the oxime oxygens are assumed to act as donors. This is similar to the structure proposed by Stratton[7] for paramagnetic bis-(salicylalhydrazone)-nickel(II), in which uncoördinated hydrazone $-NH_2$ groups are assumed to act as donors to nickel atoms of adjacent molecules, resulting in an octahedral configuration about nickel. The apparent aversion for a planar configuration shown by these compounds is considered to be most unusual.

Palladium(II) and Platinum(II) Complexes.—Palladium(II) and platinum(II) behave exactly as one might expect in their coördination with 2-pyridinaldoxime. They readily precipitate the complexes of the relationship $[M^{II}(POX)_2]$ from aqueous solutions containing two equivalents of base, in sharp contrast to the corresponding nickel(II) system.

The bis-(2-pyridinaldoxime)-palladium(II) complex is a strong dibasic acid. The titration of a mixture containing two moles of ligand and one mole of palladium(II) with sodium hydroxide proceeds to a sharp break in *p*H at two equivalents of base with no perceptible inflection in the curve at one equivalent. The shape of the curve is typical of a strong acid–strong base titration.

From the observation it might be expected that other palladium(II) complexes could not be isolated. By adding concentrated hydrochloric acid to a solution of ligand and palladium(II), however, a monoprotonated species, [Pd(POX)(HPOX)]Cl, crystallizes. When this compound is dissolved in methanol, it exhibits the conductivity of a uni-univalent electrolyte (86.5 ohms^{-1}). Although the ion $[Pd(HPOX)_2]^{++}$ is a strong dibasic acid in water, the species in methanol probably is $[Pd(POX)(HPOX)]^+Cl^-$. This point of view is supported by the realization that ionization of the ligand proton according to the equation

$$[Pd(POX)(HPOX)]Cl \rightleftharpoons [Pd(POX)_2] + H^+ + Cl^-$$

should give rise to a much higher value of the conductivity because of the high conductance of the hydrogen ion.

The only platinum(II) complex which has been isolated in pure form is the uncharged complex, $[Pt(POX)_2]$. Attempts to prepare other species have resulted only in mixtures. The *p*H of the solution must be raised to the neutral point in this preparation in order to obtain a reasonably pure product.

On recrystallization of the platinum(II) compound, a light tan material, insoluble in chloroform, is separated from the major product. Analysis of this material suggests it to be the mono-(2-pyridinaldoxime) complex salt $Na[Pt(POX)Cl_2]$. This is not surprising considering the tendency of palladium and platinum to form similar species, *i.e.*, $[Pt(bipy)Cl_2]$. A similar palladium(II) complex, $[Pd(POX)Cl]_2$, has been obtained but under somewhat different conditions. It will be described in a later paper.

Acknowledgment.—These investigations were greatly facilitated by the generous support of the National Institutes of Health.

(7) W. J. Stratton, Ph.D. dissertation, The Ohio State University, 1958.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

The Complexes of Pyridinaldazine. III. Infrared Spectra and Continued Synthetic Studies

BY WILMER J. STRATTON AND DARYLE H. BUSCH

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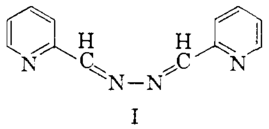
Investigations on the transition metal complexes of pyridinaldazine (PAA) have been extended to cobalt and copper, and these four new compounds are reported: $[Co_2(PAA)_3]I_2 \cdot 2H_2O$, [Cu(PAA)Cl]Cl, $[Cu_2(PAA)Cl_4]$, $[Cu_2(PAA)Cl_2]$. The new ligand, biacetylhydrazone-azine (BHA) forms bridged dinuclear complexes, $M_2(BHA)_3{}^{+4}$, with iron (II) and nickel (II), which are similar to those characterized in earlier studies with pyridinaldazine. The infrared spectra of the pyridinaldazine complexes exhibit features which support the rather unusual structures suggested for these interesting compounds. The tridentate chelation of PAA is accompanied by distinct splittings of the high frequency pyridine-ring vibration and of the C=N stretching mode of the azine link, thus distinguishing between these and the bridged dinuclear complexes, in which the PAA is symmetrically coördinated.

Introduction

It has been shown in earlier investigations[1] that 2-pyridinaldazine forms some unusual and rather interesting coördination compounds with iron(II) and nickel(II).

