Contribution from the Department of Organic Chemistry
of the University of Sydney, Sydney, Australia

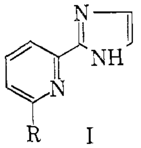
Bidentate Chelate Compounds. III.[1] Metal Complexes of Some Pyridyl–Imidazole Derivatives

By BARRY CHISWELL,[2] FRANCIS LIONS, and BENJAMIN S. MORRIS

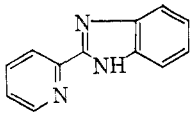
Received June 4, 1963

The bases 2-(2′-pyridyl)imidazole and 2-(6′-methyl-2′-pyridyl)imidazole have been synthesized and shown to be capable of functioning as bidentate chelating agents. The cations of certain of the complex salts they and 2-(2′-pyridyl)benzimidazole form with transition metal salts can be deprotonated with bases to "neutral" complexes. However, it has not proved possible by treatment with alkalies to deprotonate such salts so as to obtain complexed metal in the anions.

The deprotonation with bases of the complex cations of complex salts derived from certain organic chelating agents to stable neutral complexes or to complex salts with less highly charged cations has been reported.[3,4] Consideration quickly makes it apparent that there should be capable of existence many types of chelate compounds whose complex cations could be similarly deprotonated. In this paper attention is drawn to heterocyclic chelating agents of the 2-picolylamidine type such as 2-(2′-pyridyl)imidazole (I, R = H) and 2-(2′-pyridyl)benzimidazole (II).

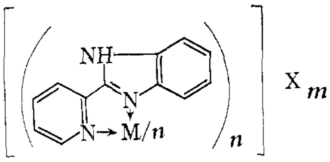


I



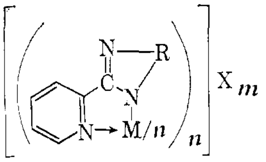
II

Leko and Vlajinats[5] appear first to have described complexes of II with copper(II) chloride and mercury(II) chloride as well as a neutral silver derivative. Later, Freiser and his co-workers[6] prepared the complex salts III (M = Ni(II), Cu(II), Co(II), or Zn(II); X = Br, I, or ClO_4; $n = 2$; $m = 2$; and M = Fe(II); X = ClO_4; $n = 3$; $m = 2$), as well as a series of 2-(2′-pyridyl)imidazoline compounds, and established the fact that coordination increases the acidity of the imino hydrogen of the imidazole or imidazoline nucleus to an extent dependent on the metal atom coordinated. They noted a shift to lower frequencies of the amine bands in the infrared spectra when coordination occurred and also recorded intensification of color with pH increase in solutions of the coordination compounds prepared from II. However, they did not record the isolation of any deprotonated complexes



III

We now report the preparation of a series of complex salts from the salts of certain transition metals and II as well as from I (R = H) and I (R = CH_3) (Tables I and II). Many of these can be deprotonated with alkali to "neutral" complexes (IV) (Table III).



IV

Alternatively, many of the "neutral" complexes can be synthesized by interaction of the ligand with a solution of a metal salt previously made ammoniacal. Attempts to deprotonate the cations of the complex salts of gold(III), rhodium(III), and iridium(III) were unsuccessful, addition of alkali to their solutions leading to decomposition and precipitation of the metal hydroxides.

When complex salts derived from bivalent metals favoring six-coordination [*e.g.*, iron(II), nickel(II)] and containing three residues of I (R = H) were treated with alkali, in each instance one ligand residue was split off and a nonvalent neutral complex with molecules containing two deprotonated ligand residues bonded to each metal atom was obtained. Similar behavior was observed with the silver complex salts derived from I (R = H) which, with alkali, gave the neutral complex containing one deprotonated I residue to each silver atom. Bonding between metal atom and chelating agent molecules does not appear to be strong enough to survive the placing of a negative charge on the complex entity. It should be remembered here that, *spatially*, the two donor nitrogens offered to a metal atom by a molecule of I or II are less favorably placed than are, for example, the bonding nitrogens in 2,2′-bipyridyl. Where *three* residues of I (R = H) are bonded to a tervalent metal ion (*e.g.*, Co^{+3}, Fe^{+3}), experiment showed that triple deprotonation can be effected and a neutral complex obtained, all three ligand residues still remaining in the complex.

Treatment of bis-[2-(2′-pyridyl)imidazolato]nickel(II)–1-water in boiling acetone with dimethyl sulfate led to rapid methylation, and, with the help of sodium perchlorate, bis-[2-(2′-pyridyl)-3-methylimidazole]-nickel(II) perchlorate was isolated from the reaction

---

[1] For the previous paper in this series, see H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **81**, 311 (1959).

[2] Petroleum Research Fund Fellow, University of Sydney.

[3] J. F. Geldard and F. Lions, *J. Am. Chem. Soc.*, **84**, 2262 (1962).

[4] J. F. Geldard and F. Lions, *Inorg. Chem.*, **2**, 270 (1963).

