PYRIDINE–METAL COMPLEXES

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AN INTERSCIENCE® PUBLICATION

JOHN WILEY & SONS
NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

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This is Part 6A of the fourteenth volume in the series

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

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A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER AND EDWARD C. TAYLOR

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Library of Congress Cataloging in Publication Data:

Tomasik, Piotr.
Pyridine–metal complexes.

(The Chemistry of heterocyclic compounds,
ISSN 0069-3154; v. 14, pt. 6)
"An Interscience publication."
Includes bibliographies.
1. Pyridine. 2. Complex compounds. 3. Organometallic compounds. I. Ratajewicz, Zbigniew.
II. Newkome, George R. (George Richard) III. Strękowski,
Lucjan. IV. Title. V. Series: Chemistry of
heterocyclic compounds; v. 14.
QD401.T66 1985 547′.593 84-26939
ISBN 0-471-05073-3

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

The Chemistry of Heterocyclic Compounds

The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds.

A field of such importance and intrinsic difficulty should be made as readily accessible as possible, and the lack of a modern detailed and comprehensive presentation of heterocyclic chemistry is therefore keenly felt. It is the intention of the present series to fill this gap by expert presentations of the various branches of heterocyclic chemistry. The subdivisions have been designed to cover the field in its entirety by monographs which reflect the importance and the interrelations of the various compounds, and accommodate the specific interests of the authors.

In order to continue to make heterocyclic chemistry as readily accessible as possible new editions are planned for those areas where the respective volumes in the first edition have become obsolete by overwhelming progress. If, however, the changes are not too great so that the first editions can be brought up-to-date by supplementary volumes, supplements to the respective volumes will be published in the first edition.

ARNOLD WEISSBERGER

Research Laboratories
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Preface

Complexes of pyridine and its derivatives are a cornerstone to diverse chemical reactions. The understanding and appreciation of the pyridine *N*-electrons have enormous long-range ramifications in the future design of industrial catalysts and drugs. This book is the first comprehensive review of the coordination compounds of pyridine, pyridine *N*-oxide, and their ring-substituted derivatives with known metals capable of forming such complexes.

The topics discussed are: a brief theoretical overview, preparative methods, structural aspects including x-ray diffraction data, physical methods of analysis, as well as chemical and physicochemical properties, and biological activity. Applications of these complexes are also noted, such as: catalysts in organic and polymer synthesis, analytical chemistry of metals, separation and isolation of metals, bright deposition of metals, and miscellaneous academic and industrial applications. All complexes are compiled in tables according to the metal providing direct access to the key references. The analytical applications of the ligands are also tabulated. Eleven thousand references are provided, thus affording interested researchers access to nearly a century of information on this topic. We apologize for small inconsistencies but the volume of chemical and structural details was herculean; we do, however, hope that they were kept to a minimum.

We believe that any academic or industrial researcher in these fields will first consult this treatise for the historic and current perspectives.

GEORGE R. NEWKOME

Baton Rouge, Louisiana

LUCJAN STREKOWSKI

Atlanta, Georgia
May 1985

Contents

Guide to Using the Book

This monograph has the following organization: Chapter 1 presents a brief theoretical introduction to coordination compounds. This is followed in Chapters 2 and 3 by a thorough presentation of pyridine σ-complexes with nontransition metals and transition, respectively. These Chapters are organized according to the Groups of the Periodic Table; thus for each Metal Group, the complexes are arranged in order from the top to bottom of the Periodic Table. The metal σ-complexes with pyridine *N*-oxides are presented in Chapter 4 and arranged similarly. Chapter 5 deals with the metal–pyridine π-complexes, while pyridine intercalation compounds and clathrates are discussed in Chapters 6 and 7, respectively.

ORGANIZATION OF THE TABLES

All the tables are integrated within the text. In Chapters 2–5 ionic "complexes" and nonionized "complex compounds" (see Section 1.5) are tabulated in the general form $\text{Metal}_m X_p \text{ (Pyridine Ligand)}_n Y_q$. In this formula X represents either a charge on the complex, an anion, or an organic moiety of a metallo-organic portion in the complex; Y is any additional nonpyridine ligand; and m, p, n, and q denote the number of respective components. These complexes are listed in the order resulting from the following sequence of criteria:

1. Metals of a given Group are arranged from a top to bottom order within the Periodic Table.
2. For a given metal, the lowest oxidation state has precedence over the higher oxidation states.
3. The complexes are listed in order of increasing metal atoms (m).
4. The complexes are listed in order of increasing pyridine ligands (n).
5. Unsubstituted pyridine is followed by increasing alkyl groups, then, vinyl-, and phenyl-substituted derivatives, and then by hetero-substituted pyridine ligands.
6. Polysubstituted pyridines are listed in order of increasing numbers of substituents.
7. The X groups are ordered following essentially the same criteria as noted for the pyridine substituents.

