Contribution from the Department of Chemistry,
University of Queensland, St. Lucia, Qld., 4067, Australia

Deprotonation of Metal Complexes Derived from Ligands Containing Pyrrole, Pyrazole and Indene Residues

B. Chiswell

Received March 21, 1972

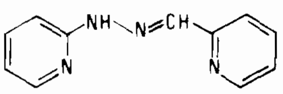
The synthesis of several new planar nitrogenous tridentate ligands, specially designed to present their donor atoms at positions very close to the normal octahedral sites of a metal atom, are described. Each of these ligand moieties, when complexed to a metal atom, also possess the potential ability to lose a proton from the periphery of the ligand molecue to yield deprotonated non-charged metal complexes.

The lack of change in colour and magnetic moment of complexes of these ligands, upon undergoing such deprotonation reactions, is compared with the marked increase in colour intensity and decrease in magnetic moment when charged complexes containing a 2-pyridylhydrazine entity in the ligand residue undergo similar deprotonation reactions.

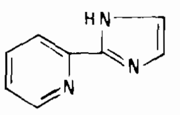
Earlier papers[1] in this series have concentrated upon the deprotonation reactions of metal complexes by the removal of the imino-hydrogen from a 2-pyridylhydrazine moiety incorporated in the ligand structure, *e.g.* the deprotonation reaction of the type:

$$[M(PAPHY)_2]^{2+} + 2OH^- \rightarrow [M(PAPY)_2] + 2H_2O$$

(where M = a divalent metal atom; PAPHY (A) and PAPY are the protonated and deprotonated forms respectively of 1,3-di(2′-pyridyl)-1,2-diazaprop-2-ene)



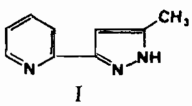
A



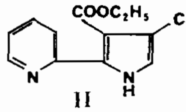
B

Complex compounds containing the deprotonated 2-pyridylhydrazine residue have been shown to be highly coloured, and in many cases to possess anomolously low magnetic moments. On the other hand, the deprotonated complexes of 2-pyridylimidazole (B) have been shown not to be highly coloured or to exhibit unusual magnetic properties.

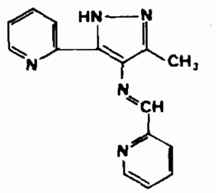
As in the complexes of the ligands derived from 2-pyridylhydrazine, the proton is removed from the chelate ring, whereas in the complexes of B the proton comes off at the periphery of the ligand structure, it was thought that the difference in colour and magnetic changes upon deprotonation may well be attributable to the different position of proton removal. It was therefore resolved to prepare a series of ligands possessing an imidazole (or similarly deprotonatable) ring system, and to study the complexes of such ligands with particular reference to their ability to be deprotonated.



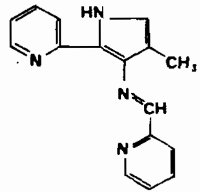
I



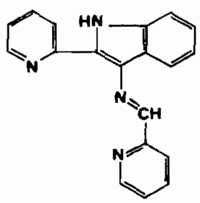
II



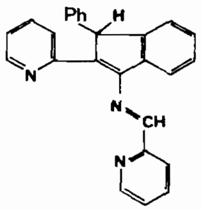
III



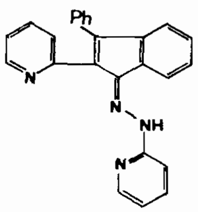
IV



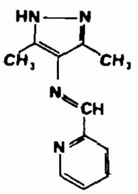
V



VI



VII



VIII

Some five new tridentate ligands (III-VII) are to be discussed in this work, while two bidentates (I and II), which are not essentially new ligands, will be briefly mentioned to correlate this work with the previous results presented for the 2-(2′-pyridyl)-imidazoles.[2] A further new bidentate (VIII) will also

---

[1] B. Chiswell and F. Lions, *Aust. J. Chem.*, 22, 71 (1969); references therein.

[2] B. Chiswell, F. Lions, and B.S. Morris, *Inorg. Chem.*, 3, 110 (1964).

Table I. Physical Properties of Complexes of Ligands I and II.