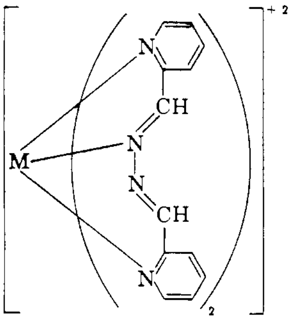


I

Upon reaction of 2-pyridinaldazine (abbreviated PAA) with iron(II) or nickel(II) salts in aqueous solution at room temperature, compounds of the type $M_2(PAA)_3X_4$ were obtained. Upon heating or prolonged standing in aqueous solution, these substances were converted into compounds of the type $M(PAA)_2X_2$. The latter compounds contained complex cations of the expected type in which each of the two ligand molecules was assumed to be coördinated in a tridentate manner to a single metal ion (structure II).

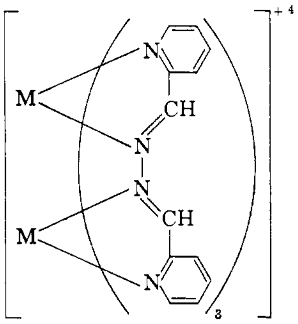
The highly unusual $M_2(PAA)_3X_4$ compounds were investigated by means of conductivity, magnetic susceptibility and spectrophotometric (visible region) measurements and, on the basis of these studies, it was concluded that they contained a

(1) W. J. Stratton and D. H. Busch, THIS JOURNAL, **80**, 1286, 3191 (1958).



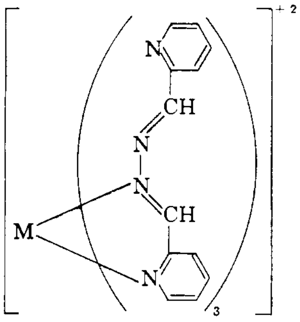
II

dinuclear complex cation, $[M_2(PAA)_3]^{+4}$. The proposed highly-ordered structure for this cation involves coördination of each of the three ligand molecules in a bidentate manner to each of the two metal ions (structure III).



III

In addition to these two types of compounds, evidence was obtained, in the case of iron(II), for the existence in solution of a third type of complex cation, $[Fe(PAA)_3]^{+2}$, in which each of the three ligand molecules presumably was coördinated in a bidentate manner to a single metal ion (structure IV). Attempts to isolate pure substances of this composition have been unsuccessful. Pyridinaldazine is believed to be nearly unique in its observed flexibility in manner of chelation, and the authors have coined the term "flexidentate" to describe this type of behavior.

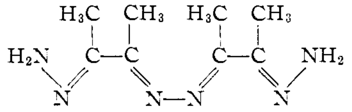


IV

Although the studies previously described were useful in determining the stoichiometric relationships in pyridinaldazine complexes, further evidence was needed in support of the proposed structures of these compounds. In particular, more concrete evidence was needed to substantiate the tetrafunctional coördination of the ligand in the $M_2(PAA)_3X_4$ compounds. The infrared absorption spectra of these compounds provide significant structural information. Certain bands in the spectra may be interpreted to give a logical and self-consistent picture indicating the manner of coördination in the various types of complexes. These data and their interpretation are presented below.

Several new cobalt and copper compounds of pyridinaldazine and their infrared spectra also are reported. The results reveal that cobalt(II) is similar to iron(II) and nickel(II) in its behavior with pyridinaldazine, while copper(II) forms a series of compounds which are analogous to, but not isostructural with, the above-mentioned series.

The unusual behavior of pyridinaldazine suggested the desirability of extending this investigation to include similar ligands, in order to examine the generality of these phenomena. Accordingly, a new ligand, biacetylhydrazoneazine (structure V), was synthesized and its chelating properties were studied briefly. It is observed in structure V that the expected chelate rings would be identical with those of pyridinaldazine if only the imino nitrogens of the hydrazone groups are coördinated.



