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Metal Complexes with Azine Ligands. II. Iron(II), Cobalt(II), and Nickel(II) Complexes with 2-Pyridyl Methyl Ketazine[1]

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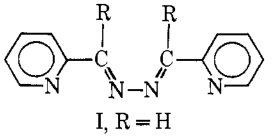
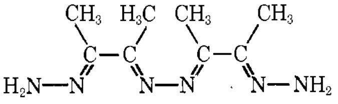
Iron(II), cobalt(II), and nickel(II) complexes of the new ketazine ligand 2-pyridyl methyl ketazine (PMK) have been synthesized and characterized by analytical, magnetic, spectrophotometric, and X-ray measurements. PMK forms dinuclear complexes of the formula $[M_2(PMK)_3]X_4$ with bridged tetrafunctional coordination of each ligand in the *trans,-trans* configuration. These complexes do not undergo a rearrangement into tridentate 1:2 complexes of the type previously reported for 2-pyridine aldazine (PAA) complexes, presumably because the methyl groups block the C=N group to prevent acid hydrolysis. *Dq* values are reported for the nickel complexes of PMK and PAA. Iron(II) also forms $[Fe(PMK)_3]I_2 \cdot 4H_2O$ and nickel(II) forms $Ni(PMK)I_2 \cdot 2H_2O$, while cobalt(II) forms neither type.

Introduction

In earlier papers[2] 2-pyridine aldazine (I, abbreviated PAA) was shown to form an unusual series of bridged octahedral complexes of the general formula $M_2(PAA)_3X_4$, where M = Fe(II), Co(II), or Ni(II).



I, R = H
III, R = CH_3



II

The dinuclear complex cations $M_2(PAA)_3{}^{4+}$ are stable in nonaqueous solvents (as well as in aqueous solutions of very high ionic strength)[1] and are believed to involve symmetric bidentate chelation of each ligand to each of the two metal ions. This requires the ligands to be in the symmetric *trans,trans* geometric isomer shown in I. In aqueous solutions of low ionic strength these complexes undergo a rearrangement into the thermodynamically stable bis-tridentate complexes, $M(PAA)_2{}^{2+}$. The essential feature of this interconversion has recently been shown to involve the acid-catalyzed hydrolysis of the ligands followed by recondensation of the ligand to form the *cis,trans* geometric isomer, with the metal ion acting as a template.[1]

A previous publication also reported studies with another azine ligand containing two α-diimine groups (-N=C—C=N-). With biacetyl hydrazone azine (II, BHA) the compounds $Fe_2(BHA)_3I_4$ and $Ni_2(BHA)_3I_4$ were isolated.[2c] These compounds are believed to contain the same type of bridged dinuclear cation with bis-bidentate chelation of the ligands as in the pyridine aldazine compounds. All attempts to isolate 1:2 compounds of II with iron(II) and nickel(II) were unsuccessful. Furthermore, the aqueous iron(II)–BHA system did not exhibit any of the color changes which characterize the aqueous iron(II)–PAA system.

In order to further define the structural parameters which control the formation of bridged 2:3 complexes and tridentate 1:2 complexes with tetrafunctional azine ligands, studies have been carried out with several new azines related to I and II. Investigations are reported here for 2-pyridyl methyl ketazine (III, PMK) which is structurally intermediate between I and II.

Experimental Section

Materials.—Pyridine-2-carboxaldehyde and 2-acetylpyridine were obtained from the Aldrich Chemical Co. and were used without further purification. Technical grade sodium fluoroborate was recrystallized before use. All other chemicals were reagent grade.

2-Pyridyl Methyl Ketazine (III).—Forty-eight grams of 2-acetylpyridine (0.40 mol) was added to 25 ml of absolute ethanol, along with 6.5 g of 95% hydrazine (0.20 mol) and a few drops of glacial acetic acid. The mixture was heated to boiling for a few minutes and then cooled to room temperature. Water was added slowly in portions, producing first an emulsion and finally crystal formation. A total of 150 ml of water was added, after which the mixture was cooled in ice. The crude product was filtered and recrystallized by dissolving in 40 ml of hot ethanol, adding water, and cooling as above. The yellow needle crystals were filtered, air dried, and finally dried *in vacuo* over P_4O_{10}; yield, *ca.* 42 g (90%), mp 53.5–54.5°. *Anal.* Calcd for $C_{14}H_{14}N_4$: C, 70.6; H, 5.9; N, 23.5. Found: C, 70.4; H, 5.8; N, 23.6.

