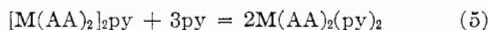


evidence that a 1:1 adduct of pyridine with  $\text{Co}(\text{AA})_2$  is formed in equilibrium with appreciable quantities of  $[\text{Co}(\text{AA})_2]_2\text{py}$  and/or  $\text{Co}(\text{AA})_2(\text{py})_2$ .

The formation of dipyridinate of  $\text{Co}(\text{AA})_2$  is shown not to be complete until very large excesses of pyridine are used, suggesting that  $\text{Co}(\text{AA})_2(\text{py})_2$  is considerably less stable than  $\text{Ni}(\text{AA})_2(\text{py})_2$ . This fact is further exemplified by comparing the formation constants for the dipyridinates of  $\text{Co}(\text{AA})_2$  and  $\text{Ni}(\text{AA})_2$  starting with the 2:1 species which appear to be formed completely. The equilibrium constant for reaction 5 in the case of nickel is  $2.7 \times 10^5 \text{ mole}^{-2} \text{ l.}^2$  while for  $\text{Co}(\text{AA})_2$



it is  $5.8 \times 10^3 \text{ mole}^{-2} \text{ l.}^2$ .

In Fig. 4 the visible spectra of  $\text{Co}(\text{AA})_2$  and  $\text{Co}(\text{AA})_2(\text{py})_2$  are compared with the spectra of  $[\text{Co}(\text{AA})_2]_2\text{py}$  and  $\text{Co}(\text{AA})_2\text{py}$  as determined at various wave lengths in this study. The similarity between the spectrum of  $\text{Co}(\text{AA})_2$  and the 2:1 adduct is particularly striking and would suggest that the coördination about the cobalt(II) is nearly the same in both cases.

The work of Cotton, *et al.*,<sup>14</sup> indicating intermolecular association of anhydrous  $\text{Co}(\text{AA})_2$  in benzene has been confirmed in this study. Cotton, *et al.*,<sup>14</sup> have shown that a temperature- and concentration-dependent association of  $\text{Co}(\text{AA})_2$  exists in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and

(14) F. A. Cotton, R. H. Soderberg, and J. A. Bertrand, to be published.

$\text{C}_6\text{H}_6$  using cryoscopic methods. They suggest that the molecular weight in  $\text{CCl}_4$  at  $77^\circ$  appears to indicate dimers ( $\pm 15\%$ ), while in freezing benzene values between that required for a trimer and that of a tetramer are obtained. Our results at  $37^\circ$  in benzene show that the average value of  $n$  ranges from 2.3 to 2.8 with concentrations ( $C_T$ ) between  $5 \times 10^{-3}$  and  $3.1 \times 10^{-2} M$ .

The spectrum deduced for the 1:1 addition product of  $\text{Co}(\text{AA})_2$  with pyridine, Fig. 4c, is almost identical with that of a 1:1 addition compound of cyclohexylamine with  $\text{Co}(\text{AA})_2$  which has been isolated by Cotton, *et al.*<sup>14</sup> An X-ray crystal structure of the latter product is being attempted.<sup>15</sup> The band systems observed in the 450–650  $m\mu$  region of the spectrum for the acetylacetonate complexes studied in this paper presumably are transitions from the  ${}^4T_{1g}$  ground state (in an octahedral field) to the  ${}^4T_{1g}(\text{P})$  level, split by reduction of symmetry and by spin-orbit coupling.<sup>16</sup> This assignment leads to a  $Dq$  value of about 950–1050  $\text{cm.}^{-1}$  for the acetylacetonate in these complexes, a value in agreement with that found previously in other acetylacetonate complexes.<sup>2</sup>

**Acknowledgment.**—This work was supported, in part, by the National Science Foundation.

(15) F. A. Cotton, private communication.

(16) C. J. Ballhausen, "Ligand Field Theory," McGraw-Hill Book Co. Inc., New York, N. Y., 1962.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF  
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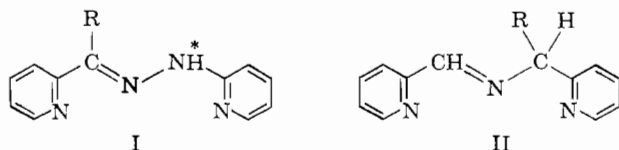
## Tridentate Chelate Compounds. III<sup>1</sup>

By JOHN F. GELDARD<sup>2</sup> AND FRANCIS LIONS

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A series of tridentate chelating agents has been prepared by condensing N-heterocyclic hydrazines of the amidrazone type, such as 2-pyridylhydrazine, with  $\alpha$ -acylated N-heterocycles, such as pyridine-2-aldehyde. These have been shown capable of coördinating with transition metal salts to give complex salts the cations of which can be de-protonated with alkalis to give intensely colored "neutral" complexes. Some of these are very stable. Some of their properties are discussed.

Coördination of the tridentate chelating agent 1,3-bis-(2'-pyridyl)-2,3-diaza-1-propene (I; R = H) with cobalt(II) salts has been shown<sup>3</sup> to lead to formation of diamagnetic cobalt(III) complex salts, the cations of which contain, coördinated with a cobalt atom, two residues of I (R = H) from one of which a proton has



(1) Previous paper in this series: H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **81**, 6415 (1959).

(2) Formerly Commonwealth Research Scholar; since 1962, Petroleum Research Fund Fellow, University of Sydney.

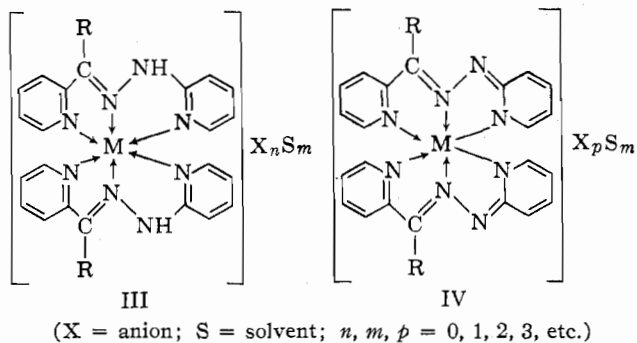
(3) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958).

been lost. We now report that bases can effect a similar deprotonation of the complex cations of salts derived by coördination of certain transition metal salts with bases of the series I (R = H or normal alkyl up to  $n$ -hexyl) or similarly constituted tridentate chelating agents prepared by interaction of a hydrazine derivative of a nitrogen heterocycle of amidrazone type with an acylated nitrogen heterocycle in which the carbonyl group is attached to a ring carbon atom adjacent to the nitrogen atom.

2-Pyridylhydrazine was condensed with 6-methylpyridine-2-aldehyde, quinoline-2-aldehyde, isoquinoline-1-aldehyde, isoquinoline-3-aldehyde, and, also, quinoline-8-aldehyde, in addition to a series of 2-acylpyridines  $\text{C}_5\text{H}_4\text{N}\cdot\text{CO}\cdot\text{R}$  (R =  $\text{CH}_3$  up to  $\text{C}_6\text{H}_{15}$ ). Pyridine-2-aldehyde also was condensed with 2-pyrimi-

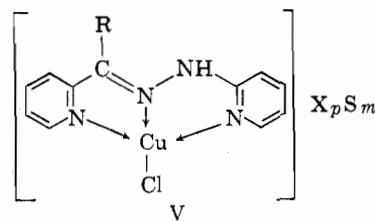
pyridylhydrazine and with 3-methyl-2-pyridylhydrazine as further examples of amidrazone-type N-heterocyclic hydrazines. Each of the resultant hydrazones (Table I) is a planar tridentate chelating agent capable of forming complex salts with the salts of transition metals. Bases can remove one proton per coordinated tridentate residue from these complex salts.

Thus, interaction of a salt such as nickel(II) perchlorate (1 mole) in hot ethanolic solution with PAPHY<sup>4</sup> (2 moles) yields the fawn-colored salt  $[\text{Ni}(\text{PAPHY})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  (III;  $\text{R} = \text{H}$ ,  $\text{M} = \text{Ni}$ ,  $\text{X} = \text{ClO}_4$ ,  $n = 2$ ,  $\text{S} = \text{H}_2\text{O}$ ,  $m = 1$ ), a paramagnetic bi-univalent electrolyte. Sodium hydroxide changes the color of its ethanolic solution to red and addition of water then causes separation of a red solid. Recrystallization of this from benzene gives intensely colored purple-green needles of the paramagnetic non-electrolyte  $[\text{Ni}(\text{PAPY})_2] \cdot 1.5\text{H}_2\text{O}$  (IV,  $\text{R} = \text{H}$ ,  $\text{M} = \text{Ni}$ ,  $p = 0$ ,  $\text{S} = \text{H}_2\text{O}$ ,  $m = 1.5$ ). This can be readily reconverted by acids to salts of the type III. Similar phenomena are observed when PAPHY (2 moles) or any other of the ligands of Table I is coordinated with salts of other



transition elements which favor six-coordination and the resultant complex salts are treated with alkalis. Intensely colored deprotonated ("neutral") complexes are obtained. Thus, the diamagnetic red complex salt III ( $\text{R} = \text{H}$ ,  $\text{M} = \text{Fe}$ ,  $\text{X} = \text{Cl}$ ,  $n = 2$ ,  $\text{S} = \text{H}_2\text{O}$ ,  $m = 2$ ) described by Lions and Martin<sup>3</sup> yields green crystalline IV ( $\text{R} = \text{H}$ ,  $\text{M} = \text{Fe}$ ,  $p = 0$ ,  $\text{S} = \text{H}_2\text{O}$ ,  $m = 1$ ), infusible below  $300^\circ$ , non-conducting in nitrobenzene solution, and paramagnetic. The complex zinc salts III ( $\text{M} = \text{Zn}$ ) are yellow. With alkalis they yield the bright red non-conducting deprotonated complexes. The deprotonated cadmium complexes are bright orange while the deprotonated manganese(II) complex  $[\text{Mn}(\text{PAPY})_2]$  is dark red. The complex salts III and complex salts of similar type prepared and studied are listed in Tables II, III, and IIIa. The deprotonated complexes obtained from them are listed in Tables IV and V.

