Preparation and properties of new transition-metal complexes with dithiocarbamates bearing carboxyl or pyridine groups

カルボキシルまたはピリジン基を有する ジチオカルバマト類を含む新規金属錯体 の合成と性質

2013, March

KEO VANTHOEUN

Graduate School of Natural Science and Technology (Doctor's Course)

OKAYAMA UNIVERSITY

Preparation and properties of new transition-metal complexes with dithiocarbamates bearing carboxyl or pyridine groups

Okayama University, Graduate School of Natural Science and Technology Division of Chemistry and Biochemistry Supervisor Name: Professor Dr. Takayoshi Suzuki

ABSTRACT

In this research new *N*,*N*-disubstituted dithiocarbamates have been designed for metal complexes with large negative charges and for multinuclear metal complexes using supramolecular aggregation.

Ten new transition-metal complexes with N,N-dialkyldithiocarbamates bearing carboxyl or pyridine groups, Ba₃[Co(Ac₂dtc)₃], Na₆[Co(Ac₂dtc)₃], Ba₂[Ni(Ac₂dtc)₂], Na₄[Ni(Ac₂dtc)₂], Ba₂[Cu(Ac₂dtc)₂], Na₄[Cu(Ac₂dtc)₂], [Fe(2,2'-dpdtc)₃], [Fe(3,3'-dpdtc)₃], [Co(2,2'-dpdtc)₃], and [Co(3,3'-dpdtc)₃], have been prepared. (Here, Ac₂dtc³⁻ = N,Ndiacetatodithio- carbamate and dpdtc = dipicolyldithiocarbamate).

The X-ray analysis of $Ba_3[Co(Ac_2dtc)_3] \cdot 16H_2O$ confirmed that the complex anion has a CoS_6 octahedral geometry with a well-organized and rigid network consisted with carboxyl groups of the complex anions, barium cations, and water molecules. Thus, the carboxyl groups do not coordinate to cobalt(III) ions.

Crystal structures of $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$, and $[Co(3,3'-dpdtc)_3]$ revealed that the central metal ions have an MS₆ (M = Fe or Co) octahedral coordination sphere. All pyridine groups do not coordinate to any metal ion. Thus, these metal complexes have been used to prepare polynuclear complexes, such as $[Fe(2,2'-dpdtc)_3]$.

 $dpdtc)_{3}Ni_{2}]Cl_{4}, \quad [Fe(2,2'-dpdtc)_{3}Cu_{2}]Cl_{4}, \quad [Fe(3,3'-dpdtc)_{3}Ni_{0.5}]Cl, \quad [Fe(3,3'-dpdtc)_{3}Cu]Cl_{2} \cdot 2H_{2}O, \\ [Co(2,2'-dpdtc)_{3}Ni]Cl_{2} \cdot H_{2}O, \quad [Co(2,2'-dpdtc)_{3}Cu_{2}]Cl_{4}, \quad [Co(3,3'-dpdtc)_{3}Ni_{2}]Cl_{4}, \quad [Co(3,3'-dpdtc)_{3}Cu_{3}]Cl_{6}. \\ \\ dpdtc)_{3}Cu_{3}]Cl_{6}. \\$

The complexes of Ba₃[Co(Ac₂dtc)₃], Na₆[Co(Ac₂dtc)₃], Ba₂[Ni(Ac₂dtc)₂], Na₄[Ni(Ac₂dtc)₂], Ba₂[Cu(Ac₂dtc)₂], and Na₄[Cu(Ac₂dtc)₂] are soluble in water but insoluble in organic solvents. In contrast, the complexes of [Fe(2,2'-dpdtc)₃], [Fe(3,3'-dpdtc)₃], [Co(2,2'-dpdtc)₃], and [Co(3,3'-dpdtc)₃] are insoluble in water but soluble in organic solvents. The solubilities of the latter class of complexes are studied in acidic, which revealed that the N,N-dipycolyldithiocarbamato metal complexes are soluble in acidic media due to the protonation of the dipicolyl nitrogen atom which are well occurred at pH 1~2.

In addition, some of the above complexes have been used to identify their effectiveness on surface tension reductions (STRs) of sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium chloride (DTAC). Moreover, the strong interaction of opposite charge of metal complexes and surfactants reveal sensitive to inclusion compounds of surfactants and α -, β -, and γ -cyclodextrins (α -, β -, and γ -CDs). For example, addition of metal complexes into a mixture of surfactants and α -, β -, or γ -CDs shows the characteristic drawing of surfactants from CDs which is due to strong interaction of metal complexes into the cationic or anionic surfactants. The easiness of drawing from inclusion compounds is shown as γ -CD > β -CD > α -CD which corresponds to the cavity diameter, 4.7 - 5.4, 6.0 - 6.5, 7.5 - 8.3 Å for α -, β -, and γ -CDs, respectively.

Preparation and properties of new transition-metal complexes with dithiocarbamates bearing carboxyl or pyridine groups

Contents

Page

Chapter 1: Introduction

1.1 Overview of dithiocarbamato complexes1
1.1.1 Preparation of dithiocarbamate
1.1.2 Dithiocarbamato Fe(III) complexes
1.1.3 Dithiocarbamato Co(III) complexes
1.1.4 Dithiocarbamato Ni(II) complexes
1.1.5 The effect of substitutes in the ligand
1.1.6 The effect of solution composition on complexation
1.1.7 Dithiocarbamate ulilizing
1.2 Overview of surface tension
1.2.1 Hydrophobic affect10
1.2.2 Surfactants
1.2.3 Interaction of metal complexes with surfactants
1.3 Overview of cyclodextrins
1.3.1 History
1.3.2 Property of cyclodextrins
1.3.3 Inclusion complex formation17
1.4 Dissertation
14.1 Structure of dissertation
References

2.1 Introduction	24
2.2 Experimental	
2.2.1 Materials and Measurements	25
2.2.2 Preparation of Na ₃ (Ac ₂ dtc) ·4H ₂ O	
2.2.3 Preparation of metal complexes	
2.2.3.1 $Na_6[Co(Ac_2dtc)_3] \cdot 10H_2O$	26
2.2.3.2 Ba ₃ [Co(Ac ₂ dtc) ₃] \cdot 16H ₂ O	27
2.2.3.3 Na ₄ [Ni(Ac ₂ dtc) ₂]H ₂ O	
2.2.3.4 Ba ₂ [Ni(Ac ₂ dtc) ₂]· $3H_2O$	
2.2.3.5 Na ₄ [Cu(Ac ₂ dtc) ₂]·4H ₂ O	
2.2.3.6 Ba ₂ [Cu(Ac ₂ dtc) ₂]	
2.2.4 Crystallography	
2.3 Results and discussion	
2.3.1 Preparation of the dithiocarbamate ligand and its complexes	
2.3.2 Absorption spectra	
2.3.3 IR spectra	
2.3.4 X-Ray structure analysis	
2.4 Conclusion	43
References	43

Chapter 2 : Preparation and Characterization of *N*,*N*-diacetatodithiocarbamato metal complexes with large negative charges.

Chapter 3: Preparation and molecular structure of *N*,*N*-dipycolyl- and N,N-3,3'dipicolyldithiocarbamato metal complexes

3.1 Introduction	46
3.2 Experimental	46
3.2.1 Materials	46
3.2.2 Measurements	46
3.3 Preparation of metal complexes	47

3.3.1 Fe(OH) ₃ and Co(OH) ₃	47
3.3.2 Synthesis of dithiocarbamato metal complexes	48
3.3.2.1 [Fe(2,2'-dpdtc) ₃]	48
3.3.2.2 [Fe(3,3'-dpdtc) ₃]	48
3.3.2.3 [Co(2,2'-dpdtc) ₃]	48
3.3.2.4 [Co(3,3'-dpdtc) ₃]	48
3.3.3 Synthesis of polynuclear complexes	50
3.3.3.1 [Fe(2,2'-dpdtc) ₃ Ni ₂]Cl ₄	50
3.3.3.2 [Fe(2,2'-dpdtc) ₃ Cu ₂]Cl ₄	50
3.3.3.3 [Fe(3,3'-dpdtc) ₃ Ni _{0.5}]Cl	50
3.3.3.4 [Fe(3,3'-dpdtc) ₃ Cu]Cl ₂ ·2H ₂ O	50
$3.3.3.5 [Co(2,2'-dpdtc)_3Ni]Cl_2 H_2O$	51
3.3.3.6 [Co(2,2'-dpdtc) ₃ Cu ₂]Cl ₄	51
3.3.3.7 [Co(3,3'-dpdtc) ₃ Ni ₂]Cl ₄	51
3.3.3.8 [Co(3,3'-dpdtc) ₃ Cu ₃]Cl ₆	51
3.3.4 Crystllography	53
3.4 Results and discussion	55
3.4.1 X-Ray diffraction analysis	56
3.4.2 Absorption spectra	57
3.4.3 Absorption spectra of polynuclear complexes by using liquid paraffin	61
3.4.4 IR spectra	64
3.4.5 Magnetic moment	67
3.4.6 Solubility	68
3.5 Conclusion	71
References	72

Chapter 4 : Control of Cyclodextrins' Inclusion with Surfactants by Metal complexes

4.1 Introduction	75
4.2 Experimental Procedure	76

4.2.1 Materials	76
4.2.2 Surface tension measurement	76
4.2.3 Method	76
4.3 Results and discussion	78
4.3.1 Surface tension of aqueous solution of Ac_2dtc^{3-} metal complexes	78
4.3.2 Surface tension reduction of SDS with Ac_2dtc^{3-} metal complexes	79
4.3.3 Surface tension Reduction of DTAC with Ac_2dtc^{3-} metal complexes	80
4.3.4 Effect of $[Co(Ac_2dtc)_3]^{6-}$ on inclusion compounds of DTAC with α -, β -, and	dγ-CDs
	81
4.3.5 Inclusion compounds of SDS with α -, β -, and γ -CDs	83
4.3.6 Effect of $[Co(NH_3)_6](ClO_4)$ on Inclusion compounds of SDS with α -, β -, and	dγ-CDs
	86
4.4 Conclusion	91
References	91

Chapter 5: Summary a	nd Conclusion	93
----------------------	---------------	----

List of figures

Page

Figure 1.1	Preparation of dithiocarbamato complex	2
Figure 1.2	Resonance structure of dithiocarbamate ligand	3
Figure 1.3	Molecular structure of [Fe(Et ₂ dtc) ₃]	4
Figure 1.4	Molecular configuration of [Co(Et ₂ dtc) ₃]	5
Figure 1.5	Planar structure of dithiocarbamato Ni(II) complex	6
Figure 1.6	Interaction among water molecules as the surface tension formation	10
Figure 1.7	Hydrophobic and hydrophilic of surfactants	12
Figure 1.8	Surface tension of aqueous solution of SDS or SBS	13
Figure 1.9	Molecular structure of cyclodextrins	14
Figure 2.1	Synthesis of the ligand	26
Figure 2.2	Synthesis of Na ₆ [Co(Ac ₂ dtc) ₃]	26
Figure 2.3	¹ H NMR of $[Co(Ac_2dtc)_3]^{6-}$ in D ₂ O	27
Figure 2.4	Synthesis of Ba ₃ [Co(Ac ₂ dtc) ₃]	27
Figure 2.5	Synthesis of Na ₄ [Ni(Ac ₂ dtc) ₂]	28
Figure 2.6	¹ H NMR of $[Ni(Ac_2dtc)_2]^{4-}$ in D ₂ O	28
Figure 2.7	Synthesis of Ba ₂ [Ni(Ac ₂ dtc) ₂]	29
Figure 2.8	Synthesis of Na ₄ [Cu(Ac ₂ dtc) ₂]	29
Figure 2.9	Synthesis of Ba ₂ [Cu(Ac ₂ dtc) ₂]	30
Figure 2.10	Absorption spectra of aqueous solution of Na ₆ [Co(Ac ₂ dtc) ₃],	
	Na ₆ [Co(Ac ₂ dtc) ₃] and Na ₄ [Cu(Ac ₂ dtc) ₂]	34
Figure 2.11	Absorption spectra of aqueous solution of Ba ₃ [Co(Ac ₂ dtc) ₃],	
	$Ba_2[Co(Ac_2dtc)_3]$ and $Ba_2[Cu(Ac_2dtc)_2]$	35
Figure 2.12	IR Spectra of Na ₆ [Co(Ac ₂ dtc) ₃] and Ba ₃ [Co(Ac ₂ dtc) ₃]	36
Figure 2.13	IR Spectra of Na ₄ [Ni(Ac ₂ dtc) ₂] and Ba ₂ [Ni(Ac ₂ dtc) ₂]	37
Figure 2.14	IR Spectra of Na ₄ [Co(Ac ₂ dtc) ₂] and Ba ₂ [Cu(Ac ₂ dtc) ₂]	38
Figure 2.15	Molecular structure of two $[Co(Ac_2dtc)_3]^{6-}$ anions bound to several	Ba ²⁺
	cations	40

Figure 2.16	Perspective drawing of the coordination envronments of Ba^{2+}	with the
	carboxyl group and hydrated molecules	41
Figure 2.17	Various coordination modes of carboxyl groups in $[Co(Ac_2dtc)_3]^{6-}$ w	vith Ba ²⁺
	ions	42

Figure 3.1	Synthesis of N,N-2,2'-dipicolyl- and N,N-3,3'-dipicolyldithio	carbamato
	complexes of iron(III) and cobalt(III)	49
Figure 3.2	Molecular structure of [Fe(2,2'-dpdtc) ₃]	56
Figure 3.3	Molecular structure of [Fe(3,3'-dpdtc) ₃]	56
Figure 3.4	Molecular structure of [Co(2,2'-dpdtc) ₃]	56
Figure 3.5	Molecular structure of [Co(3,3'-dpdtc) ₃]	56
Figure 3.6	Absorption spectra of [Fe(2,2'-dpdtc) ₃], [Fe(3,3'-dpdtc) ₃], [Co(2,2	2'-dpdtc) ₃],
	and [Co(2,2'-dpdtc) ₃] in chloroform	58
Figure 3.7	Absorption spectra of [Fe(2,2'-dpdtc) ₃], [Fe(3,3'-dpdtc) ₃], [Co(2,2	$2^{\circ}-dpdtc)_{3}],$
	and [Co(2,2'-dpdtc) ₃] in DMSO	59
Figure 3.8	Absorption spectra of $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$,	2^{-dpdtc}_{3}],
	and [Co(2,2'-dpdtc) ₃] in MeOH	59
Figure 3.8	Absorption spectrum of $[Fe(2,2'-dpdtc)_3]$ in chloroform, diffused	reflection
	spectra of [Fe(2,2'-dpdtc) ₃ Ni ₂]Cl ₄ , and [Fe(2,2'-dpdtc) ₃ Cu ₂]Cl ₄ w	vith liquid
	paraffin	59
Figure 3.9	Absorption spectrum of [Fe(3,3'-dpdtc) ₃] in chloroform and	diffused
	reflection spectra of [Fe(3,3'-dpdtc) ₃ Ni _{0.5}]Cl, and [Fe(3,3'-dpd	tc) ₃ Cu]Cl ₂
	with liquid paraffin.	61
Figure 3.10	Absorption spectra of $[Co(2,2'-dpdtc)_3]$ in chloroform and reflection	on spectra
	of $[Co(2,2'-dpdtc)_3Ni]Cl_2$ and $[Co(2,2'-dpdtc)_3Cu_2]Cl_4$ with liquid	d paraffin
		61
Figure 3.11	Absorption spectra of [Co(3,3'-dpdtc) ₃] in chloroform and reflection	on spectra
	of $[Co(3,3'-dpdtc)_3Ni_2]Cl_4$ and $[Co(3,3'-dpdtc)_3Cu_3]Cl_6$ with liquid	d paraffin
		63

Figure 3.12	Absorbance of metal complexes with pHs (pH0 -7). [Fe(2,2'-dpdtc) ₃] and
	$[Fe(3,3'-dpdtc)_3], [Co(2,2'-dpdtc)_3] and [Co(3,3'-dpdtc)_3] \dots 63$
Figure 3.13	IR spectra of $[Fe(2,2'-dpdtc)_3]$ and $[Fe(3,3'-dpdtc)_3]$
Figure 3.14	IR spectra of $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]$
Figure 3.15	Absorbance of metal complexes with pHs (0-7)69
Figure 3.16	Determination of solubility of $[Fe(2,2'-dpdtc)_3]$ in pH 1 – 765
Figure 3.17	Determination of solubility of $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]$ in
	pH 1 – 7