V

Experimental

Tris-(pyridinaldazine)-di-cobalt(II) Iodide 2-Hydrate.—Two and four-tenths grams of cobalt(II) chloride 6-hydrate (0.01 mole) was dissolved in 30 ml. of freshly prepared air-free water, and the solution was added to 2.0 g. of pyridinaldazine (0.01 mole) dissolved in 50 ml. of ethanol, producing an immediate bright red color. A solution of 13 g. of potassium iodide in 15 ml. of water was added and the stoppered flask was cooled immediately in an ice bath. Crystallization took place rapidly and, after standing overnight at 0°, the product was filtered, washed with ethanol and ether and dried *in vacuo* over P_2O_5. A dark brown crystalline product was obtained, which was seen under a microscope to consist of black needles.

Anal. Calcd. for $[Co_2(C_{12}H_{10}N_4)_3]I_4 \cdot 2H_2O$: C, 33.6; H, 2.6; N, 13.0; I, 39.3. Found: C, 33.9; H, 2.8; N, 12.9; I, 39.6. The magnetic moment was found to be 4.9 Bohr Magnetons, after making the appropriate diamagnetic corrections.

Pyridinaldazine-di-copper(II) Chloride.—Three and one-half grams of copper(II) chloride 2-hydrate (0.02 mole) was dissolved in 300 ml. of ethanol. A solution of 2 g. of pyridinaldazine (0.01 mole) in 100 ml. of ethanol was added slowly with stirring, producing an immediate yellow-green precipitate. The product was filtered and dried *in vacuo* over P_2O_5.

Anal. Calcd. for $Cu_2(C_{12}H_{10}N_4)Cl_4$: C, 30.1; H, 2.1; N, 11.7; Cl, 29.7. Found: C, 30.0; H, 2.2; N, 11.6; Cl, 29.2. $\mu_{eff.}$ = 1.7 Bohr Magneton per copper(II) ion.

Pyridinaldazine-copper(II) Chloride $^1/_2$-Hydrate.—Two grams of pyridinaldazine (0.01 mole) and 2.1 g. of copper(II) sulfate 5-hydrate (0.008 mole) were added to 100 ml. of water. The mixture was stirred for 15 minutes, during which time the color first became bright green and then changed to a deep red-brown. The solution was filtered and, upon adding a solution of 5 g. of potassium chloride in 10 ml. of water, crystals separated quickly. After cooling in an ice-bath, the product was filtered, washed with ethanol and ether and air-dried. The product consisted of minute black crystals which gave an olive-green solution when dissolved in water.

Anal. Calcd. for $Cu(C_{12}H_{10}N_4)Cl_2 \cdot {}^1/_2H_2O$: C, 40.8; H, 3.1; N, 15.8; Cl, 20.1. Found: C, 40.8; H, 3.1; N, 15.8; Cl, 19.9. $\mu_{eff.}$ = 1.9 Bohr Magnetons.

Pyridinaldazine-di-copper(I) Chloride.—Two and one-tenth grams of pyridinaldazine (0.01 mole) was dissolved in a mixture of 10 ml. of ethanol and 10 ml. of air-free distilled water by heating. The solution then was cooled quickly to produce a finely-divided precipitate of the ligand. Forty ml. of air-free water and 1.0 g. of copper(I) chloride (0.01 mole) were added, after which the flask was stoppered and the constants stirred magnetically for approximately 30 minutes at room temperature. A deep-red solution was obtained, together with a micro-crystalline precipitate. The purple-brown solid product was filtered, washed with ethanol and ether and dried *in vacuo* over P_2O_5. It is insoluble in water and ethanol, but readily soluble in pyridine and aqueous ammonia, giving red solutions in both cases. The addition of silver nitrate to the pyridine solution does not produce an immediate precipitate, but, upon standing, a white precipitate forms slowly.

Anal. Calcd. for $Cu_2(C_{12}H_{10}N_4)Cl_2$: C, 35.3; H, 2.5; N, 13.7; Cl, 17.4. Found: C, 35.2; H, 2.7; N, 14.1; Cl, 17.1. $\mu_{eff.}$ = 0.3 Bohr Magneton per metal ion.

Pyridinaldazine-di-copper(I) Bromide.—The deep-red filtrate from the preparation of pyridinaldazine-di-copper(I) chloride (above) was treated with 2 g. of potassium bromide and cooled to 0° overnight. A micro-crystalline product separated, which was filtered, washed with ethanol and ether and dried *in vacuo* over P_2O_5. The brown product, so obtained, exhibits solubilities similar to the chloride salt (above).