Tris(2-pyridyl methyl ketazine)diiron(II) Iodide Tetrahydrate.—Iron(II) sulfate heptahydrate (2.8 g, 0.010 mol) and 2-pyridyl methyl ketazine (2.4 g, 0.010 mol) were added to 100 ml of water and the mixture was stirred mechanically at room temperature for 15 min. The deep red solution was filtered to remove traces of undissolved ligand. Six grams of potassium iodide was added and the solution was cooled in ice. The resulting black crystals were filtered, washed with ethanol and ether, and dried *in vacuo* over P_4O_{10}; yield, 2.7 g. *Anal.* Calcd for $Fe_2(C_{14}H_{14}N_4)_3I_4 \cdot 4H_2O$: C, 35.9; H, 3.6; N, 12.0; Fe, 7.9. Found: C, 35.8, 35.6; H, 3.8, 3.5; N, 11.7; Fe, 7.7 (two different samples and different analysts).

The perchlorate and fluoroborate salts were prepared in an analogous manner. The infrared and electronic spectra are identical with the spectra of the iodide salt except for differences due to the anions.

Tris(2-pyridyl methyl ketazine)iron(II) Iodide Tetrahydrate.—Iron(II) sulfate heptahydrate (0.56 g, 0.0020 mol) and 2-pyridyl methyl ketazine (1.4 g, 0.0060 mol) were added to 40 ml of water. The mixture was stirred at room temperature for 30 min and then filtered to remove some undissolved ligand (*ca.* 0.3 g). One gram of potassium iodide was added and the mixture was filtered after 30 min to remove 0.7 g of $Fe_2(PMK)_3I_4$. An additional 1 g of potassium iodide was added to the filtrate which was then

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(1) For the previous paper in this series, see W. J. Stratton, M. F. Rettig, and R. F. Drury, *Inorg. Chim. Acta*, **3**, 97 (1969).

(2) (a) W. J. Stratton and D. H. Busch, *J. Amer. Chem. Soc.*, **80**, 1286 (1958); (b) *ibid.*, **80**, 3191 (1958); (c) *ibid.*, **82**, 4834 (1960).

TABLE I

MAGNETIC SUSCEPTIBILITIES OF SOLID SAMPLES AT ROOM TEMPERATURE

Compound[a]	$10^3\chi_M$	μ_{eff} per metal ion, BM
$Fe_2(PMK)_3I_4 \cdot 4H_2O$	−0.31	0.6
$Fe(PMK)_3I_2 \cdot 4H_2O$	−0.45	0.5
$Fe(PMH)_3I_2 \cdot H_2O$	−0.27	0.4
$Co_2(PMK)_3I_4 \cdot 3H_2O$	14.2	4.2
$Ni_2(PMK)_3I_4 \cdot 2H_2O$	6.98	3.0
$Ni(PMK)I_2 \cdot H_2O$	3.68	3.1

[a] PMK = 2-pyridyl methyl ketazine, PMH = 2-pyridyl methyl hydrazone.

cooled in ice overnight. Large black octahedral crystals (0.8 g) were filtered and dried *in vacuo* over P_4O_{10}. *Anal.* Calcd for $Fe(C_{14}H_{14}N_4)_3I_2 \cdot 4H_2O$: C, 46.0; H, 4.6; N, 15.3. Found: C, 46.3; H, 4.4; N, 15.3.

Tris(2-pyridyl methyl ketazine)dicobalt(II) Iodide Trihydrate.—This compound was prepared in a manner similar to the corresponding iron compound, except that the preparation was carried out under nitrogen. *Anal.* Calcd for $Co_2(C_{14}H_{14}N_4)_3I_4 \cdot 3H_2O$: C, 36.2; H, 3.5; N, 12.1. Found: C, 26.3; H, 3.7; N, 12.2.

Tris(2-pyridyl methyl ketazine)dinickel(II) Iodide Dihydrate.—This compound was prepared in a manner similar to the corresponding iron compound. An initial dark green solution was produced which gradually changed to bright red. The orange product was recrystallized from hot water. *Anal.* Calcd for $Ni_2(C_{14}H_{14}N_4)_3I_4 \cdot 2H_2O$: C, 36.7; H, 3.4; I, 36.9. Found: C, 36.5, 36.3; H, 3.5, 3.5; I, 37.1.

Tris(2-pyridyl methyl ketazine)dinickel(II) Fluoroborate Tetrahydrate.—This salt was prepared in a manner analogous to the iodide salt. *Anal.* Calcd for $Ni_2(C_{14}H_{14}N_4)_3(BF_4)_4 \cdot 4H_2O$: N, 13.4. Found: N, 13.4.