Figure 4.1	Construction of cyclodextrins77
Figure 4.2	Surface tension of Na ₆ [Co(Ac ₂ dtc) ₃], Ba ₃ [Co(Ac ₂ dtc) ₃], Na ₄ [Ni(Ac ₂ dtc) ₂],
	Ba ₂ [Ni(Ac ₂ dtc) ₂], Na ₄ [Cu(Ac ₂ dtc) ₂], and Ba ₂ [Cu(Ac ₂ dtc) ₂] in water78
Figure 4.3	Surface tension of an aqueous solution of the anionic surfactant SDS with
	Ac_2dtc^{3-} metal complexes (1.0 mM). SDS only, $Na_6[Co(Ac_2dtc)_3]$,
	$Ba_{3}[Co(Ac_{2}dtc)_{3}], Na_{4}[Ni(Ac_{2}dtc)_{2}], Ba_{2}[Ni(Ac_{2}dtc)_{2}], Na_{4}[Cu(Ac_{2}dtc)_{2}], Na_{4}[Cu(Ac_{2}dtc$
	and $Ba_2[Cu(Ac_2dtc)_2]$
Figure 4.4	Surface tension of an aqueous solution of the cationic surfactant DTAC
	with metal complexes (1.0 mM). DTAC only, $Na_6[Co(Ac_2dtc)_3]$,
	$Ba_{3}[Co(Ac_{2}dtc)_{3}], Na_{4}[Ni(Ac_{2}dtc)_{2}], Ba_{2}[Ni(Ac_{2}dtc)_{2}], Na_{4}[Cu(Ac_{2}dtc)_{2}], Na_{4}[Cu(Ac_{2}dtc$
	and $Ba_2[Cu(Ac_2dtc)_2]$ 80
Figure 4.5	Surface tension of an aqueous solution of DTAC in 1.0 mM $[Co(Ac_2dtc)_3]^{6-1}$
	with or without the presence of α -CD82
Figure 4.6	Surface tension of an aqueous solution of DTAC in 1.0 mM $[Co(Ac_2dtc)_3]^{6-1}$
	with or without the presence of $\beta\text{-CD}$
Figure 4.7	Surface tension of an aqueous solution of DTAC in 1.0 mM $[Co(Ac_2dtc)_3]^{6-1}$
	with, and without the presence of γ -CD83
Figure 4.8	Surface tension of an aqueous solution of SDS with, and without α -CD83
Figure 4.9	Surface tension of an aqueous solution of SDS with, and without $\beta\text{-CD}84$
Figure 4.10	Surface tension of an aqueous solution of SDS with, and without γ -CD85
Figure 4.11	Inclusion formation of α -, β - or γ -CDs with SDS86

- Figure 4.12 Surface tension of an aqueous solution of SDS with and without the presence of α -CD with 1.00 mM [Co(NH₃)₆]³⁺ solution.......88
- Figure 4.14 Surface tension of an aqueous solution of SDS with and without the presence of γ -CD with 1.00 mM [Co(NH₃)₆]³⁺ solution......89

List of Tables

Table 1.1	M – S bond length of transition-metal complexes	6
Table 1.2	Property of cyclodextrins	17
Table 2.1	Yields and analytical data of Ac ₂ dtc ^{3–} metal complexes	30
Table 2.2	Crystallographic data and structure refinement for Ba ₃ [Co(Ac ₂ dtc) ₃] ·16H	$[_2O$
		32
Table 2.3	Absorption spectra data	34
Table 2.4	Infrared spectra (cm ⁻¹) data	39
Table 2.5	Selected bond angles of carboxyl group in Ba ₃ [Co(Ac ₂ dtc) ₃] ·16H ₂ O	42
Table 2.6	Selected average bond lengths inn Ba ₃ [Co(Ac ₂ dtc) ₃] ·16H ₂ O	42
Table 2.7	Selected average bond angles in Ba ₃ [Co(Ac ₂ dtc) ₃] ·16H ₂ O	42
Table 3.1	Yields and analytical data of mononuclear complexes	49
Table 3.2	Yields and analytical data of polynuclear complexes	52
Table 3.3	Crystallographic and structure refinement data	54
Table 3.4	Selected average bond lengths	57
Table 3.5	Selected average bond angles	57
Table 3.6	Absorption spectra data in CHCl ₃	60
Table 3.7	Absorption spectra data in DMSO	60
Table 3.8	Absorption spectra data in MeOH	61
Table 3.9	Absorption spectra of polynuclear complexes	62
Table 3.10	Infrared spectra	64
Table 3.11	Magnetic properties of Fe(III) complexes	67
Table 3.12	Magnetic properties of Co(III) complexes	68
Table 3.13	Absorption spectra data in acidic media (pH 1)	68
Table 3.14	Absorbance at saturated concentration and defined concentration of ea	ıch
	metal complex in various pHs (pH1 – pH 7)	69

Table 4.1	Molar ratio of α -, β -, γ -CDs and surfactant (SDS) as inclusion compound	
Table 4.2	Molar ratio of α -, β -, γ -CDs and SDS as inclusion formation after adding of	
	metal complex	

Chapter 1

Introduction

1.1 Overview of dithiocarbamato complexes

During the past few decades, the design and synthesis of metal complex based on strong coordination bonds between metal and sulfur atom have become one of the most active fields in coordination chemistry. Dithiocarbamates are highly versatile ligands toward metals. They can stabilize a variety of oxidation states and coordination geometries, and seemingly small modifications to the ligand can lead to significant changes in the structure behavior of the complexes formed. Among the ligands coordinating through sulfur atoms, dithiocarbamates are deserving of much attention in recent years, and a large number of dithiocarbamato complexes have been synthesized so far; these compounds are being investigated in order to gain insight into the nature of the sulfur–metal bond in many biomolecules [1]. A developing interest in dithiocarbamate chemistry is the functionalization of the dithiocarbamate substituents which allows more complex architectures to be developed and potentially gives rise to tuneable physical properties [2–4]. This chapter focuses primarily on some metal dithiocarbamato complexes which had been synthesized, and also descript their physical properties and an interesting for new metal complexes of dithiocarbamate compounds were

illustrated. Moreover, the brief introduction of surface tension and properties of cyclodextrins are also described. Finally, the structure of dissertation of this research is clarified.

1.1.1 Preparation of dithiocarbamate

Dithiocarbamate complexes have been known for over a century, with many thousands having been synthesized, the vast majority of these contain simple alkyl substituents such as methyl and ethyl. The general method of preparation of dithiocarbamates from carbon disulphide and amines in alkaline medium (figure 1.1) is probably one of the reasons for the widespread incorrect nomenclature of these compounds. Thus a compound obtained from pyrrolidine and carbon disulphide is frequently named as pyrrolidinedithiocarbamate, whereas it is more correctly named *N*-pyrrolindinedithiocarbamate. The complexing properties of dithiocarbamate are directly connected with the presence of two donor sulphur atoms, which primarily determine the nature of the metals that can be bound, and the strength of the complexes formed. In the dithiocarbamate ion R_1 and R_2 denote various organic substituents, which do not influence significantly the metal-sulphur bonding, but may determine some analytical properties of the complexes. Most of the analytically interesting properties occur with disubstituted dithicarbamates. Monosubstituted compounds are less useful because of their stronger reducing properties and tendency to decompose to hydrogen sulphide [5].



Figure 1.1 Preparation of dithiocarbamato complex

In complexes of transition elements the bonding to the central atom is through the two sulfur atoms of the ligand and both M–S distances are equal. In the planar MS₂CN system an extensive π delocalization exists with a high contribution to the resonance structure. This property of stabilising high oxidation states in metal complexes reflects strong o-bonding characteristic of these ligands. Although the sulfur atoms of dithiocarbamate ligands possess o-donor and n-back-donation characteristics of the same order of magnitude, these ligands have a special feature in that there is an additional n-electron flow from nitrogen to sulphur *via* a planar delocalised π - orbital system (figure 1.2). This effect results in strong electron donation and hence a high electron density on the metal leading to its next higher oxidation state.



Figure 1.2 Resonance structure of dithiocarbamate ligand

1.1.2 Dithiocarbamato Fe(III) complexes

The iron(III) dithiocarbamates are the most extensively studied, largely because of their interesting magnetic properties [6]. The molecular structure of $[Fe(Et_2dtc)_3]$ had been reported by Leipoldt et al. which is a octahedral structure (figure 1.3) with the coordination geometry as FeS₆ [7] Tris(dialkyldithicarbamato) iron(III) displayed spin cross-over phenomena between high-spin and low spin states. In the complexes $[Fe(S_2CNBu_2^n)_3]$ which is large in the high-spin form at room temperature ($\mu_{eff} = 5.32$ BM) the mean Fe–S bond length is 2.42 Å whereas in the xanthate complex $[Fe(S_2COEt)_3]$, largely in the low-spin form ($\mu_{eff} = 2.75$ BM at 296 K), the mean Fe–S distance is 2.32 Å. The same difference of 0.1A in mean Fe–S

distance was observed between the high-spin ($\mu_{eff} = 3.0$ BM at 300K) tris(*N*-pyrrolidyldithiocarbamate) and the mainly low-spin ($\mu_{eff} = 3.0$ BM at 300K) *N*-methyl-*N*-phenyl derivative. In addition, there are certain alterations in the overall symmetry of the coordination polyhedrons as a consequence of the spin change. Thus the high-spin dithiocarbamate with Buⁿ as substituent has a structure intermediate between trigonal prismatic and octahedral, whereas in the low-spin xantate the structure is closer to octahedral.



Figure 1.3 Molecular structure of [Fe(Et₂dtc)₃]

1.1.3 Dithiocarbamato Co(III) complexes

Tris(dialkyldithiocarbamate)Co(III) complexes can be easily prepared in water using Na⁺R₂dtc – and CoCl₂ in the presence of O₂ or by oxidation of Co(II) using the disulfide dimer; the former method is preferable (Equation 1.1). A very large number of these green or green-brown, neutral water-insoluble complexes have been prepared. Molecular structure of $[Co(Et_2dtc)_3]$ (figure 1.4) had been reported by Brennan et al.[8] with octahedral structure as coordination geometry as CoS₆. Normally the diamagnetic tris Co(III) chelate results even when O₂ is rigorously excluded [9] but a few Co(R₂dtc)₂ have been reported when R is large. These Co(II) species are paramagnetic with one unpaired electron and probably have a square planar structure. Their stability is surprising and must reside in steric factors; no structural information is available. Several metal structures of $[Co(R_2dtc)_3]$ complexes are available in Table 1.1.



Figure 1.4 Molecular configuration of $[Co(Et_2dtc)_3]$. This is as stereo pair which may conveniently be examined with a hand-held stereo viewer

1.1.4 Dithiocarbamate Ni(II) complexes

Dithiocarbamate of nickel(II) have been well known for a long time and numerous complexes having the general formula $Ni(RR'NCS_2)_2$ have been synthesized and characterized with unsubstituted (R = R' = H), N-substituted (R = H, R' = Me, Pr, Ph) and N,N-disubstituted ((R = R' = Me, Pr, Ph, etc) dithiocarbamates. A number of analogous diselenocarbamate complexe were also reported.

The complexes have been generally prepared by direct reaction of a nickel(II) salt with an alkai metal or ammonium salt of the appropriate dithioacid in aqueous solution where the Ni(S₂CNR₂)₂ derivatives are quite insoluble. The complexes are dark coloured, often black, in the solid state and red or brownish in dilute solutions of organic solvents. All of the bis chelates are square planar as observed in the X-ray crystal structure of Ni(RR'CNC₂)₂. These complexes are strictly planar (figure 1.5) with the metal forming a four-menered chelate ring with the CS₂ moieties. The Ni–S bond distances are in the range 200–221 pm, and α and β

angles average 100° and 80° , respectively. The two C–S bond distances in each ligand molecule are equal within experimental error and in the range 169 - 171 pm [10, 11].



Figure 1.5 Planar structure of dithiocarbamato Ni(II) complex

The transition metal of dithiocarbamato complexes of the M(dtc)n (M = Fe(III), Co(II), Co(II), Ni(II), Cu(II) had also been illustrated their molecular structures. Most of tris(dithiocarbamate) Fe(III) and tiris(dithiocarbamate) Co(III) are typical hexagonal complexes containing FeS₆ and CoS₆ chromophores, respectively. Bis(dithiocarbamate) Ni(II) and bis(dithiocarbamate) Cu(II) are typical planar complexes containing CuS₄ and NiS₄, respectively. Some transition metal complexes had been characterized as shown in Table 1.1.

Table 1.1

Complex	M – S (Å)	References
$[Fe(S_2CNEt_2)_3]$	2.31 - 2.36	7
$[Fe{S_2CNCH_3(CH_2CH_2OH)}_3]$	2.32 - 3.40	13
[Fe(mebudtc) ₃]	2.35 - 2.42	13
$[Co(Et_2dtc)_3]$	2.263 - 2.270	8
$[Co\{S_2CN(CH_2CH_2CH_2NMe)_2\}_2]$	2.26 - 2.27	14
[Co(Me ₂ dtc) ₂ (hist)]ClO ₄	2.25 - 2.28	15
$[Ni\{S_2CN(CH_2CH_2OMe)_2\}_2]$	2.20 - 2.21	16

[Ni(dipdtc) ₂]	2.18 - 2.18	17
[Ni(dipdtc)(PPh ₃)] ⁺	2.20 - 2.21	17
[Ni(dipdtc)(dppe)] ⁺	2.20 - 2.21	17
$[Ni(S_2CNHC_{10}H_{15})_2]$	2.19 - 2.20	18
$[Ni\{S_2CN(CH_2CH_2NEt)_2\}_2]$	2.19 - 2.21	14
$[Pd{S2CN(CH_2CH_2CH_2NMe)_2}_2]$	2.32 - 2.33	14
$[Cu\{S_2CN(CH_2CH_2NEt)_2\}_2]$	2. – 2.32	14
$[Cu\{S_2CN(CH_2CH_2CH_2NMe)_2\}_2]$	2.29 - 2.30	14
$[Cu\{S_2CNEt(CH_2CH_2OH)\}_2]$	2.31 - 2.79	18
$[Cu\{S_2CNPr(CH_2CH_2OH)\}_2]$	2.28 - 2.31	19
$[Cu\{S_2CN(CH_2CH_2OMe)_2\}_2]$	2.72 - 2.72	16
$[Cu\{S_2CN(CH_2CH_2OMe)_2\}_2][ClO_4]$	2.55 - 2.80	16
$[Zn{S_2CN(CH_2CH_2OMe)_2}_2]$	2.33 - 2.35	16

1.1.5 The effect of substitutes in the ligand

For many years after the early work mostly only the dimethyl and diethyldithiocarbamates were used in chemical analysis. They form complexes with many metals, insoluble in water but soluble in organic solvents. To widen the applicability of these reagents attempts have been made to introduce new substituent with better analytical properties. Taking into account the properties of the complexes formed, it is possible to divide the dithiocarbamate reagents into three groups:

- Dithiocarbamates having hydrophobic substituents, which give water soluble complexes, extractable with organic solvents.
- (ii) Dithiocarbamates containing hydrophilic groups, ie., OH⁻ or COOH, which form metal complexes soluble in water but insoluble in organic solvents and therefore not extractable.

(iii) Dithiocarbamates containg two donor CS_2^- groups, which form polymeric chelates insoluble in all solvents.

This classification deals primarily with disubstituted compounds but may be extended to monosubstituted derivatives. The first group includes a great number of studied compounds. The analytical applications of the dithiocarbamates–derivatives of dimethylamine and diethylamine have been described in several hundreds of papers. The derivatives of dipropylamine and dibutylamine have also been studied. Derivatives of aromatic and heterocyclic amines such as dibenzylamine, diphenylamine, cyclohexylethylamine, pyrrolidine, piperidine, hexamethyleneamine, morpholine, thiazine, indole and substituted pyrrolidines have similar properties. There are no significant differences in the chelating properties of these compounds. Comparative studies indicate small differences in the logarithms of the metal complex`s chelate stability constants.