Anal. Calcd. for $Cu_2(C_{12}H_{10}N_4)Br_2$: C, 29.0; H, 2.0; N, 11.3; Br, 32.1. Found: C, 30.4; H, 2.5; N, 12.4; Br, 30.4.

Biacetyl-azine.—Nine milliliters of 95% hydrazine (0.27 mole) was added dropwise with rapid stirring to a mixture of 48 g. of biacetyl (0.56 mole) and 25 ml. of water, cooled in an ice-bath. The resulting pale-yellow solution was added to 500 ml. of water and, after standing for a short time, the solution became cloudy. A small quantity of a yellowish oil phase separated, which quickly solidified upon cooling in an ice-bath. The solution was decanted and the solid was treated with 200 ml. of warm (35°) water, followed by filtration through a folded filter paper to remove a trace of remaining oil. Upon cooling the two solutions to 0° overnight, long white needle crystals separated, which were filtered and air-dried very briefly. The yield of the combined products was approximately 20 g., m.p. 32–34° (lit.,[2] 39°).

Biacetylhydrazone-azine.—A solution of 20 g. of biacetyl-azine (0.12 mole) in 50 ml. of ethanol was added dropwise with stirring to a solution of 11.2 ml. of 95% hydrazine (0.34 mole) in 100 ml. of water. After cooling in an ice-bath for several hours, the resulting deep-yellow product was filtered, pressed dry on the filter and recrystallized from 50 ml. of hot absolute ethanol. Upon cooling slowly, bright yellow needle crystals were obtained, which were filtered and dried; yield, 9.5 g. Samples prepared in the same manner and found to be of essentially the same purity had melting points (none of them sharp) within the range, 127–141°. (Partial polymerization during the melting process may account for this difficulty.)

Anal. Calcd. for $C_8H_{16}N_6$: C, 48.9; H, 8.2; N, 42.8. Found: C, 48.8, 48.6; H, 8.4, 8.5; N, 42.5, 43.0.

Tris-(biacetylhydrazone-azine)-di-iron(II) Iodide.—Two grams of biacetylhydrazone-azine (0.01 mole) and 2.8 g. of iron(II) sulfate 7-hydrate (0.01 mole) were added to 50 ml. of water and, after stirring for 10 minutes at room temperature, the deep-red solution was filtered to remove undissolved ligand. A solution of 8 g. of potassium iodide in 15 ml. of water was added and the mixture cooled to 0° overnight. Upon filtration, a microcrystalline powder was obtained but, in addition, there was a considerable amount of a tar-like material left in the flask. The solid product was washed with ethanol and ether and dried *in vacuo* over P_2O_5.

Anal. Calcd. for $Fe_2(C_8H_{16}N_6)_3I_4$: C, 23.9; H, 4.0; N, 20.9; Fe, 9.2. Found: C, 24.1; H, 4.3; N, 20.9; Fe, 9.5. $\mu_{eff.}$ = 1.6 Bohr Magneton per metal ion.

Tris-(biacetylhydrazone-azine)-di-nickel(II) Iodide 4-Hydrate.—Prepared in the same manner as the Fe(II) compound. The product consisted of small yellow-brown needle crystals.

Anal. Calcd. for $Ni_2(C_8H_{16}N_6)_3I_4 \cdot 4H_2O$: C, 22.4; H, 4.4; N, 19.6; I, 39.5; Ni, 9.1. Found: C, 21.0; H, 4.1; N, 19.3; I, 44.2; Ni, 9.3.

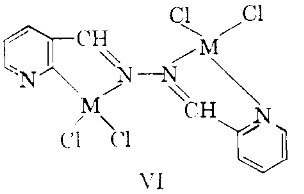
Infrared Spectra.—All spectra were obtained by means of a Perkin-Elmer infrared Spectrophotometer, Model 21, equipped with sodium chloride prisms. Solid samples in pressed potassium bromide pellets were used for all spectra. The frequencies reported for absorption maxima are corrected values, based on a polystyrene standard spectrum.

Discussion

The cobalt(II) compound of pyridinaldazine, $Co_2(PAA)_3I_4$, which is reported here is assumed to be analogous to $Fe_2(PAA)_3I_4$ and $Ni_2(PAA)_3I_4$.[1] The method of preparation was essentially the same as for the iron and nickel compounds, except that the cobalt preparation had to be carried out in an inert atmosphere to prevent oxidation of the cobalt. The compound is believed to contain a dinuclear cation with bridged tetrafunctional coördination of the ligand.