With copper(II) chloride and the ligands I complex salts (V) can be obtained readily<sup>3</sup> (Table VII), and the tridentate residue in these can be deprotonated with alkalis. Combination of copper(II) perchlorate with PAPHY (2 moles) leads to formation of a complex salt III ( $\text{R} = \text{H}$ ,  $\text{M} = \text{Cu}$ ,  $\text{X} = \text{ClO}_4$ ,  $n = 2$ ,  $\text{S} = \text{H}_2\text{O}$ ,



$m = 2$ ), which can be deprotonated by careful treatment with alkali to IV ( $\text{R} = \text{H}$ ,  $\text{M} = \text{Cu}$ ,  $\text{X} = 0$ ,  $p = 0$ ,  $\text{S} = 0$ ,  $m = 0$ ). In both this complex perchlorate and the corresponding "neutral" complex the copper(II) atoms would appear to be six-coordinated and to be exhibiting the same type of steric arrangement as those derived from metals such as iron(II) and nickel(II). Further, from the complex cobalt(III) salts previously described,<sup>3</sup> it is readily possible to prepare the doubly deprotonated complex salt IV ( $\text{R} = \text{H}$ ,  $\text{M} = \text{Co}$ ,  $\text{X} = \text{ClO}_4$ ,  $p = 1$ ,  $\text{S} = \text{H}_2\text{O}$ ,  $m = 0.5$ ).

Solution studies have shown that both the salts III and the deprotonated ("neutral") complexes IV are very stable. Quantitative evaluations of stability constants will be reported later. In solution PAPHY can readily remove metals such as nickel, iron, and cobalt from their EDTA complexes, or iron(II) from its "ferroin" complexes. The doubly deprotonated complexes (IV;  $p = 0$ ) derived from six-coordinated bivalent metals are distinguished by their ready solubility in organic solvents such as benzene, chloroform, carbon tetrachloride, lower aliphatic alcohols (up to *n*-octyl), and ketones such as cyclohexanone. However, their solubility in low-boiling petroleum fractions is slight. They are also only very sparingly soluble in water. If the alkyl chain ( $\text{R}$  in I) is increased in length, the solubility of the derived uncharged complexes (IV;  $p = 0$ ) in low-boiling saturated hydrocarbons is noticeably increased. Thus, IV ( $\text{R} = n\text{-C}_4\text{H}_9$ ,  $\text{M} = \text{Ni}$ ) was obtained in brown needles from cyclohexane; while IV ( $\text{R} = n\text{-C}_6\text{H}_{13}$ ,  $\text{M} = \text{Ni}$ ) crystallized in red needles from *n*-hexane. The molecular weight of this complex is 621. The comparable iron(II) complex IV ( $\text{R} = n\text{-C}_6\text{H}_{13}$ ,  $\text{M} = \text{Fe}$ , mol. wt. 618) crystallized in dark green prisms from *n*-hexane. It is noticeable that many of the neutral PAPY complexes crystallize with small amounts of solvent of crystallization—usually water, but sometimes benzene.

There also is recorded in the Experimental section the result of a study of the distribution of the complex iron(II) perchlorates III derived from the homologous ligands 2-7 (Table I) between water and cyclohexanone. Increasing chain length of the alkyl group lowers the solubility of the derived complex salt in water and raises the solubility in organic solvents.

Absorption spectra indicate that in the visible the intense colors of the deprotonated complexes would appear to be due to more intense absorption rather than to profound wave length displacements. However, we prefer to reserve discussion until after the accumulation of more evidence.

The complex salts, and the corresponding neutral

(4) If a residue of the pyridylhydrazone I ( $\text{R} = \text{H}$ ) is designated as PAPHY, the deprotonated residue can be designated as PAPY.

TABLE I  
LIGANDS  $R'-C=N \cdot NH-R'''$   
|  
 $R''$

No.	R'	R''	R'''	Name	Formula	Solvent <sup>a</sup>
1	2-Pyridyl	H	2-Pyridyl	1,3-Di-(2'-pyridyl)-1,2-diaza-2-propene	C <sub>11</sub> H <sub>10</sub> N <sub>4</sub>	
2	2-Pyridyl	CH <sub>3</sub>	2-Pyridyl	1,3-Di-(2'-pyridyl)-1,2-diaza-2-butene	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub>	
3	2-Pyridyl	C <sub>2</sub> H <sub>5</sub>	2-Pyridyl	1,3-Di-(2'-pyridyl)-1,2-diaza-2-pentene	C <sub>13</sub> H <sub>14</sub> N <sub>4</sub>	
4	2-Pyridyl	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	2-Pyridyl	1,3-Di-(2'-pyridyl)-1,2-diaza-2-hexene	C <sub>14</sub> H <sub>16</sub> N <sub>4</sub>	
5	2-Pyridyl	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	2-Pyridyl	1,3-Di-(2'-pyridyl)-1,2-diaza-2-heptene	C <sub>15</sub> H <sub>18</sub> N <sub>4</sub>	B
6	2-Pyridyl	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	2-Pyridyl	1,3-Di-(2'-pyridyl)-1,2-diaza-2-octene	C <sub>16</sub> H <sub>20</sub> N <sub>4</sub>	H
7	2-Pyridyl	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	2-Pyridyl	1,3-Di-(2'-pyridyl)-1,2-diaza-2-nonene	C <sub>17</sub> H <sub>22</sub> N <sub>4</sub>	
8	6-Methyl-2-pyridyl	H	2-Pyridyl	1-(2'-Pyridyl)-3-(6''-methyl-2''-pyridyl)-1,2-diaza-2-propene	C <sub>12</sub> H <sub>12</sub> N <sub>4</sub>	B
9	2-Quinoly	H	2-Pyridyl	1-(2'-Pyridyl)-3-(2''-quinolyl)-1,2-diaza-2-propene	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub>	B
10	8-Quinoly	H	2-Pyridyl	1-(2'-Pyridyl)-3-(8''-quinolyl)-1,2-diaza-2-propene	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub>	B
11	1-Isoquinoly	H	2-Pyridyl	1-(2'-Pyridyl)-3-(1''-isoquinolyl)-1,2-diaza-2-propene	C <sub>16</sub> H <sub>12</sub> N <sub>4</sub>	B
12	3-Isoquinoly	H	2-Pyridyl	1-(2'-Pyridyl)-3-(3''-isoquinolyl)-1,2-diaza-2-propene	C <sub>16</sub> H <sub>12</sub> N <sub>4</sub>	B
13	2-Pyridyl	H	2-Pyrimidyl	1-(2'-Pyrimidyl)-3-(2''-pyridyl)-1,2-diaza-2-propene	C <sub>15</sub> H <sub>9</sub> N <sub>5</sub>	F
14	2-Pyridyl	H	3-Methyl-2-pyrazinyl	1-(3'-Methyl-2'-pyrazinyl)-3-(2''-pyridyl)-1,2-diaza-2-propene	C <sub>11</sub> H <sub>11</sub> N <sub>5</sub>	A

<sup>a</sup> The *monopicate* also was prepared. Yellow needles from ethanol, m.p. 174-175°. Calcd. for C<sub>20</sub>H<sub>19</sub>N<sub>7</sub>O<sub>7</sub>: C, 51.4; H, 4.1; N,

TABLE II  
COORDINATION COMPOUNDS OF TYPE IV (X = ClO<sub>4</sub>, *n* = 2, S = H<sub>2</sub>O)