Dithiocarbamates having hydrophilic substituents has not been investigated so thoroughly. Because of the presence of OH or COOH groups the metal complexes are soluble in water and do not dissolve readily in organic solvents, because of steric factors and the rather weak complexing properties of the OH and COOH groups compared with those of the CS_2^- group it follows that the complexes formed have similar structure and properties to those of the first group. However the complexation occurs in one phase and therefore the presence of successive complexes is easily observed.

1.1.6 The effect of solution composition on complexation

Numerous experimental data on the formation of dithiocarbamate complexes enable a clear picture to be obtained of conditions under which these complexes may be formed. Nevertheless in order to understand the nature of these reactions several factors must be separately discussed:

(i) Formation of hydroxo-complexes of metals with increasing pH,

- (ii) Formation of metal complexes with ligands added as buffers, to prevent precipitation of hydroxides or to increase selectivity;
- (iii) Protonation of dithiocarbamate ions, which leads finally to decomposition of the ligand.

In most cases stepwise formation of dithiocarbamate complexes may be neglected owing to a rather drastic shift of the equilibrium towards precipitation or extraction or the metal chelate.

1.1.7 Dithiocarbamate utilizing

Organic dithiocarbamates have received much attention due to their pivotal role in agriculture and their intriguing biological activities. They have also been used as protection groups in peptide synthesis, as linkers in solid-phase organic synthesis and recently in the synthesis of ionic liquids.

The dithiocarbamate ligand has been used in the field of analytical chemistry for many years. The ability of this ligand to form neutral complexes with a wide range of metals which are then extractable into organic media has led to its widespread use in liquid-liquid extractions. Such procedures have generally been employed as a sample clean-up or preconcentration step prior to metal determination by atomic absorption spectrometry or spectrophotometry.

All transition metals form complexes with dithiocarbamate ligands, and the stabilization such coordination affords had led to the development of a wide range of application in areas as diverse as materials science, medicine, and agriculture. Given this versatility, their welldefined architecture and the extensive metal-centered electrochemistry shown by these complexes, it is surprising that they have found little use in the rapidly expanding area of supramolecular design.

1.2 Overview of surface tension

Surface tension is a fundamental obstacle in the spontaneous formation of bubbles, droplets, and crystal nuclei in liquids. It acts as a driving force to destabilize colloidal systems containing bubbles, droplets, and crystals. Such mechanisms as Ostwald ripening in emulsions, disproportionation in foams, and ice crystal growth in frozen foods during storage are the result of this phenomenon. Surface tension is a measure of the free energy of the surface per unit length and symbolized as gamma (γ). The term surface indicates that one of the phases is a gas, usually air. The unit of surface tension used in the present dissertation is mN m⁻¹. Surface tension arises from the strong interactions between water molecules, called hydrogen bonding. It is this strong interaction which also manifests in the other unusual property of water, its high boiling point. In the bulk of a liquid, each water molecule can make an optimal number of H-bonds to other water molecules (figure 1.6). On the surface, however, the interactions with the neighboring molecules are limited and weaker, resulting in a higher free energy and reduced intermolecular hydrogen bonding of the molecules. In nature, water has one of the highest surface tensions, 72.8 mN/m at 20 °C or 72.5 mN/m at 25°C.



Figure 1.6 Interaction among water molecules as the surface tension formation

1.2.1 Hydrophobic affect

The hydrophobic effect is the driving force for the formation of micelles by amphiphilic molecules and membranes by phospholipids. In these assemblies the polar, water soluble parts of the amphiphiles seek interaction with water, while in contrast, their hydrophobic, water insoluble, oily parts cluster to minimize contacts with water. The hydrophobic effect can be easily studied through changes in the surface tension for an air/water interface. More specifically, measuring changes in the surface tension of the air-water interface, allows to monitor the efficiency of the accumulation of compounds such as drugs, surfactants and lipids into the surface.

Measuring surface tension provides data reflecting thermodynamics of the compounds tested, and reveals fundamental physicochemical properties associated with processes such as adsorption, hydrogen bonding interactions, and self-assembly. The latter is particularly important for fields such as nanotechnology. Controlling surface tension by surface active materials means control of molecular level behavior and self-assembly a key to nanotechnology.

1.2.2 Surfactants

Surfactants are substances when present in low concentrations, have the ability to significantly alter the surface properties of the solvent. These compounds are generally composed of lyophobic and/or lyophilic when the lyophobic group lies within the solvent it disrupts the structure of the surface, thus decreasing the free energy of the system, while the lyophilic group prevents the complete expulsion of the surfactant from the solvent. All surfactants, however, can be categorized by the charge on the surface active component into: anionic, cationic, nonionic (figure 1.7), and zwitterionic (both positive and negative charges).

11



Figure 1.7 Hydrophobic and hydrophilic of surfactants



1.2.3 Interaction of metal complexes with surfactants

Figure 1.8. Surface tension of aqueous solutions of SDS or SBS with and without metal complexes. (1) SDS (△), (2) SBS (▽), (3) 1.25 mM $[Co(NH_3)_6]^{3+}$ + SDS (◇), (4) 2.50 mM $[Co(NH_3)_6]^{3+}$ + SDS (□), (5) 5.00 mM $[Co(NH_3)_6]^{3+}$ + SDS (○), (6) 1.25 mM $[Co(NH_3)_6]^{3+}$ + SBS (△), (7) 2.50 mM $[Co(NH_3)_6]^{3+}$ + SBS (△), (8) 5.00 mM $[Co(NH_3)_6]^{3+}$ + SBS (▲), (9) 1.25 mM $[Co(en)_3]^{3+}$ + SDS (⊲), (10) 2.50 mM $[Co(en)_3]^{3+}$ + SDS (⊲), (11) 5.00 mM $[Co(en)_3]^{3+}$ + SDS (⊲), (12) 1.25 mM $[Co(en)_3]^{3+}$ + SBS (▲), (13) 2.50 mM $[Co(en)_3]^{3+}$ + SBS (▲), and (14) 5.00 mM $[Co(en)_3]^{3+}$ + SBS (▲).

The interaction of metal complexes with surfactants had been studied extensively. The interaction of metal complexes with surfactants showed surface tension reduction (STRs) [20]. The figure 1.8 shows surface tension of aqueous solutions of SDS or SBS with 1.25–5.00 mM $[Co(NH_3)_6](ClO_4)_3$ or $[Co(en)_3](ClO_4)_3$ plotted against surfactant concentrations of 0–0.173 mM. The area drawn with a solid line for the surface tension means there was a clear solution. On the other hand, the area drawn with a dotted line shows that there was slight turbidity. The addition of metal complex reduced the surface tension of SDS or SBS aqueous solutions. So, the decrease of the surface tension at dilute concentrations of surfactants (0–0.05 mM SDS or

SBS) with high concentrations of complexes $(1.25-5.00 \text{ mM} [Co(NH_3)_6](ClO_4)_3$ or $[Co(en)_3(ClO_4)_3]$ can be explained by the formation of the 1:1 and 1:2 association complexes, $\{[\text{complex}]^{3+}(S^-)\}^{2+}$ and $\{[\text{complex}]^{3+}(S^-)_2\}^+$ and their adsorption on the water surface. The breakpoints of surface tension curves with concentration of $[Co(NH_3)_6](ClO_4)_3$ or $[Co(en)_3](ClO_4)_3$ appeared at ca. 0.03 mM of SDS or SBS. In the region of concentrations of SDS or SBS higher than 0.03 mM, the surface tension curves flattened out. This can be interpreted as showing that the adsorption of association complexes on the water surface in this region has reached saturation.

1.3 Overview of Cyclodextrins

1.3.1 History

Cyclodextrins are cyclic oligosaccharides consisting of six α -cyclodextrin, seven β cyclodextrin, eight γ -cyclodextrin or more glucopyranose units linked by α -(1,4) bonds (figure 1.9). They are also known as cycloamyloses, cyclomaltoses and Schardinger dextrins. They are produced as a result of intramolecular transglycosylation reaction from degradation of starch by cyclodextrin glucanotransferase (CGTase) enzyme. Cyclodextrins were first discovered in 1891, when in addition to reducing dextrins a small amount of crystalline material was obtained from starch digest of Bacilus amylobacter. In 1903, Schardinger was able to isolate two crystalline products, dextrins A and B, which were described with regard to their lack of reducing power. The bacterial strain capable of producing these products from starch was unfortunately not maintained. In 1904, Schardinger isolated a new organism capable of producing acetone and ethyl alcohol from sugar and starch-containing plant material. In 1911, he described that this strain, called Bacillus macerans, also produces large amounts of crystalline dextrins (25–30%) from starch. Schardinger maned his crystalline products 'crystallised dextrin α ' and 'crystallised dextrin β '. It took until 1935 before γ dextrin was isolated. At that time the structures of these compounds were still uncertain, but in 1942 the structures of α and β -cyclodextrin were determined by X-ray crystallography. In 1948, they X-ray structure of γ -cyclodextrin followed and it was recognize that CDs cam form inclusion complexes. The main interest in cyclodextrins lies in their ability to from inclusion complexes with several compounds [21, 22]. From the X-ray structures it appears that in clyclodextrins the secondary hydroxyl groups (C₂ and C₃) are located on the wider edge of the ring and the primary hydroxyl groups (C₆) on the other edge, and that the apolar C₃ and C₅ hydrogens and ether-like oxygens are at the inside of the torus-like molecules. This results in a molecule with a hydrophilic outside, which can dissolve in water, and an apolar cavity, which provides a hydrophobic matrix, described as a 'micro heterogeneous environment'. As a result of this cavity, cyclodextrins are able to form inclusion complexes with a wide variety of hydrophobic guest molecules. One or two gust molecules can be entrapped by one, two or three cyclodextrins.



Figure 1.9 Molecular structure of Cyclodextrins

1.3.2 Property of Cyclodextrins

Cyclodextrins are of three types: α -cyclodextrin, β -cyclodextrin and γ -cyclodextrin, referred to as first generation or parent cyclodextrins, as α -, β -, and γ -cyclodextrins are composed of six, seven and eight α -(1,4)-linked glycosyl units, respectively. β -Cyclodextrin is the most accessible, the lowest-priced and generally the most useful. The main properties of those cyclodextrins are given in Table 1.2.

Studies of cyclodextrins in solution are supported by a large number of crystal structure studies. Cyclodextrins crystallise in two main types of crystal packing, channel structures and cage structures, depending on the type of cyclodextrin and guest compound.

These crystal structures show that cyclodextrins in complexes adopt the expected 'round' structure with all glucopyranose units in the ${}^{4}C_{1}$ chair conformation. Furthermore, studies with linear maltohexaoses, which form an antiparallel double helix, indicate that α -cyclodextrin is the form in which the steric strain due to cyclization is least while γ -cyclodextrin is most strained [23].

Apart from these naturally occurring cyclodextrins, many cyclodextrin derivatives have been synthesised. These derivatives usually are produced by aminations, esterifications or etherifications of primary and secondary hydroxyl groups of the cyclodextrins. Depending on the substituent, the solubility of the cyclodextrin derivatives is usually different from that of their parent cyclodextrins. Virtually all derivatives have a changed hydrophobic cavity volume and also these modifications can improve solubility, stability against light or oxygen and help control the chemical activity of guest molecules [24].

Each year cyclodextrins are the subject of almost 1000 research articles and scientific abstracts, large numbers of which deal with drugs and drug-related products. In addition, numerous inventions have been described which include cyclodextrins (over 1000 patents or patent applications in the past 5 years). From a regulatory standpoint, a monograph for β -cyclodextrin is already available in both the US Pharmacopoeia/National Formulary (USP)

23/NF 18, 1995) the European Pharmacopoeia (3rd ed., 1997). A monograph for 2hydroxypropyl-*b*-cyclodextrin is in the preparation for US Pharmacopoeia/National Formulary, and various monographs for cyclodextrins are included in compendial sources, e.g. the Handbook of Pharmaceutical Excipients [25]. Thus, more than one century after their discovery cyclodextrins are finally, but rapidly, being accepted as 'new' pharmaceutical excipients.

Table 1.2

Property	a-Cyclodextrin	β-Cyclodextrin	γ-Cyclodextrin
Number of glucopyranose	6	7	8
units			
Molecular weight	972	1135	1297
Solubility in water at 25 °C	14.5	1.85	23.2
(%, w/v)			
Outer diameter (Å)	14.6	15.4	17.5
Cavity diameter (Å)	4.7–5.3	6.0–6.5	7.5–8.3
Height of torus (Å)	7.9	7.9	7.9
Cavity volume (Å ³)	174	262	427

Cycledextrins properties

1.3.3 Inclusion complex formation

The most notable feature of cyclodextrins is their ability to form solid inclusion complexes (host–guest complexes) with a very wide range of solid, liquid and gaseous compounds by a molecular complexation. In these complexes, a guest molecule is held within the cavity of the cyclodextrin host molecule. Complex formation is a dimensional fit between host cavity and guest molecule [26]. The lipophilic cavity of cyclodextrin molecules provides a microenvironment into which appropriately sized non-polar moieties can enter to form

inclusion complexes. No covalent bonds are broken or formed during formation of the inclusion complex [27]. The main driving force of complex formation is the release of enthalpy-rich water molecules from the cavity. Water molecules are displaced by more hydrophobic guest molecules present in the solution to attain an apolar–apolar association and decrease of cyclodextrin ring strain resulting in a more stable lower energy state.

The ability of a cyclodextrin to form an inclusion complex with a guest molecule is a function of two key factors. The first is steric and depends on the relative size of the cyclodextrin to the size of the guest molecule or certain key functional groups within the guest. If the guest is the wrong size, it will not fit properly into the cyclodextrin cavity. The second critical factor is the thermodynamic interactions between the different components of the system (cyclodextrin, guest, solvent). For a complex to form, there must be a favourable net energetic driving force that pulls the guest into the cyclodextrin.

While the height of the cyclodextrin cavity is the same for all three types, the number of glucose units determines the internal diameter of the cavity and its volume. Based on these dimensions, α -cyclodextrin can typically complex low molecular weight molecules or compounds with aliphatic side chains, β -cyclodextrin will complex aromatics and heterocycles and γ -cyclodextrin can accommodate larger molecules such as macrocycles and steroids.

In general, therefore, there are four energetically favourable interactions that help shift the equilibrium to form the inclusion complex:

- The displacement of polar water molecules from the apolar cyclodextrin cavity.
- The increased number of hydrogen bonds formed as the displaced water returns to the larger pool.
- A reduction of the repulsive interactions between the hydrophobic guest and the aqueous environment.
- An increase in the hydrophobic interactions as the guest inserts itself into the apolar cyclodextrin cavity.

18

1.4 Dissertation

The analytical application and molecular structures of dithiocarbamato complexes have been discussed in several textbooks and monographs on trace analysis, colorimetry, organic reagents, extraction, and in special papers. As the dissertation, new dithiocarbamato metal complexes have been prepared and illustrated their physical properties. Those metal complexes *N*,*N*-diacetatodithiocarbamato metal complexes are $(Na_6[Co(Ac_2dtc)_3],$ $Ba_3[Co(Ac_2dtc)_3],$ $Na_4[Ni(Ac_2dtc)_2],$ $Ba_2[Co(Ac_2dtc)_2],$ $Na_4[Cu(Ac_2dtc)_2],$ and $Ba_2[Cu(Ac_2dtc)_2])$ and N,N-dipycolyldithiocarbamato metal complexes ([Fe(2,2'-dpdtc)_3], $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$, and $[Co(3,3'-dpdtc)_3]$). The research questions are:

- How can the new *N*,*N*-diacetatodithiocarbamate ligand coordinate to metal cations?
 And what properties of these complexes are revealed?
- 2) How can the new *N*,*N*-dipycolyldithiocarbamate ligand coordinated to metal cations? And what properties of these complex are revealed?
- 3) Why can the metal complexes draw the surfactants from inclusion compounds of surfactants and α-, β-, and γ-cyclodextrins?

The aims of the research are: to design new *N*,*N*-diacetatodithiocarbamato and *N*,*N*-dipycolyldithiocarbamato metal complexes which are clarified by elemental analysis, to reveal their molecular structures as the X-ray diffraction, to define their absorption spectra by comparison with the previous metal complexes that had been prepared, and to identity their solubility in water and organic solvents, especially in acidic media.