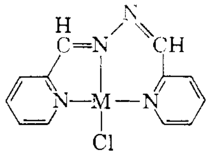
Attempts to prepare the two-to-one cobalt(II) compound were unsuccessful, because under the conditions necessary for the formation of this species (*i.e.* hot solution or slow reaction at room temperature), the cobalt is always partially oxidized by the ligand. A typical analysis shows that approximately 30% of the ligand has been converted to pyridinalhydrazone.

The first copper(II) compound, $Cu_2(PAA)Cl_4$, probably involves bridged tetrafunctional coördination (structure VI), in which the single ligand molecule coördinates in a bidentate manner to each copper atom, with the four chloride ions completing the coördination spheres of the copper ion. The *trans* structure is shown since this probably is the more stable configuration.



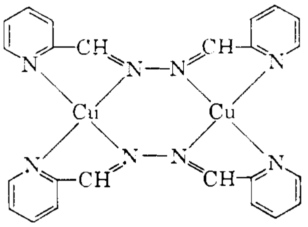
VI

The second copper(II) compound, $Cu(PAA)Cl_2 \cdot {}^1/_2H_2O$, presents an interesting structural problem. The empirical analysis would agree with two reasonable structures: one involving tridentate coördination (structure VII) and the other one a dimer involving bridged tetrafunctional coördination of the ligands in a planar structure (structure VIII). The preparative conditions were analogous to those used for the bridged octahedral



$[Cu(PAA)Cl]Cl \cdot {}^1/_2H_2O$

VII



$[Cu_2(PAA)_2]Cl_4 \cdot H_2O$

VIII

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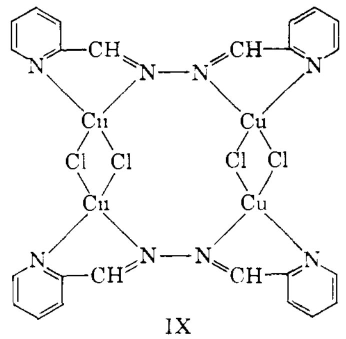
[2] O. Diels and K. Pflaumer, *Ber.*, **48**, 228 (1915).

complexes (*i.e.*, reaction at room temperature and rapid crystallization), and it is tempting to conclude that structure VIII is correct. However, the molar conductivity in methanol (90 ohm^{-1} in 10^{-3} *M* solution) agrees well with a uni-univalent electrolyte, thus supporting structure VII, containing a unipositive cation and a single free chloride ion. (Conductivity measurement in water does not give any useful information, since any coördinated chloride would be replaced by water.) The magnetic moment (1.9 Bohr Magnetons) is normal for Cu(II), whereas for structure VIII, a low moment might be expected due to metal–metal interaction.[3] This should not, however, be considered direct evidence in support of structure VII. Finally, the infrared data also seem to support structure VII, as discussed below.

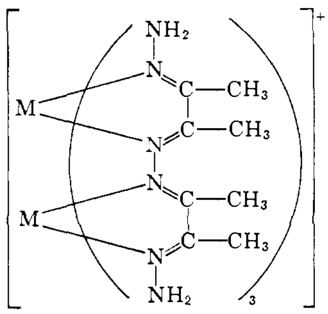
It might be mentioned that in aqueous solution the copper(II)-pyridinaldazine system appears fully as complex as that previously reported for the iron(II)–pyridinaldazine system. Evidence has been obtained for at least three compound types and the interconversions involved are now under investigation.

Preliminary work with copper(I) revealed a compound with the empirical formula $Cu_2(PAA)Cl_2$ and also the corresponding bromide compound, $Cu_2(PAA)Br_2$. In order to fill the coördination spheres of copper, the only possibility is that the halides are bridged between two copper atoms. The simplest possible structure is a dimeric one (structure IX), but a more highly polymeric structure is likely.



