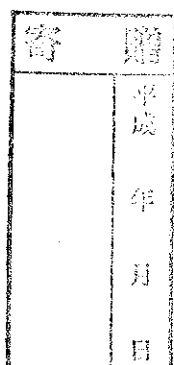


Formation and Reactivity of S-Bridged Polynuclear Structures Involving Group 6 Metal Ions

Yoshitaro MIYASHITA

A dissertation submitted to the Doctoral Program
in Chemistry, the University of Tsukuba
in partial fulfillment of the requirements for the
degree of Doctor of Philosophy (Science)

January, 1999



99311317

CONTENTS

	Page
Chapter 1. General Introduction	1
Purpose of This Work	5
References and Notes	6
Chapter 2. Incorporation of Chromium(III) Ion into S-Bridged Polynuclear Structures	8
2-1. Introduction	8
2-2. Experimental	9
2-2-1. <i>Materials</i>	9
2-2-2. <i>Preparation and Resolution of Complexes</i>	9
2-2-3. <i>Measurements</i>	12
2-2-4. <i>Crystallography</i>	13
2-3. Results and Discussion	17
2-3-1. <i>X-Ray Crystal Structures</i>	17
2-3-2. <i>Characterization</i>	21
2-3-3. <i>Formation and Reactivity</i>	26
2-3-4. <i>Electrochemical Property</i>	32
References and Notes	34
Chapter 3. Formation and Reactivity of Dinuclear Complexes with Coordinated Disulfide Bond	37
3-1. Introduction	37
3-2. Experimental	38
3-2-1. <i>Materials</i>	38
3-2-2. <i>Preparation of Complexes</i>	38
3-2-3. <i>Measurements</i>	41

3-2-4. <i>Crystallography</i>	42
3-3. Results and Discussion	45
3-3-1. <i>X-Ray Crystal Structures</i>	45
3-3-2. <i>Characterization</i>	50
3-3-3. <i>Formation of Disulfide Bond</i>	58
3-3-4. <i>Electrochemistry and Reactivity</i>	63
References and Notes	67
Chapter 4. Stereochemistry and Electrochemical Property of S-Bridged Polynuclear Molybdenum Complexes	69
4-1. Introduction	69
4-2. Experimental	70
4-2-1. <i>Materials</i>	70
4-2-2. <i>Preparation of Complexes</i>	70
4-2-3. <i>Measurements</i>	73
4-2-4. <i>Crystallography</i>	74
3-3. Results and Discussion	83
4-3-1. <i>X-Ray Crystal Structures</i>	83
4-3-2. <i>Characterization</i>	91
4-3-3. <i>Electrochemical Reactivity</i>	99
4-3-4. <i>Stereochemistry of Trinuclear Complexes</i>	105
References and Notes	107
Chapter 5. Concluding Remarks	110
References and Notes	114
Acknowledgments	115

Abbreviations

aet	2-aminoethanethiolate	$\text{NH}_2\text{CH}_2\text{CH}_2\text{S}^-$
aese	2-aminoethanesulfenate	$\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}^-$
aesi	2-aminoethanesulfinate	$\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}_2^-$
L-cys	L-cysteinate	$\text{NH}_2^*\text{CH}(\text{COO}^-)\text{CH}_2\text{S}^-$
cysta	cystamine	$\text{NH}_2\text{CH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{NH}_2$
en	ethylenediamine	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
d-tart	d-tartrate	$^-\text{OOC}^*\text{CH}(\text{O}^-)^*\text{CH}(\text{O}^-)\text{COO}^-$

Symbolism

- mer, fac*: The geometrical isomers of octahedral MX_3Y_3 type metal complexes. *fac(S)* means that three coordinated sulfur atoms occupy a face of octahedron.
- R, S*: The absolute configurations of tetrahedral sulfur atoms.
- Δ, Λ : The absolute configurations of metal complexes describing the helicity of the spiral arrangement of one octahedral edge spanned by a chelate ring relative to another.
- δ, λ : The conformations of individual chelate rings. The description of the conformation corresponds to that for the absolute configuration of a metal complex.