
PYRIDINE–METAL COMPLEXES

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PYRIDINE-METAL COMPLEXES

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THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

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A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER AND EDWARD C. TAYLOR

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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

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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.

Baton Rouge, Louisiana

GEORGE R. NEWKOME

*Atlanta, Georgia
May 1985*

LUCJAN STREKOWSKI

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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 $\text{Metal}_m\text{X}_p(\text{Pyridine Ligand})_n\text{Y}_q$. 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) clusters	3.58(750); 4.10(2154) 3.58(750); 4.10(2154)		3.62(764)
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 [<i>N</i> -(2-aminoethyl)ethylenediamine]
dm	Dipole moment
DMF	<i>N,N</i> -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 ₂ dmg	Dimethylglyoxime (2,3-butanedione dioxime)
H ₄ EDTA	Ethylenediaminetetraacetic acid
H ₂ salen	<i>N,N'</i> -Bis(salicylidene)ethylenediamine
H ₂ tsalen	<i>N,N'</i> -Bis(2-mercaptobenzylidene)ethylenediamine

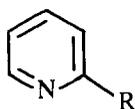
H ₂ sap	2-Hydroxy- <i>N</i> -(salicylidene)aniline
ir	Infrared spectroscopy
isoquin	Isoquinoline or isoquinolyl
K	Equilibrium constant
k	Rate constant
l	Light
lum	Luminescence spectroscopy
mcd	Magnetic circular dichroism
Me	Methyl
moe	Mossbauer spectroscopy
M.P.	Melting point
ms	Mass spectrometry
msc	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 <i>N</i> -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 (*monomethylpyridines*), lutidines (*dimethylpyridines*), and collidines (*trimethylpyridines*) 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

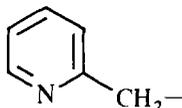
2, R = CHO

3, R = CN

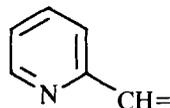
4, R = CONH₂

5, R = CSNH₂

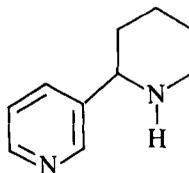
6, R = CONHNH₂



7



8



9

*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]

GEORGE R. NEWKOME
LUCJAN STREKOWSKI

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 metalloids 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, pyridyl-imidazoles, 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

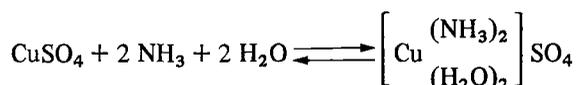


the *complex compound*, called the *Werner complex*, is formed. The ligand (NH_3) entering

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 ($109^\circ 28'$)
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*



or when CrCl_3 coordinates ammonia*

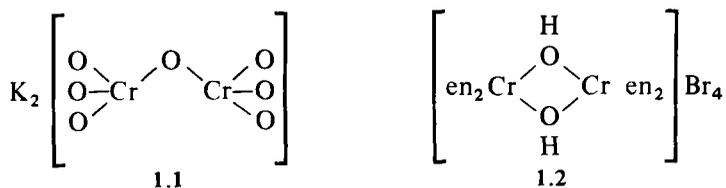
TABLE 1.2. THE RELATIONSHIP BETWEEN THE r_M/r_L RATIO, THE NUMBER OF LIGANDS (n), AND THE GEOMETRY OF THE COMPLEXES

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

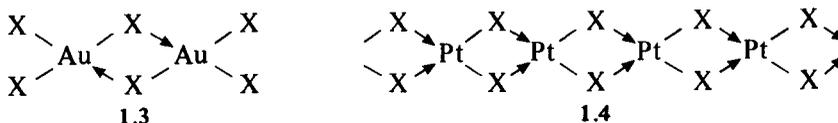
* The actual composition of the complex may vary depending upon the concentration of ammonia.

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 ($\text{H}_2[\text{PtCl}_6]$), sodium chloroaurate ($\text{Na}[\text{AuCl}_4]$), and potassium tetraiodomercurate ($\text{K}_2[\text{HgI}_4]$). Complex acids like $\text{H}_2[\text{PtCl}_6]$, $\text{H}[\text{AuCl}_4]$, and so on can react with neutral molecules (B) bearing lone electron pairs to form *onium double salts*, such as $(\text{BH})_2^+[\text{PtCl}_6]^{2-}$, $\text{BH}^+[\text{AuCl}_4]^-$, 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.