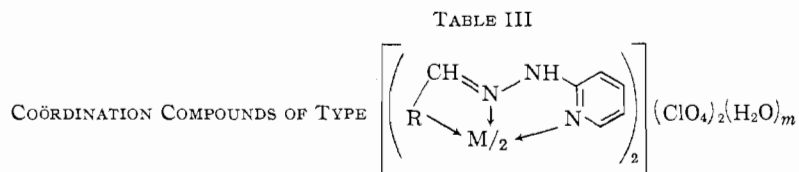
Ligand	R	Metal	<i>m</i>	Name	Formula
1	H	Ni(II)	1	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propene]-nickel(II) perchlorate-1-water	Ni[C <sub>22</sub> H <sub>20</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O
1	H	Cu(II)	2	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propene]-copper(II) perchlorate-2-water	Cu[C <sub>22</sub> H <sub>20</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O
1	H	Zn(II)	1.5	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propene]-zinc(II) perchlorate-1.5-water	Zn[C <sub>22</sub> H <sub>20</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·1.5H <sub>2</sub> O
1	H	Cd(II)	2	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propene]-cadmium(II) perchlorate-2-water	Cd[C <sub>22</sub> H <sub>20</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O
1	H	Mn(II)	2	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propene]-manganese(II) perchlorate-2-water	Mn[C <sub>22</sub> H <sub>20</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O
2	CH <sub>3</sub>	Fe(II)	0	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-butene]-iron(II) perchlorate	Fe[C <sub>24</sub> H <sub>24</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
2	CH <sub>3</sub>	Ni(II)	0	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-butene]-nickel(II) perchlorate	Ni[C <sub>24</sub> H <sub>24</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
3	C <sub>2</sub> H <sub>5</sub>	Fe(II)	0	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-pentene]-iron(II) perchlorate	Fe[C <sub>26</sub> H <sub>28</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
3	C <sub>2</sub> H <sub>5</sub>	Ni(II)	0	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-pentene]-nickel(II) perchlorate	Ni[C <sub>26</sub> H <sub>28</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
4	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	Fe(II)	0	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-hexene]-iron(II) perchlorate	Fe[C <sub>28</sub> H <sub>32</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
4	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	Ni(II)	0	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-hexene]-nickel(II) perchlorate	Ni[C <sub>28</sub> H <sub>32</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
5	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Fe(II)	1	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-heptene]-iron(II) perchlorate-1-water	Fe[C <sub>30</sub> H <sub>36</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O
5	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Ni(II)	0	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-heptene]-nickel(II) perchlorate	Ni[C <sub>30</sub> H <sub>36</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
6	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	Fe(II)	3	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-octene]-iron(II) perchlorate-3-water	Fe[C <sub>32</sub> H <sub>40</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·3H <sub>2</sub> O
6	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	Ni(II)	1	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-octene]-nickel(II) perchlorate-1-water	Ni[C <sub>32</sub> H <sub>40</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O
7	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	Fe(II)	1	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-nonene]-iron(II) perchlorate-1-water	Fe[C <sub>34</sub> H <sub>44</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O
7	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	Ni(II)	1	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-nonene]-nickel(II) perchlorate-1-water	Ni[C <sub>34</sub> H <sub>44</sub> N <sub>8</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O

M.p., °C.	Calcd.			Found			Bis-picrate of ligand							
	C	H	N	C	H	N	M.p., °C.	Formula	Solvent	Calcd.		Found		
											C	H	C	H
Oil							243	C <sub>24</sub> H <sub>18</sub> N <sub>10</sub> O <sub>14</sub>	A-B		43.0	2.7	42.7	2.8
Oil							236.5	C <sub>26</sub> H <sub>20</sub> N <sub>10</sub> O <sub>14</sub>	B		43.9	3.0	43.9	3.0
Oil							235-238 <sup>a</sup>	C <sub>26</sub> H <sub>22</sub> N <sub>10</sub> O <sub>14</sub>	B		44.7	3.2	44.8	3.4
87.5	70.8	7.1		70.6	7.1		208	C <sub>27</sub> H <sub>24</sub> N <sub>10</sub> O <sub>14</sub>	A-B		45.5	3.4	45.5	3.5
75	71.6	7.5		71.0	7.3		187.5	C <sub>28</sub> H <sub>26</sub> N <sub>10</sub> O <sub>14</sub>	A-B		46.3	3.6	46.4	3.9
Oil							183	C <sub>29</sub> H <sub>28</sub> N <sub>10</sub> O <sub>14</sub>	B		47.0	3.8	46.8	3.8
208-210	67.9	5.7	26.4	67.7	5.7	26.8								
217-218	72.6	4.9	22.6	72.5	5.0	22.5								
196-198	72.6	4.9	22.6	72.4	5.0	22.4								
197-198	72.6	4.9	22.6	72.4	5.1	21.9								
198-199	72.6	4.9	22.6	72.4	4.9	21.9								
216-220	60.3	4.6	35.2	60.2	4.5	34.8								
166-168	62.0	5.2	32.9	62.0	5.3	31.8								

20.8. Found: C, 51.9; H, 4.4; N, 20.0. <sup>b</sup> Code letters for solvents defined in Experimental section.

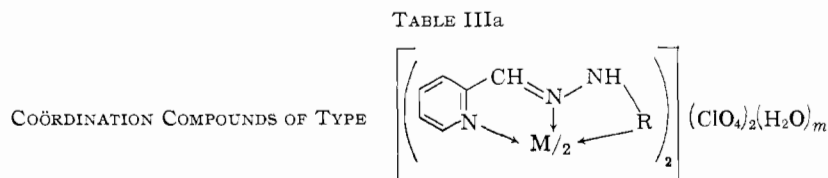
M.p., °C.	Color	Solvent	Magnetic moment, B.M.	Calcd.					Found					
				C	H	N	Cl	M	C	H	N	Cl	M	
350	Fawn	B	2.9 (20°)	39.3	3.3			8.7	39.4	3.7				8.4
	Green- brown	B		38.0	3.5	16.1	10.2	9.1	38.5	3.5	16.2	10.8		8.8
	Yellow	A-B		38.4	3.4	16.3	10.3	9.5	38.3	3.4	16.5	10.6		10.4
	Yellow	B		35.5	3.3	15.1	9.5	15.1	35.7	3.4	14.9	9.7		15.2
	Orange- red	A-B	2.1 (20°)	38.5	3.5	16.3	10.3	8.0	38.9	3.8	16.2	10.5		8.1
228	Maroon	A	1.9 (20°)	42.4	3.6			8.2	42.1	3.9				8.1
300	Fawn	A-B	3.1 (18°)	42.3	3.7			8.6	41.8	3.7				8.5
215	Maroon	A	2.3 (21°)	44.1	4.0			7.9	44.7	4.1				8.1
265	Fawn	A	3.2 (18°)	44.0	4.0			8.3	44.1	4.0				8.5
240	Maroon	A-D	1.4 (21°)	45.8	4.4			7.6	46.4	4.6				8.1
260	Fawn	A-D	3.1 (18°)	45.5	4.4			7.9	45.1	4.6				7.7
224	Red	A-B	1.6 (21°)	46.2	4.9			7.1	46.6	4.8				7.3
270	Fawn	A-B	2.7 (18°)	47.0	4.7			7.7	46.8	4.7				7.4
213	Red	A-B	0.8 (21°)	45.4	5.5			6.8	45.8	5.0				7.1
269	Fawn	A-B	3.0 (18°)	47.9	5.3			7.2	47.7	5.1				6.6
195	Red	A-B	1.4 (21°)	48.8	5.5			6.7	48.8	5.8				7.0
248	Fawn	B	3.0 (18°)	48.6	5.5			7.0	48.5	5.5				6.8

TABLE III



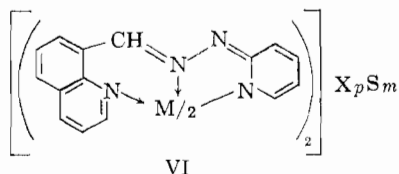
Ligand	R	Metal	<i>m</i>	Name	Formula
8	6-Methyl-2-pyridyl	Fe(II)	1	Bis-[1-(2'-pyridyl)-3-(6"-methyl-2"-pyridyl)-1,2-diaza-2-propene]-iron(II) perchlorate-1-water	$\text{Fe}[\text{C}_{24}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
8	6-Methyl-2-pyridyl	Ni(II)	2	Bis-[1-(2'-pyridyl)-3-(6"-methyl-2"-pyridyl)-1,2-diaza-2-propene]-nickel(II) perchlorate-2-water	$\text{Ni}[\text{C}_{24}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$
8	6-Methyl-2-pyridyl	Zn(II)	1	Bis-[1-(2'-pyridyl)-3-(6"-methyl-2"-pyridyl)-1,2-diaza-2-propene]-zinc(II) perchlorate-1-water	$\text{Zn}[\text{C}_{24}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
9	2-Quinolyl	Fe(II)	0.5	Bis-[1-(2'-pyridyl)-3-(2"-quinolyl)-1,2-diaza-2-propene]-iron(II) perchlorate-0.5-water	$\text{Fe}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$
9	2-Quinolyl	Ni(II)	2	Bis-[1-(2'-pyridyl)-3-(2"-quinolyl)-1,2-diaza-2-propene]-nickel(II) perchlorate-2-water	$\text{Ni}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$
9	2-Quinolyl	Zn(II)	2	Bis-[1-(2'-pyridyl)-3-(2"-quinolyl)-1,2-diaza-2-propene]-zinc(II) perchlorate-2-water	$\text{Zn}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$
10	8-Quinolyl	Fe(II)	1.5	Bis-[1-(2'-pyridyl)-3-(8"-quinolyl)-1,2-diaza-2-propene]-iron(II) perchlorate-1.5-water	$\text{Fe}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$
10	8-Quinolyl	Ni(II)	1.5	Bis-[1-(2'-pyridyl)-3-(8"-quinolyl)-1,2-diaza-2-propene]-nickel(II) perchlorate-1.5-water	$\text{Ni}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$
10	8-Quinolyl	Zn(II)	1	Bis-[1-(2'-pyridyl)-3-(8"-quinolyl)-1,2-diaza-2-propene]-zinc(II) perchlorate-1-water	$\text{Zn}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
11	1-Isoquinolyl	Fe(II)	2	Bis-[1-(2'-pyridyl)-3-(1"-isoquinolyl)-1,2-diaza-2-propene]-iron(II) perchlorate-2-water	$\text{Fe}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$
11	1-Isoquinolyl	Ni(II)	2	Bis-[1-(2'-pyridyl)-3-(1"-isoquinolyl)-1,2-diaza-2-propene]-nickel(II) perchlorate-2-water	$\text{Ni}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$
11	1-Isoquinolyl	Zn(II)	1	Bis-[1-(2'-pyridyl)-3-(1"-isoquinolyl)-1,2-diaza-2-propene]-zinc(II) perchlorate-1-water	$\text{Zn}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
12	3-Isoquinolyl	Fe(II)	2	Bis-[1-(2'-pyridyl)-3-(3"-isoquinolyl)-1,2-diaza-2-propene]-iron(II) perchlorate-2-water	$\text{Fe}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$
12	3-Isoquinolyl	Ni(II)	2	Bis-[1-(2'-pyridyl)-3-(3"-isoquinolyl)-1,2-diaza-2-propene]-nickel(II) perchlorate-2-water	$\text{Ni}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$
12	3-Isoquinolyl	Zn(II)	2	Bis-[1-(2'-pyridyl)-3-(3"-isoquinolyl)-1,2-diaza-2-propene]-zinc(II) perchlorate-2-water	$\text{Zn}[\text{C}_{30}\text{H}_{24}\text{N}_8](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$