These general tables are followed by tables listing the spectrophotometric determination of a metal using a pyridine ligand. Occasionally, tables with crystallographic data for the coordination compounds are included.

The Guide to Using the Systematic Tables is given below. The guide lists metals (in alphabetical order) and the relevant tables with a page number (in parentheses) on which listing of the particular data for a given metal begins.

GUIDE TO USING THE SYSTEMATIC TABLES

Metal	Metal Coordination Compounds		Photometric Determination of the Metal
	General Information	Crystallographic Data	
Aluminum (III)	2.11 (62); 4.3 (2078)		2.16 (96)
Americium (III)	3.44 (687); 4.8 (2139)		
(VI)	3.44 (688); 4.8 (2139)		
Antimony (III)	2.22 (140); 4.5 (2092)	4.14 (2194)	2.24 (152)
(V)	2.22 (142); 4.5 (2092)		
Arsenic (III)	2.21 (138); 4.5 (2092)		
Barium (II)	2.8 (51); 4.2 (2074)		
Berkelium (III)	3.44 (688)		
Beryllium (II)	2.4 (22); 4.2 (2072)	2.9 (54)	2.10 (60)
Bismuth (III)	2.23 (146); 4.5 (2095)	4.14 (2194)	2.24 (152)
(V)	4.5 (2095)		
Cadmium (II)	3.18 (526); 4.7 (2113)	3.19 (566); 4.14 (2195)	3.20 (567)
Calcium (0)	2.6 (42)		
(II)	2.6 (42); 4.2 (2073)	2.9 (54)	
Californium (III)	3.44 (688)		
Cerium (III)	3.28 (620); 4.8 (2124)		3.46 (693)
(IV)	3.28 (626); 4.8 (2124)		
Cesium (I)	2.2 (17); 4.1 (2071)		
Chromium (0)	3.63 (766); 5.1 (2214)		
(I)	3.64 (770)		
(II)	3.64 (770)		
(III)	3.64 (772); 3.65 (774); 4.11 (2156)	3.76 (838)	3.67 (801)
(IV)	3.66 (796)		
(V)	3.66 (796)		
(VI)	3.66 (796); 4.11 (2157)		3.67 (801)
Cobalt (0)	3.91 (1020); 5.1 (2215)		
(I)	3.91 (1020)		
(II)	3.92 (1022); 3.93 (1166) 4.13 (2170)	3.95 (1304); 4.14 (2195)	3.96 (1314)
(III)	3.93 (1166); 3.94 (1168); 4.13 (2178)	3.95 (1306)	3.97 (1323)
(IV)	3.94 (1302)		
Copper (0)	3.1 (188)		
(I)	3.1 (188); 3.3 (203); 4.6 (2096)	3.2 (202)	3.4 (206)
(II)	3.3 (203); 3.5 (208); 4.6 (2096)	3.6 (390); 4.14 (2194)	3.7 (410)
Curium (III)	3.44 (688); 4.8 (2139)		
Dysprosium (III)	3.35 (652); 4.8 (2129)		3.46 (693)
Erbium (III)	3.37 (658); 4.8 (2130)	3.45 (689)	3.46 (694)
Europium (II)	3.32 (641)		3.46 (693)
(III)	3.32 (641); 4.8 (2127)	3.45 (689)	3.46 (693)
Gadolinium (III)	3.33 (645); 4.8 (2128)	3.45 (689)	3.46 (693)