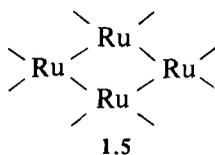
Depending on the number of central atoms involved in the complex formation, they are classified as *mono-*, *di-*, and *polynuclear complexes*. Thus, for instance, potassium dichromate (1.1) and tetrakis(ethylenediamine)- μ -dihydroxodichromium(III) bromide (1.2) are dinuclear complexes.



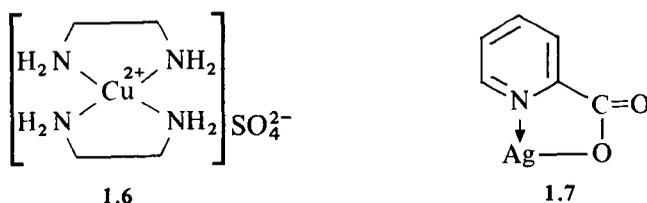
It may happen that the electronic demands of the central atom are not appeased by the ligand electrons, but by another complex. Such autoligation leads to *polynuclear complexes* like (1.3) and (1.4).



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.



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).



Some complexes crystallize from the solutions with either a stoichiometric or non-stoichiometric number of solvent molecules or components present in solution. Such "guest molecules" are imprisoned in the cage formed by the crystalline lattice of the parent complex—"host molecule" and there are no other interactions between them other than van der Waals forces. The complexes bearing caged guest molecules are called *clathrates*. *Chelatoclathrates* are also known.

Several inorganic compounds, like some sulfides of titanium, tantalum, niobium, and zinc, can crystallize in the form of layered structures, which can be intercalated entering the space between the layers by various organic and inorganic molecules. Intercalation results in the formation of either stoichiometric or nonstoichiometric compounds — *intercalates*. There is generally a charge—transfer interaction between the lattice and intercalating molecules.

Further systematics of complexes is derived from the electronic situation of the central atom at the moment of the acceptance of the ligand electrons. If the maximum number of orbitals are populated, the complexes formed with such central atoms are called *high-spin complexes*. Otherwise, the central atoms generate *low-spin complexes*. Also, the ligand electrons enter either outer or inner hybridized orbitals of the central atoms. It has an effect on the chemical and physicochemical properties of the complexes. Since spin characteristics of the complexes are dependent on the ligands, this systematics will be discussed later in more detail.

Quite often, complexes are discussed in terms of their stability (or instability). Although quantitative values are rather limited, the complexes are still considered to be more or less stable in qualitative discussions. Thus, the complexes are *stable* if their $pK > 8$, and *unstable* if the $pK < 8$.

According to Bjerrum, the complexes in solution undergo stepwise dissociation, or there is a stepwise formation of complexes, and there coexist complexes with higher and lower coordination numbers. These are called *successive complexes* (26).

1.3. SYSTEMATICS OF THE LIGANDS

In addition to the systematics of complexes introduced in the preceding paragraph to explain the nature of chelates, the ligands can be arranged based on their chemical structure. There is one essential method of systematics, which is based on their electronic properties and is related to the electronic structure of the complex formed. It is derived from either the ligand field theory (when the complexes in a solution are considered) or the crystal field theory (in the case of the solid state). Both theories rather have historical value, but they will be used here to explain some properties of the complexes. The theories deal with effects of the electric field of the ligands on the *d*-orbitals of the central atom (which actually can also be in an ionic form). The system of *d*-orbitals of the central atom is composed of energetically degenerated d_{xy} , d_{xz} , d_{yz} , d_{z^2} , and $d_{x^2-y^2}$ orbitals. However, under the influence of an octahedral electrostatic crystal field of the ligand, they split into two energetically nonequivalent groups of *d*-orbitals. In octahedral complexes (See Fig. 1.1), the energy difference between two groups of *d*-orbitals, for example, d_{γ} (or t_{2g}) and d_{ϵ} (or e_g), is characterized by the $10Dq$ (or Δ_0) parameter. In tetrahedral complexes, similar splitting of the degenerated orbitals can take place; however, the distribution of the d_{γ} and d_{ϵ} orbitals is reversed (see Fig. 1.2).