[5] A. Leko and G. Vlajinats, *Bull. soc. chim. roy. Yougoslav*, **1**, 3 (1930); **3**, 85 (1932); **4**, 17 (1933).

[6] J. L. Walter and H. Freiser, *Anal. Chem.*, **26**, 217 (1954); T. R. Harkins, J. L. Walter, O. E. Harris, and H. Freiser, *J. Am. Chem. Soc.*, **78**, 260 (1956); T. R. Harkins and H. Freiser, *ibid.*, **78**, 1143 (1956).

TABLE I

COMPLEX SALTS OF PYRIDYL–IMIDAZOLES

No.	Formula	Method of prepn.	Sol-vent[a]	Color	Conductivity, ohm^{-1} cm.^{2} (25°)	Magnetic moment, B.M.	Analyses					
							Calcd.			Found		
							C	H	M	C	H	M
1	$[Mn(C_{16}H_{14}N_6)](ClO_4)_2\cdot 2H_2O$	1a	E–W	Yellow	56.0	5.91 (19°)	33.1	3.1	9.5[b]	33.5	3.9	9.2
2	$[Co(C_{16}H_{14}N_6)](ClO_4)_2\cdot 2H_2O$	1a	E–W	Pale orange	54.8	2.11 (23°)	32.8	3.1	10.1	32.5	3.4	9.9
3	$[Ni(C_{16}H_{14}N_6)](ClO_4)_2\cdot 6H_2O$	1a	E–W	Light blue	55.2	3.28 (22°)	29.2	4.0	8.9	29.2	3.7	9.1
4	$[Ni(C_{16}H_{14}N_6)]Cl_2\cdot 2H_2O$	1a	E–W	Blue-green	57.2	3.21 (18°)	42.1	4.0	12.9[c]	41.6	4.3	12.6
5	$[Pd(C_{16}H_{14}N_6)]Cl_2$	1b	E–W	Orange	55.1	Diamag.	41.1	3.0	22.8	41.3	2.8	23.0
6	$[Cu(C_{16}H_{14}N_6)](ClO_4)_2$	1a	E–W	Light green	56.3	1.92 (20°)	34.6	3.2	11.6	34.3	3.1	11.5
7	$[Ag(C_{16}H_{14}N_6)](AgCl_2)$	4	N.r.	Colorless	27.5	Diamag.	33.4	2.4	37.4[d]	33.6	2.9	37.7
8	$[AuCl_2(C_8H_7N_3)]Cl\cdot 2H_2O$	1b	N.r.	Brown	27.2	Diamag.	19.8	2.2	40.7[e]	19.6	1.7	40.6
9	$[Cd(C_{16}H_{14}N_6)](CdCl_4)\cdot H_2O$	1a	N.r.	Colorless	54.4	Diamag.	27.7	2.6	32.5[f]	27.5	2.4	32.1
10	$[IrCl_2(C_{16}H_{14}N_6)](ClO_4)\cdot 4H_2O$	1b	E–W	Orange-yellow	29.8	Diamag.	22.1	2.5	22.1	22.1	3.1	22.4
11	$[Fe(C_{24}H_{21}N_9)](ClO_4)_2\cdot H_2O$	2a	E–W	Deep red	58.9	5.42 (20°)	40.7	3.3	7.8[g]	40.9	3.9	7.7
12	$[Fe(C_{24}H_{21}N_9)](ClO_4)_3$	2a	E–W	Deep red	89.6	2.47 (22°)	36.4	2.7	7.7	36.4	2.7	7.5
13	$[Co(C_{24}H_{21}N_9)](ClO_4)_2$	2b	E–W	Orange	56.2	4.91 (20°)	41.5	3.0	8.5	41.3	3.2	8.4
14	$[Co(C_{24}H_{21}N_9)](ClO_4)_3$	5	E	Yellow-brown	84.8	Diamag.	36.2	2.6	7.4	36.0	2.9	7.2
15	$[Ni(C_{24}H_{21}N_9)](ClO_4)_2\cdot H_2O$	2b	E–W	Mauve-pink	57.3	3.17 (22°)	40.3	3.2	8.2[h]	40.1	3.2	8.4
16	$[Rh(C_{24}H_{21}N_9)](ClO_4)_3\cdot 5H_2O$	2a	E–W	Pale yellow	77.3	Diamag.	31.0	3.3	11.1	31.0	3.2	11.2
17	$[Cu(C_{18}H_{18}N_6)](ClO_4)_2\cdot H_2O$	1a	E–W	Green	55.8	1.89 (23°)	36.0	3.3	10.6	36.0	3.6	10.8
18	$[Ag(C_{18}H_{18}N_6)](ClO_4)\cdot 0.5H_2O$	1a	N.r.	Colorless	24.9	Diamag.	40.4	3.5	20.2	40.6	3.5	20.4
19	$[Cd(C_{18}H_{18}N_6)](CdCl_4)$	1a	N.r.	Colorless	55.3	Diamag.	31.6	2.6	32.7[i]	32.1	2.8	32.7