TABLE IIIa



Ligand	R	Metal	<i>m</i>	Name	Formula
13	2-Pyrimidyl	Fe(II)	1	Bis-[1-(2'-pyrimidyl)-3-(2"-pyridyl)-1,2-diaza-2-propene]-iron(II) perchlorate-1-water	$\text{Fe}[\text{C}_{20}\text{H}_{18}\text{N}_{10}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
13	2-Pyrimidyl	Ni(II)	2	Bis-[1-(2'-pyrimidyl)-3-(2"-pyridyl)-1,2-diaza-2-propene]-nickel(II) perchlorate	$\text{Ni}[\text{C}_{20}\text{H}_{18}\text{N}_{10}](\text{ClO}_4)_2$
14	3-Methyl-2-pyrazinyl	Fe(II)	2	Bis-[1-(3'-methyl-2'-pyrazinyl)-3-(2"-pyridyl)-1,2-diaza-2-propene]-iron(II) perchlorate-2-water	$\text{Fe}[\text{C}_{22}\text{H}_{22}\text{N}_{10}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$
14	3-Methyl-2-pyrazinyl	Ni(II)	1	Bis-[1-(3'-methyl-2'-pyrazinyl)-3-(2"-pyridyl)-1,2-diaza-2-propene]-nickel(II) perchlorate-1-water	$\text{Ni}[\text{C}_{22}\text{H}_{22}\text{N}_{10}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$

complexes (VI) derived from the  $\alpha$ -pyridyl hydrazone



of quinoline-8-aldehyde appear to be very stable and possessed of high crystallizing power. Of the two "chelating loops" (or metallocyclic rings) produced by coordination of each tridentate organic residue in these complexes, one is six-membered while the other is five-membered. With the PAPY complexes each chelate loop is five-membered. The neutral complexes from

Color	Solvent	Magnetic moment, B.M. (20°)	Conductivity, ohm <sup>-1</sup> cm. <sup>2</sup> at 25°	Calcd.					Found				
				C	H	N	Cl	M	C	H	N	Cl	M
Red	A-B	0.9	52.9	41.3	3.8	16.1		8.0	41.8	4.0	16.3		8.0
Brown	A-B	3.1	48.8	40.2	3.9	15.6	9.9	8.2	40.5	4.0	15.2	9.9	8.3
Yellow	C-E		51.5	40.8	3.7		10.0	9.3	41.0	3.8		10.3	9.2
Dark red	A-B	1.3	39.4	47.4	3.3	14.8		7.8	47.2	3.8	14.7		7.3
Orange	A-B	2.8	46.4	45.6	3.6		9.0	7.4	45.9	3.8		9.0	7.3
Yellow	C-E		45.1	45.2	3.5		8.9	8.2	44.8	3.6		9.0	8.1
Dark red	A-B	1.2	47.8	46.3	3.5		9.1	7.2	46.3	3.9		9.0	7.2
Fawn	A-B	3.3	48.8	46.1	3.5		9.1	7.5	46.1	3.6		9.2	7.6
Yellow	A-B		47.9	46.3	3.4		9.1	8.4	46.2	3.5		8.8	8.5
Dark red	A-B	1.8	42.9	45.8	3.6		9.0	7.1	45.6	3.6		8.7	7.1
Maroon	A-B	3.2	39.3	45.6	3.6		9.0	7.4	46.1	3.6		9.0	7.5
Yellow	C-E		45.1	46.3	3.4	14.4	9.1	8.4	46.5	3.3	14.1	9.0	8.7
Dark red	A-B	1.1	44.7	45.8	3.6	14.2	9.0	7.1	45.9	3.6	13.8	9.5	7.2
Orange-yellow	A-B	3.2	42.7	45.6	3.6	14.2	9.0	7.4	45.9	3.5	13.6	9.2	7.3
Yellow	C-E	0	46.5	45.2	3.5		8.9	8.2	45.2	3.8		8.9	8.3

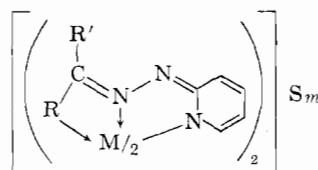
Color	Solvent	Calcd.					Found				
		C	H	N	Cl	M	C	H	N	Cl	M
Dark red	B	35.8	3.0	20.9		8.3	35.7	3.2	21.8		8.1
Fawn	A-C	36.6	2.8		10.8	9.0	36.6	3.2		10.5	8.8
Dark red	A-B	36.8	3.7	19.5	9.9	7.8	35.3	3.4	19.8	10.0	7.8
Yellow-brown	A-B	37.6	3.5	20.0	10.1	8.4	37.5	3.7	19.6	10.0	8.1

ligand 13 (prepared from 2-pyrimidylhydrazine) appear to be much more soluble in water than the corresponding PAPY complexes, while those derived ultimately from 3-methyl-2-pyrazinylhydrazine, which are about as soluble as the corresponding PAPY complexes, seem to be possessed of great crystallizing power.

Some of these neutral complexes can be sublimed

under high vacuum. Thus IV (R = H, M = Ni, S = H<sub>2</sub>O, *m* = 1.5) sublimes slowly at 0.002 mm. when carefully heated in a cold-finger apparatus in a metal bath to 300°. The sublimate was the pure anhydrous complex. The infrared absorption spectra before and after sublimation are practically identical. Similarly, bis-[1-(2'-pyridyl)-3-(2"-quinolyl)-1,2-diaza-2-propenato]-

TABLE IV  
DEPROTONATED ("NEUTRAL") METAL COMPLEXES



Ligand	R	R'	Metal	S	m	Name	Formula
1	2-Pyridyl	H	Fe(II)	H <sub>2</sub> O	1	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propenato]-iron(II)-1-water	Fe[C <sub>22</sub> H <sub>18</sub> N <sub>8</sub> ]·H <sub>2</sub> O
1	2-Pyridyl	H	Ni(II)	H <sub>2</sub> O	1.5	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propenato]-nickel(II)-1.5-water	Ni[C <sub>22</sub> H <sub>18</sub> N <sub>8</sub> ]·1.5H <sub>2</sub> O
1	2-Pyridyl	H	Zn(II)			Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propenato]-zinc(II)	Zn[C <sub>22</sub> H <sub>18</sub> N <sub>8</sub> ]
1	2-Pyridyl	H	Cd(II)			Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propenato]-cadmium(II)	Cd[C <sub>22</sub> H <sub>18</sub> N <sub>8</sub> ]
1	2-Pyridyl	H	Mn(II)	H <sub>2</sub> O	1	Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propenato]-manganese(II)-1-water	Mn[C <sub>22</sub> H <sub>18</sub> N <sub>8</sub> ]·H <sub>2</sub> O
1	2-Pyridyl	H	Cu(II)			Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propenato]-copper(II)	Cu[C <sub>22</sub> H <sub>18</sub> N <sub>8</sub> ]
5	2-Pyridyl	n-C <sub>4</sub> H <sub>9</sub>	Ni(II)			Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-heptenato]-nickel(II)	Ni[C <sub>30</sub> H <sub>34</sub> N <sub>8</sub> ]
7	2-Pyridyl	n-C <sub>6</sub> H <sub>13</sub>	Ni(II)			Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-nonenato]-nickel(II)	Ni[C <sub>34</sub> H <sub>42</sub> N <sub>8</sub> ]
7	2-Pyridyl	n-C <sub>6</sub> H <sub>13</sub>	Fe(II)			Bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-nonenato]-iron(II)	Fe[C <sub>34</sub> H <sub>44</sub> N <sub>8</sub> ]
8	6-Methyl-2-pyridyl	H	Fe(II)			Bis-[1-(2'-pyridyl)-3-(6"-methyl-2"-pyridyl)-1,2-diaza-2-propenato]-iron(II)	Fe[C <sub>24</sub> H <sub>22</sub> N <sub>8</sub> ]
8	6-Methyl-2-pyridyl	H	Ni(II)	H <sub>2</sub> O	0.5	Bis-[1-(2'-pyridyl)-3-(6"-methyl-2"-pyridyl)-1,2-diaza-2-propenato]-nickel(II)-0.5-water	Ni[C <sub>24</sub> H <sub>22</sub> N <sub>8</sub> ]·0.5H <sub>2</sub> O
8	6-Methyl-2-pyridyl	H	Zn(II)			Bis-[1-(2'-pyridyl)-3-(6"-methyl-2"-pyridyl)-1,2-diaza-2-propenato]-zinc(II)	Zn[C <sub>24</sub> H <sub>22</sub> N <sub>8</sub> ]
9	2-Quinolyl	H	Fe(II)			Bis-[1-(2'-pyridyl)-3-(2"-quinolyl)-1,2-diaza-2-propenato]-iron(II)	Fe[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]
9	2-Quinolyl	H	Ni(II)	H <sub>2</sub> O	0.5	Bis-[1-(2'-pyridyl)-3-(2"-quinolyl)-1,2-diaza-2-propenato]-nickel(II)-0.5-water	Ni[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]·0.5H <sub>2</sub> O
9	2-Quinolyl	H	Zn(II)	C <sub>6</sub> H <sub>6</sub>	0.5	Bis-[1-(2'-pyridyl)-3-(2"-quinolyl)-1,2-diaza-2-propenato]-zinc(II)-0.5-benzene	Zn[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]·0.5(C <sub>6</sub> H <sub>6</sub> )
10	8-Quinolyl	H	Fe(II)			Bis-[1-(2'-pyridyl)-3-(8"-quinolyl)-1,2-diaza-2-propenato]-iron(II)	Fe[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]
10	8-Quinolyl	H	Ni(II)	C <sub>6</sub> H <sub>6</sub>	1/3	Bis-[1-(2'-pyridyl)-3-(8"-quinolyl)-1,2-diaza-2-propenato]-nickel(II)-1/3-benzene	Ni[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]·1/3(C <sub>6</sub> H <sub>6</sub> )
10	8-Quinolyl	H	Zn(II)	C <sub>6</sub> H <sub>6</sub>	1/3	Bis-[1-(2'-pyridyl)-3-(8"-quinolyl)-1,2-diaza-2-propenato]-zinc(II)-1/3-benzene	Zn[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]·1/3(C <sub>6</sub> H <sub>6</sub> )
11	1-Isoquinolyl	H	Fe(II)	H <sub>2</sub> O	0.5	Bis-[1-(2'-pyridyl)-3-(1"-isoquinolyl)-1,2-diaza-2-propenato]-iron(II)-0.5-water	Fe[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]·0.5H <sub>2</sub> O
11	1-Isoquinolyl	H	Ni(II)	H <sub>2</sub> O	1	Bis-[1-(2'-pyridyl)-3-(1"-isoquinolyl)-1,2-diaza-2-propenato]-nickel(II)-1-water	Ni[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]·H <sub>2</sub> O
11	1-Isoquinolyl	H	Zn(II)			Bis-[1-(2'-pyridyl)-3-(1"-isoquinolyl)-1,2-diaza-2-propenato]-zinc(II)	Zn[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]
12	3-Isoquinolyl	H	Fe(II)	H <sub>2</sub> O	1	Bis-[1-(2'-pyridyl)-3-(3"-isoquinolyl)-1,2-diaza-2-propenato]-iron(II)-1-water	Fe[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]·H <sub>2</sub> O
12	3-Isoquinolyl	H	Ni(II)	H <sub>2</sub> O	1.5	Bis-[1-(2'-pyridyl)-3-(3"-isoquinolyl)-1,2-diaza-2-propenato]-nickel(II)-1.5-water	Ni[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]·1.5H <sub>2</sub> O
12	3-Isoquinolyl	H	Zn(II)	H <sub>2</sub> O	2	Bis-[1-(2'-pyridyl)-3-(3"-isoquinolyl)-1,2-diaza-2-propenato]-zinc(II)-2-water	Zn[C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> ]·2H <sub>2</sub> O