Metal	Metal Coordination Compounds		Photometric Determination of the Metal
	General Information	Crystallographic Data	
Gallium(I)	2.12(72)		
(III)	2.12(72); 4.3(2079)	2.15(88)	2.16(96)
Gold(I)	3.12(435)		3.14(441)
(III)	3.13(436); 4.6(2016)		3.14(441)
Hafnium(IV)	3.51(716); 4.9(2144)		3.54(723)
Holmium(III)	3.36(656); 4.8(2130)	3.45(689)	3.46(694)
Indium(III)	2.13(76); 4.3(2079)		2.16(97)
Iridium(0)	3.116(1710)		
(I)	3.116(1710)	3.117(1738)	
(II)	3.116(1716)		
(III)	3.116(1716); 3.116(1736); 4.13(2188)	3.117(1738)	3.118(1741)
(IV)	3.116(1736)		3.118(1741)
(V)	3.116(1736)		
Iron(0)	3.85(910); 5.1(2215)	3.88(1008)	
(I)	3.85(912)		
(II)	3.85(912); 3.86(978); 4.13(2166)	3.88(1008)	3.89(1012)
(III)	3.86(978); 3.87(980); 4.13(2166)	3.88(1008)	3.90(1018)
(IV)	3.87(1006)		
Lanthanum(III)	3.27(610); 4.8(2123)	3.45(689); 4.14(2195)	3.46(692)
Lead(II)	2.18(126); 4.4(2089)	2.19(132)	2.20(136)
(IV)	2.18(130); 4.4(2089)		
Lithium(0)	2.2(14)		
(I)	2.2(14); 4.1(2070)	2.3(18)	
Lutetium(III)	3.40(666); 4.8(2132)	3.45(689)	3.46(694)
Magnesium(0)	2.5(28)		
(II)	2.5(28); 4.2(2072)	2.9(54)	2.10(60)
Manganese(0)	3.77(840); 5.1(2215)		
(I)	3.77(841); 4.12(2160)		
(II)	3.78(844); 4.12(2160)	3.83(901)	3.84(906)
(III)	3.79(882); 4.12(2162)		3.84(907)
(IV)	3.79(885)		
Mercury(I)	3.21(569); 4.7(2115)	3.23(600)	3.24(603)
(II)	3.22(570); 4.7(2115)	3.23(600); 4.14(2195)	3.24(603)
Molybdenum(0)	3.68(802); 5.1(2214)	3.76(838)	
(I)	3.69(806)		
(II)	3.69(806); 4.11(2157)	3.76(838)	
(III)	3.70(811)	3.76(838)	
(IV)	3.71(814); 4.11(2157)		
(V)	3.71(815)		
(VI)	3.72(820); 4.11(2157)		3.73(827)
clusters	4.11(2158)		
Neodymium(III)	3.30(634); 4.8(2125)	3.45(689)	3.46(693)
Neptunium(IV)	3.44(686)		
(V)	3.44(686); 4.8(2138)		3.47(696)
(VI)	3.44(686); 4.8(2138)	4.14(2195)	
Nickel(0)	3.98(1326); 5.1(2215)		
(I)	3.98(1327)		
(II)	3.99(1328); 4.13(2180)	3.101(1522); 4.14(2195)	3.102(1530)
(III)	3.100(1518)		
(IV)	3.100(1520)	3.101(1526)	
Niobium(IV)	3.58(750)		