Formula	Colour		Analysis				Λ_M [b]	Magnetic	Method of
			%C	%H	%N	%M	(r.o.)	Moment [c]	Preparation [d]
$[Cu(HligI)_2](ClO_4)_2$ [a]	green	Calc.	37.1	3.1	14.4	10.9	55.4	1.9/293°	A, e-w
		Found	37.0	3.0	14.0	11.3			
$[Cu(ligI)_2]$	pale green	Calc.	56.8	4.2	33.2	16.7	non-elect.	1.9/293°	K, e-w
		Found	56.8	3.9	32.7	16.5			
$[Cu(ligII)_2]$	green	Calc.	59.5	5.3	8.0	12.1	non-elect.	1.9/294°	J, e-w
		Found	59.3	5.3	7.4	12.3			
$[Fe(HligI)_3](ClO_4)_2$	brown	Calc.	44.2	3.7	17.2	7.6	non-elect.	5.4/294°	C, e-w
		Found	44.0	3.6	16.5	7.9			
$[Fe(ligI)_2]$	brown	Calc.	50.6	5.2	—	13.1	non-elect.	5.3/294°	K, e-w
		Found	50.9	5.5	—	13.0			
$[FeligII)_2] . 3H_2O$	brown	Calc.	54.7	6.0	—	9.8	56.3	5.4/295°	G, e-w
		Found	54.7	6.1	—	9.5			

[a] Hlig represents the protonated form of the ligand; lig represents the deprotonated form. [b] Molar conductivity in nitrobenzene at molar strength of approx. $10^{-3}M$. [c] Expressed in Bohr Magnetons at the temperature shown. [d] See experimental section for code used.

be noted. The eight ligands are:

(i) 5-methyl-3-(2′pyridyl)-pyrazole (I);

(ii) 3-carbethoxy-4-methyl-2-(2′-pyridyl)-pyrrole (II);

(iii) 3-methyl-4-(2′-pyridylmethyleneamino)-5-(2″-pyridyl)-pyrazole (III);

(iv) 3-methyl-4-(2′-pyridylmethyleneamino)-5-(2″-pyridyl)pyrrole (IV);

(v) 3-(2′-pyridylmethyleneamino)-2-(2″-pyridyl)indole (V);

(vi) 1-phenyl-2-(2′-pyridyl)-3-(2″-pyridylmethyleneamino)-indene (VI);

(vii) 1-phenyl-2-(2′-pyridyl)-3-(2″-pyridylhydrazinyl)-indene (VII);

(viii) 2,4-dimethyl-3-(2′-pyridylmethyleneamino)-pyrazole (VIII).

It will be noted that, apart from II, the first six of these ligands could be expected to form neutral complexes by the loss of a peripheral carbon or imino-proton. VI is an attempt to prepare a tridentate nitrogenous ligand that will give complexes with a deprotonable peripheral carbon atom, while VII is a variation of VI containing a 2-pyridylhydrazine residue. This latter tridentate will give deprotonatable complexes in which the proton is lost from the imino-nitrogen in a chelate ring. It is of interest to compare the deprotonated compounds from VII with those from the other tridentate ligands.

All five tridentate ligands have a five- and a six-membered chelate ring. The latter ring in each case is constructed by the use of the edge of a further five-membered ring. This type of ligand structure places the donor bonds of the nitrogen atoms of the six-membered chelate ring almost at right angles. The suitability of this system can be seen by the comparison of the molecular models of III and 2,6-di-(2′-pyridyl)-pyridine (terpyridine).

Both 2-(2′pyridyl)-pyrrole and 3-(2′-pyridyl-pyrazole have been known for some time. As early as 1923 Tschitschibabin and Bylinkin[3] reported the preparation of the former compound and noted that it gave a platinum(II) complex, while Emmert and Brandl[4] have prepared the inner complexes of copper(II), zinc(II), iron(III) and cobalt(III) with the pyrrole. Gough and King[5] have reported the isolation of the 5-methyl derivative of the pyrazole.