1.4.1 Structure of the dissertation

To respond the questions and aims above, the dissertation consist of five main chapters: Chapter 1 is an introduction, describing the overview of dithiocarbamato complexes, such as properties of dithiocarbamato metal complexes which had been prepared, the effect of substitute in ligand molecule and the effect of solution composition on complexation are also introduced. And the overview of surface tension is also described in this chapter, as the factors which have the effects on the surface or interfacial tension. Moreover, the overview of cyclodextrins is also mentioned in the section which focuses on the general properties of α -, β -, and γ -CDs and the inclusion formation of the cyclodextrins with some surfactants

Chapter 2 describes about the preparation and characterization N, Nof diacetatodithiocarbamato metal complexes with large negative charges. This chapter, six metal complexes of N,N'-diacetatodithiocarbamato complexes have been synthesized such as $Na_{6}[Co(Ac_{2}dtc)_{3}], Ba_{3}[Co(Ac_{2}dtc)_{3}], Na_{4}[Ni(Ac_{2}dtc)_{2}], Ba_{2}[Co(Ac_{2}dtc)_{2}], Na_{4}[Cu(Ac_{2}dtc)_{2}], Na_{4}[Cu(Ac_{2}dtc$ and $Ba_2[Cu(Ac_2dtc)_2]$. These compounds were characterized by absorption spectra as the aqueous solutions. Thus, these dithiocarbamato metal complexes with carboxyl groups are soluble in water but insoluble in organic solvents. Moreover, The molecular structure of $Ba_3[Co(Ac_2dtc)_3] \cdot 16H_2O$ reveals that the complex anions capture tightly with Ba^{2+} , and confirms a well-organized and rigid network among carboxyl groups of the complex anions, barium cations, and water molecule.

about the preparation and molecular structures of Chapter 3 studies N.Ndipycolyldithiocarbamato metal complexes. Four metal complexes of N, Ndipycolyldithiocarbamato have been prepared such as, $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]$. These metal complexes are insoluble in water, thus they were dissolved in organic solvents to measure their absorption spectra. On the other hand, the solubility of these metal complexes in acidic media was estimated by the Beer-Lambert law technique, and the soluble complexes illustrate as deprotonating in pH solutions. The molecular of dithiocarbamato complexes with pyridine groups were characterized by X-ray diffraction which confirms that they have the coordination geometries around the metal centers are MS_6 (M = Fe and Co) octahedral structures and the dipicolyl groups do not coordinate. Thus, these molecules have four donor atoms as two on the sulfur atoms and other two on the nitrogen atoms of pyridine groups. Thus, they have been used to prepare polynuclear complexes, resulting as $[Fe(2,2'-dpdtc)_3Ni_2]Cl_4$, $[Fe(2,2'-dpdtc)_3Cu_2]Cl_4$, $[Fe(3,3'-dpdtc)_3Ni_{0.5}]Cl$, $[Fe(3,3'-dpdtc)_3Cu]Cl_2 \cdot 2H_2O$, $[Co(2,2'-dpdtc)_3Ni]Cl_2 \cdot H_2O$, $[Co(2,2'-dpdtc)_3Cu_2]Cl_4$, $[Co(3,3'-dpdtc)_3Ni_2]Cl_4$, $[Co(3,3'-dpdtc)_3Cu_3]Cl_6$. These polynuclear properties were illustrated by magnetic moment and diffused reflection spectra with liquid paraffin because they are insoluble in water and other organic solvents. Even, the crystal structures of polynucleare complexes were not formed, they are revealed that the dithiocarbamato metal complexes with pyridine groups can be used to prepare the polynuclear complexes.

Chapter 4 Studies about the interaction of metal complexes into the inclusion compounds of surfactants (DTAC and SDS) and α -, β -, and γ -CDs. There are two possibilities in this interaction due to the strong interaction of opposite charges of metal complexes and surfactants. Firstly, at low concentration of α -, β -, and γ -CDs, metal complexes attract easily to surfactants which can form precipitate. At high concentration of α -, β -, and γ -CDs, metal complexes can draw surfactants easily. To prevent the penetration of metal complexes which can draw surfactant from its inclusion compound, the ratios of surfactants and α -, β -, and γ -CDs have to increase to 5, 10, and 20 for α -, β -, and γ -CDs, respectively which is higher than its original inclusion as DTAC or SDS/2 α -, 2 β -, or 2 γ -CDs.

Chapter 5 is the conclusion of the dissertation, describes the summary and main results of the research discussed in the dissertation.

References:

- [1] A.M Bond, R.L. Martin, Coord. Chem. Rev. 54 (1984) 23.
- [2] J.D.E.T. Wilton-Ely, D Soklanki, E.R. Knight, K.B. Holt, AL. Thompson, G.Hogarth, Inorg. Chem. 47 (2008) 9642.
- [3] P.D Beer, N. Berry, M.G.B. Drew, O.D. FOX, M.E.Padilla-Tosta, S. Patell, Chem.Commun. (2001)199.
- [4] M.S. Vickers, J.Cookson, PD. Beer, P.T. Bishop, B.Thiebaut, J. Mater. Chem.16 (2006) 209.
- [5] A. Hulanicki, Talanta Rev, 14 (1967) 1371.
- [6] H. Nabipour, S. Ghammamy, S. Ashuri, Z. S. Aghbolaghc, Org. Chem., 2 (2010) 75.
- [7] L. Cambi, L. Szego, Ber. Dtsch. Chem. Ges., 64 (1931) 2591.
- [8] J.G. Leipoldt, P. Copppens, Inorg. Chem. 10 (1973) 2269.
- [9] T. Brennan, I. Bernal, Phys. Chem 73 (1969) 443.
- [10] L.R. Gahan, J.G. Hughes, M.J,O'Connor, P.J. Oliver. Inorg. Chem., 18 (1979) 933.
- [11] M. Martin, P.W.G. Newman, B.W. Robinson, A.H. White, J. Chem. Soc., Dalton Trans. (1972) 2233.
- [12] P.W.G. Newman, C.L. Raston, A.H. White, J. Chem. Soc., Dalton Trans. (1973) 1332.
- [13] T. Terzis, S. Filippakis, D. Mentzafos, V. Petrouleas, A. Malliaris, Inorg. Chem. 23 (1984) 334.
- [14] G. Hogarth, Inorg. Chim. Acta 362 (2009) 2020.
- [15] M.C. Hodgson, P.J. Brothers, G.R. Clark, D.C. Ware, J. inorg. Biochemistry, 102 (2008) 189.
- [16] G. Horgarth, E.J.C.R.C.R. Rainford-Brent, I. Richards, Inorg. Chim. Acta. 362 (2009) 1361.
- [17] V. Venkatachalam, K. Ramalingam, T.C.W. Mak, L. Bao-Sheng, Polyhedron., 15 (1996) 1295.

- [18] A.Z. Halimehjani, K. Marjani, A. Ashouri, V. Amani, Inorg. Chim, Acta., 373 (2011) 282.
- [19] G.M. de Lima, D.C. Menezes, C.A. Cavalcanti, J.A.F. dos Santos, I.P. Fereira, E.B. Paniago, J. L. Wardell, D.M.S.V. Vardell, Isolda.C. Mendes, H. Beraldo, J. Molecular Structure, 988 (2011) 1.
- [20] S. Sovanna, T. Suzuki, M. Kojima, S. Tachiyashiki, M. Kita, J. Colloid Interface. Sci. 2009, 332, 194.
- [21] R.A. Hedges, Industrial application of cyclodextrins. Chem Rev. 98 (1998) 2035.
- [22] X. Lu, Y. Chen, J. Chromatogr A. 955 (2002) 133.
- [23] J. Szetjli, Chem. Rev. 98 (1998) 1743.
- [24] A. Villiers, Compt Rendu. 12 (1891)112.
- [25] R.A. Nash, Press & Am. Pharm. Assoc. (1994) 145.
- [26] S.B. Munoz, B. del Castillo, M.A. Martyn, Ars Pharm 36 (1995) 187.
- [27] E. Schneiderman, A.M. Stalcup, Chromatogr B. 745 (2000) 83.
Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges

Chapter 2

Preparation and characterization of *N*,*N*diacetatodithiocarbamato metal complexes with large negative charges

Novel metal complexes with *N*,*N*-diacetatodithiocarbamate (Ac_2dtc^{3-}), including $Na_6[Co(Ac_2dtc)_3]$, $Ba_3[Co(Ac_2dtc)_3]$, $Na_4[Ni(Ac_2dtc)_2]$, $Ba_2[Ni(Ac_2dtc)_2]$, $Na_4[Cu(Ac_2dtc)_2]$, and $Ba_2[Cu(Ac_2dtc)_2]$, derived from disodium iminodiacetate monohydrate, sodium hydroxide, and carbon disulfide have been synthesized, and their molecular structures and spectroscopic properties have been characterized. The X-ray analysis of $Ba_3[Co(Ac_2dtc)_3] \cdot 16H_2O$ confirmed a well-organized and rigid network among carboxyl groups of the complex anions, barium cations, and water molecules.

2.1 Introduction

Dithiocarbamato metal complexes have been extensively studied [1] and the crystal structures of various dithiocarbamato complexes have been reported so far [2–10]. In a recent

research it has been described the synthesis of a new class of dithiocarbamato complexes, the 2-diethylaminoethyl- and 3-dimethylaminopropyl-dithiocarbamate complexes: $[M{S_2CN(CH_2CH_2NEt_2)_2}_n]$ and $[M{S_2CN(CH_2CH_2CH_2NMe_2)_2}_n]$ (M = Ni or Cu, n = 2; M = Co, n = 3) [11]. In this study, we have designed and synthesized new *N*,*N*diacetatodithiocarbamato (Ac₂dtc³⁻) complexes with a large negative charge, such as $[Co(Ac_2dtc)_3]^{6-}$, $[Ni(Ac_2dtc)_2]^{4-}$ and $[Cu(Ac_2dtc)_2]^{4-}$. The crystal structure of Ba₃[Co(Ac₂dtc)₃]·16H₂O is also reported.

2.2 Experimental

2.2.1 Materials and measurements

Disodium iminodiacetate monohydrate, sodium hydroxide, carbon disulfide were purchased from Tokyo Chemical Industry or Nacalai tesque inc. All of the chemicals were of reagent grade and were used without further purification. The UV-vis absorption spectra of aqueous solutions of *N*,*N*-diacetatodithiocarbamato complexes were measured using a Hitachi U-3410 spectrophotometer. The ¹H NMR spectra in D₂O were aquired on a Bruker AMX 400 spectrometer at 22 °C. The infrared spectra were obtained on a JASCO FT–IR FT-001 spectrophotometer as KBr discs in the 4000–400 cm⁻¹.

The metal complexes were synthesized. Yields and experimental analysis and physical properties are listed in Table 2.1

2.2.2 Preparation of Na₃(Ac₂dtc)·4H₂O

Disodium iminodiacetate monohydrate (4.88 g, 25.0 mmol) and NaOH (1.00 g, 25.0 mmol) were dissolved in 15.0 mL of water, and the resulting mixture was vigorously stirred for ca. 20 min. To this solution, CS_2 (1.90 g, 25.0 mmol) was added, followed by dropwise addition of methanol until a white precipitate was formed (figure 2.1). The precipitate was collected by filtration and washed with methanol several times. Yield: 5.44 g (70%). Found: C, 17.5; H, 3.72; N, 4.03%. Calcd for Na₃(Ac₂dtc)·4H₂O = C₅H₁₂NO₈S₂Na₃: C, 17.2; H, 3.45;

Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges

N, 4.02%. ¹H NMR (D₂O): δ 4.63 (s, S₂CNC<u>H</u>₂CO₂⁻).



Figure 2.1 Synthesis of the ligand

2.2.3 Preparation of metal complexes

2.2.3.1 Na₆[Co(Ac₂dtc)₃]·10H₂O

Na₃(Ac₂dtc)·4H₂O (5.20 g, 15.0 mmol) in 15.0 mL of water was added to a solution of $[Co(NH_3)_6]Cl_3$ (1.15 g, 5.0 mmol) in 15.0 mL of water (figure 2.2). The resulting mixture was stirred in a water bath at 40 °C until no NH₃ was detected (using pH paper). Ethanol was then slowly added to the mixture for precipitation of a green product. The precipitated product was isolated by filtration. Yield: 4.66 g (78%). Found: C, 18.1; H, 3.02; N, 4.32%. Calcd for Na₆[Co(Ac₂dtc)₃]·10H₂O = C₁₅H₃₂N₃O₂₂S₆CoNa₆: C,18.1; H, 3.24; N, 4.22%. ¹H NMR (D₂O): δ 4.18 and 4.30 (AB quartet, S₂CNC<u>H₂CO₂⁻) (figure 2.3).</u>



Figure 2.2 Synthesis of Na₆[Co(Ac₂dtc)₃]



Figure 2.3 ¹H NMR of $[Co(Ac_2dtc)_3]^{6-}$ in D₂O

2.2.3.2 Ba₃[Co(Ac₂dtc)₃]·16H₂O

 $Na_6[Co(Ac_2dtc)_3] \cdot 10H_2O$ (1.49 g, 1.50 mmol) in 10.0 mL of water and $BaCl_2$ (1.10 g, 4.50 mmol) in 10.0 mL of water were mixed (figure 2.4). Methanol was then added to the mixture until a green precipitate was deposited. This precipitate was collected by filtration and washed with methanol. Yield: 2.11 g (90%). Found: C, 13.1; H, 2.82; N, 3.03%. Calcd for $Ba_3[Co(Ac_2dtc)_3] \cdot 16H_2O = C_{15}H_{44}N_3O_{28}S_6CoBa_3$: C, 13.0; H, 3.22; N, 3.05%.



Figure 2.4 Synthesis of Ba₃[Co(Ac₂dtc)₃]

2.2.3.3 Na₄[Ni(Ac₂dtc)₂] ·H₂O

Na₃(Ac₂dtc)·4H₂O (3.47 g, 10.0 mmol) in 15.0 mL of water and [Ni(NH₃)₆]Cl₂ (1.15 g, 5.0 mmol) in 15.0 mL of water were combined (figure 2.5). The mixture was stirred at room temperature until no NH₃ was detected. Methanol (ca. 100 mL) was then slowly added into it, generating a green precipitate. The precipitated product was isolated by filtration. Yield: 2.69 g (76%). Found: C, 20.2; H, 1.46; N, 4.70%. Calcd for Na₄[Ni(Ac₂dtc)₂]·H₂O = $C_{10}H_{10}N_2O_9S_4NiNa_4$: C, 20.6; H, 1.73; N, 4.82%. ¹H NMR (D₂O): δ 4.16 (s, S₂CNC<u>H₂CO₂⁻)</u> (figure 2.6).



Figure 2.5 Synthesis of Na₄[Ni(Ac₂dtc)₂]



Figure 2.6 ¹H NMR of $[Ni(Ac_2dtc)_2]^{4-}$ in D₂O

2.2.3.4 Ba₂[Ni(Ac₂dtc)₂] \cdot 3H₂O

An aqueous solution (10.0 mL) of Na₄[Ni(Ac₂dtc)₂]·H₂O (2.03 g, 3.50 mmol) and an aqueous solution (10.0 mL) of BaCl₂ (1.71 g, 7.0 mmol) were mixed, and the resulting precipitate was filtered (figure 2.7). Yield 2.92 g (90%). Found: C, 14.9; H, 1.44; N, 3.45%. Calcd for Ba₂[Ni(Ac₂dtc)₂]·3H₂O = C₁₀H₁₄N₂O₁₁S₄NiBa₂: C, 15.0; H, 1.75; N, 3.50%.



Figure 2.7 Synthesis of Ba₂[Ni(Ac₂dtc)₂]

2.2.3.5 Na₄[Cu(Ac₂dtc)₂]·4H₂O

A solution of Na₃(Ac₂dtc)·4H₂O (3.47 g, 10.0 mmol) in 15.0 mL of water was added to an aqueous solution (15.0 mL) of [Cu(NH₃)₄]Cl₂ (1.01 g, 5.0 mmol) (figure 2.8), and the resulting mixture was stirred until no NH₃ was detected. Methanol (ca. 100 mL) was slowly added to the mixture until a sticky brown precipitate was formed, which was filtered and washed with methanol. Yield: 3.0 g (82%). Found: C, 18.7; H, 2.50; N, 4.38%. Calcd for Na₄[Cu(Ac₂dtc)₂]·4H₂O = C₁₀H₁₆N₂O₁₂S₄CuNa₄: C, 18.8; H, 2.52; N, 4.37%.