Metal	Metal Coordination Compounds		Photometric Determination of the Metal
	General Information	Crystallographic Data	
Niobium (V)	3.58 (750); 4.10 (2154)		3.62 (764)
clusters	3.58 (750); 4.10 (2154)		
Osmium (0)	3.113 (1682)		
(I)	3.113 (1682)		
(II)	3.113 (1683)	3.114 (1704)	
(III)	3.113 (1686)		
(IV)	3.113 (1689)		3.115 (1708)
(VI)	3.113 (1689)	3.114 (1704)	3.115 (1708)
(VIII)	3.113 (1703)		3.115 (1708)
Palladium (0)	3.110 (1626)		
(I)	3.110 (1626)		
(II)	3.110 (1626); 4.13 (2186)	3.111 (1672)	3.112 (1676)
(IV)	3.110 (1670)		
Platinum (0)	3.119 (1742); 5.1 (2215)	3.122 (1830)	
(I)	3.119 (1742)		
(II)	3.119 (1742); 3.120 (1804) 4.13 (2188)	3.122 (1830); 4.14 (2195)	3.123 (1838)
(III)	3.120 (1804)		
(IV)	3.120 (1804); 3.120 (1805) 3.121 (1806); 4.13 (2192)		3.123 (1838)
Plutonium (III)	3.44 (687)		
(IV)	4.8 (2138)		
(VI)	3.44 (687); 4.8 (2138)		
Potassium (0)	2.2 (16)		
(I)	2.2 (16); 4.1 (2070)		
Praseodymium (III)	3.29 (628); 4.8 (2124)	3.45 (689)	3.46 (693)
Rhenium (0)	3.81 (887); 5.1 (2215)		
(I)	3.81 (887); 4.12 (2163)		
(II)	3.81 (889); 4.12 (2163)		
(III)	3.81 (890); 4.12 (2163)		3.84 (907)
(IV)	3.81 (891)		
(V)	3.81 (893); 3.82 (894)	3.83 (901)	3.84 (907)
(VI)	3.82 (900)		
(VII)	3.82 (900)		
Rhodium (I)	3.106 (1568); 4.13 (2186)	3.108 (1620)	3.109 (1624)
(II)	3.106 (1586)		
(III)	3.107 (1590); 4.13 (2186)	3.108 (1620)	3.109 (1624)
(IV)	3.107 (1618)		
Rubidium (I)	2.2 (17); 4.1 (2071)		
Ruthenium (0)	3.103 (1536)		
(I)	3.103 (1536)		
(II)	3.103 (1536); 3.103 (1550); 4.13 (2186)	3.104 (1562)	
(III)	3.103 (1550); 3.103 (1552); 4.13 (2186)		3.105 (1566)
(IV)	3.103 (1558)		3.105 (1566)
(VI)	3.103 (1560)		
(VIII)	3.103 (1560)		
Samarium (III)	3.31 (638); 4.8 (2126)	3.45 (689)	3.46 (693)
Scandium (III)	3.25 (606); 4.8 (2122)	3.45 (689)	3.46 (692)
Silver (I)	3.8 (414); 4.6 (2015)	3.10 (430)	3.11 (434)
(II)	3.9 (428); 4.6 (2016)	3.10 (430)	3.11 (434)

Metal	Metal Coordination Compounds		Photometric Determination of the Metal
	General Information	Crystallographic Data	
Sodium (0)	2.2 (14)		
(I)	2.2 (15); 4.1 (2070)		
Strontium (II)	2.7 (50); 4.2 (2074)	2.9 (54)	
Tantalum (II)	3.59 (756)		
(IV)	3.59 (756)		
(V)	3.59 (756); 4.10 (2154)		3.62 (765)
Technetium (I)	3.80 (886)		
(V)	3.80 (886)	3.83 (901)	
Tellurium (IV)	2.25 (154); 4.5 (2092)		
(VI)	2.25 (155)	2.26 (156)	
Terbium (III)	3.34 (648); 4.8 (2128)	3.45 (689)	3.46 (693)
Thallium (I)	2.14 (82); 4.3 (2080)		
(III)	2.14 (82); 4.3 (2080)	2.15 (88)	2.16 (99)
Thorium (IV)	3.41 (668); 4.8 (2132)		3.47 (695)
Thulium (III)	3.38 (661); 4.8 (2131)		3.46 (694)
Tin (II)	2.17 (102); 4.4 (2082)		
(IV)	2.17 (103); 4.4 (2083)	2.19 (132); 4.14 (2194)	2.20 (136)
Titanium (I)	3.48 (697)		
(II)	3.48 (697)		
(III)	3.48 (697)	3.52 (717)	
(IV)	3.49 (700); 4.9 (2142)	3.52 (717)	3.53 (721)
Tungsten (0)	3.74 (828); 5.1 (2215)		
(I)	3.75 (832)		
(II)	3.75 (832)		
(III)	3.75 (833)	3.76 (838)	
(IV)	3.75 (834)		
(V)	3.75 (835)		
(VI)	3.75 (835); 4.11 (2159)		
Uranium (III)	3.42 (672)		
(IV)	3.42 (672); 4.8 (2133)		
(V)	3.42 (673)		
(VI)	3.43 (674); 4.8 (2133)	3.45 (689); 4.14 (2195)	3.47 (695)
Vanadium (0)	3.55 (724)		
(I)	3.55 (724)		
(II)	3.55 (724)	3.60 (759)	
(III)	3.55 (725); 4.10 (2146)	3.60 (759)	3.61 (760)
(IV)	3.56 (730); 4.10 (2146)	3.60 (759)	3.61 (760)
(V)	3.57 (744); 4.10 (2153)		3.61 (760)
Ytterbium (III)	3.39 (663); 4.8 (2131)	3.45 (689)	3.46 (694)
Yttrium (III)	3.26 (608); 4.8 (2122)		3.46 (692)
Zinc (II)	3.15 (444); 4.7 (2110)	3.16 (516); 4.14 (2194)	3.17 (522)
Zirconium (III)	3.50 (708)		
(IV)	3.50 (708); 4.9 (2144)		3.54 (723)