The 2-(2′-pyridyl)-pyrroles tend to form inner complexes upon interaction with transition metal ions, losing the imino-proton during complex formation. Upon the other hand the 3-(2′-pyridyl)-pyrazoles can form normal chelate complexes in which the non-bonding nitrogen atom of the pyrazole ring retains the proton. Such complexes are readily deprotonated by removal of this proton in alkaline solution. The compounds from ligands I and II are in Table I.

It can be seen that the neutral complexes have normal magnetic moments and do not possess intense colours. These compounds are very similar to the corresponding compounds from the 2-(2′-pyridyl)-imidazoles.[2]

The compounds obtained from the tridentate ligand III have been studied in slightly more detail than have those from the two similar ligands IV and V. Thus they are listed separately in Table II, while those from the latter two ligands are presented together in Table III.

It will be noted that none of the deprotonated complexes of these three ligands have anomalous magnetic moments. The small magnetic moments of the spin-paired, theoretically diamagnetic iron(II) complexes , is typical of such compounds.* Except in the case of the iron(II) complex of III which is deep blue when protonated and green when deprotonated, there appears to be no marked changes in colour intensities upon deprotonation of the peripheral imino-nitrogen atoms. However, this feature requires further study of absorption spectra.

The bidentate ligand VIII, which can be seen to be similar to III but with a co-ordinating pyridine ring replaced by a methyl group, was prepared for the purposes of comparison with this latter ligand. If

---

(3) A.E. Tschitschibabin and J.G. Bylinkin, *Chem. Berichte*, *56B*, 1745 (1923).

* Compare $Fe(terpyridine)_2(ClO_4)_2 . 2H_2O$; μ = 1.33 E.M./294°[6]

(4) B. Emmert and F. Brandl, *Chem. Berichte*, *60*, 2211 (1927).

(5) G.A.C. Gough and H. King, *J. Chem. Soc.*, 350 (1933).

(6) T.N. Lockyer, Thesis, Univ. of N.S.W., Sydney, 1962.

Table II. Physical Properties of Complexes of Ligand III *.

Formula	Colour		Analysis %C	%H	%N	%M	Λ_M [b]	Magnetic Moment [c]	Method of Preparation [d]
Fe(HligIII)$_2$(ClO$_4$)$_2$ [a]	deep blue	Calc.	46.0	3.3	17.9	7.1	56.4	0.7/297°	A, e-w
		Found	46.1	3.0	17.0	7.0			
Fe(ligIII)$_2$. 2H$_2$O	green	Calc.	58.1	4.8	22.6	9.0	non-elect	0.8/297°	K, e-w
		Found	58.0	4.7	21.8	9.1			
Co(HligIII)$_2$(ClO$_4$)$_2$	brown	Calc.	45.8	3.3	17.8	7.5	53.2	4.9/299°	A, e-w
		Found	45.8	3.2	17.2	7.3			
Co(ligIII)$_2$. 3H$_2$O	brown	Calc.	56.5	4.7	—	9.2	non-elect	4.9/299°	K, e-w
		Found	56.3	5.0	—	9.2			
Ni(HligIII)$_2$(ClO$_4$)$_2$	mauve	Calc.	45.8	3.3	—	7.5	54.6	3.1/298°	A, e-w
		Found	45.5	3.3	—	7.6			
Ni(ligIII)$_2$. 2H$_2$O	brown	Calc.	58.1	4.5	22.6	9.5	non-elect	3.0/297°	K, e-w
		Found	58.3	4.5	22.0	9.2			
Cu(HligIII)(ClO$_4$)$_2$. 2H$_2$O	green	Calc.	31.9	3.0	—	11.3	54.9	—	A, e-w
		Found	31.7	3.1	—	11.0			
Cu(ligIII)OH	pale green	Calc.	52.5	3.8	—	18.5	non-elect	—	K, e-w
		Found	52.7	3.9	—	18.2			

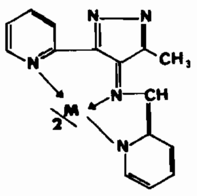
* For notec [a], [b], [c] and [d] see footnote to table I.