Figure 2.8 Synthesis of Na₄[Cu(Ac₂dtc)₂]

2.2.3.6 Ba₂[Cu(Ac₂dtc)₂]

Na₄[Cu(Ac₂dtc)₂]·2H₂O (1.81 g, 3.0 mmol) in 10.0 mL of water was added to a solution of BaCl₂ (1.46 g, 6.00 mmol) in 10.0 mL of water (figure 2.9), and the resulting mixture was stirred for 10 min. Methanol (ca. 100 mL) was slowly added to the resulting clear solution until a black solid precipitate was formed. Yield: 2.12g (80%). Found: C, 15.9; H, 1.03; N, 3.51%. Calcd for Ba₂[Cu(Ac₂dtc)₂] = C₁₀H₈N₂O₈S₄CuBa₂: C, 16.0; H, 1.07; N, 3.71%.



Figure 2.9 Synthesis of Ba₂[Cu(Ac₂dtc)₂]

Table 2.1

Yields analytical data of Ac₂dtc metal complexes.

Compound Formula	Color	Yield	C%	H%	N%
		(%)	Found	Found	Found
			(Calc.)	(Calc.)	(Calc.)
Na ₆ [Co(AC ₂ dtc) ₃]·10H ₂ O	Green	4.66 g	18.1	3.05	4.32
		78.5%	(18.1)	(3.20)	(4.25)
$Ba_{3}[Co(AC_{2}dtc)_{3}]\cdot 16H_{2}O$	Green	2.11 g	13.2	2.87	3.31
		90.0%	(13.3)	(2.90)	(3.20)

Na ₄ [Ni(Ac ₂ dtc) ₂]·H ₂ O	Green	2.69	20.1	1.46	4.68
		76.0%	(20.1)	(1.47)	(4.67)
Ba ₂ [Ni(Ac ₂ dtc) ₂]·3H ₂ O	Green	90.0%	14.9	1.44	3.45
		2.92	(15.0)	(1.53)	(3.50)
$Na_4[Cu(Ac_2dtc)_2]\cdot 2H_2O$	Brown	3.01 g	18.7	1.52	4.38
		82.1%	(18.8)	(1.42)	(4.37)
$Ba_2(Cu(Ac_2dtc)_2]$	Black	2.12 g	15.9	1.03	3.51
		82.5%	(16.0)	(1.07)	(3.70)

Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges

2.2.4 Crystallography

Crystallographic data and details of structure refinement for Ba₃[Co(Ac₂dtc)₃]·16H₂O are listed in Table 2.2. A green block crystal of Ba₃[Co(Ac₂dtc)₃]·16H₂O having approximate dimensions of $0.35 \times 0.30 \times 0.25$ mm was mounted with a cryoloop and flash cooled by a cold nitrogen gas stream. The X-ray diffraction data were obtained at -85 ± 2 °C using a Rigaku R-axis rapid imaging plate area detector with graphite monochromated Mo K α radiation ($\lambda =$ 0.71075 Å). All structural calculations were carried out using Crystal Structure software package [12]. The structure was solved using a direct method employing the SIR2004 software package [13] and refined on F^2 (with all independent reflections) by using the SHELXL 97 software package [14]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the Ac₂dtc³⁻ moieties were introduced at the calculated positions and treated using the riding models on the attached C atoms, whereas the hydrogen atoms of hydrated water molecules were not included in the calculation.

Table 2.2

Crystallographic data and structure refinement for Ba₃[Co(Ac₂dtc)₃]·16H₂O

Formula	$Ba_{3}CoS_{6}O_{28}N_{3}C_{15}H_{44}$	Formula Weight	1377.84
Crystal system	Monoclinic	<i>a</i> (Å)	12.2337(6)
$b(\text{\AA})$	23.5120(11)	$c(\text{\AA})$	15.7200(6)
$\beta(^{\circ})$	108.0956(17)	$V(\text{\AA}^3)$	4298.1(3)
Ζ	4	$D_{\rm calc}$ (g/cm ³)	2.129
Space Group	<i>P</i> 2 ₁	F(000)	2680
<i>R</i> _{int}	0.028	μ (Mo–K α) (cm ⁻¹)	34.718
$R1 (I > 2\sigma(I))$	0.032	wR2 (all reflns,)	0.0833
Reflection/ parameter	19477/1010	GoF	1.084

2.3 Results and discussion

2.3.1 Preparation of the dithiocarbamate ligand and its complexes

The synthetic procedures for metal complexes of Ac_2dtc^{3-} were somewhat similar to those of the other dithiocarbamate complexes, requiring the sodium salt of Na₃(Ac₂dtc) to be prepared advance. Complexes of $Na_6[Co(Ac_2dtc)_3],$ $Na_4[Ni(Ac_2dtc)_2],$ in and $Na_4[Cu(Ac_2dtc)_2]$ were synthesized by the reaction of $Na_3(Ac_2dtc)$ with $[Co(NH_3)_6]Cl_3$ (3:1) ratio), [Ni(NH₃)₆]Cl₂ (2:1 ratio), and [Cu(NH₃)₄]Cl₂ (2:1 ratio), respectively. The crude products obtained directly from aqueous reaction mixtures were consistently waxy, rendering them unsuitable for elemental analysis; thus methanol or ethanol was added to induce formation of a precipitate that could be filtered and washed as needed. A cation exchange could be succeeded by addition of BaCl₂ to an aqueous solution of the Na⁺ salt, inducing the precipitation of the Ba^{2+} salt: $Ba_3[Co(Ac_2dtc)_3]$, $Ba_2[Ni(Ac_2dtc)_2]$ and $Ba_2[Cu(Ac_2dtc)_2]$. The metal complexes with Ac_2dtc^{3-} are soluble in water but insoluble in some organic solvents such as methanol, ethanol, chloroform, and dimethyl sulfoxide. Saturated aqueous solutions of these complexes were evaporated in a desiccator over $CaCl_2$. A green crystal of $Ba_3[Co(Ac_2dtc)_3] \cdot 16H_2O$ was formed which was appropriate for the X-ray diffraction study.

2.3.2 Absorption and IR spectra

Comparisons of the absorption spectra of dithiocarbamato complexes were made to those reported by Kita et al. [15], Oktavec et al. [16] and Jeliazkova et al. [17]; they studied tris(N,N-diethyldithiocarbamato)cobalt(III), bis(N,N-dialkyldithiocarbamato) nickel(II) and bis(N,N-diethyldithiocarbamato)copper(II), respectively. The absorption spectra of the present Ac₂dtc complexes of Co(III), Ni(II), and Cu(II) are shown in figure 2.10, and the spectral data are listed in Table 2.2. The lowest energy absorption band of the cobalt(III) complex at 15800 cm^{-1} is almost similar in energy to the absorption band of [Co(Et₂dtc)₃] at 15600 cm⁻¹. Thus, the absorption band corresponds to the d-d transition. A similarly weak absorption band was also observed around 15800 cm⁻¹ in the spectra of nickel(II) and copper(II) complexes, as similar to the previously reported $[M{(C_6H_5CH=NCH_2CH_2)_2NCS_2}(S_2CNH_2)]$ (M=Ni or Cu) The strong bands at 25300, 26300 and 30050 cm^{-1} for Na₆[Co(Ac₂dtc)₃], [18]. Na₄[Ni(Ac₂dtc)₂] and Na₄[Cu(Ac₂dtc)₂], respectively, were attributed to the charge transfer process. On the other hand, the absorption bands of Ba₃[Co(Ac₂dtc)₃], Ba₂[Ni(Ac₂dtc)₂], and $Ba_2[Cu(Ac_2dtc)_2]$ are similar to $Na_6[Co(Ac_2dtc)_3]$, $Na_4[Ni(Ac_2dtc)_2]$, and $Na_4[Cu(Ac_2dtc)_2]$, respectively, as shown in figure 2.11 and data lists in Table 2.3 The results confirm that the counter ions in the metal complexes have not any effect on the metal coordination absorption bands.

By using the Beer-Lambert Law, the amount of metal complexes dissolved in water is shown in Table 2.3. The concentration of metal complexes with sodium counter ions is not listed due to its high solubility in water. These results suggest that Ac_2dtc^{3-} capture more strongly to barium ions than to sodium ions.

Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges



Figure 2.10 Absorption spectra of aqueous solutions of Na₆[Co(Ac₂dtc)₃] (—), Na₄[Ni(Ac₂dtc)₂] (—), and Na₄[Cu(Ac₂dtc)₂] (—)

Table 2.3

Absorption data

Complex	σ/1	[C] saturated/			
					mM
Na ₆ [Co(Ac ₂ dtc) ₃]	15.8(2.79)	18.5(2.31) ^{sh}	25.3(4.05)	30.8(4.43)	hs
Na ₄ [Ni(Ac ₂ dtc) ₂]	15.8(1.94)	18.3(1.80) ^{sh}	26.3(3.86)	28.1(3.80) ^{sh}	hs
Na ₄ [Cu(Ac ₂ dtc) ₂]	15.8(2.83)	23.3(3.97)	30.05(3.12) ^{sh}	38.8(4.47)	hs
Ba ₃ [Co(Ac ₂ dtc) ₃]	15.3(2.70)	17.4(2.20) ^{sh}	25.0(4.10)	30.0(4.10)	2.9
Ba ₂ [Ni(Ac ₂ dtc) ₂]	16.1(2.20)	18.5(2.10) ^{sh}	26.5(3.80)	28.5(3.40) ^{sh}	0.08
Ba ₂ [Cu(Ac ₂ dtc) ₂]	15.3(2.95)	23.0(4.10)	30.0(3.45) ^{sh}	38.2(4.82)	2.7

sh: shoulder

hs: high solubility, [C]: concentration

Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges



Figure 2.11 Absorption spectra of aqueous solutions of Ba[Co(Ac₂dtc)₃] (—), Ba₂[Ni(Ac₂dtc)₂] (—), and Ba₂[Cu(Ac₂dtc)₂] (—)

2.3.3 IR spectra

Infrared spectra of metal complexes with dithiocarbamate ligands have been extensively studied [19]. The IR spectral data of the Ac_2dtc^{3-} metal complexes are given in Table 2.4. In $[Co(Ac_2dtc)_3]^{6-}$ the band at 1030 and 1500 cm⁻¹ are associated for C–S and C–N stretching (figure 2.12), respectively. These bands are higher than those of $[Co(Et_2dtc)_3]$ [20]. Also, the C–S and C–N bands of $[Ni(Ac_2dtc)_2]^{4-}$ (figure 2.13) are stronger than those of $[Ni(4-PhPipdtc)_2]$ (4-PhPipdtc = 4-phenylpiperidinedithiocarbamate) [21] due probably to the acetate ions. For $[Cu(Ac_2dtc)_2]^{4-}$ (figure 2.14), the 1002 and 1019 cm⁻¹ bands are attributed to the C–S bonds. These bands are also higher than those of $[Cu(4-PhPipdtc)_2]$ [21]. These

Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges

results suggest that the highly negative charges give an effect on strengths of the C–S bands, due to an interaction of negatively charged dithiocarbamato complex anions with counter cation of Na^+ .



Figure 2.12 IR spectra of Na₆[Co(Ac₂dtc)₃] and Ba₃[Co(Ac₂dtc)₃]

Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges



Figure 2.13 IR spectra of Na₄[Ni(Ac₂dtc)₂] and Ba₂[Ni(Ac₂dtc)₂]

Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges



Wave number (Cm⁻¹)

Figure 2.14 IR spectra of $Na_4[Cu(Ac_2dtc)_2]$ and $Ba_2[Cu(Ac_2dtc)_2]$

Table 2.4

Infrared Spectra (cm ⁻¹) Dat
--

Complex	υ(C ≔ S)	υ(C ''' N)
Na ₆ [Co(Ac ₂ dtc) ₃]	1030	1500
$Ba_3[Co(Ac_2dtc)_3]$	1028	1499
Na ₄ [Ni(Ac ₂ dtc) ₂]	1021, 1172	1497
$Ba_2[Ni(Ac_2dtc)_2]$	1025	1507
$Na_4[Cu(Ac_2dtc)_2]$	1002, 1019	1485
$Ba_2[Cu(Ac_2dtc)_2]$	1002	1488

2.3.4 X-Ray structure analysis

Figure 2.15 illustrates two types of complex anions of $[Co(Ac_2dtc)_3]^{6^-}$ in the asymmetric unit of the monoclinic enantiomorphic space group $P2_1$, which correspond to the tris(chelate)type CoS₆ octahedral coordination geometry with a Δ and Λ configuration, respectively. figures 2.15 and 2.16 show that Ba²⁺ ions were tightly captured by carboxyl groups and water molecules. This indicates that 2 $[Co(Ac_2dtc)_3]^{6^-}$, 6 Ba²⁺ and 32 H₂O formed a well-organized and rigid network in the crystal. The complex anion having Co1 connects with 11 Ba²⁺ ions and the anion with Co2 connects with 9 Ba²⁺ ions, as shown in Figure 2.15. The Ba1, Ba2 and Ba3 ions have coordination number of eight and the Ba4, Ba5 and Ba6 ions have nine. Oxygen atoms from O1 to O24 associate with carboxyl groups and oxygen atoms from O25 to O56 come from water molecules (figure 2.16). Figure 2.17 shows six different bonding modes of carboxyl groups with Ba²⁺ ions. The variety of bond lengths between Ba²⁺ and O atoms of

Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges

carboxyl groups is due to the bond angle of C–O–Ba (Table 2.5) and suggests that, the smaller the bond angle of C–O–Ba, the longer the bond length of O–Ba in carboxyl groups. Tables 2.6 and 2.7 provide the averaged data for the bond lengths and bond angles of the complex. The bond angles of S–Co–S, S–C–S, and Co–S–C are similar to those in $[Co(Et_2dtc)_3]$ [16] and $[Co{S_2CN(CH_2CH_2CH_2NMe)_2}_3]$ [11]. The angles around the N atom of $[Co(Ac_2dtc)_3]^{6-}$ are approximately 120° and the angles around the carboxyl carbon are also approximately 120°. These results show high possibility of six carboxyl group in $[Co(Ac_2dtc)_3]^{6-}$ can capture effectively with cations.



Figure 2.15 Molecular structures of two $[Co(Ac_2dtc)_3]^{6-}$ anions bound to several Ba²⁺cations.

Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges



Figure 2.16 Perspective drawing of the coordination environments of Ba^{2+} with the carboxyl group and hydrated water molecules.



Figure 2.17 Various coordination modes of carboxyl groups in $[Co(Ac_2dtc)_3]^{6-}$ with Ba²⁺ ions.

Table 2.5

Selected bond angles (°) of carboxyl group in Ba₃[Co(Ac₂dtc)₃]·16H₂O

Bond	Angle	Bond	Angle
C(10)–O(8)–Ba(6)	144.5(4)	C(3)–O(1)–Ba(1)	101.6(3)
C(3)–O(2)–Ba(1)	150.2(3)	C(13)–O(11)–Ba(3)	162.2(4)
C(13)–O(12)–Ba(2)	103.0(3)	C(13)–O(12)–Ba(1)	133.9(3)
C(8)–O(5)–Ba(2)	91.2(3)	C(8)–O(6)–Ba(2)	93.5(3)
C(18)–O(13)–Ba(3)	101.6(3)	C(18)–O(13)–Ba(2)	143.7(3)

Table 2.6

Selected averaged bond lengths (Å) in Ba₃[Co(Ac₂dtc)₃]·16H₂O

Bond	Bond length	Bond	Bond length
Co(1)– S	2.273(15)	S – C	1.712(8)
Co(2)– S	2.271(16)	N – C	1.322(7)
C – C	1.527(8)	C – O	1.245(7)

Table 2.7

Selected averaged bond angles (°) in Ba₃[Co(Ac₂dtc)₃]·16H₂O

0		101		
Bond	Angle	Bond	Angle	
S - Co(1) - S	76.48(5)	Co(1) - S - C	86.42(12)	
S - Co(2) - S	76.47(5)	Co(2) - S - C	86.45(10)	
S - C - S	110.6(3)	S - C - N	124.6(4)	
(C)C - N - C(C)	117.1(4)	N-C-C	113.5(4)	

Chapter 2: Preparation and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges

(S)C - N - C(C)	121.2(4)	O – C – O	124.5(5)
C - C - O	118.3(5)		

2.4 Conclusion

New diacetatodithiocarbamato metal complexes with carboxyl groups have been synthesized such as Na₆[Co(Ac₂dtc)₃], Ba₃[Co(Ac₂dtc)₃], Na₄[Ni(Ac₂dtc)₂], Ba₂[Cu(Ac₂dtc)₂], Na₄[Cu(Ac₂dtc)₂], and Ba₂[Cu(Ac₂dtc)₂] which illustrate the large negative charges. The crystal structure of Ba₃[Co(Ac₂dtc)₃] · 16H₂O revealed that the complex anion capture Ba²⁺ cation very tightly. Thus these metal complexes can catch or coordinate with cationic metals or positive ions.