ABBREVIATIONS

Physical properties and physicochemical methods for these coordination compounds, as well as commonly used substituents and ligands, are abbreviated. The following abbreviations (listed in alphabetical order) are used:

acr	Acridine or acridinyl
b	Bright
bipy	2,2′-Bipyridine
bk	Black
B.P.	Boiling point
Bu	Butyl
bu	Blue
bush	Bluish
bw	Brown
bwsh	Brownish
ca	Correlation analysis
cal	Calorimetry
cd	Circular dichroism
chr	Chromatography
cond	Conductance (electric)
d	Dark
dc	Distribution coefficient
dec	Decomposition
dien	Diethylenetriamine [*N*-(2-aminoethyl)ethylenediamine]
dm	Dipole moment
DMF	*N*,*N*-Dimethylformamide
ed	Electron diffraction
em	Electron microscopy
en	Ethylenediamine
epr	Electron paramagnetic resonance
Et	Ethyl
g	Green
gsh	Greenish
gy	Grey
gysh	Greyish
Hacac	Acetylacetone (2,4-pentanedione)
H_2dmg	Dimethylglyoxime (2,3-butanedione dioxime)
H_4EDTA	Ethylenediaminetetraacetic acid
H_2salen	*N*,*N*′-Bis(salicylidene)ethylenediamine
H_2tsalen	*N*,*N*′-Bis(2-mercaptobenzylidyne)ethylenediamine

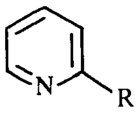
H_2sap	2-Hydroxy-*N*-(salicylidene)aniline
ir	Infrared spectroscopy
isoquin	Isoquinoline or isoquinolyl
K	Equilibrium constant
k	Rate constant
l	Light
lum	Luminescence spectroscopy
mcd	Magnetic circular dichroism
Me	Methyl
moe	Mossbauer spectroscopy
M.P.	Melting point
ms	Mass spectrometry
msc	Magnetic susceptibility
n	Refractive index
nd	Neutron diffraction
nmr	Nuclear magnetic resonance
nqr	Nuclear quadrupole resonance
o	Orange
ol	Olive
ord	Optical rotatory dispersion
p	Potentiometry
PAN	1-(2-Pyridylazo)-2-naphthol
PAR	4-(2-Pyridylazo)resorcinol
pc	Phthalocyanine
Ph	Phenyl
phen	1,10-Phenanthroline
pic	Picoline
pk	Pink
pmr	Proton magnetic resonance
porph	Porphine
pp	Purple
Pr	Propyl
py	Pyridine or pyridyl
pyO	Pyridine *N*-oxide
qch	Quantum chemical calculations
quin	Quinoline or quinolyl
r	red
ram	Raman spectroscopy
rsh	Reddish
R.T.	Room temperature
sol	Solubility

T	Temperature
terpy	2,2′:6′,2″-Terpyridine
th	Thermodynamic studies
tha	Thermal analysis
thioph	Thiophene or thienyl
urtp	Urotropine (hexamethylenetetramine)
uv	Ultraviolet spectroscopy
v	Violet
visc	Viscosity
w	White
xr	Powder x-ray diffraction studies
xr	Single crystal x-ray diffraction studies
xrp	X-ray photoelectron spectroscopy
y	Yellow
ysh	Yellowish

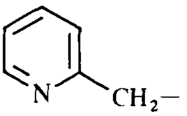
NOTE ON THE NOMENCLATURE

The I.U.P.A.C. recommendations for the nomenclature of organic chemistry* have generally been used throughout this treatise. However, a few inconsistencies with these recommendations have herein been used, generally to simplify user interpretation or to remain consistent throughout an inconsistent recommendation.*

