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Metal Complexes with Azine Ligands. I. Ligand Hydrolysis and Template Synthesis in the Iron(II)-2-Pyridinaldazine System

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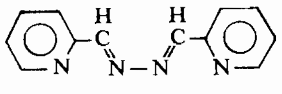
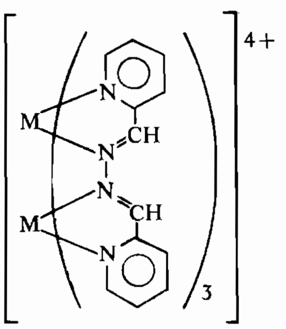
The dinuclear iron(II) complex of 2-pyridinaldazine, $Fe_2(PAA)_3^{4+}$*, has been shown to undergo conversion in aqueous solution to the more stable* $Fe(PAA)_2^{2+}$ *by a 3-step process involving initial dissociation of one metal ion, followed by hydrolysis of the three ligand molecules to give the tris-pyridinalhydrazone complex, and finally recondensation of two aldhehyde fragments to give the bis-tridentate complex. Geometric considerations show that the ligand must exist in different geometric isomers in the initial and final compounds. It is proposed that the metal ion acts as a template for formation of the less stable ligand isomer in* $Fe(PAA)_2^{2+}$*. Spectrophotometric evidence is presented to support the existence of the 3:2 complex ion in solution and to show that this ion is stabilized in solutions of high ionic strenght. As part of the evidence for the above sequence of reactions, a model 3:1 iron(II) complex was synthesized from the new azine ligand 2-pyridinalbenzaldazine.*

Introduction

In earlier investigations[2,4] 2-pyridinaldazine (I, abbreviated « PAA ») was shown to form at least two distinct types of octahedral coordination compounds. Upon reaction of PAA with iron(II) or nickel(II) salts in aqueous solution at room temperature, followed by addition of KI or $NaClO_4$, compounds of the type $[M_2(PAA)_3]X_4$ were obtained. After heating or prolonged standing in aqueous solution, these substances were converted into compounds of the type $[M(PAA)_2]X_2$. Evidence was presented in support of a structure for the $[M_2(PAA)_3]X_4$ compounds containing a bridged dinuclear cation in which each of three ligands is bonded in a bidentate manner to each of the two metal ions(II).



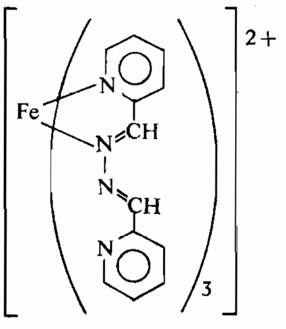
I



II

The $[M(PAA)_2]X_2$ compounds were assumed to involve tridentate chelation of each ligand molecule along an edge of the metal ion octahedron. Magnetic and infrared data for the solid compounds were in agreement with these structures.

The previous work on the iron(II) system also led to the conclusion that a third complex exists in solution as an intermediate in the conversion of the 3:2 complex to the 2:1 complex. Magnetic and spectrophotometric mole ratio studies indicated a 3:1 ratio of ligand to metal for this substance which was assumed to be $Fe(PAA)_3^{2+}$(III). However, no mechanism was proposed by which the tris-bidentate complex (III) is converted into the bis-tridentate complex, $[M(PAA)_2]X_2$.



III

Further studies on this system, together with geometric considerations, now lead us to believe that the previous interpretation of the behavior in solution was partially incorrect. A sequence of reactions is here proposed which involves hydrolysis of the ligand and re-synthesis of the ligand in a new geometric isomer with the metal ion acting as a template.

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(1) (a) Undergraduate research assistant, 1963. Present address: University of California at Riverside. (b) Undergraduate research assistant, 1966. Present address: University of Chicago.
(2) W. J. Stratton and. D. H. Busch, *J. Am. Chem. Soc.*, *80*, 1286 (1958).
(3) W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc.*, *80*, 3191 (1958).
(4) W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc.*, *82*, 4834) (1960).