Table III. Physical Properties of Complexes of Ligands IV and V.*

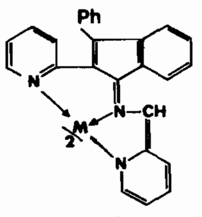
Formula	Colour		Analysis %C	%H	%N	%M	Λ_M [b] (r.o.)	Magnetic Moment [c]	Method of Preparation [d]
Fe(HligIV)$_2$(ClO$_4$)$_2$ [a]	brown	Calc.	49.2	3.6	—	7.1	57.6	0.8/297°	A, e-w
		Found	49.1	3.5	—	6.8			
Fe(ligIV)$_2$. H$_2$O	pale-brown	Calc.	64.4	4.7	—	9.4	non-elect	0.8/297°	A, e-w
		Found	64.6	4.8	—	9.6			
Fe(HligV)$_2$(ClO$_4$)$_2$	reddish brown	Calc.	53.4	3.3	13.2	6.6	non-elect	0.9/298°	A, e-w
		Found	53.5	3.6	12.6	6.8			
Fe(ligV)$_2$. H$_2$O	pale-brown	Calc.	68.2	4.2	16.7	8.3	non-elect	0.9/298°	A, e-w
		Found	68.0	4.3	16.0	8.0			
Ni(HligIV)$_2$(ClO$_4$)$_2$	mauve	Calc.	49.0	3.6	14.3	7.5	non-elect	2.9/300°	A, e-w
		Found	49.2	3.8	13.8	7.2			
Ni(ligIV)$_2$	brown	Calc.	66.1	4.5	19.3	10.1	58.7	3.0/300°	K, e-w
		Found	66.4	4.3	18.9	9.7			
Ni(HligV)$_2$(ClO$_4$)$_2$	mauve	Calc.	53.3	3.3	—	6.9	55.7	3.1/295°	K, e-w
		Found	53.2	3.0	—	6.8			
Ni(ligV)$_2$	brown	Calc.	69.8	4.0	—	9.0	—	3.0/294°	K, e-w
		Found	69.7	4.4	—	9.2			
Cu(HligIV)(H$_2$O)$_2$(ClO$_4$)$_2$	green	Calc.	34.2	3.2	—	11.3	—	—	K, e-w
		Found	34.6	3.2	—	11.3			
Cu(ligIV)OH	pale green	Calc.	56.1	3.8	—	16.4	56.8	—	K, e-w
		Found	56.3	3.8	—	16.3			

* For notes [a], [b], [c] and [d] see footnote to table I.

we consider the deprotonated complexes of III (see IIIa) it can be seen that resonance stabilisation of them can take place through the 2-pyridylmethyleneamino-chain. The α-pyridyl group in the 5-position of the pyrazole ring does not in this picture, enter into the resonance system.



III a



VI a

Thus it would be expected that stable deprotonated complexes of VIII could be prepared. This does not appear to be the case. Although protonated copper(II) and iron(II) compounds were isolated (see Table IV), attemps to deprotonate them in alkaline solution did not yield stable neutral compounds. The importance of the bonding pyridine ring in the stabilisation of the deprotonated system is clearly seen.

The ligand VI was prepared in the hope that it might form stable deprotonated compounds in which a proton was lost from the carbon atom in the 1-position of the indene ring system (see VIa). Such a system would possess resonance stabilisation very similar to that exhibited by IIIa. VI readly gave protonated compounds with copper(II) (green) and iron(II) redish-brown) perchlorates (see Table IV). The addition of alkail to solutions of the compounds led to the formation of intense violet colours which rapidly disappeared. Although no deprotonated complexes could be isolated, it would appear that deprotonation does occur and that the entities formed are very unstable.

Ligand VII is similar in structure to the other tridentates, however it possesses a 2-pyridylhdrazine

Table IV. Physical Properties of Complexes of Ligands VI and VIII.*

Formula	Colour		Analysis %C	%H	%N	%M	Method of Preparation [d]
$Fe(HligVI)_2(ClO_4)_2$ [a]	reddish-brown	Calc.	62.3	3.8	8.4	5.6	A, n.r.
		Found	62.0	3.5	7.8	5.9	
$Cu(HligVI)_2H_2O(ClO_4)_2$	green	Calc.	47.6	3.2	—	9.7	A, e
		Found	47.7	3.2	—	9.4	
$Fe(HligVIII)_3(ClO_4)_2 . H_2O$	brown	Calc.	45.3	4.3	19.2	6.4	C, e-w
		Found	45.3	4.6	18.8	6.1	
$Cu(HligVIII)_2(ClO_4)_2 . H_2O$	green	Calc.	38.7	3.8	—	9.3	A, e-w
		Found	38.9	3.7	—	9.1	

* For notes [a] and [d] see footnote to table I.