(2-Pyridyl methyl ketazine)nickel(II) Iodide Hydrate.—Nickel(II) chloride hexahydrate (0.9 g, 0.0037 mol) and 2-pyridyl methyl ketazine (0.6 g, 0.0025 mol) were added to 20 ml of water and the mixture was stirred at room temperature for 30 min. The deep green solution was filtered to remove traces of ligand. Potassium iodide (10 g) was added and the resulting dark olive brown solid was filtered, washed with ethanol and ether, and dried *in vacuo* over P_4O_{10}. *Anal.* Calcd for $Ni(C_{14}H_{14}N_4)I_2 \cdot H_2O$: C, 29.6; H, 2.8; N, 9.9. Found: C, 29.6; H, 2.1; N, 9.9.

Tris(2-pyridyl methyl hydrazone)iron(II) Iodide Hydrate.—2-Acetylpyridine, hydrazine, and iron(II) chloride were combined in stoichiometric amounts in hot aqueous solution. The mixture was filtered to remove a precipitate of hydrous iron oxide. Addition of potassium iodide gave the desired product, which was recrystallized from hot water. *Anal.* Calcd for $Fe(C_7H_9N_3)_3I_2 \cdot H_2O$: C, 34.4; H, 4.0; N, 17.2. Found: C, 34.6; H, 4.2; N, 17.2.

Physical Measurements.—Infrared spectra were run on a Perkin-Elmer Model 457 spectrophotometer, using the KBr-pellet technique. The instrument was calibrated against polystyrene film. Ligand field spectra of nickel complexes were determined using a Beckman DU monochromator fitted with a Guilford Model 222 photometer attachment. All other electronic spectra were recorded using a Beckman DB spectrophotometer and Sargent SRL recorder. Magnetic susceptibilities of solid compounds were determined by the Gouy method, using a 5-mm diameter tube in a field of approximately 8000 G. Mercury tetrathiocyanatocobalt(II) was used as calibrant.[3] Diamagnetic corrections were applied in the usual manner[4] using: PMK, -133×10^{-6}; PMH, -76×10^{-6}; I^-, -45×10^{-6}; metal ions, -13×10^{-6}; H_2O, -13×10^{-6}.

Results and Discussion

2-Pyridyl methyl ketazine (III, PMK) forms complexes with iron(II), cobalt(II), and nickel(II) of the general formula $M_2(PMK)_3X_4$, where $X^- = I^-$, ClO_4^-, or BF_4^-. The compounds appear to be analogous to the series of 2-pyridine aldazine complexes of similar stoichiometry.[2] The magnetic susceptibilities of the iron and nickel complexes (Table I) indicate in each case that both metal ions are in an octahedral, strong-field environment. The magnetic susceptibility of the cobalt complex, however, is considerably below the normal range of 4.7–5.2 BM for octahedral cobalt(II) complexes, indicating either substantial spin–spin interaction between cobalt ions of the type discussed by Ball and Blake for dimeric nickel complexes,[5] or an equilibrium between two cobalt spin states of the type discussed by Stoufer, *et al.*[6] The pyridine aldazine complex, $Co_2(PAA)_3I_4$, has a normal magnetic moment of 4.9 BM,[2c] consistent with other information on the relative bond strengths of PAA and PMK complexes.

Infrared spectra (Table II) are quite similar to the spectra of the corresponding pyridine aldazine complexes which have been discussed previously.[1,2c] For the cobalt and nickel complexes, the unsplit bands in the 1620–1500-cm^{-1} region and a pyridine ring-breathing band shifted entirely from 991 to 1018 cm^{-1} all indicate symmetric bis-bidentate bonding. The 2:3 iron complex shows similar behavior of the higher frequency pyridine bands and has the 1552-cm^{-1} band expected for coordinated C=N with iron(II), but this compound also unexpectedly shows two equal-intensity (and relatively broad, asymmetric) bands at 1019 and 988 cm^{-1}. The appearance of these two bands suggests unsymmetric coordination of the ligand, but the iron complex was found to be isostructural with the cobalt and nickel complexes (as shown by identical X-ray powder diffraction patterns for the iodide salts) and in most other ways the complexes behave similarly.