Experimental Section

Materials. $[Fe_2(PAA)_3]I_4$ and $[Fe(PAA)_2]I_2$ were prepared as described previously.[2] Tris-(pyridinalhydrazone)-iron(II) iodide was prepared according to the method of Stoufer and Busch.[5]. Pyridine-2-aldehyde and 2-pyridinaldazine were obtained from the Aldrich Chemical Company. All other chemicals were reagent grade.

2-Pyridinalbenzaldazine(VII). A mixture of 5.0 grams of hydrazine (0.15 mole) and 13.9 grams of 2-pyridinaldehyde (0.13 mole) in 100 ml. of ethanol was heated under reflux for a short time. The solution was cooled in a salt-ice bath and kept cold while 15.9 grams of benzaldehyde (0.15 mole) was added dropwise. Upon standing overnight at 0°C, yellow crystals were deposited, which were then recrystallized twice from absolute ethanol. Yield, 6.3 grams. M.p. 93-98°C.

Anal. Calcd. for $C_{13}H_{11}N_3$: C, 74.6; H, 5.3; N, 20.1. Found: C, 74.2; H, 5.4; N, 20.0.

Tris-(pyridinalbenzaldazine)-Iron(II) Iodide 1-Hydrate. Five grams of the ligand were added to 1.6 grams of iron(II) chloride 4-hydrate in 80 ml. of ethanol, producing an intense red color. After stirring for 5 minutes, the solution was filtered to remove approximately one gram of a maroon powder which was probably the chloride salt of the complex. The filtrate was added with vigorous stirring to a large excess of ice-cold aqueous potassium iodide solution. The resulting maroon-colored solid was filtered, washed thorouhly with cold water, then with ether until the ether washes were colorless, and finally dried in a vacuum over P_4O_{10}.

Anal. Calcd. for $[Fe(C_{13}H_{11}N_3)_3]I_2 \cdot H_2O$: C, 49.0; H, 3.7; N, 13.2; I, 26.6. Found: C, 48.6; H, 4.2; N, 13.2; I, 26.7. The compound is quite soluble in ethanol and only sparingly soluble in water.

Spectrophotometric Studies. Ultraviolet and visible absorption spectra were obtained with a Beckman DB spectrophotometer and a Sargent SRL recorder. The cell compartment was thermostatted at 30.0°C by means of a circulating water bath. Matched 1 cm. silica cells were used for approximately 10^{-4} *M* solutions in the visible region and 10^{-5} *M* in the ultraviolet. Insertion of matched 9 mm. silica blocks permitted measurements with a 10-fold increase in concentration. In addition, a Beckman sandwich cell with silica plates and a 0.101 mm. spacer permitted spectra to be obtained up to concentrations of 10^{-2} *M* in the visible and 10^{-3} *M* in the ultraviolet regions.

Attempts to obtain electronic spectra of solid samples by smearing Nujol mulls on filter paper were unsuccessful. We therefore used a modification of the method of Dyer *et al.*[6,7] in which a fine dispersion of the compound was precipitated directly on filter paper. For the spectrum of $[Fe_2(PAA)_3]I_4$, a weighed sample was added to water to give a 0.01 *M* solution and the mixture was stirred for one minute. A strip of Whatman No. 1 filter paper was dipped into the solution and dried quickly under an infrared lamp. A small piece was then cut from the paper and inserted into a 1 cm. glass cell filled with Nujol. A reference cell was prepared in a similar manner using blank filter paper. The usefulness of this method rests on the assumption that the material precipitated from solution onto the paper has the desired composition; thus the method is applicable only where a sample can be put into solution and recovered unchanged.

Infrared spectra were obtained with a Perkin Elmer Model 521 spectrophotometer using pressed KBr discs.

