Gmelin Handbook of Inorganic Chemistry

8th Edition

Mn
Manganese

D 4

Coordination Compounds 4

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With 27 illustrations

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Coordination Compounds 4 – 1985 (**present volume**)

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IN SOME CASES MORE RECENT DATA HAVE BEEN CONSIDERED

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Preface

The present volume, "Manganese" D 4, continues the description of the manganese complexes. The arrangement of the complexes in these D volumes is based on the ligand type. The introduction, on p. 1, shows the classes of complexes which have already been described in Chapters 1 through 16 in the Volumes D 1 (1979), D 2 (1980), and D 3 (1982).

In Chapters 16.2 to 16.8 of this volume, the description of the manganese complexes with N-heterocycles is continued. Included are complexes with nucleosides and nucleotides of pyrimidine and purine bases, and large sections on complexes with porphyrins and phthalocyanines. Manganese complexes with porphyrins and phthalocyanines continue to receive a great deal of attention. They are used as commercial dyes, optical and electrical materials, and as catalysts. Another importance ascribed to these manganese complexes is their role as models for the iron-porphyrin containing heme proteins.

In Chapters 17 to 19, complexes with amino alcohols, -phenols, -ethers, aminooxo compounds and amino acids are described. Chapters 20 and 21 give some information on manganese complexes with peptides and proteins. These chapters, along with the sections on complexes with nucleosides, nucleotides, and nucleic acids, should permit the reader access to the literature in the field of bioinorganic chemistry of manganese.

A formula index at the end of this volume lists the ligands and their empirical molecular formulas.

Complexes with amine-N-carboxylic acids and with Schiff bases will be described in "Manganese" D 5 together with other complex types.

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Coordination Compounds of Manganese

(Continued)

Introduction

Arrangement. In Series D coordination compounds of manganese, with the exception of the organometallic compounds, are described. The volumes "Mangan" D 1 to D 3 contain the following chapters:

"Mangan" D 1, 1979	1) Review
	2) Complexes with H_2O
	3) Complexes with Alcohols
	4) Complexes and Salts with Phenols and Other Aromatic Hydroxy Compounds
	5) Complexes with Aldehydes
	6) Complexes with Ketones
	7) Complexes with Quinones
	8) Complexes with Ethers and O-Heterocycles
"Mangan" D 2, 1980	9) Complexes and Salts of Carboxylic Acids and Their Derivatives
	10) Cyanomanganate Complexes
	11) Cyanato, Thiocyanato, and Selenocyanato Complexes
"Manganese" D 3, 1982	12) Complexes with Ammonia
	13) Complexes with Amines
	14) Complexes with Hydrazine and Its Derivatives
	15) Complexes with Hydroxylamine
	16) Complexes with N-Heterocycles

This volume continues the description of complexes with N-heterocycles. They are arranged by the number of N atoms in the ring. Ligands with the same number of N atoms are arranged by ring size. For ligands containing several heterocyclic rings, that with the largest number of N atoms takes precedence. Complexes with heterocycles containing N and O hetero atoms are placed at the end of Chapter 16. Chapters 17 to 21 describe complexes with amino alcohols, aminophenols, aminoketones, aminoethers, amino acids, peptides, and proteins.

Mixed ligand complexes are generally arranged according to the principle of last position. For example, the complexes containing both amino acids and N-heterocyclic ligands are placed in Chapter 19 "Complexes with Amino Acids". The index at the end of this volume, which lists the empirical formulas of the ligands, is intended to expedite locating specific compounds.

Rules and Definitions. Generally the names of the ligands correspond to IUPAC nomenclature; trivial names are also used.

The stepwise stability (formation) constants K_n for the formation of complexes in solution from a central atom M and ligands L and the cumulative constants β_n are defined as follows:

$$K_n = [ML_n]/[ML_{n-1}] \cdot [L] \text{ in L/mol for equilibria } ML_{n-1} + L \rightleftharpoons ML_n \ (n = 1, 2, 3, \ldots)$$

$$\beta_n = [ML_n]/[M] \cdot [L]^n \text{ in } L^n/mol^n \text{ for equilibria } M + nL \rightleftharpoons ML_n \ (n = 1, 2, 3, \ldots)$$

The formation of complexes with protonated ligands is described by:

$$K^M_{MH_pL} = [MH_pL]/[M] \cdot [H_pL] \text{ for equilibria } M + H_pL \rightleftharpoons MH_pL \ (p = 1, 2, 3, \ldots)$$

Enthalpy (ΔH), free enthalpy (ΔG), or entropy changes (ΔS) are given the same subscript as the corresponding K: e.g., ΔH_1 for constant K_1. For reactions represented by cumulative constants β, the notation $\Delta H_{\beta n}$ is used. Ionic strengths are given in mol/L.

Abbreviations and Dimensions. Temperatures are normally given in °C; K stands for Kelvin. Abbreviations used with temperatures are m.p. for melting point and dec. for decomposition. With thermodynamic data, (s) is used to label solids, (g) is used to designate the gaseous state, and (l) is used for liquids.