TABLE II

SELECTED INFRARED ABSORPTION BANDS

Compound	C=N	I[a]	II[a]	C=N	Ring breathing
PMK	1612 m	1582 s	1565 s		991 m
$Fe_2(PMK)_3I_4 \cdot 4H_2O$	1622 w	1602 s	1585 m	1552 m	1019 m, 988 m
$Co_2(PMK)_3I_4 \cdot 3H_2O$	1618 w	1591 s	1565 m		1018 s
$Ni_2(PMK)_3I_4 \cdot 2H_2O$	1620 m	1595 s	1568 m		1019 s
$Fe(PMK)_3I_2 \cdot 4H_2O$	1620 m 1615 m	1602 s 1583 m	1580 m 1567 m	1560 sh	992 m
$Ni(PMK)I_2 \cdot H_2O$	1620 m	1592 s	1568 m		1020 s

[a] Characteristic pyridine ring vibrations.

The evidence indicates that these $M_2(PMK)_3X_4$ compounds contain the same bridged dinuclear complex ion (IV) as found with 2-pyridine aldazine,[2] with the ligands in the *trans,trans* geometric isomer. It is of particular interest to note that the methyl groups of the ketazine do not prohibit this manner of chelation, even though considerable steric strain must be involved.

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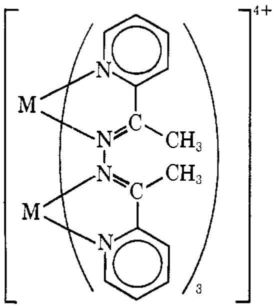
(3) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(4) B. N. Figgis and J. N. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p 416.

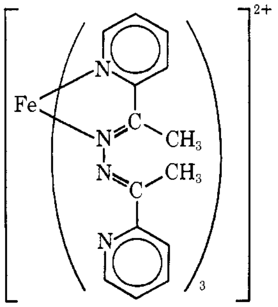
(5) P. W. Ball and A. B. Blake, *J. Chem. Soc., A*, 1415 (1969).

(6) R. C. Stoufer, D. W. Smith, E. A. Clevenger, and T. E. Norris, *Inorg. Chem.*, **5**, 1167 (1966).

Models show that these methyl groups would prohibit bridged tetrafunctional chelation with coplanarity of the ligands, but that bridging is possible with a twisted conformation of the ligands. This lends support to the proposed[2b] spiral structure of the bridged M_2L_3 ion.



IV



V

2-Pyridyl methyl ketazine and 2-pyridine aldazine both form very strong coordinate bonds, as evidenced by the large ligand field splitting parameter, *Dq*, for their nickel complexes (Table III). The $^3A_{2g} \rightarrow {}^2T_{2g}$ transition was assigned from solution spectra in accord with the assignments of Robinson, Curry, and Busch.[7] The values of *Dq* for $Ni_2(PMK)_3{}^{4+}$ and $Ni_2(PAA)_3{}^{4+}$ indicate similar ligand field strengths with PMK being slightly stronger. These may be compared (Table III) with results for other strong-field tris-bidentate nickel complexes. 2,2′-Bipyridine, 1,10-phenanthroline, 2-pyridyl methyl hydrazone, and 2-pyridinal hydrazone are structurally similar to PAA and PMK (the latter two being nearly identical with half of PMK and PAA), but all four show slightly stronger ligand field strengths than the two azines in their 2:3 complexes. This difference may be attributed to the strained nature of the bridged 2:3 structure. (It is of interest to note that the *cis,trans* tridentate form of PAA in $Ni(PAA)_2{}^{2+}$ produces a significantly stronger *Dq* than does the *trans,-trans* form and that this is one of the largest *Dq* values of any nickel(II) complex yet reported.)

TABLE III

LIGAND FIELD SPLITTING PARAMETERS FOR SOME OCTAHEDRAL NICKEL(II) COMPLEXES

Complex[a]	*Dq*	Ref
$Ni_2(PAA)_3{}^{4+}$	1205	*b*
$Ni_2(PMK)_3{}^{4+}$	1235	*b*
$Ni(bipy)_3{}^{2+}$	1265	*d*
$Ni(o\text{-phen})_3{}^{2+}$	1270	*d*
$Ni(PAH)_3{}^{2+}$	1272	*c*
$Ni(PMH)_3{}^{2+}$	1275	*b*
$Ni(PAA)_2{}^{2+}$	1279	*b*

[a] PAA, 2-pyridine aldazine; PMK, 2-pyridyl methyl ketazine; PMH, 2-pyridyl methyl hydrazone; PAH, 2-pyridinal hydrazone; *o*-phen, 1,10-phenanthroline; bipy, 2,2′-bipyridine. [b] This work. [c] See ref 7. [d] C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