Table V. Physical Properties of Complexes of Ligands VII.*

Formula	Colour		%C	Analysis %H	%N	%M	Λ_M [b] (r.o.)	Magnetic Moment [c]	Method of Preparation [d]
$Ni(HligVII)_2(ClO_4)_2$ [a]	brownish-red	Calc.	59.6	3.6	11.1	5.8	47.3	3.1/295°	A, e-w
		Found	59.8	3.8	10.7	5.6	47.		
$Co(HligVII)_2(ClO_4)_2 . 2H_2O$	brown	Calc.	57.5	3.8	—	5.6	47.9	4.9/297°	A, e-w
		Found	57.6	4.0	—	5.4			
$Fe(ligVII)_2 . 2H_2O$	violet-black	Calc.	71.5	4.5	—	6.7	non-elect	0.9/296°	A, e
		Found	71.5	4.3	—	6.8			
$Co(ligVII)_2$	reddish-violet	Calc.	74.5	4.2	—	7.3	non-elect	3.4/296°	K, n.r.
		Found	74.8	4.2	—	7.6			
$Ni(ligVII)_2$	reddish-violet	Calc.	74.5	4.2	—	7.3	non-elect	2.5/296°	K, n.r.
		Found	74.5	4.0	—	7.1			
$Cu(ligVII)H_2O . ClO_4$	reddish-violet	Calc.	50.8	3.2	9.5	10.7	27.4	—	A, e-w
		Found	50.7	3.0	88.	10.6			

* For notes [a]. [b], [c] and [d] see footnote to table I.

chain in place of the 2-pyridlymethyleneamino chains of these other ligands and the imino-nitrogen of the hydrazine chain is the proton loser upon deprotonation of its complexes. Keeping in mind that proton loss in such cases is from a chelate ring, it is interesting to note that all the deprotonated compounds from this ligand possess intensely coloured solutions. Furthermore, both the neutral cobal(II) and nickel(II) compounds have anomalously low magnetic moments (see Table V). These two features support the theory that the preparation of neutral complexes by the deprotonation of an atom in a chelate ring is likely, depending on the sixe of the possible resonance system thereby set-up, to yield highly coloured compounds with intense colours in solution. Cobalt(II) and nickel(II) compounds with anomalous moments may also be exepected.

Although charged compounds of cobalt(II) and nickel(II) were obtained from VII, the interaction of the ligand with iron(II) perchlorate and copper(II) perchlorate led to the direct formation of the deprotonated compounds.

Experimental Section

Preparation of Ligands

(i) *3-methyl-5-(2′-pyridyl)-pyrazole* (I) Picolinyl acetone was prepared by a Claisen condensation of ethyl picolinate and acetone. Clean dry sodium (4.9 g.) in very small globules ("molecular sodium") and dry ether (70 ml) were vigorously stirred in a reaction flask under nitrogen while dry ethanol (12.5 ml) was added over 15 min. The solution was stirred for some 4-5 hours until the sodium had dissolved. Dry acetone (12.5 g.) in dry benzene (100 ml) was then added rapidly, followed by purified ethyl picolinate (25.0 g.). The mixture was stirred and the sodium salt of the condensation product separated slowly. The mixture was refluxed with stirring for a further 2 hours. The cream coloured product was dissolved in water and the aqueous solution so obtained extracted with ether. The remaining aqueous layer was made just acid with acetic acid and a light red oil separated out. The aqueous solution was again extracted with ether (2×200 ml.), the extracts comined, dried over sodium sulphate and the ether evaporated off. The dark red oil obtained was distilled under vacuum, b.p. 112-114/2 mm. Yield 16.0 g. straw coloured oil. This product is the diketone picolinyl acetone.

