CH=CH—CH=CH[e]		446	12.6	3.0
	Tetracyano(α-iminocarboxylato)ferrates(II)			
CH_3	H	462	23.5	2.4
CH_3	CH_3	442	25	2.55
CH=CH—CH=CH[e]		439	28	2.55

[a] Solvent, water; temperature, 25°. [b] «Normal» species, see text. [c] Solvent, 10% by volume of ethanol in water. [d] Spectral data obtained by extrapolation. [e] Ligand, picolinic acid.

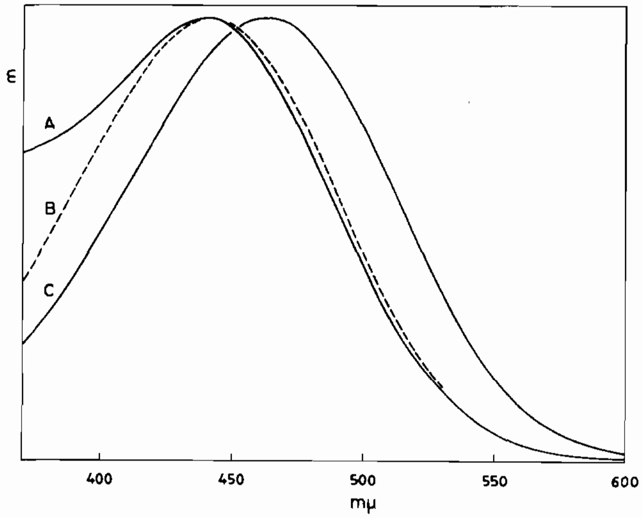

Figure 4. Absorption spectra of tetracyano(α-iminocarboxylato) ferrates(II). Organic ligand : A, picolinic acid ; B, N-pyruvylidenemethylamine ; C, N-glyoxylidenemethylamine. Curves are drawn to equal height at the absorption maximum. Numerical values of the molar absorbancy indices are given in Table I.

Aqueous solutions of the mixed cyano complexes are perfectly stable in air. This contrasts sharply with the great lability toward oxygen of the corresponding cyanide-free complexes; oxygen destroys the brownish-red color within a few sec., turning the solutions into a pale yellow. The rate of the acid hydrolysis of the mixed cyano complexes is likewise considerably slower. At 25° and in an acetate buffer of pH 4.8, the mixed cyano complex derived from pyruvic acid and methylamine has a half-life of approximately one hour. Under the same conditions, the cyanide-free complex was practically completely destroyed in about 10 sec.

Discussion

The Nature of the Iron(II)-Oxocarboxylate-Amine Complexes. The spectroscopic results presented in the preceding section prove the existence of complex species in which amine and metal are combined in the ratio of 3: 1 and also provide evidence for the formation of other complexes with a lower ratio of amine to metal. Amine and oxocarboxylate may, in principle, have either reacted to form a Schiff base, i.e. the anion of an α-iminocarboxylic acid (2), or else a carbinolamine, $R'HNC(OH)R.COO^-$. Leussing et al,[12] in a study of the complex equilibria between α-oxo acids, amino acids and some divalent metal ions, have shown that both, the Schiff base and the carbinolamine are capable of forming complexes with the metal. However, it seems very unlikely that iron(II) complexes of the saturated carbinolamines might give rise to the observed, fairly strong absorption in the visible spectral region. On the other hand, iron(II) complexes of ligands which contain conjugated—C=N—groupings are well known to be strongly colored.[7,13,14] It seems thus reasonable to ascribe the color observed in the afore mentioned systems to the formation of iron(II) complexes of α-iminocarboxylic acids. Accordingly, the complex species containing amine and metal in the ratio of 3: 1 would be formulated as tris(α-iminocarboxylato)ferrate(II) anions, $[Fe(R'N=CR.COO)_3]^-$ [15]

Comparison of the absorption spectra of the supposed tris(α-iminocarboxylato)ferrates(II) with the spectrum of tris(picolinato)ferrate(II), lends some support to this assumption. The spectra of the complexes of the simple iminocarboxylic acids are all similarely shaped and display two shoulders, one on each side of the absorption maximum. The spectra of the N-pyruvylidenemethylamine and N-pyruvylideneaniline complexes, shown in Figure 1, are representative for the whole series. The spectrum of the picolinato complex, shown in the same Figure, displays clearly a shoulder on the long wave length wing of the main absorption band. Any shoulder present on the short wave length wing would be masked by the second, broad band which now appears in the near ultraviolet. As can be seen from the data in Table I, the spectral half widths, δ(-), of all tris(α-iminocarboxylato)ferrates(II), inclusive of the picolinato complex, are very nearly the same; molar absorptivities at the band maximum are all around $1 \times 10.^3$