The names of the compounds listed above are (1) bis-[2-(2′-pyridyl)imidazole]manganese(II) perchlorate–2-water; (2) bis-[2-(2′-pyridyl)imidazole]cobalt(II) perchlorate–2-water; (3) bis-[2-(2′-pyridyl)imidazole]nickel(II) perchlorate–6-water; (4) bis-[2-(2′-pyridyl)imidazole]nickel(II) chloride–2-water; (5) bis-[2-(2′-pyridyl)imidazole]palladium(II) chloride; (6) bis-[2-(2′-pyridyl)imidazole]copper(II) perchlorate; (7) bis-[2-(2′-pyridyl)imidazole]silver(I) dichloroargenate(I); (8) dichloro-2-(2′-pyridyl)imidazolegold(III) chloride–2-water; (9) bis-[2-(2′-pyridyl)imidazole]cadmium(II) tetrachlorocadmiate(II)–1-water; (10) dichloro-bis-[2-(2′-pyridyl)imidazole]iridium(III) perchlorate–4-water; (11) tris-[2-(2′-pyridyl)imidazole]iron(II) perchlorate–1-water; (12) tris-[2-(2′-pyridyl)imidazole]iron(III) perchlorate; (13) tris-[2-(2′-pyridyl)imidazole]cobalt(II) perchlorate; (14) tris-[2-(2′-pyridyl)imidazole]-cobalt(III) perchlorate; (15) tris-[2-(2′-pyridyl)imidazole]nickel(II) perchlorate–1-water; (16) tris-(2-(2′-pyridyl)imidazole]rhodium-(III) perchlorate–5-water; (17) bis-[2-(6′-methyl-2′-pyridyl)imidazole]copper(II) perchlorate–1-water; (18) bis-[2-(6′-methyl-2′-pyridyl)imidazole]silver(I) perchlorate–0.5-water; (19) bis-[2-(6′-methyl-2′-pyridyl)imidazole]cadmium(II) tetrachlorocadmiate(II).

[a] Solvents used for recrystallization of complexes were ethanol (E), water (W), and benzene (B). Mixed solvents are indicated by use of both letters. When the complex was difficult to recrystallize but was obtainable pure by precipitation and washing the letters N.r. (not recrystallized) are used. [b] Nitrogen: calcd., 14.5; found, 14.8. [c] Nitrogen: calcd., 18.4; found, 18.4. Chlorine: calcd., 15.6; found, 15.8. [d] Nitrogen: calcd., 14.6; found, 14.6. Chlorine: calcd., 12.3; found, 12.4. [e] Nitrogen: calcd., 8.7; found, 8.9. Chlorine: calcd., 22.0; found, 22.0. [f] Nitrogen: calcd., 12.1; found, 12.1. Chlorine: calcd., 20.5; found, 20.6. [g] Nitrogen: calcd., 17.8; found, 17.7. [h] Nitrogen: calcd., 17.7; found, 17.2. [i] Chlorine: calcd., 20.8; found, 20.9.

TABLE II

Formula	Method of prepn.	Solvent	Color	Analyses					
				Calcd.			Found		
				C	H	M	C	H	M
(a) Bis-[2-(2′-pyridyl)benzimidazole]metal salts									
$[Mn(C_{24}H_{18}N_6)]Cl_2\cdot 6H_2O$	1a	E–W	Yellow	46.2	4.8	8.9	45.9	4.7	9.0
$[Co(C_{24}H_{18}N_6)]Cl_2$	1a	E	Red	55.5	3.5	11.3	54.9	3.4	11.2
$[Co(C_{24}H_{18}N_6)](CNS)_2$	1a	N.r.	Pink	55.2	3.2	10.5	55.4	3.2	10.8
$[Ni(C_{24}H_{18}N_6)]Cl_2$	1a	N.r.	Blue-green	55.5	3.5	11.3	55.4	3.4	10.8
$[Cu(C_{24}H_{18}N_6)]Cl_2$	1a	E	Green	54.9	3.4	12.1	54.7	3.4	12.1
$[Cu(C_{24}H_{18}N_6)]SO_4\cdot 2H_2O$	1a	N.r.	Green	49.3	3.8	10.9	49.5	4.0	10.6
$[Cu(C_{24}H_{18}N_6)](NO_3)_2$	1a	E–W	Green	49.9	3.1	11.0	49.5	3.6	11.0
$[Cu(C_{24}H_{18}N_6)]I_2$	6	E	Green	40.6	2.5	8.9	40.5	2.5	8.7
$[Ag(C_{24}H_{18}N_6)]NO_3$	1a	E–W	Colorless	47.0	3.9	23.5	46.5	4.0	22.9
$[Ag(C_{24}H_{18}N_6)]_2S_2O_8$	7	N.r.	Yellow-brown			18.1[a]			18.2
$[Be(C_{24}H_{18}N_6)]SO_4$	1a	E–W	Yellow	58.2	3.6	1.8	59.0	3.6	1.8
(b) Tris-[2-(2′-pyridyl)benzimidazole]metal salts									
$[Fe(C_{36}H_{27}N_9)]Cl_2\cdot 6H_2O$	8	N.r.	Red	53.5	4.8	7.0	53.5	4.9	7.1
$[Fe(C_{36}H_{27}N_9]Cl_3$	9	E	Dark red	57.8	3.6	7.5	57.3	3.6	7.6
$[Co(C_{36}H_{27}N_9)]Cl_3$	10	E–W	Red-brown	57.6	3.6	7.9	58.3	3.7	7.7
$[Ni(C_{36}H_{27}N_9)]Cl_2\cdot 2H_2O$	2a	E	Pink	57.8	4.1	7.8	58.4	4.1	7.7