References

- D. Coucouvanis, Prog. Inorg. Chem., 11 (1970) 233; D. Coucouvanis, Prog. Inorg.
 Chem., 26 (1979) 301; G. Hogarth, Prog. Inorg. Chem., 53 (2007) 71.
- J.D.E.T. Wilton-Ely, D. Soklanki, E.R. Knight, K.B. Holt, A.L. Thompson, G. Hogarth, Inorg. Chem., 47 (2008) 9642.
- [3] P.D. Beer, N. Berry, M.G.B. Drew, O.D. Fox, M.E.P. Tosta, S. Patell, Chem. Commun., (2001) 199.
- [4] R.A. Howie, G.M. de Lima, D.C. Menezes, J.L. Wardell, S.M.S. Wardell, D.J. Young,E.R.T. Tiekink, CrystEngComm, 10 (2008) 1626.
- [5] B. Macias, M.V. Villa, E. Chicote, S.Martin–Velasco, A. Castineiras, J. Borras, Polyhedron, 21 (2002) 1899.
- [6] A.A. Achilleos, L. Gahan, T.W. Hambley, P.C. Healy, D.M. Weedon, Inorg. Chim. Acta, 157 (1989) 209.
- [7] M.C. Hodgson, P.J. Brothers, G.R. Clark, D.C. Ware, J. Inorg. Biochem., 102 (2008)

789.

- [8] J.L. Serrano, L. Garcia, J. Perez, E. Perez, G. Sanchez, J. Garcia, G. Lopez, G. Garcia,
 E. Molins, Inorg. Chim. Acta, 355 (2003) 33.
- [9] L.M.G. Cunha, M.M.M. Rubinger, J.R. Sabino, L.L.Y. Visconte, M.R.L. Oliveira, Polyhedron, 29 (2010) 2282.
- [10] V. Venkatachalam, K. Ramalingam, T.C.W. Mak, L. Bao-Sheng, Polyhedron, 15 (1996) 1295.
- [11] G. Hogarth, E.J.C.R.C.R. Rainford-Brent, S.E. Kabir, I. Richards, J.D.E.T. Wilton-Ely, Q. Zhang, Inorg. Chim. Acta, 362 (2009) 2020.
- [12] Rigaku and Rigaku/MSC, CrystalStructure, Crystal structure analysis package, ver.3.7.0, The Woodlands, TX, USA, 2000–2005.
- [13] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. de Caro, C. Giacovazzo, G. Polidori, R. Apagna, J. Appl. Cryst., 38 (2005) 381.
- [14] G.M. Scheldrick, Acta Crystallogr., Sect., A 64 (2008) 112.
- [15] M. Kita, K. Yamanari, Y. Shimura, Bull. Chem. Soc. Jpn., 62 (1989) 23.
- [16] D. Oktavec, B. Siles, J. Stefanec, E. Korgova, J. Garaj, Collec. Czech, Chem. Commun., 45 (1980) 791.
- [17] B.G. Jeliazkova, N.D. Yordanow, Inorg. Chim. Acta, 203 (1993) 201.
- [18] G.E. Manoussakis, C.A. Bolos, Inorg. Chim. Acta, 108 (1985) 215.
- [19] F. Bonati, R. Ugo, J. Organomet. Chem., 10 (1967) 257.
- [20] P. Deplano, E. F. Trogu, A. Lai, Inorg. Chim. Acta, 68 (1983) 147.
- [21] A. C. Fabretti, F. Forghieri, A. Giusti, C. Preti, G. Tosi, Inorg. Chim. Acta, 86 (1984)127.

Chapter 3

Preparation and molecular structures of *N*,*N*-2,2'-dipicolyl- and *N*,*N*-3,3'- dipicolyldithiocarbamato metal complexes

New iron(III) and cobalt(III) complexes, $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$, and $[Co(3,3'-dpdtc)_3]$ (dpdtc = dipicolyldithiocarbamate) have been synthesized and their molecular structures have been characterized. The solubility of these complexes in acidic solution was also carried out. These metal complexes have been elucidated by X-ray crystallography which confirm that they have the coordination geometries around the metal centers are MS₆ (M = Fe and Co) octahedral structures and the dipicolyl groups do not coordinate. These mononuclear complexes were used to synthesize some polynuclear dithiocarbamato complexes ($[M(2,2'-dpdtc)_3M'_mX_{2m}]$ and $[M(3,3'-dpdtc)_3M'_mX_{2m}]$: M = Fe(III) or Co(III), M' = Ni(II) or Cu(II), m = 0.5, 1, 2 or 3, X = Cl) which were characterized by elemental analysis, diffused reflection spectra, and magnetic susceptibility. The properties of these mononuclear and corresponding polynuclear complexes are compared using absorption diffused reflection spectra and effective magnetic moment.

3.1 Introduction

Dithiocarbamates are known as bidentate ligands through sulfur and a number of transition metal dithiocarbamato complexes have been studied and characterized [1-8]. In recent research, the synthesis and characterization of N,N-diacetatodithiocarbamato metal complexes with large negative charges has been reported [9]. The ligand, 2,2'-dpdtc has been studied as a spontaneously assembling dithiocarbamate ligand on gold surface [10]. But there are no reports of metal complexes with the new ligands, N,N-2,2'-dipicolyl- and N,N-3,3'-dipicolyldithiocarbamate. We have designed these ligands to be tetradentate. Possible bonding modes are through two sulfurs and two picolyl nitrogen atoms and these ligands can bridge with different metals to form polynuclear complexes.

In this study, novel of N,N-2,2'-dipicolyl- and N,N-3,3'-dipicolyldithiocarbamato iron(III) and cobalt(III) complexes have been prepared as $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$, and $[Co(3,3'-dpdtc)_3]$. Our interest in these complexes is due to the possibility for different coordination structures and properties with the position of picolyl groups. Moreover these metal complexes can be used to prepare the polynuclear complexes and as an indicator in acidic solutions caused by their deep color in acidic media.

3.2 Experimental

3.2.1 Materials

Complexes of $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]$ were prepared using procedures similar to those in the literature [11,12]. The compounds, 2,2'-dipicolylamine, 3,3'-dipocolylamine, carbon disulfide (CS₂) and chloroform (CHCl₃) were purchased from Tokyo Chemical Industry and Nacalai tesque inc.

3.2.2 Measurements

The UV-vis absorption spectra of $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]$ in CHCl₃ solution were measured using a Hitachi U-3900H

spectrophotometer. The solubility of these complexes was measured in hydrochloric acid solution adjusted to different pHs (pH 1–7). The mixture of a metal complex and an acidic solution was stirred for an hour and the resulting mixture was filtered off using a glass microfibre filter (GFA, Whatman, 25 mm, \emptyset Circles). The absorbance of the filtrate was measured at 490 nm and 650 nm for Fe(III) and Co(III) complexes, respectively. [Fe(3,3'dpdtc)₃] decomposed in acidic aqueous solution. The infrared spectra were obtained on a JASCO FT–IR FT-001 spectrophotometer as KBr discs in the 4000–400 cm⁻¹.

The magnetic susceptibility of mono and polynuclear complexes of Fe(III) and Co(III) of *N*,*N*-2,2'-dipicolyl- and *N*,*N*-3,3'-dipicolyl dithiocarbamato was compared by using a magnetic susceptibility balance (Sherwood Scientific, Cambridge UK) at room temperature. From the mass susceptibility data, the molar magnetic susceptibility and effective magnetic susceptibility can be denoted for comparison of mono and polynuclear complexes.

3.3 Preparation of metal complexes

3.3.1 Fe(OH)₃ and Co(OH)₃

 $FeCl_3 \cdot 6H_2O$ and NaOH were mixed in the molar ratio 1 : 3 in water, affording a reddish precipitate of $Fe(OH)_3$. The precipitate was collected by repeated centrifugation and was washed with distilled water.

 $CoCl_2 \cdot 6H_2O$ and NaOH were mixed in the molar ratio 1 : 2 in water, producing a bluish precipitate of $Co(OH)_2$. 3% of hydrogen peroxide (H_2O_2) solution was slowly added to the mixture in the stoichiometric ratio 1 : 0.5, producing a greenish precipitate of $Co(OH)_3$. The precipitate was collected by repeated centrifugation and was washed with distilled water.

These hydroxide metals were used to synthesized the mononuclear of *N*,*N*-2,2'-dpdtc and 3,3'-dpdtc metal complexes. And these mononuclear were used to prepare the polynuclears. Yields and analytical data of mono and polynuclear complexes are listed in Table 3.1 and Table 3.2, respectively.

3.3.2 Synthesis of dithiocarbamato metal complexes

3.3.2.1 [Fe(2,2-dpdtc)₃]

2.50 g (13.0 mmol) of 2,2'-dipicolylamine and 1.00 g (13.0 mmol) of CS₂ were dissolved separately in 10.0 mL of MeOH. Both solutions were added, with stirring, into a MeOH solution suspension containing freshly prepared Fe(OH)₃ (4.30 mmol) (figure 3.1). A black solid was collected by filtration. Yield: 2.00 g (50%). Anal. Calcd for $[Fe(2,2'-dpdtc)_3](\%) = C_{39}H_{36}N_9S_6Fe: C, 53.7; H, 4.13; N, 14.4.$ Found: C, 52.5; H, 3.60; N, 14.1.

3.3.2.2 [Fe(3,3'-dpdtc)₃]

This complex was prepared by using 3,3'-dipicolylamine instead of 2,2'-dipicolylamine, following similar procedure (2.3.2.1). A brown precipitation was collected. Yield: 2.50 g (63%). Anal. Calcd for $[Fe(3,3'-dpdtc)_3] \cdot H_2O(\%) = C_{39}H_{38}N_9S_6FeO$: C, 52.2; H, 4.27; N, 14.1. Found: C, 52.6; H, 4.01; N, 14.0.

3.3.2.3 [Co(2,2'-dpdtc)₃]

This complex was prepared similarly to the method in $[Fe(2,2'-dpdtc)_3]$, by using Co(OH)₃ instead of Fe(OH)₃. A green solid was collected by filtration. Yield: 2.10 g (53%). Anal. Calcd for $[Co(2,2'-dpdtc)_3](\%) = C_{39}H_{36}N_9S_6Co$: C, 53.1; H, 4.11; N, 14.2. Found: C, 51.7; H, 3.76; N, 14.0.

3.3.2.4 [Co(3,3'-dpdtc)₃]

 $[Co(3,3'-dpdtc)_3]$ was prepared in a similar procedure to that of $[Co(2,2'-dpdtc)_3]$, by using 3,3'-dipicolylamine instead of 2,2'-dipicolylamine. A green solid was collected by filtration. Yield: 2.40 g (60%). Anal. Calcd for $[Co(3,3'-dpdtc)_3] \cdot H_2O(\%) = C_{39}H_{36}N_9S_6CoO: C, 52.0; H, 4.40; N, 13.7. Found: C, 52.9; H, 3.71; N, 14.0.$

Table 3.1

Yields and analytical data of mononuclear complexes

Complexes	Color	Yield	С%	H%	N%
		(%)	Calc.	Calc.	Calc.
			(Found)	Found	(Found)
[Fe(2,2'-dpdtc) ₃]	Black	2.00 g	53.7	4.13	14.4
		(50%)	(52.5)	(3.60)	(14.1)
[Fe(3,3'-dpdtc) ₃]	Brown	2.50 g	52.2	4.22	14.1
		(63%)	(52.6)	(4.01)	(14.0)
[Co(2,2'-dpdtc) ₃]	Green	2.10	53.1	4.11	14.2
		(50%)	(51.7)	(3.76)	(14.0)
[Co(3,3'-dpdtc) ₃]	Green	2.40	52.0	4.40	13.7
		(60%)	(52.9)	(3.71)	(13.71)





3.3.3 Synthesis of polynuclear Complexes of [M(n,n'-dpdtc)₃]•(M'Cl₂)_m 3.3.3.1 [Fe(2,2'-dpdtc)₃Ni₂]Cl₄

0.10 g (0.11 mmol) of $[Fe(2,2'-dpdtc)_3]$ was dissolved in chloroform and 0.08 g (0.33 mmol) of NiCl₂•6H₂O was dissolved in methanol. Both solutions were mixed. Diethyl ether was then added to the mixture until a brownish precipitate was deposited. This precipitate was collected by filtration and washed with diethyl ether. Yield 0.13g (72%). Anal. Calcd for $[Fe(2,2'-dpdtc)_3Ni_2]Cl_4 = C_{39}H_{36}N_9S_6FeNi_3Cl_6$: C, 41.1; H, 3.18; N, 11.0%. Found: C, 40.9; H, 2.98; N, 10.6%.

3.3.3.2 [Fe(2,2'-dpdtc)₃Cu₂]Cl₄

0.10 g (0.11 mmol) of $[Fe(2,2'-dpdtc)_3]$ was dissolved in chloroform and 0.06 g (0.33 mmol) of CuCl₂•2H₂O was dissolved in methanol. Both solutions were mixed. Diethyl ether was then added slowly to generate a brown precipitate. The precipitated product was isolated by filtration. Yield 0.11g (69%). Anal. Calcd for $[Co(2,2'-dpdtc)_3Cu_2]Cl_4 = C_{39}H_{36}N_9S_6CoCu_2Cl_4$: C, 41.0; H, 3.16; N, 10.9%. Found: C, 41.9; H, 3.35; N, 11.2%.

3.3.3.3 [Fe(3,3'-dpdtc)₃Ni_{0.5}]Cl

0.10 g (0.11 mmol) of $[Co(3,3'-dpdtc)_3]$ was dissolved in chloroform and 0.08 g (0.33 mmol) of NiCl₂•6H₂O was dissolved in methanol. Both solutions were mixed, a brown precipitate was formed and washed by diethyl ether. Yield 0.11 g (61%). Anal. Calcd for $[Fe(3,3-dpdtc)_3Ni_{0.5}]Cl = C_{39}H_{36}N_9S_6FeNiCl$: C, 50.0; H, 3.78; N, 13.1%. Found: C, 49.6; H, 3.84; N, 13.3 %.

3.3.3.4 [Fe(3,3'- dpdtc)₃Cu]Cl₂•2H₂O

0.10 g (0.11 mmol) of $[\text{Fe}(3,3'-\text{dpdtc})_3]$ was dissolved in chloroform and 0.06 g (0.33 mmol) of CuCl₂•2H₂O was dissolved in methanol. Both solutions were mixed, a brown precipitate was formed and washed by diethyl ether. Yield 0.12 g (76%). Anal. Calcd for

 $[Fe(3,3'-dpdtc)_3Cu]Cl_2 \cdot 2H_2O = C_{39}H_{40}N_9S_6FeCu_2Cl_4O_2: C, 44.6; H, 3.88; N, 12.0\%.$ Found: C, 44.3; H, 3.46; N, 11.6 %.

3.3.3.5 [Co(2,2'-dpdtc)₃Ni]Cl₂•H₂O

0.10 g (0.11 mmol) of $[Co(2,2'-dpdtc)_3]$ was dissolved in chloroform and 0.08 g (0.33 mmol) of NiCl₂•6H₂O was dissolved in methanol. Both solutions were mixed. Acetone was added slowly to the resultant solution until the greenish precipitate was formed. The solid was collected and washed by acetone. Yield 0.08 g (45%). Anal. Calcd for $[Co(2,2'-dpdtc)_3Ni]Cl_2•H_2O = C_{39}H_{38}N_9S_6OCoNiCl_2$: C, 45.4; H, 3.72; N, 12.2%. Found: C, 45.2; H, 3.99; N, 12.0 %.