zinc(II) hemibenzene was sublimed to give the analytically pure red dichroic neutral complex without any benzene of crystallization.

In a third experiment bis[1-(2'-pyridyl)-3-(8"-quinolyl)-1,2-diaza-2-propenato]-iron(II) was sublimed, but in this instance some decomposition also occurred as the sublimate was not quite analytically pure.

The susceptibility of the complexes IV to proton attack with re-formation of the salts III makes it possible to transfer coordinated metal as neutral complex IV into water-immiscible solvents from aqueous solutions of the

salts III with alkali and then to recover it from the organic solvent into aqueous solution as salt III again with acid. This is a process of potential value for metal extractions and purification. Potentialities in analytical work are suggested by the observation that formation of a highly colored neutral [Zn(PAPY)<sub>2</sub>] complex serves to distinguish zinc from aluminum because the latter does not complex with PAPHY owing to its well known aversion to the formation of stable chelate compounds with chelating agents which can offer only nitrogen atoms as donors. The ability to transfer com-

M.p., °C.	Color	Solvent	Magnetic moment, B.M.	Con- ductivity, ohm <sup>-1</sup> cm. <sup>2</sup> at 25°	Calcd.				Found			
					C	H	N	M	C	H	N	M
>300	Dark green	A-B	1.9(18°)		56.4	4.3		11.9	56.2	4.1		12.1
>300	Red-green	F	2.9(20°)	0.1	55.0	4.4	23.3	12.2	54.8	4.4	22.8	11.3
141-145	Red	F-J			57.5	4.0	24.4	14.2	57.4	4.0	23.1	14.1
126-128	Red	F-J		.1	52.1	3.6	22.1	22.2	52.0	4.1	21.0	21.0
	Dark red	F-J			56.5	4.3	24.0	11.8	57.1	4.6	22.7	12.0
	Dark red- brown	F-J			57.7	4.0		13.9	58.2	4.4		13.6
249-250	Red-green	G		.3	63.7	6.1	19.8	10.4	63.6	6.2	19.7	10.5
192-193	Red-green	H		.3	65.7	6.8	18.0	9.5	65.4	7.2	18.4	9.1
185-186	Dark green	H		.3	66.0	6.8	18.1	9.0	65.7	6.9	18.2	9.2
	Green	A-B	0.9(24°)	.2	60.3	4.6	23.4	11.7	60.0	4.8	22.8	11.9
	Red	A-B		0	58.8	4.7	22.9	12.0	59.0	5.0	23.3	11.9
220-230	Orange	F-J		0.2	59.1	4.6		13.4	59.3	4.8		13.6
	Black	A-D	1.8(24°)	0	65.5	4.0	20.4	10.2	65.3	4.3	19.3	9.7
	Green	F-J		0.1	64.1	4.1	19.9	10.4	63.9	4.3	20.1	10.6
302-305	Red	F-J		0	66.2	4.2	18.7	10.9	66.3	4.4	18.1	11.2
	Dark green	F-J		0.3	65.5	4.0		10.2	65.4	4.4		10.3
	Dark green	F-J		.7	66.4	4.2		10.1	66.5	4.4		10.5
	Dark green	F-J		.2	66.2	4.2		11.2	65.7	4.7		10.8
	Green- black	A-B	1.5(24°)	.2	64.4	4.1		10.0	64.2	4.4		10.2
	Dark red	F-J		.8	63.1	4.2	19.6	10.3	62.9	4.4	20.2	10.3
280-282	Dark red	F-J		.1	64.4	4.0		11.7	64.0	4.2		11.7
	Black	F-J			63.4	4.3		9.8	63.9	4.5		10.0
	Orange-red	F-J		1.3	62.1	4.3		10.1	61.8	4.6		10.0
198-202	Orange- yellow	F-J		0.6	60.5	4.4	18.8	11.0	60.6	4.6	18.7	11.1

plexed metal atoms from aqueous media to lipid material or in the reverse direction according to hydrogen ion concentration also would appear to offer important possibilities for experimentation in biological systems.

### Discussion

In considering the nature of the deprotonated complexes IV, the following facts are pertinent. First, the positive charge located originally on the central metal ion of any complex cation tends to be dissipated over the

whole cation by withdrawal of negative charge from the periphery. There is a substantial body of evidence<sup>5</sup> to support this contention, commencing with the demonstration by Bjerrum in 1906 that aquated chromium-(III) ions can split off as protons peripheral hydrogen atoms (from the coordinated water molecules).<sup>6</sup> Attention also should be drawn to the complex compounds

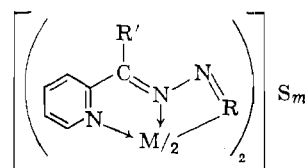
(5) For an account, see F. Basolo in J. C. Bailar, Jr., "Chemistry of the Coordination Compounds," Reinhold Publishing Corp., New York, N. Y., 1956, pp. 424-431.

(6) N. Bjerrum, *Kgl. Danske Videnskab. Selskabs Skrifter*, [7] 4, 1 (1906).



TABLE V

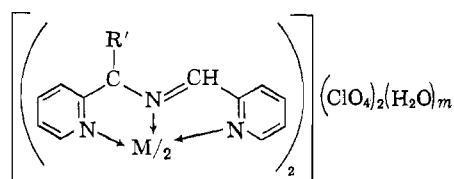
DEPROTONATED ("NEUTRAL") METAL COMPLEXES OF TYPE



Ligand	R	R'	Metal	S	m	Name	Formula
13	2-Pyrimidyl	H	Fe(II)	H <sub>2</sub> O	1.5	Bis-[1-(2'-pyrimidyl)-3-(2''-pyridyl)-1,2-diaza-2-propenato]-iron(II)-1.5 water	Fe[C <sub>20</sub> H <sub>16</sub> N <sub>10</sub> ] · 1.5H <sub>2</sub> O
14	3-Methyl-2-pyrazinyl	H	Fe(II)	H <sub>2</sub> O	0.5	Bis-[1-(3'-methyl-2'-pyrazinyl)-3-(2''-pyridyl)-1,2-diaza-2-propenato]-iron(II)-0.5-water	Fe[C <sub>22</sub> H <sub>20</sub> N <sub>10</sub> ] · 0.5H <sub>2</sub> O
14	3-Methyl-2-pyrazinyl	H	Ni(II)	C <sub>6</sub> H <sub>6</sub>	1	Bis-[1-(3'-methyl-2'-pyrazinyl)-3-(2''-pyridyl)-1,2-diaza-2-propenato]-nickel(II)-1-benzene	Ni[C <sub>22</sub> H <sub>20</sub> N <sub>10</sub> ] · C <sub>6</sub> H <sub>6</sub>