[a] Persulfate: calcd., 16.2; found, 16.6.

product. By decomposition of this in solution with hydrogen sulfide there was obtained the same 1-methyl-2-(2′-pyridyl)imidazole (V) that is obtained from I (R = H) by direct methylation. The identity of the two methylated bases is shown, among other evidence, by the identity of the infrared spectra of their complex nickel(II) perchlorates and iron(II) perchlorates, which, as expected, contain no >N–H bands.

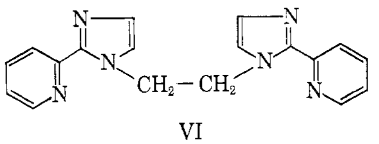
TABLE III

DEPROTONATED ("NEUTRAL") COMPLEXES IV

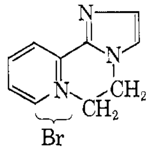
Formula	Method of prepn.	Solvent of recrystn.	Color	Magnetic moment, B.M.	Analyses					
					Calcd.			Found		
					C	H	M	C	H	M
			(a) Bis-[2-(2′-pyridyl)imidazolato]metals							
$[Fe(C_{16}H_{12}N_6)] \cdot 2H_2O$	11, 13	B	Deep brown	5.26 (20°)	50.6	4.2	14.7	50.6	4.3	14.5
$[Co(C_{16}H_{12}N_6)] \cdot 2H_2O$	13, 15	B	Brown	2.06 (23°)	49.8	4.2	15.3	50.0	4.3	15.0
$[Ni(C_{16}H_{12}N_6)] \cdot H_2O$	13, 15	B	Brown	3.15 (18°)	52.6	3.8	13.8	52.6	4.5	13.9
$[Pd(C_{16}H_{12}N_6)]$	11, 13	B	Yellow	Diamag.	48.6	3.0	26.8	48.5	3.2	27.0
$[Cu(C_{16}H_{12}N_6)] \cdot H_2O$	13, 15	B	Light green	1.93 (20°)	51.9	3.8	14.6	51.7	3.8	14.6
$[Cd(C_{16}H_{12}N_6)] \cdot 2H_2O$	15	B	Colorless	Diamag.	43.8	3.7	25.6	43.4	4.0	25.6
			(b) Tris-[2-(2′-pyridyl)imidazolato]metals							
$[Fe(C_{24}H_{18}N_9)] \cdot 0.5H_2O$	12, 13	B	Red-violet	2.52 (22°)	57.6	3.8	11.2	57.6	3.7	11.4
$[Co(C_{24}H_{18}N_9)] \cdot 3H_2O$	14	E–W	Brown		54.0	4.5	11.0	54.2	4.6	11.2
			(c) Bis-[2-(2′-pyridyl)benzimidazolato]metals							
$[Ni(C_{24}H_{16}N_6)]$	15	N.r.	Green-yellow		64.4	3.6	13.2	64.2	3.6	12.9
$[Cu(C_{24}H_{16}N_6)]$	15	N.r.	Green		63.7	3.5	14.1	64.1	3.6	13.8
$[Zn(C_{24}H_{16}N_6)]$	15	E	Yellow		63.5	3.5	14.4	64.6	3.4	14.2
			(d) Bis-[2-(6′-methyl-2′-pyridyl)imidazolato]metals							
$[Cu(C_{18}H_{16}N_6)] \cdot 0.5H_2O$	13, 15	B	Green	1.91 (23°)	55.5	4.4	16.3	55.1	4.7	16.2
$[Cd(C_{18}H_{16}N_6)] \cdot 1.5H_2O$	13, 15	B	Colorless	Diamag.	47.5	4.2	24.7	47.5	4.3	24.5
			(e) Pyridylimidazolato silver complexes							
$[Ag(C_8H_6N_3)] \cdot 0.5(H_2O)^a$	15	B	Colorless	Diamag.	36.8	2.7	41.3	36.9	2.3	41.5
$[Ag(C_{12}H_8N_3)]^b$	15	N.r.	Colorless		47.7	2.6	35.8	48.2	2.6	36.4
$[Ag(C_9H_8N_3)] \cdot 1.5H_2O^c$	13, 15	B	Colorless	Diamag.	36.8	3.8	36.8	36.8	3.9	36.6

[a] Ligand I (R = H). [b] Ligand II. [c] Ligand I ($R = CH_3$).