3.3.3.6 [Co(2,2'-dpdtc)₃Cu₂]Cl₄

0.10 g (0.11 mmol) of $[Co(2,2'-dpdtc)_3]$ was dissolved in chloroform and 0.06 g (0.33 mmol) of CuCl₂•2H₂O was dissolved in methanol. Both solutions were mixed, a green precipitate was form. The solid was collected and washed by acetone. Yield 0.07 g (40%). Anal. Calcd for $[Co(2,2'-dpdtc)_3Cu_2]Cl_4 = C_{39}H_{36}N_9S_6CoCu_2Cl_4$: C, 40.7; H, 3.33; N, 11.0%. Found: C, 41.1; H, 3.86; N, 11.2%.

3.3.3.7 [Co(3,3'-dpdtc)₃Ni₂]Cl₄

0.10 g (0.11 mmol) of $[Co(3,3'-dpdtc)_3]$ was dissolved in chloroform and 0.08 g (0.33 mmol) of NiCl₂•6H₂O was dissolved in methanol. Both solutions were mixed, a green solid was formed and washed by diethyl ether. Yield 0.16 g (86%). Anal. Calcd for $[Co(3,3'-dpdtc)_3Ni_2]Cl_4 = C_{39}H_{36}N_9S_6CoNi_2Cl_4$: C, 41.4; H, 3.18; N, 11.0%. Found: C, 42.2; H, 3.17; N, 11.2%.

3.3.3.8 [Co(3,3'-dpdtc)₃Cu₃]Cl₆

0.10 g (0.11 mmol) of $[\text{Co}(3,3'-\text{dpdtc})_3]$ was dissolved in chloroform and 0.08 g (0.33 mmol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in methanol. Both solutions were mixed, a green solid was formed and washed by diethyl ether. Yield 0.14 g (80%). Anal. Calcd for

 $[Co(3,3'-dpdtc)_3Cu_3]Cl_6 = C_{39}H_{36}N_9S_6CoCu_3Cl_6 : C, 35.6; H, 2.89; N, 9.54\%.$ Found: C, 36.1; H, 2.94; N, 9.37 %.

Table 3.2

Yields and analytical data of polynuclear complexes

Complexes	Color	Yield	C%	H%	N%
		(%)	Calc.	Calc.	Calc.
			(Found)	(Found)	(Found)
[Fe(2,2'-dpdtc) ₃ Ni ₂]Cl ₄	Brown	0.13 g	41.1	3.18	11.0
		(72%)	(40.9)	(2.98)	(10.6)
[Fe(2,2'-dpdtc) ₃ Cu ₂]Cl ₄	Brown	0.11 g	41.0	3.16	10.9
		(69%)	(41.9)	(3.35)	(11.2)
[Fe(3,3'-dpdtc) ₃ Ni _{0.5}]Cl	Brown	0.11 g	50.0	3.78	13.1
		(61%)	(49.6)	(3.84)	(13.3)
[Fe(3,3'-dpdtc) ₃ Cu]Cl ₂ •2H ₂ O	Brown	0.12 g	44.6	3.88	12.0
		76%	(44.3)	(3.46)	(11.6)
[Co(2,2'-dpdtc) ₃ Ni]Cl ₂ •H ₂ O	Green	45%	45.4	3.72	12.2
			(45.2)	(3.99)	(12.0)
[Co(2,2'-dpdtc) ₃ Cu ₂]Cl ₄	Green	0.08 g	41.0	3.33	11.0
		40%	(41.1)	(3.86)	(11.2)
[Co(3,3'-dpdtc) ₃ Ni ₂]Cl ₄	Green	0.16 g	41.4	3.18	11.0
		86%	(42.2)	(3.17)	(11.2)
[Co(3,3'-dpdtc) ₃ Cu ₃]Cl ₆	Green	0.14 g	35.6	2.89	9.54
		80%	(36.1)	(2.94)	(9.37)

3.3.4 Crystallography

Crystallographic and structure refinement data for $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]\cdot H_2O$, $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]\cdot H_2O$ are listed in Table 3.3. A black prismatic crystal of $[Fe(2,2'-dpdtc)_3]$ with approximate dimensions of $0.30 \times 0.20 \times 0.20$ mm, and a black prismatic crystal of $[Fe(3,3'-dpdtc)_3]\cdot H_2O$ (approximately $0.20 \times 0.20 \times 0.20 \times 0.20$ mm) were each mounted using a cryoloop and liquid paraffin, and flash-cooled with a cold nitrogen stream. X-ray diffraction data ($6^\circ < 2\theta < 55^\circ$) were obtained at -80 ± 1 °C on a Rigaku Varimax 724 diffractometer with multi-layer mirror monochromated Mo–Ka radiation ($\lambda = 0.71075$ Å).

A green platelet crystal of $[Co(2,2'-dpdtc)_3]$ with approximate dimensions of $0.35 \times 0.20 \times 0.10$ mm was glued to the top of a glass fiber and mounted on a Rigaku R-axis rapid and analyzed using graphite monochromated Mo–K α radiation ($\lambda = 0.71075$ Å). X-ray diffraction data ($8^\circ < 2\theta < 55^\circ$) were obtained at $23\pm1^\circ$ C.

A green platelet crystal of $[Co(3,3'-dpdtc)_3]\cdot H_2O$ with approximate dimensions of 0.35 × 0.20 × 0.20 mm was mounted using a cryoloop and liquid paraffin, and flash-cooled with a cold nitrogen gas stream. X-ray diffraction data were obtained at $-87\pm1^{\circ}C$ using a Rigaku R-axis rapid imaging plate area detector with graphite monochromated Mo–K α radiation ($\lambda = 0.71075$ Å).

All structural calculations were carried out using the Crystal Structure software package [13]. The structures were solved by a direct method, using the SIR 2004 software package [14], and refined on F^2 (with all independent reflections) using the SHELXL 97 software package [15]. All non-hydrogen atoms were refined anisotopically. The hydrogen atoms of the dpdtc moieties were introduced at the calculated positions and treated using the riding model on the attached C atoms, while those of the hydrated water molecules were not included in the calculation.

Table 3.3

Complexes	[Fe(2,2'-dpdtc) ₃]	[Fe(3,3'-dpdtc) ₃]·H ₂ O	[Co(2,2'-dpdtc) ₃]	[Co(3,3'-dpdtc) ₃]·H ₂ O
Formula	$C_{39}H_{36}FeS_6N_9$	$C_{39}H_{38}FeS_6ON_9$	C39H36CoS6N9	$C_{39}H_{38}CoS_6ON_9$
Formula	878.98	896.99	882.06	900.07
Weight				
Color	Black	Black	Green	Green
T/°C	-80 (1)	-80 (1)	23 (1)	-87 (1)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space Group	Pī	$P2_{1}/c$	Pī	$P\overline{1}$
Ζ	2	4	2	2
a(Å)	7.968(2)	19.0661(15)	7.9361(13)	10.9326(10)
$b(\text{\AA})$	11.293(3)	7.9907(4)	11.410(2)	14.0321(11)
$c(\text{\AA})$	23.298(6)	27.851(2)	23.418(4)	14.9484(14)
α(°)	79.454(6)	90	79.252(5)	116.250(3)
$\beta(^{\circ})$	86.899(8)	93.892(4)	86.346(5)	96.855(2)
γ(°)	77.439(7)	90	76.376(5)	96.600(3)
$V(\text{\AA}^3)$	2011.5(9)	4233.5(5)	2024.2(6)	2005.4(3)
$D_{\rm calc}({\rm g/cm}^3)$	1.451	1.407	1.447	1.520
F(000)	910	1860	912	932
R _{int}	0.033	0.067	0.032	0.027
μ(ΜοΚα)	7.283	6.953	7.756	7.862
(cm^{-1})				
$R1(I>2\sigma(I))$	0.0324	0.0649	0.0380	0.0393
w $R_2(all$	0.0872	0.1915	0.1194	0.1229
reflections)				
Goodness of fit	1.045	1.145	1.092	1.135
(GOF) on F ²				

Crystallographic and structure refinement data

3.4 Results and discussion

N,*N*-2,2'-dipicolyl- and *N*,*N*-3,3'-dipicolyldithiocarbamato metal complexes were synthesized by the reaction of 2,2'-dipicolylamine or 3,3'-dipicolylamine and CS₂ with $Fe(OH)_3$ or Co(OH)_3, in the stoichiometric molar ratio 3 : 3 : 1 (amine : CS₂ : M(OH)_3). The resulting complexes were $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]$ respectively. These metal complexes are insoluble in water, but soluble in methanol, ethanol, chloroform, and dimethyl sulfoxide. They were recrystallized from a chloroform solution by slowly mixing with diethyl ether in a closed vessel.

3.4.1 X-Ray diffraction analysis

Figures 3.2–3.5 illustrate the molecular structures of $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]$ respectively. The structures of $[Fe(2,2'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3] \cdot H_2O$ crystallize in the triclinic space group $P\overline{1}$ with Z = 2 and $[Fe(3,3'-dpdtc)_3] \cdot H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with Z = 4.

Tables 3.4 and 3.5, list the selected average bond lengths and bond angles of these complexes. The coordination arrangement of these complexes are normal tris(dithiocarbamate) MS₆ structures. The dipicolyl groups do not coordinate to any metal. S-Fe-S and S-Co-S bond angles are similar to those of tris(N,N-The diethyldithiocarbamato)iron(III) ([Fe(Et₂dtc)₃]) [16] and tris(*N*,*N*-diethyldithiocarbamato) cron(III) ([Co(Et₂dtc)₃]) [17] respectively.

Chapter 3: Preparation and molecular structures of N,N-2,2'-dipicolyl- and N,N-3,3'dipicolyldithiocarbamato metal complexes



Figure 3.2 Molecular structure

of [Fe(2,2'-dpdtc)₃]



Figure 3.3 Molecular structure of

[Fe(3,3'-dpdtc)₃]



Figure 3.4 Molecular structure

of [Co(2,2'-dpdtc)₃]

Figure 3.5 Molecular structure

of $[Co(3,3'-dpdtc)_3]$

Table 3.4

Bond length	M–S	S–C	(C)N–C(S)	(C)N–C(C)
$[Fe(2,2'-dpdtc)_3]$	2.311(5)	1.719(8)	1.324(8)	1.368(2)
$[Fe(3,3'-dpdtc)_3]$	2.301(8)	1.714(3)	1.329(4)	1.3797(5)
$[Fe(Et_2dtc)_3]$	2.309(1)	1.720(4)	1.326(6)	1.480(7)
$[Co(2,2'-dpdtc)_3]$	2.267(8)	1.707(3)	1.325(3)	1.387(4)
$[Co(3,3'-dpdtc)_3]$	2.265(9)	1.709(3)	1.335(4)	1.378(6)
$[Co(Et_2dtc)_3]$	2.268(8)	1.706(7)	1.315(15)	1.345(14)

Selected average bond lengths (Å)

Table 3.5

Selected average bond angles (°)

Bond angle	S-M-S	M–S–C	S-C-S	S-C-N	N–C–C
$[Fe(2,2'-dpdtc)_3]$	75.59(7)	86.47(6)	111.2(8)	124.5(4)	117.6(6)
$[Fe(3,3'-dpdtc)_3]$	75.69(3)	86.43(5)	110.8(8)	124.5(2)	120.2(4)
[Fe(Et ₂ dtc) ₃]	75.91(1)	86.51(1)	110.9(2)	124.3(2)	111.6(5)
$[Co(2,2)^{-}dpdtc)_{3}]$	76.51(2)	86.24(10)	110.6(14)	124.6(2)	121.6(2)
[Co(3,3'-dpdtc) ₃]	76.62(3)	86.23(10)	110.6(12)	124.7(2)	121.4(2)
[Co(Et ₂ dtc) _{3]}	76.50(1)	86.30(3)	110.9(3)	124.5(3)	112.6(11)

3.4.2 Absorption spectra

Absorption spectra of $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]$ in chloroform are shown in figure 3.6 and the spectral data are listed in Table 3.6. The iron(III) complexes with 2,2'-dpdtc and 3,3'-dpdtc show a typical FeS₆ chromophore. The lower energy transition bands at 16250 cm⁻¹ and 19500 cm⁻¹ are similar in energy to those of $[Fe(Et_2dtc)_3]$ reported by Kunkely et al. [18] and Miessler et al. [19]. The cobalt(III) complexes with 2,2'-dpdtc and 3,3'-dpdtc show a typical CoS₆ chromophore. The lower energy transition bands at 16150 cm⁻¹ and 20500 cm⁻¹ are similar

Chapter 3: Preparation and molecular structures of N,N-2,2'-dipicolyl- and N,N-3,3'dipicolyldithiocarbamato metal complexes

to those found in the absorption spectra of Na₆[Co(Ac₂dtc)₃] reported by Vanthoeun et al. [9].

Figures 3.7, 3.8 show the absorption spectra of $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$, and $[Co(3,3'-dpdtc)_3]$ in dimethyl sulfoxide and methanol, respectively. Their absorption spectra are listed in Table 7 and 8. These results are similar in the chloroform solvent.



Figure 3.6 Absorption spectra of [Fe(2,2'-dpdtc)₃] (–), [Fe(3,3'-dpdtc)₃] (–), [Co(2,2'-dpdtc)₃] (–), and [Co(3,3'-dpdtc)₃] (–) in chloroform.



Figure 3.7 Absorption spectra of [Fe(2,2'-dpdtc)₃] (–), [Fe(3,3'-dpdtc)₃] (–), [Co(2,2'-dpdtc)₃] (–), and [Co(3,3'-dpdtc)₃] (–) in DMSO.



Figure 3.8 Absorption spectra of [Fe(2,2'-dpdtc)₃] (–), [Fe(3,3'-dpdtc)₃] (–), [Co(2,2'-dpdtc)₃] (–), and [Co(3,3'-dpdtc)₃] (–) in MeOH.
Table 3.6

Absorption spectroscopic data in CHCl₃

Complexes		$\sigma/10^3 \mathrm{cm}^{-3}$	$1 (\log (\epsilon/cm^{-1} m))$	$\operatorname{nol}^{-1} \operatorname{dm}^{3}))$		Ref.
[Fe(2,2'-dpdtc) ₃]	16.25(3.45)	19.50(3.65)	21.0(3.60) ^{sh}	28.50(4.27)	37.0(4.95)	This
						work
[Fe(3,3'-dpdtc) ₃]	16.25(3.35)	19.50(3.55)	21.0(3.55) ^{sh}	28.50(4.25)	37.0(5.00)	This
						work
[Fe(Et ₂ dtc) ₃]	16.94	19.45 ^{sh}	25.70	28.57	34.96	[22]
[Co(2,2'-dpdtc) ₃]	16.10(3.20)	18.50(3.0) ^{sh}	20.05(3.35)	27.0(4.60)	30.05(4.60)	This
						work
[Co(3,3'-dpdtc) ₃]	16.10(3.25)	18.50(3.05) ^{sh}	20.05(3.40)	27.0(4.45)	30.05(4.75)	This
						work
Na ₆ [Co(Ac ₂ dtc) ₃]	15.8(2.79)	18.5(2.31) ^{sh}	25.3(4.05)	30.8(4.43)	36.3(4.2)	[0]
sh: shoulder						

Table 3.7

Absorption spectroscopic data in DMSO

Complexes		$\sigma/10^3 \mathrm{cm}^{-1}$	$(\log (\epsilon/cm^{-1}))$	$ol^{-1} dm^3))$	
[Fe(2,2'-dpdtc) ₃]	20.0(3.50)	24.0(2.95) ^{sh}	28.5(4.20)	32.5(4.25)	37.0(4.75)
[Fe(3,3'-dpdtc) ₃]	20.0(3.50)	25.0(2.95) ^{sh}	28.0(4.05))	32.6(4.20)	38.0(4.70)
[Co(2,2'-dpdtc) ₃]	16.5(3.15)	19.5(2.85) ^{sh}	22.0(3.20)	31.1(4.40)	33.0(4.50)
[Co(3,3'-dpdtc) ₃]	16.5(3.20)	19.5(3.00) ^{sh}	22.0(3.30)	31.1(4.55)	35.0(4.70)

sh: shoulder

Table 3.8

Complexes		$\sigma/10^3 \mathrm{cm}^{-1}$	^ι (log (ε/cm ⁻¹ n	$\operatorname{nol}^{-1} \operatorname{dm}^3))$	
[Fe(2,2'-dpdtc) ₃]	19.5(3.40)	21.5(3.40) ^{sh}	25.0(4.25)	28.0(4.35)	35.0(4.95)
[Fe(3,3'-dpdtc) ₃]	19.5((3.50)	21.5(3.50) ^{sh}	25.0(4.20)	28.0(4.35)	36.0(5.00)
[Co(2,2'-dpdtc) ₃]	16.5(3.30)	20.0(3.20) ^{sh}	22.0(3.40)	29.5(4.55)	32.5(4.75)
[Co(3,3'-dpdtc) ₃]	16.5(3.25)	20.0(3.00) ^{sh}	22.0(3.35)	30.0(4.50)	34.0(4.70)

Absorption spectroscopic data in MeOH

sh: shoulder

3.4.3 Absorption spectra of polynuclear complexes by using liquid paraffin







Figure 3.10 Absorption spectrum of [Fe(3,3'-dpdtc)₃] (-) in chloroform, diffused reflection spectra of [Fe(3,3'-dpdtc)₃Ni_{0.5}]Cl (---) and [Fe(3,3'-dpdtc)₃Cu]Cl₂(...) with liquid paraffin.