Results and Discussion

Spectrophotometric Results. It had been previously reported[3] that when $[Fe_2(PAA)_3]^{4+}$ salts were dissolved in water the color slowly changed from red to orange. The visible absorption spectrum showed a slight blue shift in the charge transfer band (from 510 to 475 mμ) and a large increase in intensity. This change occurred over a period of several hours at room temperature and, on the basis of the then available data, had been assumed to be associated with release of one metal ion from the dinuclear complex, $Fe_2(PAA)_3^{4+} \rightarrow Fe(PAA)_3^{2+} + Fe^{2+}$. This change was followed by a much slower color change from orange to blue, as the peak at 475 mμ disappeared and a new peak appeared at 650 mμ. which was postulated to be due to the formation of the tridentate complex, $[Fe(PAA)_2]^{2+}$. These previous studies were limited to very dilute solutions (*ca.* 10^{-4} M) because of the availability of only 1 cm. cells and the high extinction coefficient of the charge transfer band.

In the present work, spectrophotometer cells of approximately 1 mm. and 0.1 mm. path lengths were employed to permit studies up to 10^{-2} *M* concentration. It was found that the spectral change with time varied quite significantly with concentration and that adequate interpretations could not be based solely on 10^{-4} *M* spectra. Typical results are shown in Figure 1, in which repetitive scans of the spectral region of interest have been made at three concentrations. It is observed that at 10^{-3} *M* an initial peak at 520 mμ rapidly disappears, with appearance of a 475 mμ peak. At 10^{-4} *M*, no 520 mμ peak is observed and there is a simple increase in the 475 mμ peak. At both of these concentrations the changes shown in Figure 1 are followed by a slow decrease in the 475 mμ peak with simultaneous appearance of a new peak at 650 mμ. At 10^{-2} *M*, the initial peak at *ca.* 530 mμ slowly decreases and shifts to *ca.* 510 mμ, along with a simultaneous increase in absorbance at 650 mμ.

These observations can best be accounted for by a proposed reaction sequence involving first dissociation of the 3:2 complex (λ_{max} = 540 mμ) into the 3:1 complex (λ_{max} = 520 mμ) and free iron(II), followed by hydrolysis of the uncomplexed $-C=N-$ group in each ligand to give 3 moles of pyridinaldehyde (« PA ») and the tris-(2-pyridinalhydrazone)-iron(II) ion (IV) which adsorbs at 475 mμ.

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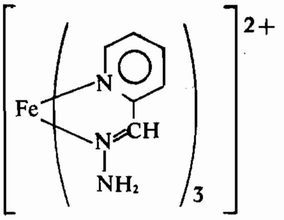
(5) R. C. Stoufer and D. H. Busch, *J. Am. Chem. Soc.*, *78*, 6016 (1956).

(6) G. Dyer, J. G. Hartley, L. M. Venanzi, *J. Chem. Soc.* 1293 (1965).

(7) M. T. Halfpenny, J. G. Hartley, L. M. Venanzi, *J. Chem. Soc.*, *A*, 627 (1967).



IV, $Fe(PAH)_3^{2+}$

Finally $Fe(PAH)_3^{2+}$ recombines with pyridinaldehyde to form $Fe(PAA)_2^{2+}$ (λ_{max} = 650 mμ). The net equations to describe these three steps are:

$Fe_2(PAA)_3^{4+} \rightarrow Fe(PAA)_3^{2+} + Fe^{2+}$ (Step 1)

$Fe(PAA)_3^{2+} + 3H_2O \rightarrow Fe(PAH)_3^{2+} + 3PA$ (Step 2)

$Fe(PAH)_3^{2+} + 2PA \rightarrow Fe(PAA)_2^{2+} + 2H_2O + PAH$ (Step 3)

The following evidence supports this hypothesis.