Heat treatment of I (R = H) with ethylene dibromide yields 1,2-bis-[2-(2′-pyridyl)-1-imidazolyl]ethane (VI). The cyclic quaternary salt VII is not formed. This behavior is in marked contrast to that exhibited by the bidentate chelating agent 8-thiolquinoline,[7]



VI



VII

which forms the cyclic quaternary salt with such ease that it is not possible to prepare 1,4-bis-(8′-quinolyl)-1,4-dithiabutane by direct alkylation with ethylene dibromide and alkali. Presumably, again, the wider spatial gap between the pyridine nitrogen and either of the imidazole nitrogens in I (R = H) militates against ring formation.

The base I ($R = CH_3$) in which the methyl group in the 6-position of the pyridine ring may be regarded as a "blocking group" was found, as anticipated,[8] not to form isolable complexes with manganese(II) salts or with salts of group VIII metals. However, it readily formed complex salts with salts of group IB and group IIB metals (Table I) and these could be deprotonated to neutral complexes (Table III).

Finally, it should be noted that the complex compounds recorded in this paper, in general, melted (or decomposed) above 300° and that their measured conductivities in nitrobenzene and magnetic moments were normal.

Experimental

2-(2′-Pyridyl)imidazole (I, **R = H**). A procedure similar to that described by Radziszewski[9] was used. Ice-cold solutions of pyridine-2-aldehyde (10.7 g.) in ethanol (10 ml.) and glyoxal (20 ml. of 30% aqueous solution) in ethanol (10 ml.) were mixed and then, without delay, ice-cold concentrated aqueous ammonia solution (30 ml. of 20 *N*) was added. The yellow-brown solution was kept at 0° for 30 min., then allowed to stand overnight at room temperature. Most of the ethanol was distilled off and the cold residue extracted many times with ether. The solvent was removed from the combined, dried, ether extracts and the residual oil distilled *in vacuo*. A pale yellow oil (8 g.), b.p. 130–132° (0.5 mm.), was collected. It soon solidified and was obtained by recrystallization from ethyl acetate as yellow prisms, m.p. 134–135°.

Anal. Calcd. for $C_8H_7N_3$: C, 66.2; H, 4.8; N, 29.0. Found: C, 66.3; H, 4.9; N, 28.7.

2-(6′-Methyl-2′-pyridyl)imidazole (**I, R** = CH_3) was prepared similarly from 6-methyl-pyridine-2-aldehyde; yellow prisms, m.p. 170°.

Anal. Calcd. for $C_9H_9N_3$: C, 67.9; H, 5.7; N, 26.4. Found: C, 67.8; H, 5.8; N, 25.9.

2-(2′-Pyridyl)benzimidazole has been prepared by many different methods. The material used for the experiments recorded in this paper was made in rather poor yield by heating *o*-phenylenediamine and 2-picolinic acid together.[10] A much more convenient method consists in carefully heating together equimolecular amounts of *o*-phenylenediamine and 2-picolinthioamide. The purified product melted at 221°.

Preparation of Chelate Compounds Recorded in Tables I and II.—Several variant methods were employed. Briefly these were:

(1a) A solution of the metal salt (1 mole) in water was mixed with a solution of the ligand (2 moles) in ethanol; evaporation followed by cooling then yielded the crude product.

(1b) This method was similar to 1a except that the metal was present in the complex anion (*e.g.*, $[PdCl_4]^{-2}$, $[AuCl_4]^-$, etc.) of the salt used.

(2a) Similar to 1a except that *three* molecular proportions of ligand to *one* of metal salt were used.

---

(7) *Cf.* H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **82**, 5018 (1960).

(8) *Cf.*, *e.g.*, H. M. Irving, M. J. Cabell, and D. H. Mellor, *J. Chem. Soc.*, 3417 (1953); E. J. O'Reilly and R. A. Plowman, *Australian J. Chem.*, **13**, 145 (1960); D. B. Fox, J. R. Hall, and R. A. Plowman, *ibid.*, **15**, 235 (1962).

(9) B. Radziszewski, *Ber.*, **15**, 2706 (1882).

(10) B. S. Morris, Thesis, University of Sydney, Australia, 1940.

(2b) The product obtained by process 1a was treated in ethanol solution with a further proportion of ligand followed by evaporation to yield the required (tris-ligand) complex.

(3) An ethanolic solution of the ligand (2 moles) was treated with an aqueous solution of the complex ammine salt (1 mole) of the metal. Concentration by evaporation followed by cooling yielded the required complex salt.

(4) An ethanolic solution of the ligand (2 moles) was added to an aqueous solution of silver(I) nitrate (1 mole) after which hydrochloric acid (0.5 mole; 50% of theory) was gradually and carefully stirred in to precipitate the complex.