As recommended, "nicotinic acid" and "isonicotinic acid" are used for 3- and 4-pyridinecarboxylic acids, respectively. Since the list of accepted trivial names for heterocyclic carboxylic acids is nonlimiting,* picolinic acid is proposed herein as the accepted trivial name for 2-pyridinecarboxylic acid (**1**). Accordingly, the derivatives are thus named picolinaldehyde (**2**), picolinonitrile (**3**), picolinamide (**4**), thiopicolinamide (**5**), and picolinohydrazide (**6**). The trivial names of picolines (*mono*methylpyridines), lutidines (*di*methylpyridines), and collidines (*tri*methylpyridines) are retained because they are vastly preferred in the literature. For the same reason, a pyridylmethyl group is called picolyl (**7**, 2-isomer shown); however, 2-pyridylmethylene is the only name used for moiety **8**. For the sake of simplicity the name anabasine is herein used for **9** but its



1, R = COOH
2, R = CHO
3, R = CN
4, $R = CONH_2$
5, $R = CSNH_2$
6, $R = CONHNH_2$



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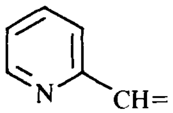

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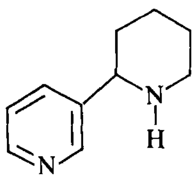

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*International Union of Pure and Applied Chemistry, *Nomenclature of Organic Chemistry*, Pergamon Press, Oxford, 1979.

tabulated, substituted derivatives are named according to the more cumbersome systematic approach.

The tables listing spectrophotometric determination of metals contain full names of the ligands. When a structurally complicated co-factor is used for such determination, its short, trivial name is given. These compounds are listed below, together with the respective Chemical Abstracts Indexes:

Abietic acid	[514-10-3]
Azotol A	[92-77-3]
Azotol OA	[135-62-6]
Azotol OT	[135-61-5]
Azotol PA	[92-79-5]
Chromazurol S	[1667-99-8]
Crystal Violet	[14426-25-6]
Gossypol	[303-45-7]
Pyrocatechol Violet	[115-41-3]
Rhodamine B	[81-88-9]
Triton B	[64-02-8]

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CHAPTER 1

Essentials of Coordination Chemistry

Many chemists involved in studies of the chemical behavior and physicochemical properties of pyridines assumed that all the data collected dealt with pyridines themselves. Such an assumption can be incorrect, unless the investigations are carried out either in the vapor phase or with a good deal of approximation in nonpolar solvents. Because of its geometry, the orbital of the lone electron pair of the ring nitrogen atom is not involved in resonance with the ring π-electron system, and it is easily accessible for interactions with solvent molecules and various species present in solutions. Such interactions readily, and often significantly, influence the reactivity and various properties of pyridines under study. This is well illustrated by attempts to describe electronic properties of the ring nitrogen atom in terms of various σ-substituent constants (1,2), as well as by the dependence on the solvent of σ constants for the pyridyl groups (3).

Changes in the chemical properties of chemical compounds by the complexation were very soon realized. The amount of work dealing with the changes in the central atom and not in the ligand is striking. Meerwein (4) was one of the first to have paid attention to variations of the electronic structure of the ligand and he interpreted them on the basis of electronic theory.

Investigations of salts, complexes, and chelates of pyridines can be very helpful in understanding and appreciating the effect of engagement of the lone pair of *N*-electrons on the properties and behavior of pyridines. Moreover, these compounds are interesting for a wide range of practical applications.

This chapter is devoted to pyridine coordination compounds with a metal as the central atom. Clathrates and intercalates are also included.

The selection between metals and metaloids is based on the current conductivity criterium. Thus, apart from transition metals, all metals of the first and second group of the Periodical Table are considered. The pyridine complex species of boron, silicon, and germanium are beyond the scope of this chapter, since these elements are nonmetals. The metals of the fifth group are represented by arsenic, antimony, and bismuth, and in the sixth group, only tellurium and polonium are metals.

Because of the tremendous amount of data dealing with the complexes of both the pyridine and pyridine *N*-oxide series, the systems containing the pyridine ring bonded to another heteroaromatic ring are not considered. For this reason, bipyridyls, pyridylimidazoles, pyridyltriazines, and so on are not discussed in this chapter. Pyridinium salts and pyridinium double salts (e.g., chloroplatinates, chloroaurates, etc.) are also beyond our scope. They can be interesting for many reasons, but they are not pyridine–metal complexes in character. Several pyridine derivatives, for instance, pyridinols and pyridones, coordinate metals through heteroatoms other than the ring nitrogen atom. The pyridine ligands, that are not coordinated through the ring nitrogen, the oxygen of the 1-oxide, or the ring π-electron system are also omitted.