The diketone (5 g.) was treated with hydrazine hydrate (10 g.) in concentrated hydrochloric acid (20 ml.). The solution so obtained was made alkaline and extracted with ether, which upon evaporation yielded a yellow oil which crystallised slowly. Yield of colourless pyrazole was 3.8 g., m.p. 96-97°.

Analysis. Calcd for $C_9H_9N_3$: C, 67.9; H, 5.7; N, 26.4. Found C, 68.2; H, 5.6; N, 26.1%.

(ii) *3-(carbethoxy)-4-methyl-2-(2′-pyridyl)-pyrrole* (II) Acetone monoxime (4.5 g) in concentrated acetic acid (40 ml) plus water (10 ml) was treated all at once with ethyl picolinyl acetate[*] (10 g) with vigorous stir-

---

[*] This product was obtained by a similar method used above for picolinyl acetone, but replacing the acetone by ethyl acetate (22.8 g.). The compound is a light red oil, b.p. 129-132°/2.0 mm. A yield of 20.1 g. was obtained using the same quantities as in the earlier preparation.

ring. Zinc dust (10 g) was added slowly keeping the temperature of reaction below 60° The solution was well-stirred and refluxed for 2 hours after addition of the zinc. The required pyrrole deposited when the solution was cooled. Yield 10.5 g of colourless crystals, m.p. 247-248°, after recrystallisation from alcohol.

Analysis. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.8; H, 6.1; N, 12.1. Found: C, 67.8; H, 6.0; N, 11.8%.

(iii) *3-methyl-4-(2′-pyridylmethylene-amino)5-(2″-pyridyl)-pyrazole (III).* Picolinyl acetone (8 g) in dilute acetic acid was treated with sodium nitrite (3.1 g) in a small volume of water. The crystalline oxime was filtered off and dissolved in alcohol. The alcoholic solution was treated with hydrazine hydrate (8 g) and concentrated hydrochloric acid (20 ml) and a deep green colour developed. Overnight the colour disappeared and yellow crystals deposited (0.5 g). This was found to be the *3-methyl-4-amino-5-(2′-pyridyl)-pyrazole.*

Analysis. Calcd for $C_9H_{10}N_4$: C, 62.0; H, 5.8; N, 32.2. Found: C, 62.6; H, 5.8; N, 32.1%.

The amine 6.0 g was obtained by evaporation of the above solution. This product (5.5 g) was mixed with pyridine-2-aldehyde (3.4 g) in alcohol and heated to boiling with a few drops of acetic acid. Upon cooling the required ligand (III) deposited. It was recrystallised from alcohol. Yield 6.8 g of cream needles, m.p. 177-178°.

Analysis. Calcd for $C_{15}H_{13}N_5$: C, 68.5; H, 5.0; N, 26.6. Found: C, 68.5; H, 5.3; N, 24.4%.

(iv) *3-methyl-4-(2′-pyridylmethyleneamino)-5-(2″-pyridyl)-pyrrole (IV).* This was prepared from the amine obtained by the Curtius rearrangement of the azide prepared from the hydrazide of 3-(carbethoxy)-4-methyl-2-(2″-pyridyl)-pyrrole.

(a) *Hydrazide of 3-carbethoxy-4-methyl-2-(2″-pyridyl)-pyrrole.* This pyrrole (10 g) in dilute hydrochloric acid was treated with hydrazine hydrate (10 g). The solution became hot and upon standing deposited a clean white crystalline material (8.5 g) m.p. 300°.

Analysis. Calcd for $C_{11}H_{12}N_4O$: C, 6.1; H, 5.6. Found: C, 61.0; H, 5.3%.

(b) *Preparation of Azide.* The hydrazide (8.0 g) in water (50 ml) and dilute hydrochloric acid (15 ml) were placed in an ice-bath. Ether (40 ml) was added followed by a concentrated aqueous solution of sodium nitrite (2.8 g). The solution was stirred vigorously for 30 min and the crystalline deposit obtained filtered off. The aqueous layer was separated and extracted with fresh ether. When allowed to stand overnight the combined ether extracts deposited crystals (6.0 g) of the azide.