(5) The method of Bauer and Drinkard[11] was used.

(6) A concentrated aqueous solution of potassium iodide (1.7 g.) was added to an aqueous ethanolic solution of bis-[2-(2′-pyridyl)benzimidazole]copper(II) nitrate (2 g.). Flat green plates of the complex iodide were deposited.

(7) Bis-[2-(2′-pyridyl)benzimidazole]silver(I) nitrate was allowed to stand in contact with excess of a solution of ammonium persulfate. After several days the white starting material had changed to the yellow-brown microcrystalline persulfate.

(8) A solution of 2-(2′-pyridyl)benzimidazole (1.5 g.) in aqueous ethanol was added to a solution of iron(II) sulfate–7-water (0.7 g.) in water. A solution of barium chloride–2-water (0.63 g.) was added, and the precipitated barium sulfate was removed and the filtrate evaporated to small bulk. Small red crystals of the complex chloride crystallized.

(9) Benzene solutions of II (1.5 g.) and anhydrous iron(III) chloride (0.4 g.) were mixed. The complex salt formed a dark red-brown precipitate.

(10) Solutions of II (2 g.) in aqueous ethanol and hexaamminecobalt(III) chloride (0.9 g.) in water were mixed and heated on a water bath, the volume being maintained constant until evolution of ammonia ceased. It was then evaporated to small volume. Red-brown crystals of the product separated.

Preparation of Deprotonated Metal Complexes (Table III).—The following variant methods were used:

(11) Solutions of II (2 moles) in ethanol and the metal perchlorate (1 mole) in water were mixed and 5 *N* sodium hydroxide solution was added. The neutral compound was then extracted into benzene. After washing and drying of this solution, solvent was removed by evaporation. The solid compound then crystallized on cooling.

(12) The method was similar to method 11 except that three molecular proportions (instead of two) of ligand were used to one of metal perchlorate.

(13) A solution in aqueous ethanol of the preformed, corresponding complex metal salt (see Table I) was treated with sodium hydroxide solution and the neutral metal complex extracted into benzene.

(14) Solutions of II (0.5 g.) in ethanol (20 ml.) and cobalt(II) perchlorate-6-water (0.35 g.) in water (10 ml.) were mixed and treated with hydrogen peroxide solution (10 ml. of 3%). Excess 5 *N* ammonium hydroxide solution was then added and the neutral complex extracted into benzene.

(15) A solution of II (2 moles) in ethanol was added to an aqueous ammoniacal solution of a complex ammine salt (1 mole) of the required metal. Partial evaporation of the solution followed by cooling yielded the required noncharged complex.

1-Methyl-2-(2′-pyridyl)imidazole (V).—(a) I (R = H, 1.5 g.) was added to solution of sodium methoxide [from sodium (0.25 g.) and dry methanol (20 ml.)] and then freshly redistilled dimethyl sulfate (1.3 g.) was added. The solution was refluxed 15 min., concentrated, and cooled. Colorless V, m.p. 167°, crystallized. Its infrared spectrum showed no >N–H bands.

Anal. Calcd. for $C_9H_9N_3$: C, 67.9; H, 5.7; N, 26.4. Found: C, 67.8; H, 5.8; N, 25.9.

(b) Bis-[2-(2′-pyridyl)imidazolato]nickel(II)–1-water (1 g.) was dissolved in boiling acetone (50 ml.) and dimethyl sulfate (0.4 g.) was added. A green hygroscopic sludge separated. It was taken up in aqueous ethanol and sodium perchlorate added. Light blue **bis[1-methyl-2-(2′-pyridyl)imidazole]nickel(II) perchlorate–1-water** (0.5 g.) crystallized from this solution.

TABLE IV[a]

INFRARED ABSORPTION PEAKS

Compound	3 μ N—H str., cm.$^{-1}$	5–7 μ C═N str., cm.$^{-1}$	7–15 μ pyr. breathing, cm.$^{-1}$
PIMIN	3328	1664	996
$[(\mathrm{PIMIN})_3\mathrm{Co}]\mathrm{I}_2$	3190	1631	1010
$[(\mathrm{PIMIN})_3\mathrm{Ni}]\mathrm{I}_2$	3185	1634	1012
$[(\mathrm{PIMIN})_2\mathrm{Zn}]\mathrm{Br}_2$	3186	1631	1010
PHIM	3353	1690	988
$\mathrm{Cu(PHIM)_2(ClO_4)_2}$	3209	1615	1012
$\mathrm{Cu(PIM)_2 \cdot H_2O}$	. . .	1599	1008
$\mathrm{Fe(PHIM)_3(ClO_4)_2 \cdot H_2O}$	3204	1603	1008
$\mathrm{Fe(PIM)_2 \cdot 2H_2O}$	. . .	1605	1009
$\mathrm{Ni(PHIM)_2(ClO_4)_2 \cdot 6H_2O}$	3205	1613	1012
$\mathrm{Ni(PHIM)_3(ClO_4)_2 \cdot H_2O}$	3205	1603	1010
$\mathrm{Ni(PIM)_2 \cdot H_2O}$	. . .	1605	1011
$\mathrm{Ag(PHIM)_2AgCl_2}$	3205	1600	988
$\mathrm{Ag(PIM) \cdot 0.5H_2O}$	. . .	1595	988
MPHIM	3455	1690	987
$\mathrm{Ag(MPHIM)_2(ClO_4) \cdot 0.5H_2O}$	3247	1597	987
$\mathrm{Ag(MPIM) \cdot 1.5H_2O}$	. . .	1590	987
$\mathrm{Cd(MPHIM)_2CdCl_4}$	3205	1610	1001
$\mathrm{Cd(MPIM)_2 \cdot 1.5H_2O}$	. . .	1600	1002
MePIM	. . .	1690	990
$\mathrm{Ni(MePIM)_2(ClO_4)_2 \cdot H_2O}$	. . .	1610	1005
$\mathrm{Fe(MePIM)_3(ClO_4)_2}$	. . .	1598	1004