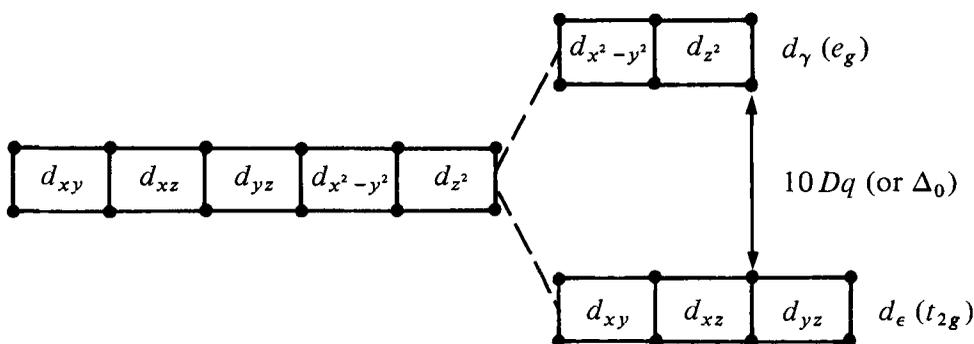


Fig. 1.1

The other symmetry types of coordinated groups have a more complicated pattern of splitting the energy levels of d -orbitals. Thus, one or another mode of differentiation between d -orbitals is due solely to how coordinated groups arrange their positions with respect to the central atom. The ligands enter the electric field of the central atom along the axis occupied by both the $d_{x^2-y^2}$ and d_{z^2} orbitals in the octahedral complexes, and along the axes of all d_{xy} , d_{xz} , and d_{yz} orbitals in tetrahedral complexes. It may be assumed that the hybridization of the central atom (and in consequence one of few possible configurations of the complex) can be influenced by either the approaching or already coordinated ligands. The electric field of the ligand has quite an effect on the $10Dq$ parameter. The ligand, which causes the splitting to exceed the $10Dq$ value, is called a *strong-field ligand* and those producing a splitting below this value belong to the *weak-field ligands*. The field strength of the ligand depends on the central atom. Therefore, it is more convenient to discuss the properties of the ligands in the context of the central atom. Complexes with ligands that behave as strong-field ligands have paired electrons in the orbitals of the central atom and are *low-spin complexes*. Complexes bearing ligands with a weak field have unpaired electrons and belong to the *high-spin complexes*.

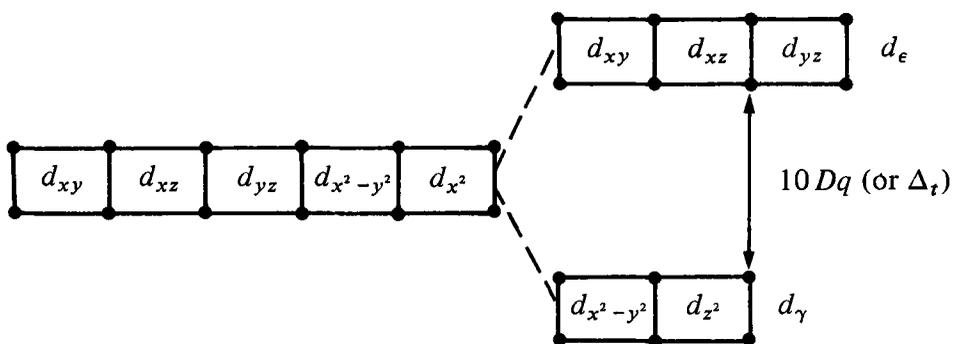


Fig. 1.2

1.4. STABILITY OF COMPLEXES

Complex stability is the most fundamental and most widely studied property of the complexes. If properly interpreted and understood, it can afford valuable information on the electronic properties of all ligands and central atoms and the nature of the interactions between them. Unfortunately, stability of complexes may result from a combination of many factors, which sometimes are not unequivocally interpreted. Thus far, the chemistry of complexes suffers from a lack of any general theory of stability. Several empirical structure–stability relationships have quite limited practical applications. The most essential factors influencing complex stability are given below.