Electronic spectra of the $Fe_2(PMK)_3X_4$ salts show a strong charge-transfer band at 503 mμ (ε 1.5 × 10^4) with a very pronounced shoulder at 545 mμ (Figure 1, curve B). Many octahedral iron(II) complexes with α-diimine ligands exhibit intense charge-transfer bands of a characteristic unsymmetric shape with a shoulder on the high-energy side.[8-10] Typical of these is the spectrum of the 2,2′-bipyridine complex, $Fe(bipy)_3{}^{2+}$ (Figure 1, curve E). The $Fe_2(PMK)_3{}^{4+}$ absorption band is of similar intensity (per mole of metal) but has a distinctly different shape, with a shoulder on the low-energy side. The absorption band of the corresponding PAA complex (Figure 1, curve A) does not show the same asymmetry. The spectrum of $Fe_2PMK_3I_4$ was found to be independent of solvent, concentration, temperature, and ionic strength; thus the double peak does not indicate an equilibrium mixture.

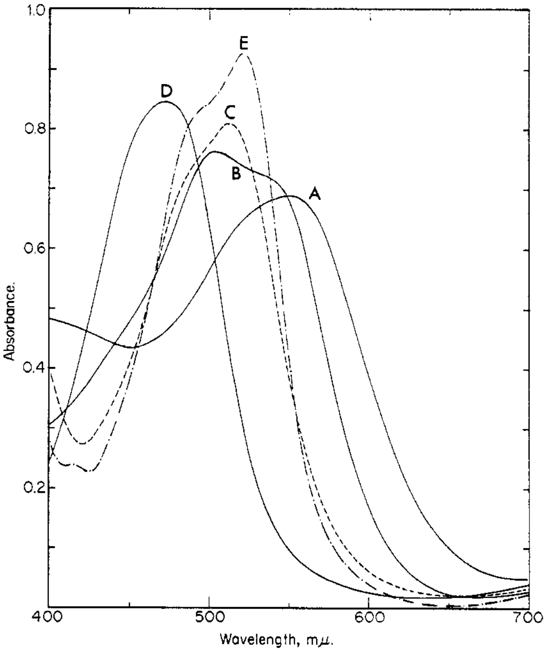


Figure 1.—Electronic spectra of: (A) $Fe_2(PAA)_3I_4$, 5 × 10^{-4} *M*, 1-mm cell; (B) $Fe_2(PMK)_3I_4$, 5 × 10^{-4} *M*, 1-mm cell; (C) $Fe(PMK)_3I_2$, 10^{-4} *M*, 10-mm cell; (D) $Fe(PMH)_3I_2$, 10^{-3} *M*, 1-mm cell; (E) $Fe(bipy)_3I_2$, 10^{-4} *M*, 10-mm cell. (A) and (C) in nitromethane; others in water.

Although PMK and PAA form similar bridged 2:3 complexes, there is one dramatic difference between the two ligands. Whereas the $M_2(PAA)_3{}^{4+}$ complexes rapidly convert in solution into compounds of the type $M(PAA)_2{}^{2+}$, no such conversion has been observed with the PMK complexes. Aqueous solutions of $[Fe_2(PMK)_3]I_4$ showed no change in the electronic absorption spectrum after several weeks at room temperature or several hours at 100°, and the starting material could be recovered unchanged. No change was observed even in 50% H_2SO_4 or in HCl up to 4 *M* concentration. Magnetic susceptibility measurements on a 10^{-2} *M* solution of $Fe_2(PMK)_3I_4$ at room temperature showed only a very small amount of paramagnetism (corresponding to *ca.* 1% spin-free iron) at the end of 72 hr. The corresponding $Fe_2(PAA)_3I_4$ system under the same conditions shows *ca.* 30% spin-free iron in 1 hr.

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(7) M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, **2**, 1178 (1963).

(8) P. Krumholz, *J. Amer. Chem. Soc.*, **75**, 2163 (1953).

(9) D. H. Busch and J. C. Bailar, *ibid.*, **78**, 1137 (1956).

(10) S. M. Nelson and J. Rogers, *J. Chem. Soc., A*, 272 (1968).