[a] Figures for the first four compounds listed are taken directly from the paper by Lane, *et al.*[12] Code names for the ligands used are: 2-(2′-pyridyl)imidazoline, PIMIN; 2-(2′-pyridyl)-imidazole, PHIM; 2-(6′-methyl-2′-pyridyl)imidazole, MPHIM; 2-(2′-pyridyl)-1-methylimidazole, MePIM. Deprotonated "neutral" complexes derived from either the second or third ligand lose the H from the code name. Thus, bis-[2-(2′-pyridyl)-imidazolato]copper(II)–1-water is tabulated as $\mathrm{Cu(PIM)_2 \cdot H_2O}$.

Anal. Calcd. for $[\mathrm{NiC_{18}H_{18}N_6}](\mathrm{ClO_4})_2$: C, 37.4; H, 3.4; Ni, 10.2. Found: C, 37.3; H, 3.7; Ni, 9.8.

A solution of this salt in aqueous ethanol was made slightly alkaline and gaseous hydrogen sulfide passed through it for 5 min. After removal of the nickel(II) sulfide, addition of water, and extraction with ether, V (0.2 g.) was recovered as colorless needles, m.p. 167°. The infrared spectrum was identical with that of the specimen prepared by method (a).

Anal. Found: C, 67.7; H, 5.8; N, 26.0.

Interaction of V prepared by method (a) with nickel(II) perchlorate gave the same light blue bis-[1-methyl-2-(2′-pyridyl)-imidazole]nickel(II) perchlorate–1-water described above. The infrared spectra were identical.

V (prepared by either method) reacted with iron(II) perchlorate to give dark red **bis-[1-methyl-2-(2′-pyridyl)imidazole]-iron(II) perchlorate.**

Anal. Calcd. for $[\mathrm{FeC_{27}H_{27}N_9}](\mathrm{ClO_4})_2$: C, 44.2; H, 3.7; Fe, 7.6. Found: C, 44.4; H, 4.1; Fe, 7.5.

1,2-Bis-[2′-(2″-pyridyl)-1′-imidazolyl]ethane Dihydrobromide Hydrate.—In a typical experiment equimolar quantities of I (R = H) and ethylene dibromide were heated together in a sealed tube at 100°. The resultant solid was recrystallized from aqueous ethanol and obtained as colorless needles, m.p. 235°.

Anal. Calcd. for $\mathrm{C_{18}H_{16}N_6 \cdot 2HBr \cdot H_2O}$: C, 43.6; H, 4.0; N, 16.9; Br, 32.3. Found: C, 43.7; H, 4.5; N, 14.7; Br, 32.2.

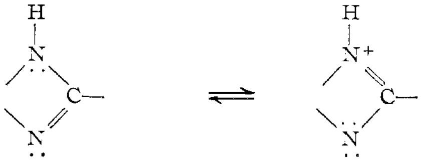
Infrared Spectra.—Lane, *et al.*,[12] have recently reported infrared studies of the ligands 2-(2′-pyridyl)imidazoline, 2-(2′-pyridyl) benzimidazole (II), and some other imidazole derivatives and

---

[11] H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

[12] T. J. Lane, I. Nakagawa, J. L. Walter, and A. J. Kandathil, *Inorg. Chem.*, **1**, 267 (1962).

some of the derived metal chelate compounds. They characterized various bands for the first of these ligands in the 3, 5–7, and 7–15 μ spectral regions. In the 3 μ region the band at 3328 cm.$^{-1}$ attributed to the N–H stretching frequency dropped in frequency upon coordination with Ni(II), Co(II), and Zn(II) (see Table IV). This was attributed to the resonance structure on the right (below) making a greater contribution on coordination with a metal ion than before.