1.4.1. Properties of the Central Atom

Some metal ions have unpaired electrons in their hybridized orbitals and, therefore, are not immediately capable of complexation. First, the energy has to be delivered for pairing these electrons, so as to make available empty orbitals for the incoming ligand electrons. The energy necessary for this rearrangement of the valence shell makes the reaction of such a cation with the ligands difficult. On the other hand, the energy already accumulated in the complex destabilizes the complex. Since the formation of the complex may mainly be considered as the reaction of a cation with either an anion or a neutral ligand, it is quite reasonable that the cation with high charge has a better chance to form strong bonds. Such an assumption is essentially correct, but frequently there are pre-dominating factors. The strength of the bonds formed with the hybridized *d*-orbitals of the inner sphere is higher than that of the bonds with hybridized outer sphere *d*-orbitals. The bonds in which *s*- and *p*-orbitals of the central atom take part are generally weaker. However, the partial positive cation charge can increase the strength of the bonds.

The central atom is almost always capable of bonding to more than one ligand. The ligands already bonded to the central atom significantly change the attitude toward bonding to subsequent ligands by lowering its charge and the number of accessible orbitals. The steric factors also play an important role. An increase of bond strength and, consequently, the lower energy of the complex, which becomes more stable, may additionally come from the deformation of valence orbitals (polarization). The cations prepare entering groups for the reaction by polarizing their electrical system. This effect favors the reaction and it is dependent on the charge-to-radius ratio of the cation. It is quite rational that ions of the transition elements and the ions of the 18-electron elements cause higher polarization than the cations of the electronic structure of a noble gas.

1.4.2. Properties of the Ligands

The bond strength between the central atom and ligand depends on both the density and localization of the charge. The polarizability of the ligand favors formation of the stable ligand–central atom bond. Moreover, the ligand electric field polarizes the central atom, thus increasing the stability of the complex. The shape and size of the ligand can create problems associated with the steric factors. The type of orbital (*s*, *p*, and *d*) involved in bond formation with the central atom also affects the strength of the resultant

bond. Since the overlap of the d -orbitals and their hybrids with the orbitals of the central atom used to be most effective, their participation in the formation of the complex is most profitable for the stability of resulting compound.

Two and more atoms of the same ligand capable of playing the donor role to the central atom can lead to the formation of very stable complexes – chelates. These donor atoms must be situated in the ligand in such a manner that the ring system can be formed; however, steric reasons can prohibit the formation of the chelate ring, even if the conditions for the chelating are apparently present.

1.5. COMPLEXES AND COMPLEX COMPOUNDS

Most authors do not distinguish between complexes and complex compounds. Such differentiation is introduced in this chapter to allow the reader to follow the systematics of the complex species shown in the tables.

Numerous equilibrium, kinetic, and other studies carried out in dilute solution are reported in the literature; therefore, the properties measured relate to ions if the ionization has occurred. Since the attention of many investigators is focused on the complexes, the data in such cases concern complex ionic species, called “complexes” throughout this chapter. Contrary to “complexes” in the sense herein presented, all neutral, nonionizable complexes, which are ionizable but not ionized, are considered here as “complex compounds”. The data concerning these compounds result from full, uncharged structure.

1.6. ISOMERISM IN THE COMPLEX COMPOUNDS

Several types of isomerism of the complex compounds are known:

Ionization Isomerism. The compounds $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_2$ yield a good example of such isomerism. The composition of both compounds is identical; however, the first bears the SO_4^{2-} anion beyond the coordination sphere, whereas the second has the NO_2^- ion not coordinated in the inner sphere. Thus, they are entirely different. The dissociation of both affords different ionic species.

Coordination Isomerism. Both the complex compounds $[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{CN})_6]^{3-}$ are again different, in spite of identical qualitative and quantitative composition.

Structural Isomerism. This type of isomerism can be met when ambident anions are coordinated to the central atom. Such an anion can be coordinated to the central atom through either its more nucleophilic or electronegative site. It is well-illustrated by the pair of isomeric cobalt(III) complex compounds: $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $(\text{Co}(\text{NH}_3)_5\text{NO}_2)\text{Cl}_2$.

Polymerization Isomerism. Two complex compounds may have the same empirical formula, but the actual chemical composition of one isomer is, for instance, duplicated in relation to the composition of the other isomer. Both the Pt(II) complex compounds, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]_2$, are different species. Since the ammonia molecules and the chlorine atoms are coordinated to platinum, the monomeric species does not

undergo dissociation in solution, but the dimer dissociates into $[\text{Pt}(\text{NH}_3)_4]^{2+}$ and $[\text{PtCl}_4]^{2-}$ ions.