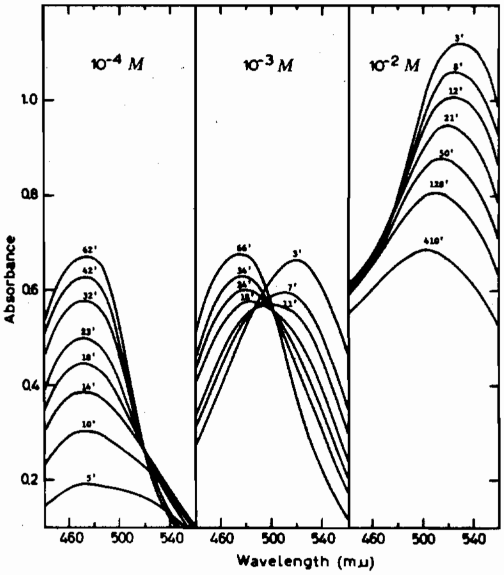


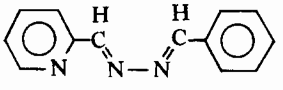
Figure 1. Time dependence in the absorption spectrum of aqueous $[Fe_2(PAA)_3]I_4$ at 30°C and *ca.* pH 6. (A) 1.00 cm cell, (B) 0.100 cm. cell, (C) 0.0101 cm. cell. Time given in minutes.

Evidence for Ligand Hydrolysis Mechanism. (1) A sample of $[Fe(PAH)_3]I_2$ prepared according to the method of Stoufer and Busch[5] was found to possess an absorption band at 475 mμ, and the spectrum of a 10^{-4} *M* solution agreed well with the uppermost curve in Figure 1(a). The previous[3] assignment of the 475 mμ peak to $Fe(PAA)_3^{2+}$ is thus in error.

(2) A 10^{-3} *M* solution of $[Fe_2(PAA)_3]I_4$ was allowed to stand until its spectrum showed maximum absorbance at 475 mμ (5 hours at 25°C) and then was passed through a cation exchange column packed with Dowex 50 X-8 in the Na^+ form to remove all cationic complex species. The solution was then passed through an anion column containing Dowex 1 X-8 in the Cl^- form to remove iodide ion. An ultraviolet spectrum of the resulting solution was in good agreement with the spectrum of pyridinaldehyde, (λ_{max} = 234, 265 mμ), and indicated recovery of approximately 70% of the theoretical amount of pyridinaldehyde.

(3) A solution of $[Fe(PAH)_3]I_2$ mixed with pyridinaldehyde was observed to slowly turn blue, and to produce an absorption spectrum identical with that of $[Fe(PAA)_2]I_2$ (λ_{max} = 650 mμ). Spectrophotometric rate studies were carried out in which the appearance of $Fe(PAA)_2^{2+}$ was followed at 650 mμ in buffered solutions at pH 4.7 and a temperature of 30°C. A solution of $[Fe_2(PAA)_3]I_4$ (1×10^{-3} *M*) was compared with a synthetic mixture consisting of $[Fe(PAH)_3]I_2$ (1×10^{-3} *M*), $FeCl_2$(1×10^{-3} *M*) and pyridinaldehyde (3×10^{-3} *M*). The data from both systems gave good pseudo first order plots over at least 3 half lives and the observed rate constants agreed within 1% (8.54×10^{-3} min^{-1} and 8.46×10^{-3} min^{-1}).

(4) We have been unable to isolate any pure salts of $Fe(PAA)_3^{2+}$. (All attempts to precipitate this complex have given either $[Fe_2(PAA)_3]X_4$, $[Fe(PAH)_3]X_2$, or a mixture of these with the desired product). We therefore prepared the three-to-one complex of the previously-unreported unsymmetrical ligand 2-pyridinalbenzaldazine (V, « PBA »).