The vibrational spectra are labeled as IR (infrared) or R (Raman). The assigned bands (wave numbers in cm^{-1}) are labeled with the symbols ν, for stretching vibrations, and δ, for deformation vibrations. The intensities are placed in parentheses (w = weak, m = medium, s = strong, vs = very strong, etc.); sh means shoulder; br means broad. The UV absorption maxima of the electronic spectra are given in nm (λ_{max}) or cm^{-1} (ν_{max}); the extinction coefficient ε ($L \cdot mol^{-1} \cdot cm^{-1}$) or log ε is in parentheses.

Abbreviations for ligands, solvents, and methods frequently used in this volume are listed below. Additional abbreviations, which are used only in the chapter on complexes with porphyrins are tabulated on p. 93.

Hacac	acetylacetone = 2,4-pentanedione
H_4edta	ethylenediaminetetraacetic acid
bpy	2,2'-bipyridyl
en	ethylenediamine
phen	1,10-phenanthroline
py	pyridine
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
THF	tetrahydrofuran
DMA	dimethylacetamide

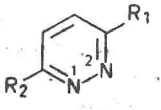
DTA	differential thermoanalysis
TG	thermogravimetry
DTG	differential thermogravimetry
DSC	differential scanning calorimetry
ESR	electron spin resonance
NMR	nuclear magnetic resonance
PRR	proton relaxation rate

16 Complexes with N-Heterocycles (Continued)

16.2 Complexes with Heterocycles Containing Two N Atoms in the Ring

Remark. Complexes with 1H-pyrazole, 1H-imidazole, 1H-benzimidazole, and derivatives of these ligands are described in "Manganese" D 3, 1982, see Sections 16.2.1 to 16.2.16, pp. 271 to 320.

16.2.17 With Pyridazine and Its 3,6-Bis(2-pyridyl) Derivative



R_1, R_2 = H; (= $C_4H_4N_2$)
R_1, R_2 = 2-C_5H_4N; (= $C_{14}H_{10}N_4$)

$Mn(C_4H_4N_2)X_2$ (X = Cl, Br) and **$Mn(C_4H_4N_2)SO_4$**. The chloro and bromo complexes were precipitated by mixing solutions of hydrated manganese(II) halide and pyridazine in absolute ethanol [1, 2]. The precipitates were washed with a mixture of ethanol and ether and dried at 80°C [1], or washed with ethanol and dried in vacuo at room temperature [2]. The chloro complex may be precipitated by adding pyridazine to an aqueous solution of $MnCl_2 \cdot 4H_2O$ [3]. The sulfato complex was obtained by dissolving hydrated manganese(II) sulfate in a minimum amount of water, adding a filtered ethanol solution of the ligand, and adding ethanol until precipitation began. The complex was washed and dried as above [1].

The complexes are all colorless. Their magnetic moments μ_{eff} (in μ_B) at 25°C, the assigned band maxima in the electronic reflectance spectra (in cm^{-1}) and the assigned far IR absorption maxima in the 400 to 40 cm^{-1} region (in cm^{-1}, polyethylene discs) are listed in the following table [1]:

complex	μ_{eff}	electronic transitions from $^6A_{1g}$(S) to			molecular vibrations	
		$^4T_{1g}$(G)	$^4T_{2g}$(G)	^4E_g(G), $^4A_{1g}$(G)	ν(Mn-N)	ν(Mn-X)
$Mn(C_4H_4N_2)Cl_2$	5.8	18800	21600	23600	260, 232	196, 148
$Mn(C_4H_4N_2)Br_2$	5.7	18800	20700	23200	236, 200*)	148, 116*)
$Mn(C_4H_4N_2)SO_4$	5.8	19600	22000	24000	—	—

*) In the original paper assigned to the pyrazine complex, probably in error.

Similar magnetic moments and electronic spectra, the latter with an additional band in the 27000 cm^{-1} region, had also been found for the chloro and bromo compounds by [2], but the strong bands at 237 and 189 cm^{-1} in the far IR spectrum (recorded in the 650 to 80 cm^{-1} region) were assigned to ν(Mn-Cl) and ν(Mn-N), respectively [2], contrary to the assignments of [1]. Other bands occurring in the far IR spectra are ligand bands or could not be assigned [2]. The sulfato complex shows only the very strong IR band of the $\nu_3(SO_4^{2-})$ vibration at about 1100 cm^{-1}; other sulfate modes apparently are masked by ligand peaks [1]. The magnetic moments and absorption spectra of the compounds suggest high-spin polymeric octahedral complexes, which must involve bridging anions (Cl^-, Br^-, SO_4^{2-}) and possibly also bridging ligands [1, 2]. $Mn(C_4H_4N_2)Cl_2$ is sparingly soluble in water [3].

$Mn(C_{14}H_{10}N_4)_2(NO_3)_2$ was prepared by blending hot solutions of $Mn(NO_3)_2 \cdot 6H_2O$ and 3,6-bis-(2-pyridyl)pyridazine in a mixture of methanol and $HC(OC_2H_5)_3$. On cooling overnight, yellow air-stable crystals appeared. According to Weissenberg and precession photographs these are triclinic, space group $P\bar{1}$-C_i^1 (No. 2), with lattice constants a = 8.88, b = 11.95, c = 14.20 Å (each ±0.03 Å), α = 107.0°, β = 87.6°, γ = 103.0° (±0.3°); Z = 2. V = 1404 ± 11 $Å^3$. The atomic positions,