Solvation Isomerism. Several complex compounds crystallize with solvent molecules, which can be bonded either in or beyond the coordination sphere, and a distribution between the inner and outer coordination spheres is also possible. For example, three hydration isomers with the general formula of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ are known. Their structures, $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$, can be proved by quantitative analysis of chloride ion.

Geometrical Isomerism. Generally, this type of isomerism deals with the complex compounds having the central atoms of the 4 and 6 coordination numbers. When the orbitals of the 4 coordinating central atom are dsp^2 hybridized, they occupy the angles of a square. If pairs of two different ligands are coordinated to a central atom, a pair of isomers may be anticipated (Fig. 1.3).

The coordination number of 6 for the central atom implies an octahedral structure of the complex compound, designated by six d^2sp^3 hybridized orbitals. There are several possible isomers of such complex compounds, depending on the differentiation of all six ligands. If there are five a and one b , isomerism cannot occur. When four a and two b are coordinated, the pair of isomers should be available, as shown in Fig. 1.3. The number of isomers will increase by increasing the different types of ligands.

Cis and *trans* isomers are formally distinguished by the distance between both b substituents.

The reactivity and physicochemical properties of *cis* and *trans* isomers are entirely different. According to Chernyaev (6, 7), the mutual effects of the *trans* ligands make them more labile in various ligand exchange reactions. Such trends have solely qualitative meaning and are obeyed for the limited number of central atoms, such as Pt(IV), Pd(II), Ir(III), Rh, and a few others.

Optical Isomerism. Complexes and complex compounds can exhibit the optical activity, if they do not possess any center and plane of symmetry. Optical isomerism is found among the complex species having coordination numbers of four or higher.

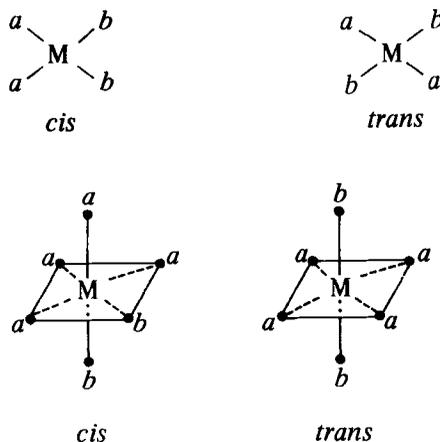


Fig. 1.3

1.7. PYRIDINE AND ITS DERIVATIVES AS THE LIGANDS

Pyridine is capable of acting as either a π or σ ligand. However, only randomly does it donate its π -electron system to the electronic shell of a metal atom. The higher affinity of pyridine toward donation of σ electrons is due to its inherent structure. Pyridine forms a dipole with the electron density localized on the nitrogen atom. Moreover, the lone pair of N -electrons has a geometry that makes it easily accessible for donation to a central metal atom in the resultant complex. The Graham σ -inductive and π -resonance parameters calculated for the $\text{pyM}(\text{CO})_5$ complex compounds, where $M = \text{Cr}, \text{Mo},$ or W , illustrate the differences (8–12) (see Section 1.5).

It is practically impossible to determine the strength of the pyridine ligand by means of any universal parameters. It varies from one metal to another and depends also on steric interactions in the inner coordination sphere. Substituents, which reside on the ring, are also important.

The stability and formation constants of the complexes and complex compounds are more or less roughly linearly dependent on the substituent effects, which can be correlated by means of thermodynamic relationships like the Hammett and Taft equations. Pyridine is specific from the point of view of such equations. The composition of the inductive and resonance interactions transmitted from the substituent to the nitrogen atom differs from that found in the series of benzoic acids and their esters. Therefore, Hammett σ -constants do not reflect properly substituent effects upon the basicity of pyridine (13). The π -back donation from some central atoms to the pyridine nucleus additionally affects the correlations. These and other effects evoked attempts at correcting the thermodynamic relationships to achieve a higher precision for the series of complexes. Thus Da Silva et al (14, 15) have introduced a new S_f parameter reflecting the intervention of π -back donation. The correlations are conducted for only 3- and 4-substituted pyridines. The anomalous stability and formation constants for the complexes with 2-mono- and 2,6-disubstituted pyridines are interpreted in terms of steric hindrances around the nitrogen atom. However, this need not be the only reason for the anomalies observed (13).