V

This ligand should be electronically and sterically similar to PAA except that it cannot form the bridged $Fe_2L_3^{4+}$ chelates. The complex $[Fe(PBA)_3]I_2$ was prepared in analytically pure form. When dissolved in aqueous solution, this compound showed an initial peak in the visible absorption spectrum at *ca.* 520 mμ, but the solution quickly changed color from red to orange and the absorption peak shifted to 475 mμ (Figure 2). The characteristic odor of benzaldehyde was easily detected in the orange solution. It is reasonable to propose that the hydrolysis reaction $Fe(PBA)_3^{2+} \rightarrow Fe(PAH)_3^{2+} + 3BA$, had occurred (BA = benzaldehyde), analogous to the second reaction in the Fe-PAA system. The absorption peak of $Fe(PBA)_3^{2+}$ at 520 mμ is consistent with the 520 mμ peak observed initially in 10^{-3} *M* $Fe_2PAA_3^{4+}$, and the equilibrium spectrum is identical with that of $Fe(PAH)_3^{2+}$.

Evidence for $Fe_2(PAA)_3^{4+}$ in Solution. The results reported in the previous publications provided no clear evidence for the existence of the dinuclear complex ion in solution. Magnetic and infrared data supported its existence in the solid state, but all previous data from aqueous solution studies showed only a 3:1 complex.[3] We have now obtained the following spectrophotometric evidence for $Fe(_2(PAA)_3^{4+}$ in solution.

When $[Fe_2(PAA)_3]I_4$ is dissolved in nitromethane the color remains stable with time, and the visible absorption spectrum shows a peak at *ca.* 540 mμ. The same mμ peak is found in the transmission spectrum of solid $[Fe_2(PAA)_3]I_4$ dispersed on filter paper (as described in the experimental section).

Although $Fe_2(PAA)_3^{4+}$ reacts rapidly in aqueous solution, as evidenced by the disappearance of the 540 mμ peak, it was found that the 540 mμ peak could be stabilized in aqueous solutions of high ionic strength. At $10^{-2}\,M$ complex and 5 M LiCl the 540 mμ peak is indefinitely stable, while at $10^{-4}\,M$ complex and 5 M LiCl the spectrum exhibits a time dependence with slow disappearance of the 540 mμ peak.

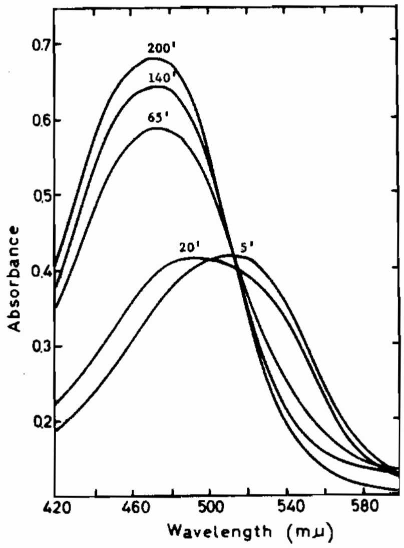


Figure 2. Time dependence in the absorption spectrum of aqueous $[Fe(PBA)_3]I_2$, 25°C, *ca.* pH 6, *ca.* $10^{-3}\,M$. Time given in minutes.

Further evidence of an ionic strenght effect was obtained from magnetic susceptibility measurements. Earlier work[3] showed that the paramagnetic susceptibility of aqueous 0.01 M $[Fe_2(PAA)_3]I_4$ increased with time, consistent with the release of high-spin aqueous iron(II) from the low-spin dinuclear complex. In the present work, a 0.01 M solution of $[Fe_2(PAA)_3]I_4$ was prepared in 5 M LiCl. The magnetic susceptibility remained nearly zero, increasing gradually to only 6 percent of the maximum paramagnetism for a corresponding solution of the complex at low ionic strength.

These results at high ionic strength support the existence of the dinuclear tetrapositive complex ion, since interionic attractive forces should stabilize the 4+ ion in preference to two dipositive ions (step 1 in the proposed mechanism). It should be noted that lithium chloride was not a good choice for the suporting electrolyte, but was chosen because it was available and would not precipitate the iron complex. Chloride complexing with iron should favor the dissociation reaction, but the experimental results indicate that this effect is insignificant compared with the charge stabilization.