IX

The studies with biacetylhydrazone-azine (structure V) revealed that this ligand forms compounds with iron(II) and nickel(II) of the general type $M_2(BHA)_3I_4$. The preparative procedures were analogous to those used for the bridged pyridinaldazine complexes, and it is assumed that these compounds also contain bridged tetrafunctional coördination (structure X). Unlike pyridinaldazine, however, this appears to be the only stable mode of chelation for this ligand. All attempts to prepare compounds of the type $M(BHA)_2X_2$ have been unsuccessful, and the absence of any time dependence in the absorption spectrum of $Fe_2(BHA)_3I_4$ suggests the presence of only one complex species.



X

Infrared spectra were obtained for two iron(II) complexes, two nickel(II) complexes, one cobalt(II) complex, and three copper compounds. No attempt has been made to do a complete analysis of these spectra; however, a few of the bands appear to be sensitive to the type of chelate structure and will be discussed in some detail. Table I lists the bands of interest in the 1400–1700 cm.$^{-1}$ region for pyridine, 2-pyridinaldehyde, 2-pyridinal methylimine and 2-pyridinaldazine. (Data for 2-pyridinal methylimine and its complexes are included only for reference purposes. This work will be reported elsewhere.[4]) Pyridine has four bands associated with the heterocyclic ring vibrations, as tabulated in Table I.[5] These same four bands appear more or less unaltered in the three pyridine derivatives, and there seems little doubt that they are assigned correctly in the ligands of interest. In addition, 2-pyridinal methylimine and 2-pyridinaldazine also show a strong band at about 1630 cm.$^{-1}$ which is assigned to the C═N stretching vibration. Bellamy[6] gives a range of 1640–1690 cm.$^{-1}$ for C═N stretching vibrations, and a recent paper on azine compounds by Bacon and Lindsay[7] reports a range of 1580–1670 cm.$^{-1}$, with the lower frequencies for more highly conjugated azines.

TABLE I

INFRARED ABSORPTION BANDS, 1400–1700 CM.$^{-1}$ REGION

		Pyridine ring vibrations			
	C═N Stretch	I	II	III	IV
Pyridine		1582	1570	1484	1437
2-Pyridinaldehyde		1582 s	1570 sh	1468 m	1435 s
2-Pyridinal methylimine	1634 s	1587 s	1567 s	1468 s	1435 s
2-Pyridinaldazine	1631 s	1580 s	1570 sh	1486 s	1454 s

The bands in the same region of the spectrum for the metal complexes of pyridinal methylimine and pyridinaldazine are tabulated by metals in Table II. The data for the iron compounds can be interpreted most clearly and they will therefore be discussed in detail, with only brief mention of the others. The pyridinal methylimine compound is assumed to contain a single 5-membered chelate ring per ligand molecule (structure XI), whereas the first pyridinaldazine compound is postulated to contain two 5-membered chelate rings per ligand molecule in a bridged structure (structure XII), and the second pyridinaldazine compound is postu-

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(3) A number of papers have appeared recently on low magnetic moments for copper(II) compounds, due to metal–metal interaction, *e.g.*, B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956); Martin and Waterman, *ibid.*, 2545 (1957); O. Asai, M. Kishita and M. Kubo, *J. Phys. Chem.*, **63**, 96 (1959).

(4) P. Figgins and D. H. Busch, unpublished results.

(5) I. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 226.

(6) Bellamy, ref. 5, p. 234.

(7) R. G. R. Bacon and W. S. Lindsay, *J. Chem. Soc.*, 1382 (1958).

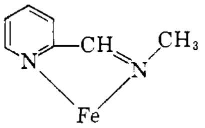
TABLE II

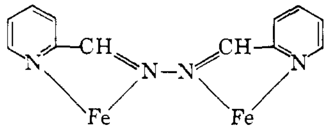
INFRARED ABSORPTION BANDS, 1400–1700 CM.$^{-1}$ REGION[a]