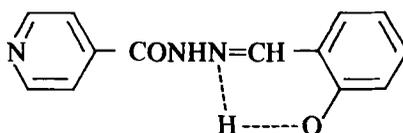
Substituents located in the α -positions of the pyridine can affect the site of coordination. It should be noted that some substituents on pyridine prohibit the N -coordination on the metal. This is quite common in the case of 2-pyridone. This compound always becomes a ligand through the oxygen atom, and the possibility of the chelation involving the ring nitrogen atom is rejected independently of the higher affinity of a given metal to oxygen or nitrogen (16–22). 2,3-Pyridinediol behaves similarly (23), but this is not the case for 2-pyridinethione, which can react via the sulfur or nitrogen atoms. Some interaction is postulated between the nitrogen atom and $\text{Sn}(\text{IV})$ and $\text{Hg}(\text{II})$, whereas $\text{Pd}(\text{II})$ definitely selects the nitrogen atom. The coordination site in 2-cyanopyridine is also variable and shifts from the CN-side to the ring, depending on the coordinating metal. Thus, methylmagnesium iodide coordinates to the cyano group, whereas LiAlH_4 employs the ring nitrogen exclusively (24). The same is true for isonicotinohydrazide. Zinc coordinates preferably the β -amino group of the hydrazino function, whereas cadmium coordinates to the ring nitrogen.

The varying function of a pyridine derivative, as ligand, can also result from the influence of the metal on the tautomeric equilibrium, which eventually occurs. 2-Acetylpyridine is complexed in both its ketonic and enolic forms; enolization during complex-

ation occurs only under the influence of a metal ion, that is not bonded to halogen. The ketonic complexes in aqueous solution are not stable and can be transformed into the enolic isomers (25).

The behavior of pyridine monocarboxylic acids as the ligands depends on the metal atom. There is no doubt in the case of both nicotinic and isonicotinic acids that they form salts with Group I and II metals. The salts of these acids with some other metals are sometimes claimed to coordinate another molecule of such acids or their salts via the nitrogen atom. Pyridine dicarboxylic acids also form salts and chelates, dependent on the nature of the metal atom.

Some attention has been paid to hydrazones of *o*-hydroxybenzaldehyde derived from nicotino- and isonicotinohydrazide (see structure 1.8).



1.8

In most cases, the chelation does not use the ring nitrogen and such compounds are not considered unless there is clear evidence that the pyridine ring nitrogen is involved with chelated metal.

These and many other examples are discussed in more detail in relevant sections.

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σ -Pyridine Coordination Compounds with Nontransition Metals

2.1. COORDINATION COMPOUNDS WITH THE METALS OF NONTRANSITION GROUP I

2.1.1. Introduction

Alkaline metal ions do not exhibit any remarkable tendency toward complexation. It could be anticipated that owing to the size-to-charge ratio, their valence shells would resemble those of the noble gases and would possess a low charge. Thus, among the ions of the Group I elements, lithium ion most readily forms solvates, whereas the rubidium and cesium cations only randomly solvate. It should, however, be noted that solvent molecules can also be bonded to the counter anion. Although this circumstance is not a measure of the ability of the cation to form complexes, it may, however, throw light on the anion polarization by the cation. The polarization decreases as the number of solvating molecules surrounding the cation increases. In the first coordination sphere, lithium, sodium, and potassium cations coordinate four molecules of water and other solvents (1), but not pyridine and its derivatives. Lithium salts can deviate from such behavior upon solution. This is manifested by abnormal colligative properties like very low vapor pressure, freezing point, and so on. Only in the case of hydration (Table 2.1) are the number of water molecules without orientational polarizability and coordination numbers in the inner hydration sphere, which are well-known for all of the alkali metal ions.

TABLE 2.1. NUMBERS (z_f) OF WATER MOLECULES WITHOUT ORIENTATIONAL POLARIZABILITY, TOTAL NUMBERS (z_+) OF WATER MOLECULES (COORDINATION NUMBERS) IN THE INNER HYDRATION SPHERE OF THE ALKALI ION (2)

T(°C)	$z_f (\pm 0.5)$				
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
0	6.2	5.7	—	—	—
25	5.6	4.6	3.2	2.3	1.6
50	5.6	4.6	—	—	1.6
z_+	4.9	6.8	7.7	8.2	9.3