The influence of the nature of the ligand substituents, R and R′ in 2, on the position and intensity of the visible absorption band is similar to that found in the series of tris(2-pyridylaldimine) and tris(2-pyridylketoimine) iron(II) complexes.[16,17] Replacement of methyl by phenyl on the imino nitrogen, produces in both cases a bathochromic shift accompanied by a decrease of the spectral intensity. It is noted from Table I that the wave length shift is considerably larger (31 mμ) when the substituent on the carbon atom, R, is hydrogen than when it is methyl (18 mμ). A similar observation was made in the series of the afore mentioned iron(II)-α-diimine complexes and explained[17] by the steric hindrance of the bulky methyl group to a coplanar arrangement of the phenyl ring and the $X_2C=NX$ skeleton of the ligand. It is also noted from Table I that the complexes of the simple, aliphatic α-imino acids absorb at considerably longer wave length than the complex of their heterocyclic analogue, picolinic acid. The same observation was made in the series of tris(α-diimine)iron(II) complexes[7] and has been interpreted by Busch and Bailar[14] in terms of a cross-conjugation effect. Finally, it is seen from Figure 1 that the spectrum of the tris(picolinato) complex displays a second band of comparable intensity in the near UV which is lacking, or considerably weaker in the spectrum of the complexes of aliphatic α-imino acids. This again paralleles the behaviour found in the series of the iron(II)-α-diimine complexes.

In the case of the mixed cyano complexes, the similarity between the spectra of the complexes derived from simple α-iminocarboxylic acids on the one hand, and from picolinic acid on the other, is still more pronounced. The spectra of the mixed cyano complexes derived from N-pyruvylidenemethylamine and N-glyoxylidenemethylamine (curve B and C in Figure 4) consist of a single band of nearly perfect Gaussian shape. The spectrum of tetracyano (picolinato)ferrate(II) (curve A in Figure 4) looks very much alike, except for an enhanced absorption at the short wave length wing which indicates the presence of another band in the near UV. Inspection of the data in Table I shows that the spectral intensities and band widths of all three mixed cyano complexes are quite similar. On the strength of the spectroscopic and of chemical evidence it is concluded that the mixed cyano complexes derived from picolinic acid on the one hand, and from the aliphatic iminocarboxylic acids on the other, have the same molecular composition. Accordingly, the latter are formulated as tetracyano(α-iminocarboxylato)ferrate(II) anions, $[Fe(CN)_4(R'N=CR.COO)]^{3-}$. It is interesting to note that the spectral intensities of the mixed cyano complexes are about twice as high as these of the cyanide-free complexes (see Table I), although the former contain but one and the latter three organic ligands.

On the whole, spectral evidence strongly supports the supposition that the complex species formed in the iron(II)-oxocarboxylate-amine systems are derived from conjugating imine ligands, viz. α-iminocarboxylic acids.

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[12] D. L. Leussing and C. K. Stanfield, *J. Am. Chem. Soc.*, *86*, 2805 (1964); D. L. Leussing and D. C. Schultz, *ibid.*, *86*, 4846 (1964); D. L. Leussing and E. M. Hanna, *ibid.*, *88*, 693, 696 (1966).

[13] R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

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

[15] The term α-iminocarboxylic acid will be used when the class of compounds 2 is considered. In naming specific compounds, names such as N-glyoxylidenemethylamine or N-pyruvyldeneaniline, which are self-explanatory, will be used (see ref. 12).

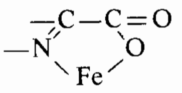
[16] P. Krumholz in «Theory and Structure of Complex Compounds», B. Jezowska-Trzebiatowska Ed., Pergamon Press, Warszawa 1965, p. 217.

[17] P. Krumholz, Inorg. Chem., *4*, 609 (1965).

and form a single class with the complexes of their heterocyclic analogues represented by picolinic acid.

The lability of the tris(α-iminocarboxylato)ferrates(II) suggests that, contrary to the behaviour of the tris(α-diimine)iron(II) complexes,[18] the former complexes are of the high spin type. This supposition is corroborated by the normal trend of the stability constants of the picolinato complexes[5] which contrasts sharply with the strong enhancement of the constant for the addition of a third ligand, found in the iron(II) complexes of heterocyclic α-diimine ligands.[19,20] The comparative inertness of the tetracyano (α-iminocarboxylato)ferrates(II) and, particularely, their strongly enhanced spectral intensity make it very probable that these complexes are of the low spin type.

The Nature of the Spectral Tansitions. The color of the ferrous complexes of α-iminocarboxylic acids can, formally, be connected with the presence of the «chromophoric» chelate ring A. As in the case of the iron(II)-α-diimine[7] (or iron(II)-methine)[14] chromophore, it is possible to write down back-bonded resonance structures, like B, which may be thought to contribute primarely to the excited state, or states, of the molecule.[16]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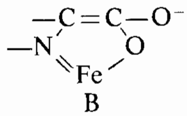
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According to Williams[13] and Jorgensen,[21] the visible absorption of ferrous complexes of conjugating imine ligands is caused by an electron transfer from orbitals mainly localized on the metal to orbitals mainly localized on the ligands and π-antibonding. Williams[13] has commented on the low spectral intensities of the ferrous complexes of heterocyclic imino acids, e.g. picolinic acid, as compared with the much higher intensities (ε_{max} approx. 10^4) of tris(α-diimine)iron(II) complexes. It was assumed that the absorption is caused in both cases by the low spin form of the complex. The comparatively weak absorption of the iminocarboxylato ferrates(II) was explained by the presence of a small proportion of the latter form.