In order to demonstrate that the 540 mμ band does in fact represent the $Fe_2(PAA)_3^{4+}$ ion, a spectrophotometric mole ratio study was carried out after the method of Yoe and Jones.[8] Solid samples of pyridinaldazine were added to freshly-mixed aqueous solutions $1.5\times10^{-2}\,M$ in iron(II) ammonium sulfate and 5.0 M in LiCl. The mixtures were stirred for 8 minutes, then filtered to remove unreacted pyrinaldazine and the spectra run immediately. All spectra showed a single peak at *ca.* 540 mμ. The results (Figure 3) clearly indicate that the species absorbing at 540 mμ contains three pyridinaldazine ligands per two iron(II) ions.

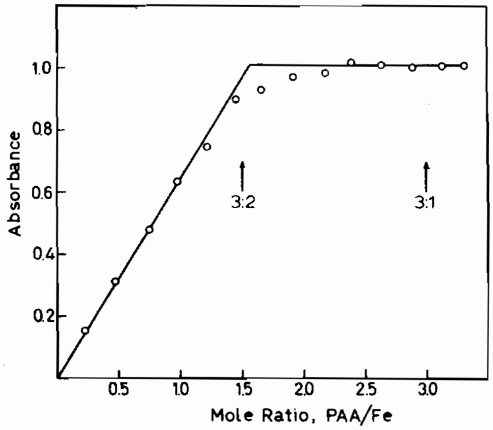


Figure 3. Mole ratio study at 540 mμ. All solutions $1.5\times10^{-2}\,M$ in $Fe(NH_4)_2(SO_{42}$ and 5 M in LiCl.

Rate Data. The spectrophotometric time studies shown in Figure 1 may now be interpreted as follows. At 10^{-3} M, the dissociation of one metal ion (step 1) occurs so rapidly that it was essentially complete and the 540 mμ peak had disappeared before the first scan could be made. What is shown at this concentration is the conversion of $Fe(PAA)_3^{2+}$ (λ_{max} = 520 mμ) into $Fe(PAH)_3^{2+}$ (γ_{max} = 475 mμ). At $10^{-4}\,M$ the evidence suggests that the complex initially dissociates to a large extent into free ligands and iron ions, and only as the ligand hydrolyzes does it recombine with iron to form the more stable $Fe(PAH)_3^{2+}$. When the 3 : 2 compound is dissolved in water at this concentration, the solution is initially red but very rapidly fades so that by the time a spectrum can be recorded the solution is nearly colorless. This same effect is not observed at 10^{-3} M or higher concentrations. At both 10^{-4} M and 10^{-3} M concentrations, the existence of the 475 mμ peak and its slow disappearance indicate that the last step in the reaction sequence is the slowest one and thus the rate-determining step for formation of $Fe(PAA)_2^{2+}$.

At 10^{-2} M, the absence of a 475 mμ peak indicates that step (3) is fast compared to the first two steps. The slow shift in the absorption peak from 530 mμ to 510 mμ indicates the conversion of $Fe_2(PAA)_3^{4+}$ into $Fe(PAA)_3^{2+}$ with a small amount of $Fe(PAH)_3^{2+}$ present in the latter runs. The simultaneous decrease in absorbance is due to formation of the final product, $Fe(PAA)_2^{2+}$.

A preliminary kinetic study of this system carried out in our laboratory has shown that step (2) is pseudo first order (with a complex pH dependence as expected for a Schiff base hydrolysis mechanism[9]) and step (3) is approximately second order (also with a complex

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[8] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed., 16,* 111 (1944).

[9] J. B. Conant and P. D. Bartlett, *J. Am. Chem. Soc., 54,* 2881 (1932).

pH dependence). These results qualitatively account for the shift in relative rates for steps (2) and (3) with change in concentration. Spectrophotometric rate data were collected for the system 1×10^{-3} *M* $[Fe_2(PAA)_3]I_4$ in air-free acetate buffer solutions of ionic strength 0.1 at 30.0 °C. Step (2) was followed at 520 mμ and step (3) was followed at 640 mμ. At both wavelengths a pseudo first order relationship was obeyed over approximately two half lives. At pH 6.0, k_{obs} = 0.046 min^{-1} for step (2) and 0.0017 min^{-1} for step (3). At pH 5.0, k_{obs} = 0.092 min^{-1} for step (2) and 0.0054 min^{-1} for step (3).