TABLE VI

COÖRDINATION COMPOUNDS OF TYPE

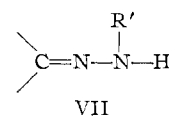


R	Metal	m	Name	Formula
CH <sub>3</sub>	Fe(II)	3	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-butene]-iron(II) perchlorate-3-water	Fe[C <sub>26</sub> H <sub>26</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> · 3H <sub>2</sub> O
CH <sub>3</sub>	Ni(II)	1	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-butene]-nickel(II) perchlorate-1-water	Ni[C <sub>26</sub> H <sub>26</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O
C <sub>2</sub> H <sub>5</sub>	Fe(II)	2	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-pentene]-iron(II) perchlorate-2-water	Fe[C <sub>28</sub> H <sub>30</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O
C <sub>2</sub> H <sub>5</sub>	Ni(II)	1	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-pentene]-nickel(II) perchlorate	Ni[C <sub>28</sub> H <sub>30</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
n-C <sub>3</sub> H <sub>7</sub>	Fe(II)	2	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-hexene]-iron(II) perchlorate-2-water	Fe[C <sub>30</sub> H <sub>34</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O
n-C <sub>3</sub> H <sub>7</sub>	Ni(II)	1	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-hexene]-nickel(II) perchlorate	Ni[C <sub>30</sub> H <sub>34</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
n-C <sub>4</sub> H <sub>9</sub>	Fe(II)	1	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-heptene]-iron(II) perchlorate-1-water	Fe[C <sub>32</sub> H <sub>38</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O
n-C <sub>4</sub> H <sub>9</sub>	Ni(II)	1	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-heptene]-nickel(II) perchlorate-1-water	Ni[C <sub>32</sub> H <sub>38</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O
n-C <sub>5</sub> H <sub>11</sub>	Fe(II)	3	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-octene]-iron(II) perchlorate-3-water	Fe[C <sub>34</sub> H <sub>42</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> · 3H <sub>2</sub> O
n-C <sub>5</sub> H <sub>11</sub>	Ni(II)	1	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-octene]-nickel(II) perchlorate	Ni[C <sub>34</sub> H <sub>42</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
n-C <sub>6</sub> H <sub>13</sub>	Fe(II)	1	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-nonene]-iron(II) perchlorate	Fe[C <sub>36</sub> H <sub>46</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
n-C <sub>6</sub> H <sub>13</sub>	Ni(II)	1	Bis-[1,3-di-(2'-pyridyl)-2-aza-1-nonene]-nickel(II) perchlorate	Ni[C <sub>36</sub> H <sub>46</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
C <sub>6</sub> H <sub>5</sub>	Ni(II)	2	Bis-[1,3-di-(2'-pyridyl)-3-phenyl-2-aza-1-propene]-nickel(II) perchlorate-2-water	Ni[C <sub>36</sub> H <sub>30</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> · 2H <sub>2</sub> O
C <sub>6</sub> H <sub>5</sub>	Zn(II)	1	Bis-[1,3-di-(2'-pyridyl)-3-phenyl-2-aza-1-propene]-zinc(II) perchlorate-1-water	Zn[C <sub>36</sub> H <sub>30</sub> N <sub>6</sub> ](ClO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O

derived from biguanides and guanlyureas and transition metal elements.<sup>7</sup>

If after coordination with a metal ion a chelate group still possesses peripheral hydrogen atoms so located that under favorable circumstances they can be caused to dissociate as protons, the higher the positive charge on the central metal atom the greater will be the tendency toward such dissociation. The nature of the atom of the ligand to which such a peripheral hydrogen atom is attached also is important. Suitably located multiple

bonds (electron sinks) in the ligand structure increase this tendency for hydrogen to ionize. Hydrazones of aldehydes and ketones already possess the partial structure VII.



This is of the X=Y-Z-H type, in which, no matter what the nature of the atoms X, Y, and Z, the hydrogen

(7) P. Ray, *Chem. Rev.*, **61**, 313 (1961).

M.p., °C.	Color	Solvent	Magnetic moment, B.M.	Con- ductivity, ohm <sup>-1</sup> cm. <sup>2</sup> at 25°	Calcd.				Found			
					C	H	N	M	C	H	N	M
	Purple	A-B			50.1	4.0			50.3	4.1		
	Dark red- green	A-B		0.3	54.0	4.3	28.6	11.4	53.8	4.6	28.1	11.1
	Green	F-J		0.6	59.9	4.7	25.0	10.5	59.7	5.0	25.4	10.2

M.p., °C.	Color	Solvent	Calcd.			Found						
			C	H	M	N	Cl	C	H	M	N	Cl
250	Purple	A-B	42.7	4.4	7.6			42.8	4.1	7.4		
300	Fawn	A-B	44.7	4.1	8.4			45.0	4.0	8.0		
208	Purple	A-B	45.4	4.6	7.5			45.8	4.5	7.6		
250	Fawn	A-B	47.5	4.3	8.3			47.0	4.3	8.3		
205	Purple	A-D	46.8	5.0	7.3			46.9	4.6	7.5		
295	Fawn	A-D	49.1	4.7	8.0			48.6	4.7	7.6		
205	Purple	A-D	49.3	5.2	7.2			49.5	5.0	6.8		
276	Fawn	A-D	49.2	5.2	7.5			49.3	5.1	7.6		
202	Purple	A-D	48.4	5.7	6.6			47.6	5.3	6.6		
258	Fawn	A-D	51.7	5.3	7.4			51.7	5.4	7.3		
195	Purple	A-D	52.9	5.7	6.8			52.2	5.5	7.0		
254	Fawn	A-D	52.7	5.6	7.2			52.7	5.6	7.5		
273-278	Pale green	A-B	51.5	4.1	7.0	10.0	8.4	51.5	4.4	7.1	10.0	8.4
258-263	White	A-B	52.2	3.9	7.9	10.1	8.6	52.3	4.3	7.8	9.7	8.4

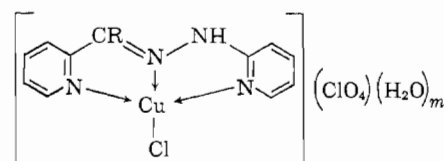
always *tends* to be acidic. If the substituent R' group is also electron-withdrawing, the ability of the hydrazone to function as an acid can be quite marked. Thus, the 2,4-dinitrophenylhydrazones of aldehydes and ketones can be titrated as acids with alkalis, and analytical methods are based upon this fact.<sup>8</sup>

In the bases I, the R' group of the partial formula VII is  $\alpha$ -pyridyl, which can be considered only mildly electron-withdrawing, so that these bases function only as

weak acids. However, when a molecule of any of the bases I becomes coordinated with a metal ion, this tendency for electrons to be withdrawn from the >N-H bond becomes markedly enhanced. Because the structures of the bases I are such that a new stable resonating system of aromatic type can be formed by detachment of a proton from this imino group after coordination and then redistribution of the electron pair previously shared by it, proton removal with alkali becomes relatively easy. Formula IV is a representation of one canonical form only of such aromatic systems.

(8) A. J. Sensabough, R. H. Cundiff, and P. C. Markunas, *Anal. Chem.*, **30**, 1445 (1958).

TABLE VII  
COPPER(II) COÖRDINATION COMPLEXES OF TYPE



Ligand	R	m	Name	Formula	M.p., °C.	Calcd.		Found	
						C	H	C	H
2	CH <sub>3</sub>		[Chloro-1,3-di-(2'-pyridyl)-1,2-diaza-2-butene]-copper(II) perchlorate	Cu[Cl(C <sub>12</sub> H <sub>12</sub> N <sub>4</sub> )]ClO <sub>4</sub>	265 dec.	35.1	3.0	35.8	3.1
3	C <sub>2</sub> H <sub>5</sub>		[Chloro-1,3-di-(2'-pyridyl)-1,2-diaza-2-pentene]-copper(II) perchlorate	Cu[Cl(C <sub>13</sub> H <sub>14</sub> N <sub>4</sub> )]ClO <sub>4</sub>	265 dec.	36.8	3.3	37.1	3.3
4	n-C <sub>3</sub> H <sub>7</sub>		[Chloro-1,3-di-(2'-pyridyl)-1,2-diaza-2-hexene]-copper(II) perchlorate	Cu[Cl(C <sub>14</sub> H <sub>16</sub> N <sub>4</sub> )]ClO <sub>4</sub>	272 dec.	38.3	3.7	38.7	3.7
5	n-C <sub>4</sub> H <sub>9</sub>		[Chloro-1,3-di-(2'-pyridyl)-1,2-diaza-2-heptene]-copper(II) perchlorate	Cu[Cl(C <sub>15</sub> H <sub>18</sub> N <sub>4</sub> )]ClO <sub>4</sub>	249 dec.	40.2	4.1	39.8	4.0
6	n-C <sub>5</sub> H <sub>11</sub>		[Chloro-1,3-di-(2'-pyridyl)-1,2-diaza-2-octene]-copper(II) perchlorate	Cu[Cl(C <sub>16</sub> H <sub>20</sub> N <sub>4</sub> )]ClO <sub>4</sub>	252 dec.	41.2	4.3	41.1	4.3
7	n-C <sub>6</sub> H <sub>13</sub>	1	[Chloro-1,3-di-(2'-pyridyl)-1,2-diaza-2-nonene]-copper(II) perchlorate	Cu[Cl(C <sub>17</sub> H <sub>22</sub> N <sub>4</sub> )]ClO <sub>4</sub> ·H <sub>2</sub> O	245 dec.	40.9	4.9	40.9	4.8

Evidence bearing on this potential acidity of the hydrogen atom marked with an asterisk in I is to be found in the capacity of alcoholic solutions of PAPHY to dissolve metal powders, such as zinc, iron, and nickel powders, to give alcoholic solutions of the intensely colored complexes IV. Hydrogen does not appear to be released during the solution process and apparently is used up in the reduction of some PAPHY in solution. Nevertheless, the method, with zinc, for example, is preparative.