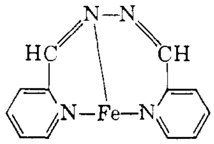
	C=N Stretch	Pyridine ring I	Pyridine ring II	C=N Stretch (5-membered ring)	Pyridine ring III	Pyridine ring IV
$Fe(PMI)_3^{+2}$	....	1619 s	1599 w	1558 w	1475 s	1436 s
$Fe_2(PAA)_3^{+4}$	....	1605 s	1572 m	1544 m	1471 s	1443 m
$Fe(PAA)_2^{+2}$	1628 s	1605 1595 s	1570 sh	1527 m	1475 s	1435 s
$Co(PMI)_3^{+2}$	1652 m	1602 s	1570 w	....	1480 m	1446 s
$Co_2(PAA)_3^{+4}$	1623 m	1585 s	1560 m	....	1479 s	1436 m
$Ni(PMI)_3^{+2}$	1654 s	1604 s	1570 w	....	1482 m	1441 s
$Ni_2(PAA)_3^{+4}$	1625 w	1592 s	1568 m	?	1479 m	1445 s
$Ni(PAA)_2^{+2}$	1637 s	1598 1587 s	1563 sh	?	1482 s	1440 s
$[Cu(PMI)Cl_2]$	1655 m	1609 s	1573 w	....	1481 m	1447 s
$[Cu_2(PAA)Cl_4]$	1637 s	1595 s	1567 sh	?	1477 m	1443 s
$[Cu(PAA)Cl]^+$	1636 s	1595 1582 s	1567 sh	?	1479 m	1429 m

[a] Abbreviations: PMI, 2-pyridinal methylimine; PAA, 2-pyridinaldazine; s, strong; m, medium; w, weak; sh, shoulder; ?, uncertain band.

lated to contain one 5-membered and one 6-membered ring per ligand molecule (structure XIII).


$Fe(PMI)_3^{+2}$
XI


$Fe_2(PAA)_3^{+4}$
XII


$Fe(PAA)^{+2}$
XIII

The four pyridine ring vibrational bands (Table II) agree well with those of the free ligands (Table I), the only significant difference being a shift of the first pyridine band to slightly higher frequencies. It is observed, however, that in the last compound the first pyridine band is split into a doublet. As shown in structure XIII, this compound is postulated to have dissimilar chelate rings—one five-membered and one six-membered. The two pyridine rings are effectively fused to the chelate rings and should therefore have slightly different vibrational energies, which is in agreement with the observed doublet.

The most striking change in this region of the spectrum as a result of chelation is the behavior of the C=N stretching vibration. In the case of pyridinal methylimine with iron(II), the strong band at 1634 cm.$^{-1}$ disappears entirely. This may be explained on the basis that metal-ligand π-electron interaction in the 5-membered chelate ring greatly alters the vibrational frequency of the C=N group. A new band appears, however, at 1558 cm.$^{-1}$, as shown, and since all other bands in this region of the spectrum are accounted for, it seems reasonable to assign this band to the coordinated C=N vibration. Exactly the same thing occurs in the first pyridinaldazine compound, *i.e.*, the C=N band of the ligand disappears and a new band appears at 1544 cm.$^{-1}$. This agrees with the postulated structure (XII), containing two identical 5-membered rings. The third iron compound has two C=N bands, one at 1628 cm.$^{-1}$ essentially the same as in the free ligand and one at 1527 cm.$^{-1}$. This suggests that the two C=N groups are not identical in this compound. The band at 1527 cm.$^{-1}$ agrees with the presence of a 5-membered ring, and the band at 1628 cm.$^{-1}$ might be interpreted to indicate that the conjugative effects of a 6-membered chelate ring are more limited and do not greatly alter the vibration of the C=N group. The presence of two C=N bands would then agree with dissimilar chelate rings (structure XIII). Unfortunately no reference data are available on 6-membered chelate rings of this type, but such data obviously would be very useful in further interpretation of this shift.

The data for the corresponding cobalt(II), nickel(II) and copper(II) compounds cannot be interpreted quite as simply and unambiguously as in the case of iron(II). This probably is due in large measure to the weaker interactions of these ions with ligands of the conjugated aromatic amine type. In particular, it is observed that these compounds do not show the marked shift of the C=N band to a lower frequency for 5-membered chelate rings, as was found in the case of iron(II). As expected, the last (nickel compound, $Ni(PAA)_2^{+2}$ (Table II)) shows a splitting of the first pyridine band, thus indicating dissimilar chelate rings. Similarly, the last copper compound (Table II) also exhibits a splitting of the first pyridine band, thus supporting the postulated mono-nuclear structure, $[Cu(PAA)Cl]^+$, for this compound, as discussed above.