As is seen in Table I, the variation of spectral intensities within the series of tris(α-iminocarboxylato) ferrates(II) is, altogether, rather small. It was also found that the spectral intensity per coordinated ligand of tris(picolinato)ferrate(II) on the one hand, and of the mono(picolinato) complex on the other, are not substantially different.[22] In view of these findings, the hypothesis of an intensity determining equilibrium between low spin and high spin forms of the complexes seems rather untenable.[23] Consequently, the electron transfer transitions of the α-iminocarboxylato ferrates(II) are taken as genuinely belonging to the high spin form of the complexes. The comparatively low intensity of these transitions might be connected with a larger metal-ligand distance in the high spin (d^6) complexes, resulting from the presence of antibonding d electrons.[24]

As noted in the preceding section, the electron transfer band of tris(α-iminocarboxylato)ferrates(II) displays clearly three components. A Gaussian analysis of the spectrum of the N-pyruvylidenemethylamine complex allows one to localize the three components at approximately 18.800 ± 200, 21.100 ± 200 and 23.500 ± 400 cm^{-1}. There are signs of another weak component (or components) around 26.000 cm^{-1}. We shall briefly consider the possible origin of this composite spectral pattern.

In the first place, one has to consider the likely presence of the two geometrical isomers of octahedral complexes of unsymmetrical bidentate ligands. Isomerism by itself could only account for the presence of two band components. Moreover, the average distance between the components of approximately 2350 ± 300 cm^{-1} seems unusually large for an energy difference between equivalent transitions of isomeric species.[25]

Secondly, the observed band components might originate from different electronic transitions of a single complex species. In order to examine this possibility, we use the crude picture of an excited electron transfer state, composed of an iron(III) ion and of a group of ligands holding an extra electron in their π^* orbital system. In the weak field limit, the totally symmetric ground state of iron(III), ^6S, can not be split by any crystal field or by spin orbit coupling alone. Since in octahedral high spin ferric complexes with oxygen donors, the next higher state, $^4T_1$, lies some 10.500 to 12.500 cm^{-1} above the ground state,[26] the observed band splitting can hardly come from the central metal. However, the band components could derive from the lowest π^* levels of the ligands in the complex, split in consequence of metal-ligand or ligand-ligand interactions. In particular, the C_1 symmetrv of the trans isomer would allow for three distinct π^* levels.

Finally, the observed spectral pattern might represent a vibrational structure. A vibronic interaction is expected to involve either the C=O (or OCO) or the C=N stretching vibrations of the ligands,[16] with frequencies between about 1400 and 1700 cm^{-1}. This is considerably less than the average distance between the band components, obtained by Gaussian analysis. However, because of the uncertainty of a Gaussian resolution of complex spectral patterns, a vibrational origin of the observed band structure cannot be excluded.

The spectral intensity per coordinated ligand of the electron transfer transitions in the tetracyano(iminocarboxylato)ferrates(II) is roughly the same as the intensity of such transitions in low spin iron(II)-

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(18) K. Sone, M. Kishita and M. Kato, *Naturwiss.*, *43*, 104 (1956).

(19) P. Krumholz, *Ann. Academia Bras. Ciências*, *22*, 263 (1950).

(20) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).

(21) C. K. Jørgensen, *Acta Chem. Scand.*, *11*, 166 (1957).

(22) For mono(picolinato)iron(II) (see Experimental Section), ε_{max} approx. 330 ± 30, at λ_{max} 397 mμ.

(23) This hypothesis would lead to the conflicting requirements that 10 Dq for $[Fe(picol)_3]^-$ is close a) to the spin-pairing energy of iron(II) and b) to 10 Dq of $[Fe(H_2O)_6]^{2+}$. Actually, the values under a) and b) differ by at least 3000 cm^{-1}; see M. A. Robinson, J. D. Curry and D. H. Busch, *Inorg. Chem.*, *2*, 1178 (1963).

(24) J. H. van Santen and J. S. van Wieringen, *Rec. Trav. Chim. Pays Bas*, ***71***, **420** (1952).

(25) In isomeric tris(2-pyridylketoimine)iron(II) complexes this difference amounts to a few hundred cm^{-1}.[17] However, the energies of the «inverse» charge transfer transitions in the two isomers of $Irpy_3Br_3$ differ by as much as 1400 cm^{-1}; see C. K. Jørgensen, *Acta Chem. Scand.*, *11*, 151 (1957).

(26) See C. K. Jørgensen, «Absorption Spectra and Chemical Bonding in Complexes», Pergamon Press, Oxford 1962.

α-diimine complexes. Since the cubic ground state of low spin iron(III) is an orbitally threefold degenerate $^2T_2$ state, one would expect a splitting of an excited electron transfer state (vide supra) under the low symmetry (C_S or C_1) of the mixed cyano complexes. Actually, the electron transfer band of tetracyano-(α-iminocarboxylato)ferrates(II) has a nearly perfect Gaussian form. However, this does not entitle one to conclude that this band originates from a single electronic transition, because splittings considerably smaller than the half width of the band will not seriously disturb its Gaussian form.