In the 5–7 μ region the band at 1664 cm.$^{-1}$ attributed to the C=N stretching frequency of the imidazoline ring dropped upon coordination. In the 7–15 μ region a peak at 996 cm.$^{-1}$ was assigned to the pyridine breathing mode. Coordination caused it to increase. This was explained as being due to the coordination bonding of the pyridine ring nitrogen atom to the metal ion, causing restriction in the breathing mode.

2-(2′-Pyridyl)imidazoline is a dihydro-2-(2′-pyridyl)imidazole with very similar structural features to those of I (R = H). Each compound may be regarded as a substituted 2-picolinamidine with practically identical structures in the donor nitrogen atoms section of the molecules. It is, therefore, not unreasonable to expect very similar infrared peaks in the spectral regions discussed above and similar shifts upon coordination. The observed frequencies are tabulated (Table IV). The observations were made in Nujol mulls using a Perkin-Elmer Model 221 spectrophotometer.

It is worth commenting that deprotonation of the cations of the complex salts giving neutral complexes strips each imidazole N–H group of its hydrogen. This is shown in the spectra by the disappearance of the N–H stretching peak in the 3 μ region. Replacement of this N–H by N–CH_3 (2-(2′-pyridyl)-1-methylimidazole) causes a similar disappearance of this band. Also, in the four silver complexes examined there is no change in frequency shown upon coordination in the pyridine breathing frequency, suggesting that the silver atom in these complexes is not bonded to the pyridine nitrogen atom.

Acknowledgments.—The authors gratefully acknowledge the assistance of the Petroleum Research Fund of the American Chemical Society for a grant which has made this work possible and the considerable help of Miss B. Stevenson, M.Sc., for all the organic microanalyses and spectral data recorded.

Contribution No. 1566 from the Department of Chemistry,
University of California, Los Angeles 24, California

Complexes of Chromium(II) and (III) with Ethylenediaminetetraacetic Acid[1]

By ROBERT L. PECSOK, L. DONALD SHIELDS,[2] and WILLIAM P. SCHAEFER

Received July 19, 1963

A potentiometric and polarographic study of the Cr(II)-EDTA complex has yielded a value of 13.61 for log formation constant and 3.00 for minus log acidity constant. The log formation constant of the Cr(III)–EDTA complex is 23.40.

Introduction

In previous polarographic studies of chromium(II) in various complexing media,[3–5] we have noted that the Cr(II)–EDTA is a very powerful reductant with a half-wave potential of −1.48 v. *vs.* s.c.e. Its very fast reactions with oxygen, hydrogen ion, and/or hydroxide ion have made quantitative measurements very difficult. For example, although nearly all of the stability constants of the metal–EDTA complexes have been measured,[6] no values have yet been reported for either the Cr(II)–EDTA or the Cr(III)–EDTA complexes. With the results of this study, we now have a complete list of constants for divalent metal complexes of the first transition series.

Experimental

Reagents.—Chromium(II) chloride solutions were prepared from primary standard grade potassium dichromate as previously described[5] by reduction with hydrogen peroxide and a mercury cathode. The Cr(II) content was determined by indirect potentiometric titration with ceric solution after adding an excess of ferric ion. The Cr(III) content was determined spectrophotometrically and found to be less than 0.1% of the total Cr. Hydrogen ion was determined by potentiometric titration with sodium hydroxide.

Reagent grade disodium EDTA was assayed by titration with base. All solutions were finally adjusted to 0.1 *F* ionic strength with reagent grade potassium chloride.

pH Measurements.—We define pH as the negative logarithm of the hydrogen ion *concentration*. All pH measurements were made with a Radiometer PHM4C meter using a Radiometer G202B glass electrode. Solutions were adjusted to 0.100 *F* ionic strength at 20.00 ± 0.02°. The electrode was calibrated under the same conditions over the pH range 1 to 4, with a linear response of 58.20 mv./pH unit. Measurements were reproducible to ±0.2 mv.

Polarography.—The polarographic cell consisted of a thermostated beaker with an external saturated calomel electrode connected by a double compartment salt bridge filled with KCl solution. The cell resistance was 690 ohms. Polarograms were recorded on a Sargent XXI polarograph without damping. The slide wire was calibrated by checking the applied potential at two

---

[1] Presented in part at the Sixteenth Annual Summer Symposium of the Division of Analytical Chemistry, American Chemical Society, Tucson, Arizona, June, 1963. This research was supported by the National Science Foundation. Abstracted from a thesis presented by L. D. Shields to the Graduate Division, University of California, Los Angeles, for the Ph.D. degree, Sept., 1963.

[2] du Pont Teaching Fellow, 1961–1962.

[3] R. L. Pecsok and J. J. Lingane, *J. Am. Chem. Soc.*, **72**, 189 (1950).

[4] R. L. Pecsok, *J. Chem. Educ.*, **29**, 597 (1952).

[5] R. L. Pecsok and W. P. Schaefer, *J. Am. Chem. Soc.*, **83**, 62 (1961).

[6] S. Chaberek and A. E. Martell, "Organic Sequestering Agents," John Wiley and Sons, New York, N. Y., 1959, p. 572.