(c) *Preparation of 3-methyl-4-amino-5-(2′-pyridyl)-pyrrole.* The azide(6.0 g) was boiled strongly in dry ethanol solution (100 ml) and the excess ethanol distilled off. The solid residue was refluxed with concentrated hydrochloric acid (20 ml) until the oily layer had disappeared (15 hr). Neutralisation of the hydrolysis mixture with sodium hydroxide solution was carried out in an ice-bath. The amine was extracted from the alkaline solution with ether. Yield of viscous red oil 3.2 g. Attempts to vacuum distil this oil were unsuccessful.

(d) *Preparation of IV.* The above crude amine (3.0 g) in alcohol with a few drops of acetic acid was treated with pyridine-2-aldehyde (2.0 g). The solution was brought to the boil and upon cooling deposited the required pyrrole (3.7 g); *3-methyl-4-(2′-pyridylmethyleneamino)-5-(2″-pyridyl)pyrrole m.p. 208°.*

Analysis. Calcd for $C_{16}H_{14}N_4$: C, 73.2; H, 5.3; N, 21.4. Found: C, 73.0; H, 5.4; N, 20.9%.

(v) *3-(2′-pyridylmethyleneamino)-2-(2″-pyridyl)-indole (V).* 2-(2′-pyridyl)-indole (3.3 g) (prepared by the Fischer indole synthesis[7]) in dilute potassium hydroxide (5 g in 800 ml water) and sodium acetate (50 g) was treated slowly in an ice-bath with ice-cold diazotised sulphanilic acid solution (from sodium nitrite (2.5 g) and sulphanilic acid (3.25 g) in water). The yellowish-red solution was allowed to come to room temperature and tin(II) chloride (8.0 g) was added. When made strongly acidic with hydrochloric acid the solution rapidly decolourised as reduction of the diazo-compound took place. The solution was made strongly alkaline with potassium hydroxide so that the tin hydroxide redissolved. Extractions of the solution with ether followed by evaporation of the combined ether extracts yielded the amine as a viscous oil. This oil was reacted with pyridine-2-aldehyde (3 g) in alcohol with a few drops of acetic acid. A slow yellow deposit of the required indole separated (2.6 g). This gave colourless crystals upon recrystallisation from alcohol m.p. 210°

Analysis. Calcd for $C_{19}H_{14}N_4$: C, 76.4; H, 4.7; N, 18.8. Found: C, 76.3; H, 4.5; N, 18.2%.

(vi) *2,4-dimethyl-3-(2′pyridylmethyleneamino)-pyrazole (VIII).* Acetylacetone (10 g) was treated with sodium nitrite (6.9 g) in dilute acetic acid (20 ml). The oxime of acetylacetone separated as white crystals. This product was treated with hydrazine hydrate (20 g) in dilute hydrochloric acid (20 ml). The solution obtained was made alkaline with potassium hydroxide and extracted with ether to obtain the 2,4-dimethyl-3-amino-pyrazole as a yellow oil (9.2 g). The interaction of this oil with pyridine-2-aldehyde (7.8 g) in alcohol plus a few drops of acetic acid yielded the required compound (VIII). This was recrystallised from aqueous acohol to yield a colourless crystalline material (13.9 g) m.p. 183°

Analysis. Calcd for $C_{11}H_{12}N_4$: C, 66.0; H, 6.0; N, 28.0. Found C, 66.4; H, 6.2; N, 28.4%.