1.1. FORMATION OF THE COMPLEXES

The driving force of the atoms to form molecules originates from their tendency to reach an energetically favored state, that is, to create the electronic structure of the noble gas on either the atomic or molecular orbitals. This tendency is responsible for the formation of molecules with valence bonds. Formation of molecules in such a way does not always satisfy the electronic demands of the molecules resulting from vacancies in the form of hybridized orbitals which surround molecules or ions. They remain empty even if the possibilities for the formation of valence bonds are already exhausted. Such molecules and ions (Lewis acids) are capable of accepting electrons from either other ions or neutral molecules, disposing preferably with nonbonding electrons (Lewis bases). When a Lewis base donates electrons to the Lewis acid, a complex species is formed by means of a coordination bond. If the lone electron pair of the Lewis base (ligand) is engaged in the coordination bond, the coordination compound is called a *σ-complex*. In some cases, the electrons of the π system can enter hybridized vacancies of the Lewis acid to form a *π-complex*. The number of unoccupied vacancies estimates the potential number of ligands that can be bonded to the Lewis acid, that is, its *coordination number*. It may or may not correspond to the actual coordination number of given Lewis acid, owing to both electronic and steric reasons as well as to the concentration of the ligand in the course of complex formation. However, the presence of empty hybridized orbitals is not a necessary condition to form coordination compounds. Several complexes are formed because of the interactions between ions (electrostatic forces) and molecules with high dipole or induced dipole moments. The species formed in such a way are called *adducts*, *solvates*, and so on.

The electric field of the species formed in classical ways from the central atom and the ligands (so-called *primary complex*) can be felt by ions and neutral molecules beyond the inner sphere of the complex. In such cases, some regular arrangement around the primary complex can be met. In this manner, a *secondary complex*, containing molecules in the outer sphere, is built up.

1.2. SYSTEMATICS OF THE COMPLEXES

The types of complexes may be related to the central atom coordination number, which may result from the type of hybridization of all unoccupied orbitals and orbitals occupied by lone *N*-electrons (5). The type of hybridization implies simultaneously the geometry of the complexes, as shown in Table 1.1. The configuration of solvates and adducts is governed first by the steric effect of the ligands, which again is dependent on the ratio of the radius of the central atom (r_M) and the radii of the ligands (r_L). Table 1.2 shows such a relationship. The rule mentioned above may also be valid in complexes with coordination bonds. The geometries listed in Tables 1.1 and 1.2 may be distorted for more or less recognized reasons.

Another systematics of the complexes is based on the behavior of the Lewis acid when attached to the Lewis base. Thus, in the reaction

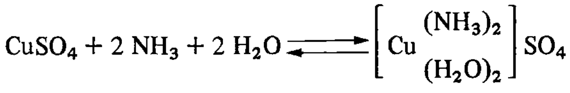
$$PtCl_2 + 2\,NH_3 \longrightarrow [Pt(NH_3)_2Cl_2]$$

the *complex compound*, called the *Werner complex*, is formed. The ligand (NH_3) entering

TABLE 1.1. THE RELATIONSHIP BETWEEN THE HYBRIDIZATION OF THE CENTRAL ATOM, ITS COORDINATION NUMBER, AND THE GEOMETRY OF THE COMPLEX

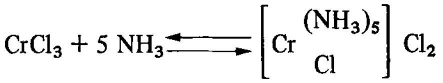
Type of Hybridization	Coordination Number	Geometry
sp or dp	1	Linear
p^2, ds, or d^2	2	Nonlinear
p^2, dp^2, d^2s, or d^2	3	Planar trigonal (120°)
dsp	3	Dissymmetric planar
p^3 or d^2p	3	Trigonal pyramid
sp^3 or d^3s	4	Tetrahedral (109°28′)
dsp^2 or d^2p^2	4	Planar tetragonal
d^2sp, dp^3, or d^3p	4	Distorted tetrahedral
d^4	4	Tetragonal pyramid
dsp^3 or d^3sp	5	Trigonal bipyramid
d^2sp^2, d^4s, d^2p^3, or d^4p	5	Tetragonal pyramid
d^3p^2	5	Planar pentagonal
d^5	5	Pentagonal pyramid
d^2sp^3	6	Octahedral
d^4sp or d^5p	6	Trigonal prismatic
d^3p^3	6	Trigonal antiprismatic
d^4sp^3	8	Dodecahedral
d^5p^3	8	Antiprismatic
d^5sp^2	8	Flat centered prismatic