That this same proximal nitrogen atom of the hydrazine residue is, however, the site for attack by electrophilic reagents is shown by the experimental fact that heating of a dry xylene solution of the neutral complex bis-[1-(2'-pyridyl)-3-(8''-quinolyl)-1,2-diaza-2-propenato]-nickel(II) (1 mole) (chosen for the experiment because it is anhydrous) with dimethyl sulfate (2 moles) for a few minutes leads to loss of the intense color and formation of a yellow-brown salt from which analytically pure bis-[1-(2'-pyridyl)-3-(8''-quinolyl)-1-methyl-1,2-diaza-2-propene]-nickel(II) perchlorate-1-water can be prepared. This latter salt does not undergo the typical intense color change associated with deprotonation when treated in solution with alkalis. Its infrared spectrum shows stretching absorptions at 2720 and 2660 cm.<sup>-1</sup> which are characteristic of >N-CH<sub>3</sub> groups.

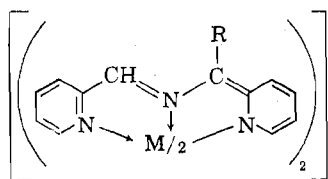
It is important to note that the deprotonated complexes IV contain *two* flat resonating systems at right angles to each other and linked by one common atom—the metal atom. Because the PAPHY residues are dissymmetrical, both the molecules of these complexes and the cations of the complex salts III must exist in enantiomorphous forms. Similar systems are known in which *two* flat aromatic-type rings are held at right angles through a common metal atom ring member; for example, the chelate compounds derived from β-diketones and bivalent 4-coördinate metals, such as zinc or beryllium, which dispose their covalences tetrahedrally, and the dipyrromethene derivatives of the same metals.

Analogies can be drawn between the coördination

compounds derived from the bases I on the one hand and those derived from the dipyrromethenes and the porphyrin type compounds on the other. However, dissociation of hydrogen from nitrogen must *precede* coördination of the latter as the protons come from nitrogen atoms which then become donors. With coordination compounds derived from the bases I, eventual detachment of protons occurs from nitrogen atoms which are on the periphery of the complex ion and these protons can be detached and reattached without rupture of the nitrogen-metal bonds which hold the complex ion together.

We also have coördinated the series of bases II (R = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, up to n-C<sub>6</sub>H<sub>13</sub>) with the salts of some transition metals (Table VI) and have studied the effect of increase of pH on solutions of the derived complex salts. Color changes strongly indicate that deprotonation of the complex ions does occur as the pH of the solution is increased. Thus, addition of a solution of II (R = H) in ethanol to ethanolic solutions of the perchlorates of iron(II), cobalt(II), nickel(II), and zinc(II) led to separation of solid complex perchlorates which were colored, respectively, dark green, brown, orange, and yellowish orange. Addition of ethanolic sodium ethoxide to each of these slurries led, in each instance, to re-solution of the separated solid and change of color to intense dark brown, reddish purple, clear red, and orange-red, respectively. Addition of benzene and then shaking out with water showed that the color-responsible substances were benzene-soluble. However, the complex cobalt compound decomposed very rapidly indeed, and gradual loss of color indicated breakdown of the others. Formation of the complex salts in aqueous solution and then treatment with aqueous alkali led again to intense color production which, however, faded rapidly. Because of the instability of the derived "neutral" complexes, we have not isolated any in the pure state. However, they can be formulated as resonating complexes VIII constituted analogously to IV

We then synthesized 1-phenyl-1,3-bis-(2'-pyridyl)-2-aza-1-propene (II: R = C<sub>6</sub>H<sub>5</sub>) and have studied its co-



VIII

ordination with some transition metal salts. Contrary to the statement of Boyer and Wolford,<sup>9</sup> we have found it readily possible to reduce the oximes of 2-benzoylpyridine with zinc dust and ethanolic acetic acid to *dl*-phenyl- $\alpha$ -pyridylmethylamine. The derived Schiff's base II ( $R = C_6H_5$ ) readily coordinates with nickel(II), iron(II), and zinc(II) salts to give stable complex salts (Table VI). Treatment of these in solution with alkali leads to deprotonation of the complex cations and intensely colored neutral complexes are formed. However, although these can be separated and even recrystallized, it has not so far proved possible to obtain them in analytically pure form.

It should finally be pointed out that it is readily possible to devise other organic chelating agents capable of coordination with transition metal salts to give complex salts the complex ions of which can be deprotonated to stable "neutral" complexes. We already have reported one such complex.<sup>10</sup>

### Experimental

Melting points are uncorrected. Magnetic moments were measured on a Gouy balance at room temperature. Starting materials were either purchased and purified or synthesized. Isoquinoline-1-aldehyde and isoquinoline-3-aldehyde were made by selenium dioxide oxidation of the corresponding methyl isoquinolines.<sup>11</sup> Quinoline-8-aldehyde was obtained by a similar oxidation of 8-methylquinoline.<sup>12</sup> 2-Pyridylhydrazine was obtained by interaction of 2-bromopyridine and hydrazine hydrate according to the method of Fargher and Furness.<sup>13</sup> It was purified by distillation *in vacuo* and kept in sealed ampoules in the dark. 2-Pyrimidylhydrazine was prepared from 2-aminopyrimidine by first converting it to 2-chloropyrimidine<sup>14</sup> and then causing this to react with hydrazine hydrate according to the method of Shirokawa, Bau, and Yoneda.<sup>15</sup>

**3-Methyl-2-pyrazinyl-hydrazine.**—2-Chloro-3-methyl-pyrazine (40 g.) and hydrazine hydrate (150 ml. of 100%) were heated together under reflux until the mixture had become homogeneous. Its color was then dark brown. It was cooled and the solid which separated was collected (19 g.; 50% of theory) and recrystallized from benzene. It formed yellow plates, m.p. 142–144°.

*Anal.* Calcd. for  $C_5H_8N_4$ : C, 48.4; H, 6.5; N, 45.1. Found: C, 48.6; H, 6.5; N, 45.0.

$R''$

**Ligands of the Type  $R'-C=N-NH-R''$ .**—The general method of formation of these hydrazones was to heat together

in fairly concentrated ethanolic solution stoichiometrical proportions of the carbonyl compound and the hydrazine. After about 5 min. under reflux, the solution was cooled and usually water was added. If the hydrazone crystallized it was collected and recrystallized from a suitable solvent. Uncrystallizable oils were converted to the bis-picrates for analysis. Table I contains the relevant data.

**Solvents** used for recrystallization are indicated in the Tables by code letters as: A, water; B, ethanol; C, acetone; D, dimethylformamide; E, ethyl acetate; F, benzene; G, cyclohexane; H, *n*-hexane; J, petroleum ether. Use of mixed solvents is indicated by the use of both code letters, e.g., A-B indicates aqueous ethanol; F-J indicates use of a benzene-petroleum ether mixture.

**Preparation of Complex Perchlorates.**—The general method evolved was to mix hot solutions in ethanol of the previously prepared metal perchlorate hydrate and of the ligand in stoichiometrical proportions and then allow to cool. Usually the complex salt crystallized out, was collected, and recrystallized from ethanol, aqueous ethanol, or water. Tables II, III, and IIIa list the diazapropene complex salts prepared in this way, while Table VI lists the azapropene complex perchlorates.

**Distribution Coefficients.**—Distribution of the complex iron(II) perchlorates derived from the ligands 2–7 (see Table I) between water and cyclohexanone was studied as follows. A color intensity-molar concentration curve was derived for each of the six complex iron(II) perchlorates in slightly acid water (pH 6.5) and in cyclohexanone at 25°. The colorimeter was a Hilger "Spekker" with a Spectrum Green 604 filter protected by a heat filter H 503 ( $\lambda_{max}$  518 m $\mu$ ). The aqueous solutions were found to obey Beer's law. However, the cyclohexanone solutions deviated slightly at higher concentrations. A weighed sample (a few milligrams) of the iron(II) complex being studied then was distributed between water (10 ml.) and cyclohexanone (10 ml.) by shaking together at 25°. The two phases were separated and the concentration of solute in the aqueous phase determined using the colorimeter and the calibration curve. The distribution coefficients were determined as the ratio: molar concentration in water/molar concentration in cyclohexanone. These values for the various ligands (number of ligand given first) were found as: 2, 0.72; 3, 0.64; 4, 0.42; 5, 0.09; 6, 0.00; 7, 0.00.

**Deprotonation of Complex Salts to "Neutral" Complexes.**—Usually the salt was dissolved in water or aqueous alcohol and then 10% sodium hydroxide solution was dropped into the stirred solution. If no precipitate formed at once, dilution with water usually caused one to separate. The neutral complexes from ligand no. 13 were notable exceptions, being very soluble in water. Their isolation necessitated the use of very concentrated solutions. Usually, after precipitation the complex was collected, washed with a small amount of water, and recrystallized to purity from a suitable solvent (indicated in Tables IV and V).