Two possibilities exist for step (1): either a rate-determining unimolecular dissociation or a rapid pre-equilibrium followed by a rate-determining step (2). The latter seems more likely on the basis of the available evidence. Thus at concentrations of 10^{-3} *M* or lower the equilibrium favors the dissociation products for step (1) and equilibration is fast compared with the time required for spectrophotometric measurements. At concentrations above 10^{-2} *M*, the equilibrium dissociation for step (1) is relatively small and the rate of disappearance of $Fe_2(PAA)_3^{4+}$ is controlled by step (2).

Infrared Data. In an earlier publication,[4] infrared evidence was presented in support of the proposed structures of $[Fe_2(PAA)_3]I_4$ (II) and $[Fe(PAA)_2]I_2$ (III), as well as for the corresponding nickel salts. The conclusions were based primarily on the C=N stretching vibration at *ca.* 1600 cm^{-1} and the highest frequency pyridine ring vibration at *ca.* 1580 cm^{-1}. We now report additional evidence based on an analysis of the band near 1000 cm^{-1} which has been assigned[10] to the symmetric inplane breathing frequency of the pyridine rings. This band appears at 995 cm^{-1} upon coordination of the pyridine nitrogen to a metal ion. This shift constitutes a sensitive indicator of pyridine coordination.

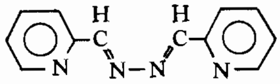
The frequencies of the ring breathing vibration for pyridinaldazine and some of its complexes are given in Table I. The iron and nickel 3:2 compounds show a blue shift of *ca.* 30 cm^{-1}. There is no evidence of a band at 993 cm^{-1} in these compounds, thus both of the pyridine nitrogens must be coordinated to metal ions. (We have recently prepared a new iron(II)-PAA compound in which one end of the ligand is believed to be uncoordinated. This compound has absorption bands at both 990 and 1022 cm^{-1}.)[14] For the 2 : 1 compounds, the band is shifted approximately the same amount but is split into a doublet. Again the absence of any band at 993 cm^{-1} shows that both pyridine nitrogens are coordinated. The doublet nature of this band indicates that the two ends of the molecule are in dissimilar environments in the 2 : 1 compounds and further supports the proposed structure III.

Table I. Infrared Frequencies - Pyridine Ring Breathing Vibration

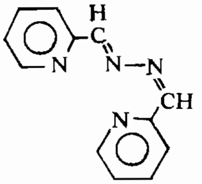
Compound[a]	Frequency (cm^{-1})
PAA	993
$Fe_2(PAA)_3I_4$	1022
$Ni_2(PAA)_3I_4$	1023
$Fe(PAA)_2I_2$	1028 1013
$Ni(PAA)_2I_2$	1020 1030

[a] PAA = 2-pyridinaldazine.

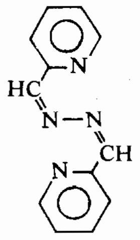
Geometric Considerations. In the previous publications,[2-4] no consideration was given to the geometric factors associated with the conversion of the 3 : 2 dinuclear compounds into the 2 : 1 bis-tridentate compounds, other than to suggest the intermediate formation of a 3 : 1 compound. In particular, no mention was made of the fact that pyridinaldazine may exist in three geometric isomers, depending on the orientations of the substituents about each C=N unit. The *trans-trans* isomer (VI) is likely to exist in two rotational conformations, by rotation through 180° about the N–N bond axis, still maintaining the planar configuration expected of a highly conjugated molecule. The *cis-trans* (VII) and *cis-cis* (VIII) isomers, on the other hand, may exist in only one planar conformation because of steric hindrance. The *cis-cis* isomer is less likely to form stable complex ions.