(vii) *1-phenyl-2-(2′-pyridyl)-3-(2″-pyridylmethyleneamino)-indene VI.* Pyrothalone (12.5 g) from the interaction of 2-methyl-pyridine and phthalic anhydride was added to a freshly prepared ether solution of phenyl lithium from phenyl bromide (19.2 g) and lithium (1.7 g) under nitrogen. The mixture was gently refluxed for 2 hours and then cooled in an ice-bath and treated with excess ammonium chloride solution. The original solid deposit dissolved and a

---

(7) S. Sugasowa, M. Terashima, and Y. Kanoaka, *Pharm. Bull* (Japan), *4*, 16 (1956).

new solid precipitated upon this treatment. The reaction mixture was stirred for an hour and the solid carbinol filtered off, washed with water and dried This product was dehydrated by dissolution in concentrated hydrochloric acid, stirring for 15 min. and neutralising with sodium hydroxide. The solid dehydrated carbinol from the neutralisation was recrystallised from aqueous alcohol. Yield 12.2 g., m.p. 148°. This is the *3-ketone of 1-phenyl-2-(2′-pyridyl)-indene.*

The 3-ketone (8.2 g) was just dissolved in alcohol and treated with a concentrated aqueous solution of hydroxylamine hydrochloride (16 g) and sodium acetate (30 g). The mixture was boiled for 5 min. and upon cooling the yellow 3-oxime (8.1 g) deposited.

The oxime was suspended in water (100 ml) and zinc dust (30 g) and acetic acid (200 ml of concentrated) added. The mixture was heated on the water-bath to initiate reaction and left for 30 min. by which time all the oxime had dissolved. The unreacted zinc precipitates redissolved. The solution was then extracted with ether (3×200 ml), the extracts combined, dried over sodium sulphate and evaporated to yield the *3-amino-1-phenyl-2-(2′-pyridyl)-indene* as a viscous oil (6.1 g). This oil was treated with pyridine-2-aldehyde (2.3 g) in alcohol plus a few drops of acetic acid to give the required indene (VI). The product separates as cream needles upon recrystallisation from alcohol. Yield 7.0 g m.p. 148°.

Analysis. Calcd for $C_{26}H_{19}N_3$: C, 83.5; H, 5.1; N, 11.3. Found C, 83.7; H, 5.4; N, 10.48%.

(viii) *1-phenyl-2-(2′-pyridyl)-3-(2″-pyridylhydrazinyl)-indene (VII).* Treatment of the 3-keto-compound (3.7 g), obtained during the foregoing preparation with 2-pyridylhydrazine (1.5 g) in alcohol with a few drops of acetic acid added, led to the slow deposition of VII. Recrystallisation from aqueous olcohol yielded yellow needles (3.6 g) of the hemihydrate, m.p. 155-156°.

Analysis. Calcd for $C_{25}H_{18}N_4 . \frac{1}{2}H_2O$: C, 78.2; H, 4.9; N, 14.6. Found: C, 78.6; H, 4.9; N, 14.2%.

Preparation of Complex Compounds. The code to the methods of preparation is given below.

A

The ligand (2 molecular proportions) in ethanol solution was treated with a solution of the metal perchlorate (1 molecular proportion) in water. If the required compound failed to precipitate, partial evaporation of the solution followed by cooling then yielded the crude product.

C. Similar to method A but using 3 molecular proportions of the ligand.

G

The ligand (2 molecular proportions) in ethanol was treated with metal perchlorate (1 molecular proportion) in water, and the solution was made slightly alkaline with aqueous 5N sodium hydroxide solution. A change in the colour of the solution was noted and the substance giving rise to this new colour was extracted into benzene. Partial evaporation of the dried (sodium sulphate) benzene extracts followed by cooling yielded the required compound.

J

The ligand (2 molecular proportions) in ethanol was treated with an aqueous solution of the required complex ammine salt of the metal (1 molecular proportion). Partial evaporation of the resultant solution, followed by cooling yielded the required compound. The aqueous solution of the complex ammine salt of the required metal was prepared by treating a solution of the metal ion (1 molecular proportion) with ammonia solution until the ammonia was in slight excess.

K

The corresponding charged complex in aqueous solution was treated with 5N sodium hydroxide solution until weakly alkaline. The substance giving rise to the changed colour of the solution was extracted into either benzene or chloroform solution and this solution was dried over sodium sulphate. Partial evapration followed by cooling of the sodium yielded the required compound.

Solvents for Recrystallisation. These are shown in small type after the code letter for the method of preparation: e- ethanol; e-w - aqueous ethanol; n.r. - not recrystallised.

Acknowledgments. The author wishes to acknowledge the Petroleum Research Fund for granting support for this work.