Previous work[1] demonstrated that the 2:3 PAA compounds undergo conversion to the 1:2 compounds by a sequence of reactions involving dissociation of one metal ion, hydrolysis of the uncoordinated end of each ligand, and subsequent re-formation of the ligand as the *cis,-trans* geometric isomer so as to permit tridentate chelation. The absence of any such hydrolysis and rearrangement reactions for the PMK complexes is attributed to a steric effect of the methyl groups which block the C=N group so as to prevent hydrolysis of the latter. According to this hypothesis, the mechanism of the rearrangement in pyridine aldazine complexes must involve initial hydrolysis of the C=N groups while the ligands are still tetrafunctionally coordinated. Thus although the tridentate structure $M(PMK)_2^{2+}$ is sterically quite feasible, apparently no kinetic pathway exists for its formation. This hypothesis also explains the behavior of biacetyl hydrazone azine (II), which contains methyl groups in exactly the same blocking positions as in PMK, thus preventing rearrangement of its 2:3 complexes.

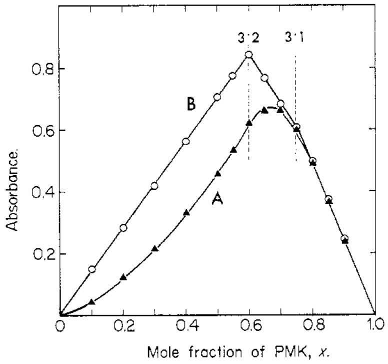

Figure 2.—Spectrophotometric continuous-variations study of the system 2-pyridyl methyl ketazine (x) and iron(II) sulfate ($1 - x$), both 3×10^{-2} *M*: (A) 5 min after mixing, 520 mμ; (B) 2 hr after mixing, 504 mμ.

In addition to the 2:3 complex, iron(II) and PMK also form a 1:3 complex, $[Fe(PMK)_3]I_2$. This compound is diamagnetic (Table I) and the visible electronic spectrum is very similar in shape and intensity to the spectrum of $Fe(bipy)_3I_2$ (Figure 1, curves C and E). The infrared bands (Table II) in the 1630–1500-cm^{-1} region indicate bidentate chelation of the ligand with one end uncoordinated (structure V). In the 1100–900-cm^{-1} region the spectrum is identical with that of free PMK, with no shift of the 991-cm^{-1} band. No explanation can be offered for this observation but it is undoubtedly related to the anomalous spectrum of $Fe_2(PMK)_3I_4$ in the same region. All other evidence on the compound is consistent with structure V.

The formation of the two iron–PMK complex ions in water at room temperature is controlled largely by the stoichiometric ratio of the reactants. Nearly pure $Fe_2(PMK)_3^{4+}$ is formed when the PMK:Fe ratio is 1:1, but when the ratio is 2:1 (the maximum ratio at which the ligand completely dissolves under preparative conditions), the two complex ions form in approximately equal amounts. Fractional precipitation with potassium iodide yielded analytically pure $Fe(PMK)_3I_2 \cdot 4H_2O$ as the more soluble component. At 50° in aqueous solution the equilibrium is shifted almost entirely to the 2:3 complex regardless of the ligand: metal ratio. In order to explore further the iron(II)–PMK system in solution, a spectrophotometric continuous-variations study was carried out. Aqueous solutions of iron(II) ammonium sulfate and pyridyl methyl ketazine (the latter containing 25% ethanol), both 3×10^{-2} *M*, were mixed and allowed to stand at 22°. Spectra were recorded for each solution at the end of 5 min and after 2 hr. Figure 2 shows that the major species present after 2 hr (curve B) is $Fe_2(PMK)_3^{4+}$ but that the second complex ion, $Fe(PMK)_3^{2+}$, is also present in small amount. The graph for the initial solutions after 5 min (curve A) shows roughly an equal mixture of the two complex ions. Similar plots at other wavelengths show essentially the same results for both curves.

Attempts to prepare 1:3 complexes of cobalt(II) and nickel(II) with PMK gave no evidence for the existence of such complexes with these metals. Likewise, attempts to prepare an analogous 1:3 complex of iron(II) with PAA were unsuccessful.

One additional unique type of pyridyl methyl ketazine complex, $Ni(PMK)I_2 \cdot H_2O$, was isolated from solutions having an Ni:PMK ratio $\geqslant 1$. The infrared spectrum of this compound is virtually identical with that of $Ni_2(PMK)_3I_4$ but the X-ray powder patterns are different and the two compounds have different solubility characteristics. Preliminary information indicates that the structure is a dimer with coordinated water and iodide ions. Further studies on this and related compounds will be reported in a separate publication. No evidence was obtained for similar 1:1 PMK compounds with iron(II) or cobalt(II). Likewise, no evidence was obtained for a 1:1 nickel(II) compound with PAA.

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