VI, (*trans-trans*)

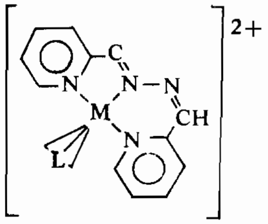


VII, (*cis-trans*)



VIII, (*cis-cis*)

Only the *trans-trans* isomer (VI) is capable of forming the bridged structure (II) as postulated for the $[M_2(PAA)_3]X_4$ compounds. Precision spacefilling Courtauld atomic models show that formation of II is in fact possible, although some bond-angle strain and steric interaction between ligands is involved. The resulting structure has a spiral configuration, as suggested previously.[3] For $[M(PAA)_2]X_2$ compounds with the postulated tridentate structure, the ligand must be in the *cis-trans* configuration (IX). Chelation of this



IX, L = second ligand at 90° angle

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(10) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1130 (1960).
(11) T. J. Lane, I. Nakagawa, J. L. Walter, and A. J. Kandathil, *Inorg. Chem.*, *1*, 267 (1962).
(12) B. Chiswell, F. Lions, and B. Morris, *Inorg. Chem.*, *3*, 110 (1964).
(13) F. Farha and R. T. Iwamoto, *Inorg. Chem.*, *4*, 844 (1965).
(14) W. J. Stratton, to be published.

isomer to produce both 5 and 6-membered chelate rings creates very little bond angle distortion.

In order for conversion to take place from the 3 : 2 to the 2 : 1 compounds, the ligand must change from one geometric isomer to another. The ligand hydrolysis mechanism provides a reasonable explanation for this interconversion. Thus, the *trans-trans* isomer is apparently the more stable form of the free ligand and reacts with various metal ions to form octahedral bridged $M_2(PAA)_3$ chelates. In aqueous solution these complexes dissociate one metal ion; the ligands then hydrolyze to form the tris-hydrazone complex, and finally two aldehyde fragments recondense onto the complex in the *cis-trans* configuration, with elimination of one pyridinalhydrazone molecule. The most interesting and significant aspect of the final step is that the metal ion acts as a template for the formation of an unstable isomer of the ligand. Only when bonded to a metal ion does the ligand exist in the *cis-trans* isomer, and in the case of iron(II) the interconversion takes place by a remarkably well delineated sequence of reactions. A number of other examples of template synthesis have been reported in which an unstable Schiff base is formed by coordination to a metal ion.[15-18] The present study may be the first reported example in which a stable Schiff base rearranges to a different geometric isomer under the influence of a metal ion template.

It is of interest to consider why the final thermodynamically stable product involves the unstable *cis-trans* isomer. In order to utilize three or more nitrogen atoms in coordination, only two possibilities appear to exist, namely structures II and IX. Structure II involves some steric strain, but the largest factor contributing to its equilibrium instability is probably the metal-metal repulsion. Thus II is kinetically favored in the formation reaction because of the initial ligand configuration, but is thermodynamically less stable than structure IX which has very little bond angle strain and no metal-metal repulsion. It is not surprising that the free ligand exists largely as the *trans-trans* isomer, since the *trans*-rotational form of this isomer has the least intramolecular interaction of any possible configuration.

All attempts so far to isolate the *cis-trans* isomer of the free ligand have been unsuccessful. These have included various treatments of the free ligand and extraction of the ligand from solutions of $Fe(PAA)_2^{2+}$. In each case the material had the same melting point as normal pyridinaldazine and gave the characteristic red color with iron(II). That the free ligand may exist at least momentarily in the *cis-trans* configuration is demonstrated by the fact that when certain zinc complexes containing the *cis-trans* isomer of pyridinaldazine are added to iron(II) salts in aqueous solution, the blue color characteristic of $Fe(PAA)_2^{2+}$ is obtained immediately with no trace of red, whereas other zinc complexes with the *trans-trans* isomer give a red color with iron.[19]

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