**Bis[1,3-di-(2'-pyridyl)-1,2-diaza-2-propenato]-cobalt(III) Perchlorate-0.5-Water.**—A solution of PAPHY (0.4 g.) in aqueous perchloric acid (1.1 g of 36%) was added to a hot suspension of sodium triscarbonatocobaltate(III)-3-water<sup>16</sup> (0.36 g.). A vigorous evolution of carbon dioxide occurred and a red solution was formed. On cooling a green solid separated. It was collected and recrystallized from aqueous ethanol and obtained in diamagnetic green plates with a metallic luster.

*Anal.* Calcd. for  $Co[C_{22}H_{18}N_8](ClO_4) \cdot 0.5H_2O$ : C, 47.0; H, 3.4; N, 20.0; Cl, 6.3; Co, 10.5. Found: C, 47.1; H, 3.3; N, 19.5; Cl, 6.5; Co, 10.5.

**Sublimation of "Neutral" Complexes.**—The sample (10–15 mg.) was heated in a highly evacuated cold-finger apparatus in a metal bath, the temperature being gradually raised to, and held at, about 300° for some hours. Thus, bis-[1,3-di-(2'-pyridyl)-1,2-diaza-2-propenato]-nickel(II)-1.5-water yielded the anhydrous neutral complex.

(9) J. H. Boyer and L. J. Wolford, *J. Org. Chem.*, **23**, 1053 (1958).

(10) J. F. Geldard and F. Lions, *J. Am. Chem. Soc.*, **84**, 2262 (1962)\*

(11) Cf. R. S. Barrows and H. G. Lindwall, *ibid.*, **64**, 2430 (1942); C. E. Teague and A. Roe, *ibid.*, **73**, 688 (1951).

(12) V. M. Rodionov and M. A. Berkengeim, *J. Gen. Chem. USSR*, **14**, 330 (1944) [*Chem. Abstr.*, **39**, 4076 (1945)].

(13) R. G. Fargher and R. Furness, *J. Chem. Soc.*, **107**, 691 (1915).

(14) N. Sperber, D. Papa, E. Schwenk, M. Sherlock, and R. Fricano, *J. Am. Chem. Soc.*, **73**, 5755 (1951).

(15) K. Shirokawa, S. Bau, and M. Yoneda, *J. Pharm. Soc. Japan*, **73**, 598 (1953) [*Chem. Abstr.*, **48**, 9362 (1954)].

(16) Cf. H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

*Anal.* Calcd. for  $\text{Ni}[\text{C}_{22}\text{H}_{18}\text{N}_8]$ : C, 58.3; H, 4.0; N, 24.7. Found: C, 58.3; H, 4.4; N, 24.1.

Similarly, bis-[1-(2'-pyridyl)-3-(2''-quinolyl)-1,2-diaza-2-propenato]-zinc(II)-0.5-benzene gave the solvent-free complex.

*Anal.* Calcd. for  $\text{Zn}[\text{C}_{30}\text{H}_{22}\text{N}_8]$ : C, 64.4; H, 4.0. Found: C, 64.2; H, 4.3.

**Bis-[2-(2'-pyridyl)-4-(8''-quinolyl)-2,3-diaza-3-butene]-nickel(II) Perchlorate-1-Water.**—To a hot solution in dry xylene of bis-[1-(2'-pyridyl)-3-(8''-quinolyl)-1,2-diaza-2-propenato]-nickel(II)- $1\frac{1}{3}$ -benzene was added a slight excess of freshly distilled methyl sulfate. The intense color soon faded and a yellow solid was precipitated. This was collected, washed well with dry ether, and then dissolved in hot aqueous ethanol. Addition of sodium perchlorate in excess led to precipitation of a yellow solid which was recrystallized from aqueous ethanol.

*Anal.* Calcd. for  $\text{Ni}[\text{C}_{22}\text{H}_{18}\text{N}_8](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ : C, 48.0; H, 3.8; N, 14.0; Cl, 8.9. Found: C, 47.9; H, 4.0; N, 13.8; Cl, 8.8.

R''

**Ligands of the Type R'-CH=N-CH-R''' (II).**—The 2-acylpyridines required as starting materials were synthesized by the action of the appropriate Grignard reagents (2 moles) on pure 2-cyanopyridine according to the method of Craig.<sup>17</sup> 2-Pyridyl *n*-amyl ketone (yield 81%, b.p. 134° (12 mm.); 2,4-dinitrophenylhydrazone, m.p. 124°; *Anal.* Calcd. for  $\text{C}_{17}\text{H}_{19}\text{N}_5\text{O}_4$ : C, 57.1; H, 5.4. Found: C, 57.1; H, 5.4) appears to be new. The ketones were converted to their oximes by warming in aqueous ethanol solution with hydroxylamine hydrochloride and sodium carbonate. Each oxime then was reduced in hot ethanol solution by adding glacial acetic acid and then stirring in zinc dust according to the method of Craig and Hixon.<sup>18</sup> The 2-( $\alpha$ -aminoalkyl) pyridines eventually were recovered as colorless oils by distillation under vacuum. They had characteristic amine-like odors. 1-Amino-1-(2'-pyridyl) ethane, b.p. 100–104° (18 mm.), and 1-amino-1-(2'-pyridyl) propane, b.p. 69° (1 mm.), already have been described by Bower and Ramage.<sup>19</sup>

**1-Amino-1-(2'-pyridyl)-butane** (b.p. 129–132° (22 mm.), bis-picrate m.p. 202–205°; *Anal.* Calcd. for  $\text{C}_{21}\text{H}_{20}\text{N}_8\text{O}_{14}$ : C, 41.5; H, 3.3. Found: C, 41.5; H, 3.6); **1-amino-1-(2'-pyridyl)-pentane** (b.p. 97–100° (1 mm.), bis-picrate, m.p. 193°;

(17) L. C. Craig, *J. Am. Chem. Soc.*, **56**, 1144 (1934).

(18) L. C. Craig and R. M. Hixon, *ibid.*, **53**, 4387 (1931).

(19) J. D. Bower and J. R. Ramage, *J. Chem. Soc.*, 2834 (1955).

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{22}\text{N}_8\text{O}_{14}$ : C, 42.5; H, 3.6. Found: C, 42.4; H, 3.7); **1-amino-1-(2'-pyridyl)-hexane** (b.p. 110° (1.5 mm.), oily bis-picrate); and **1-amino-1-(2'-pyridyl)-heptane** (b.p. 118° (1 mm.) oily bis-picrate) appear to be new.

Each of these primary amines was caused to react in hot ethanol with one molecular proportion of pyridine-2-aldehyde, heat being evolved. The resultant Schiff's bases were pale yellow oils which were not further purified but used in the crude condition for coordination with metal perchlorates. Details concerning the complex perchlorates prepared are set out in Table VI.

**1,3-Di-(2'-pyridyl)-3-phenyl-2-aza-1-propene (II; R = C<sub>6</sub>H<sub>5</sub>).**—*dl*-Phenyl-(2-pyridyl)-methylamine, b.p. 118–120° (0.6 mm.), was prepared by the Craig and Hixon method<sup>18</sup> in 75% yield. Its picrate formed yellow needles, m.p. 198–200° (lit.<sup>9</sup> 181°) (*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{15}\text{N}_5\text{O}_7$ : C, 52.3; H, 3.7; N, 16.9. Found: C, 52.3; H, 3.6; N, 17.0). The **5-bromosalicylidene derivative**, pale yellow prisms from 95% ethanol, had m.p. 132–135° (*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{15}\text{ON}_2\text{Br}$ : C, 62.1; H, 4.1; N, 7.6. Found: C, 61.7; H, 4.1; N, 7.8). Admixture of ethanol solutions of the base (1 mole) and pyridine-2-aldehyde (1 mole) led to evolution of heat and development of a yellow color. The solution was boiled for 1 min., cooled, and allowed to stand. The solid which separated was taken up in *n*-hexane and the solution chilled to –40°. White needles, m.p. 80–81°, separated and were collected.

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{15}\text{N}_3$ : C, 79.1; H, 5.5; N, 15.4. Found: C, 79.0; H, 5.7; N, 15.0.

**Copper(II) Coordination Complexes of Type V.**—Hot ethanolic solutions of copper(II) chloride (1 mole) and the ligand (2, 3, 4, 5, 6, or 7; 1 mole) were mixed and sodium perchlorate in slight excess was added to the hot solution, which then was allowed to cool. The green complex salt which crystallized was collected and recrystallized from hot water. The melting points recorded in Table VII are virtually decomposition points.

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## The Donor Properties of 2,2'-Bipyridine N,N'-Dioxide

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A number of coordination compounds of 2,2'-bipyridine N,N'-dioxide (bipyO<sub>2</sub>) with metal salts have been prepared, and their structure determined by analysis, conductivity, and magnetic susceptibility measurements. The compounds were found to be electrolytes, containing the following complex cations:  $[\text{M}(\text{bipyO}_2)_3]^{n+}$  (M = Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>),  $[\text{Cr}(\text{bipyO}_2)_2\text{Cl}_2]^+$ , and  $[\text{Cu}(\text{bipyO}_2)_2]^{2+}$ , and the anions ClO<sub>4</sub><sup>–</sup> and PtCl<sub>4</sub><sup>–2</sup>.

### Introduction

Pyridine N-oxide is known to form coordination compounds with many metal ions and their preparation, properties, and infrared spectra have been reported recently.<sup>1,2</sup> The present paper reports the results of a similar study on the compounds of 2,2'-bipyridine

N,N'-dioxide (bipyO<sub>2</sub>) with some metals of the first transition series, namely, Cr(III), Mn(II), Fe(III), Co(II), and Ni(II), as well as with Cu(II), Zn(II),

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(2) S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, in press; Y. Kakiuti, S. Kida, and J. V. Quagliano, *ibid.*, in press.