One other band of structural interest is the strong band found at 685 cm.$^{-1}$ in the ligand (Table III). In all of the compounds which are believed to involve tridentate coördination, this band remains as a medium intensity band at a slightly lowered frequency; whereas in all of the bridged compounds it completely disappears from the spectrum. (It cannot, of course, be ascertained whether the band has actually diappeared, or merely been displaced beyond the end of the spectrum, *i.e.* below 650 cm.$^{-1}$.) Pyridine has a strong band at 670 cm.$^{-1}$ which has been assigned to a hydrogen out-of-plane vibration[8]; however, it is not immediately apparent why such a vibration should be sensitive to the type of chelate compound. It can be shown with models that in the case of the octahedral complexes with a bridged structure the three pyridine rings attached to each metal ion occupy a face of the octahedron, whereas in the tridentate two-to-one compounds, even though there are more pyridine groups per metal ion, there is less crowding. Thus, steric factors may be significant. However, no explanation can be given for the shift in this band for $Cu_2(PAA)Cl_4$, which should have the least steric hindrance of any of the compounds. This suggests that the effect may, in fact, be electronic rather than steric.

TABLE III

LOW FREQUENCY INFRARED ABSORPTION BAND

Pyridinaldazine	685 s
Tridentate compounds	
$Fe(PAA)_2^{+2}$	664 m
$Co(PAA)_2^{+2}$	658 m
$Ni(PAA)_2^{+2}$	665 m
$Cu(PAA)Cl^{+}$	664 m
Bridged compounds	
$Fe_2(PAA)_3^{+4}$	. . .
$Co_2(PAA)_3^{+4}$	. . .
$Ni_2(PAA)_3^{+4}$	. . .
$Cu_2(PAA)Cl_4$	. . .

To summarize: both the C=N band and high frequency pyridine ring vibration in pyridinaldazine have been shown to be sensitive to the structure of the chelate compound. In both cases the changes have been interpreted to be entirely consistent with the proposed structures for the two types of complexes. One additional band, from hydrogen out-of-plane vibration on the pyridine rings, also has been shown to be structurally sensitive to the type of complex, but no conclusive explanation can be given at this time. Although these observations do not in themelves prove the postulated structures, nevertheless they do contribute significantly to the total structural information about these very interesting and unusual compounds.

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Inner Complexes. III. Ring Bromination of β-Dicarbonyl Chelates

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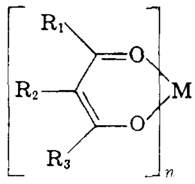
N-Bromosuccinimide is a general reagent for replacing the ring hydrogen of metal β-dicarbonyl chelates with bromine. Tracer studies indicate that this substitution can occur without any intermediate ring cleavage.

Inner complexes frequently possess physical properties such as solubility, melting point and hydrolytic stability characteristic of organic compounds rather than inorganic salts.[1,2] This analogy is extended by the reported reactivity of metal chelates having pendant functional groups in characteristic organic reactions involving these groups, wherein the chelate ring remains intact.[3-6] Less common, however, are substitution reactions on the ring itself in which the reaction proceeds without apparent cleavage of the chelate ring.

Considering specifically the metal β-dicarbonyl compounds (A), most reported reactions with reagents such as bromine,[7] acetyl chloride[8] and sulfur chloride,[9] lead to products of ring cleavage. As an exception, the bromination of chromium(III) tris-(2,4-pentanedionate) with elemental bromine produces the tribromide A($M = Cr$, $R_1 = R_3 = CH_3$, $R_2 = Br$, $n = 3$).[10] Nitrogen tetroxide and copper bis-(2,4-pentanedionate) are reported to form the dinitro derivative A ($M = Cu$, $R_1 = R_3 = CH_3$, $R_2 = NO_2$, $n = 2$).[11] Kinetic data also support the formation of the brominated intermediate A ($M = Cu$, $R_1 = CH_3$, $R_2 = Br$, $R_3 = OC_2H_5$, $n = 2$) in the cupric ion catalyzed bromination of ethyl 3-ketobutyrate.[12] None of these reactions appears to be generally applicable to metal β-dicarbonyl chelates, nor has any conclusive evidence been published to demonstrate that substitution occurs directly on the chelate ring rather than through ring cleavage with subsequent reformation of the ring.



(A)

It has now been found that N-bromosuccinimide reacts with stoichiometric amounts of metal β-dicarbonyl chelates A ($R_2 = H$) to form ring brominated derivatives A ($R_2 = Br$). The success

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