hybridized orbitals of the Pt atom does not remove the chlorine atoms from the coordination sphere denoted by the bracket, and the resulting compound does not dissociate in solution. This is not the case when $CuSO_4$ reacts with aqueous ammonia*



$$CuSO_4 + 2\,NH_3 + 2\,H_2O \rightleftharpoons \left[Cu\begin{matrix}(NH_3)_2\\(H_2O)_2\end{matrix}\right]SO_4$$

or when $CrCl_3$ coordinates ammonia*



$$CrCl_3 + 5\,NH_3 \rightleftharpoons \left[Cr\begin{matrix}(NH_3)_5\\Cl\end{matrix}\right]Cl_2$$

TABLE 1.2. THE RELATIONSHIP BETWEEN THE r_M/r_L RATIO, THE NUMBER OF LIGANDS (n), AND THE GEOMETRY OF THE COMPLEXES

r_M/r_L	n	Geometry
Arbitrary	2	Linear
0.15	3	Trigonal
0.22	4	Tetrahedral
0.41	5	Trigonal bipyramid
>0.41	6	Octahedral
0.73	8	Cubic

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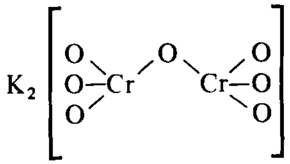
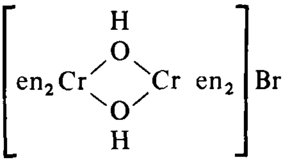
[*] The actual composition of the complex may vary depending upon the concentration of ammonia.

Such complexes are known as *cationic complexes*. One might imagine complexes containing any cation and complex anion; these *anionic complexes* may be represented by chloroplatinic acid ($H_2[PtCl_6]$), sodium chloroaurate ($Na[AuCl_4]$), and potassium tetraiodomercurate ($K_2[HgI_4]$). Complex acids like $H_2[PtCl_6]$, $H[AuCl_4]$, and so on can react with neutral molecules (B) bearing lone electron pairs to form *onium double salts*, such as $(BH)_2^+[PtCl_6]^{2-}$, $BH^+[AuCl_4]^-$, and others, respectively. Although the complex character of the anion is retained, they have the character of the salt with respect to the B species.

Depending on the number of central atoms involved in the complex formation, they are classified as *mono-*, *di-*, and *polynuclear complexes*. Thus, for instance, potassium dichromate (**1.1**) and tetrakis(ethylenediamine)-μ-dihydroxodichromium(III) bromide (**1.2**) are dinuclear complexes.

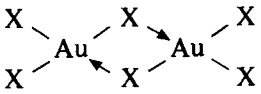


1.1

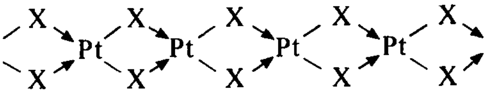


1.2

It may happen that the electronic demands of the central atom are not appeased by the ligand electrons, but by another complex. Such autoligation leads to *polynuclear complexes* like (**1.3**) and (**1.4**).

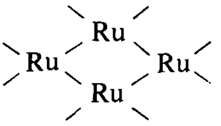


1.3



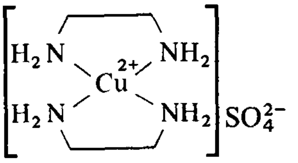
1.4

Another central atom can act as the source of electrons, thus two or more complexes polymerize into *cluster complexes* like (**1.5**), in which direct metal–metal bonds exist.

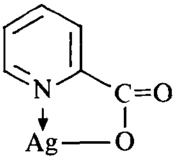


1.5

The following systematics of complexes arises from the nature of the ligands. Ligands disposed with more than one electron pair, which can fill hybridized orbitals of the central metal, are called *bi-*, *tri-*, *quatro-*, and generally *multidentate ligands*. In particular cases resulting from steric conditions, two or more lone electron pairs of one ligand can be coordinated with hybridized orbitals of one atom to form *chelates* like (**1.6**) and (**1.7**).



1.6



1.7