Chapter 3: Preparation and molecular structures of N,N-2,2'-dipicolyl- and N,N-3,3'dipicolyldithiocarbamato metal complexes

The polynuclear complexes $[M(n,n'-dpdtc)_3M'_mX_{2m}]$ were prepared by reacting $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$ or $[Co(3,3'-dpdtc)_3]$ with $[Pd(PhCN_2)Cl_2]$, NiCl_2·6H₂O or CuCl_2·2H₂O. The polynuclear products were insoluble in water and organic solvents. The molecular structures of these polynuclear complexes could not be determined, so diffused reflection spectra of the complexes are used to carry out comparisons with the corresponding mononuclear complexes.

The absorption spectra of $[Fe(2,2'-dpdtc)_3]$, $[Fe(2,2'-dpdtc)_3Ni_2]Cl_4$, $[Fe(2,2'-dpdtc)_3Cu_2]Cl_4$, $[Fe(3,3'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3Ni_{0.5}]Cl$, and $[Fe(3,3'-dpdtc)_3Cu]Cl_2$ are shown in figures 3.9, 3.10 and spectral data in Table 3.9. The polynuclear complexes show the absorption spectrum band with medium intensity at 21100 cm⁻¹, at 17000 cm⁻¹, at 18700 cm⁻¹, and at 21000 cm⁻¹ for $[Fe(2,2'-dpdtc)_3Ni_2]Cl_4$, $[Fe(2,2'-dpdtc)_3Cu_2]Cl_4$, $[Fe(3,3'-dpdtc)_3Ni_{0.5}]Cl$, and $[Fe(3,3'-dpdtc)_3Cu]Cl_2$ respectively which are different from absorption band of $[Fe(2,2'-dpdtc)_3]$ and $[Fe(3,3'-dpdtc)_3]$ (16250 cm⁻¹). The variety of absorption spectra of mono and polynuclear due to polymerization forms by an effects of other transition metals (nickel(II) or copper(II)) on the FeS₆ chromophore of $[Fe(2,2'-dpdtc)_3]$.

Table 3.9

Complexes	$\sigma/10^3 \text{cm}^{-1}$	$^{-1}$ (log (ε /cm ⁻¹ mol ⁻¹ d	lm ³))
[Fe(2,2'-dpdtc) ₃ Ni ₂]Cl ₄	18.0(3.95) ^{sh}	21.10(4.15)	-
[Fe(2,2'-dpdtc) ₃ Cu ₂]Cl ₄	17.0(4.05)	17.50(4.0) ^{sh}	21.50(4.25)
[Fe(3,3'-dpdtc) ₃ Ni _{0.5}]Cl	18.75(3.8)	24.0(3.85) ^{sh}	-
[Fe(3,3'-dpdtc) ₃ Cu]Cl ₂	21.0(4.25)	24.0(4.20) ^{sh}	-
[Co(2,2'-dpdtc) ₃ Ni]Cl ₂	17.50(3.95)	19.20(3.90) ^{sh}	-
[Co(2,2'-dpdtc) ₃ Cu ₂]Cl ₄	18.60(4.35)	21.0(4.30)	23.0(4.27) ^{sh}
[Co(3,3'-dpdtc) ₃ Ni ₂]Cl ₄	16.0(3.80) ^{sh}	23.0(4.25)	-
$[Co(3,3'-dpdtc)_3Cu_3]Cl_6$	17.0(4.20) ^{sh}	19.10(4.36)	23.0(4.25) ^{sh}

Absorpti	ion Spe	ctral Data
----------	---------	------------

sh: shoulder

Chapter 3: Preparation and molecular structures of N,N-2,2'-dipicolyl- and N,N-3,3'dipicolyldithiocarbamato metal complexes







Figure 3.12 Absorption spectra of $[Co(3,3'-dpdtc)_3]$ (-) in chloroform, reflection spectra of $[Co(3,3'-dpdtc)_3Ni_2]Cl_4$ (---) and $[Co(3,3'-dpdtc)_3Cu_3]Cl_6$ (...) with liquid paraffin.

The absorption spectra of $[Co(2,2'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3Ni]Cl_2$, $[Co(2,2'-dpdtc)_3Cu_2]Cl_4$, $[Co(3,3'-dpdtc)_3]$, $[Co(3,3'-dpdtc)_3Ni_2]Cl_4$, and $[Co(3,3'-dpdtc)_3Cu_3]Cl_6$ are shown in figures 3.11, 3.12 and spectral data in Table 3.9. The polynuclear complexes show the absorption spectrum band with medium intensity at 17500 cm⁻¹, at 18600 cm⁻¹, at 16000 cm⁻¹, and at 17000 cm⁻¹ for $[Co(2,2'-dpdtc)_3Ni]Cl_2$, $[Co(2,2'-dpdtc)_3Cu_2]Cl_4$, $[Co(3,3'-dpdtc)_3Ni_2]Cl_4$, and $[Co(3,3'-dpdtc)_3Cu_3]Cl_2$, respectively, which are different from absorption band of $[Co(2,2'-dpdtc)_3]$ and $Co[(3,3'-dpdtc)_3]$ (16100 cm⁻¹). The variety of absorption spectra of mono and polynuclear suggests that the interaction of adding of another transition metal form a polymerization which effects on the CoS₆ chromophore of $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]$.

3.4.4 IR spectra

Infrared spectra of metal complexes with dithiocarbamate ligands have been extensively studied [19]. The IR spectral data of the *N*,*N*-2,2'-, and *N*,*N*-3,3'-dipicolyldithiocarbamato metal complexes are listed in Table 3.10. S. Singhal et al. [21] suggested the resonance of tris(*N*,*N*'-dialkyldithiocarbamato) rion (III) complex structures on the ligand indication considerable double bond character in the (S₂)C^{...}N(R₂) bond as $\upsilon_{(N^{12}C)}$ band in the region 1499 cm⁻¹, and $\upsilon_{(C-S)}$ at 985 cm⁻¹. We have observed $\upsilon_{(N^{12}C)}$ of 2,2'-, and *N*,*N*-3,3'-dipicolyldithiocarbamato iron(III) complexes at 1473.35, and 1479.62cm⁻¹, and strong bands of $\upsilon_{(C-S)}$ at 992.40 cm⁻¹ and 997.98 cm⁻¹, respectively (figure 3.13). Thus these results match well with the literature. Moreover, The I.R spectral assignment of Co(Et₂dtc)₃ [22] complexes have been established that the band in the 1498 cm⁻¹ region to stretching vibration of the C^{...}N band and $\upsilon_{(C-S)}$ at 950 cm⁻¹. For 2,2'- and *N*,*N*-3,3'-dipicolyldithiocarbamato cobalt(III) complexes, the $\upsilon_{(C-S)}$ bands are at 1477.69 cm⁻¹ and 1479.62 cm⁻¹ and $\upsilon_{(C-S)}$ at 993.64 and 995.56 cm⁻¹, respectively (figure 3.14). These bands are similar to the literature.

Table 3.10

Complexes	v(C-N)	v(C-S)	Ref.
[Fe(2,2'-dpdtc) ₃]	1473.35	992.40	This work
[Fe(3,3'-dpdtc) ₃]	1479.62	997.98	This work
[Fe(Et ₂ dtc) ₃]	1499	985	[21]
[Co(2,2'-dpdtc) ₃]	1477.69	995	This work
[Co(3,3'-dpdtc) ₃]	1479.62	993	This work
[Co(Et ₂ dtc) ₃	1498	950	[22]

Infrared spectra (cm^{-1})



Figure 3.13 IR spectra of $[Fe(2,2'-dpdtc)_3]$ and $[Fe(3,3'-dpdtc)_3]$



Figure 3.14 IR spectra of $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3]$

3.4.5 Magnetic moment

Table 3.11 lists some data of magnetic properties of mononuclear and polynuclear complexes of Fe(III) of N,N-(2,2'-dipicolyl) and N,N-(3,3'-dipicolyl) dithiocarbamato complexes. Effective magnetic moments of Fe(III) complexes increase from mono to polynuclear with another transition metal content but they are as same as the paramagnetic compounds of Fe(III). The results are consistent with the trend of paramagnetic tetrahedral of Ni(II) or paramagnetic square planar Cu(II) in correspond polymerization.

Table 3.11

Metal complexes	Effective magnetic	The number of
	moment (µ _{eff})	unpaired electrons
$[Fe(2,2)^{2}-dpadtc)_{3}]$	4.0	3
[Fe(2,2'-dpadtc) ₃ Ni ₂]Cl ₄	4.26	3
[Fe(2,2'-dpadtc) ₃ Cu ₂]Cl ₄	4.43	3
$[Fe(3,3'-dpadtc)_3]$	3.89	3
[Fe(3,3'-dpadtc) ₃ Ni _{0.5}]Cl	4.12	3
[Fe(3,3'-dpadtc) ₃ Cu]Cl ₂	4.35	3

Magnetic properties of Fe(III) complexes

Table 3.12

Metal complexes	Effective magnetic	The number of
	moment (µ _{eff})	unpaired electrons
$[Co(2,2)^{2}-dpadtc)_{3}]$	0	0
[Co(3,3'-dpadtc) ₃ Cu ₂]Cl ₄	2.92	2
$[Co(3,3'-dpadtc)_3]$	0	0
[Co(3,3'-dpadtc) ₃ Ni ₂]Cl ₃	2.63	2
[Co(3,3'-dpadtc) ₃ Cu ₃]Cl ₆	2.53	2

Magnetic properties of Co(III) complexes

Table 3.12 lists some data of magnetic properties of mononuclear and polynuclear complexes of Co(III) of N,N-(2,2'-dipicolyl) and N,N-(3,3'-dipicolyl) dithiocarbamato complexes. The effective magnetic moment and the number of unpaired electrons of $[Co(2,2'-\text{dpdtc})_3]$ and $[Co(3,3'-\text{dpdtc})_3]$ are equal to zero, meaning that mononuclear complexes of Co(III) are diamagnetic compounds. But in the cluster compounds they contain two unpaired electrons due to the increase of the effective magnetic moment from mono to polynuclear. These results suggest by the interaction of paramagnetic tetrahedral of Ni(II), and paramagnetic square planar of Cu(II) in correspond polymerization.

3.4.6 Solubility

Table 3.13								
Absorption	spectral	data	in	acidic	media	(pH	1)	

Complexes	$\sigma/10^3 \text{cm}^{-1} (\log (\epsilon/\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^3))$					
[Fe(2,2'-dpdtc) ₃]	18.5(2.55)	23.5(3.25)	30.0(3.60)	34.0(3.90)	-	-
[Co(2,2'-dpdtc) ₃]	16.1(2.25)	18.50(2.10) ^{sh}	20.0(2.30)	27.0(3.45)	28.0(3.40) ^{sh}	30.0(3.55)
[Co(3,3'-dpdtc) ₃]	16.1(2.35)	18.50(2.15) ^{sh}	20.0(2.35)	27.0(3.55)	28.0(3.50) ^{sh}	30.0(3.75)

Table 3.14



Absorbance at saturated concentrations and defined concentration of each metal complex in various pHs (pH 1-7)

Figure 3.15 Absorbance of metal complexes with pHs (pH 0-7). [Fe(2,2'-dpdtc)₃] (\circ) (at 490 nm), [Co(2,2'-dpdtc)₃] (\bullet) and [Co(3,3'-dpdtc)₃] (\Box) (at 650 nm).



Figure 3.16 Determination of solubility of $[Fe(2,2'-dpdtc)_3]$ (0) in pH 1 – 7

Although solubility is not a colligative property, our metal complex solubility was estimated by the Beer-Lambert law technique as using a molar absorption coefficient (Table 3.13). The *N*,*N*-2,2'-dipicolyl- and *N*,*N*-3,3'-dipicolyldithiocarbamato iron(III) and cobalt(III) complexes are insoluble in water, but they are soluble in hydrochloric acid. Table 3.14 lists the absorbance values at saturated concentration and defined concentration of each metal complex in the pH 1 – 7. Figure 3.15 shows high absorbance of saturated concentration of these metal complexes at pH 1 and pH 2. Figure 3.16 – 3.17 carry out high soluble at pH 1 and pH 2 of Fe(III) and Co(III) metal complexes respectively. These results suggest that the solubility of these metal complexes due to the protonation of the dipicolyl nitrogen atom in the acidic media. Thus the protonation can be well occurred at pH 1 and pH 2.

Chapter 3: Preparation and molecular structures of N,N-2,2'-dipicolyl- and N,N-3,3'dipicolyldithiocarbamato metal complexes



Figure 3.17 Determination of solubility of $[Co(2,2'-dpdtc)_3] (\bullet)$, $[Co(3,3'-dpdtc)_3] (\Box)$ in pH 1 – 7

3.5 Conclusion

The ligands, 2,2'-dpdtc and 3,3'-dpdtc can coordinate through two sulfur and two picolyl nitrogen atoms but the present complexes have MS_6 coordination environment. These metal complexes are insoluble in water and alkaline solution but act as indicators in acidic media due to the deeper color in acidic aqueous solution below pH 2. Moreover, these complexes are good starting materials to build polynuclear complexes due to the bidentate on the nitrogen atom of pyridine. The crystal structure of these polynuclear complexes has not been studied because they are either insoluble in water or organic solvents.

References

- D. Coucouvanis, Prog. Inorg. Chem. 11 (1970) 233; D. Coucouvanis, Prog. Inorg. Chem. 26 (1979) 301; G. Hogarth, Prog. Inorg. Chem. 53 (2007) 71.
- [2] S. Singhal, C.L. Sharma, A.N. Garg, K. Chandra, Polyhedron 21 (2002) 2489.
- [3] R. Chant, A.R. Hendrickson, R.L. Martin, N.M Rohde, Inorg. Chem. 14 (1975) 1894.
- [4] P.C. Healy, E. Sinn, Inorg. Chem. 14 (1975) 109.
- [5] M.C. Hodgson, P.J. Brothers, G.R. Clark, D.C. Ware, J. Inorg. Biochem. 102 (2008) 789.
- [6] P. Deplano, E. Trogu, A. Lai, Inorg. Chim. Acta 68 (1983) 147.
- [7] M. Kita, K. Yamanari, Y. Shimura, Bull. Chem. Soc. Jpn. 62 (1989) 23.
- [8] M. Kita, H. Tamai, F. Ueta, A. Fuyuhiro, K. Yamanari, K. Nakajima, M. Kojima, K. Murata, S. Yamashita, Inorg. Chim. Acta 314 (2001) 139.
- [9] K. Vanthoeun, T. Bunho, R. Mitsuhashi, T. Suzuki, M. Kita, Inorg. Chim. Acta 394 (2013) 410.
- [10] Y. Zhao, W.P. Segarra, Q. Shi, A. Wei, J. Am. Chem. Soc. 127 (2005) 7328.
- [11] R.D. Bereman, D. Nalewajek, Inorg. Chem. 17 (1978) 1085.
- [12] P. Giboreau, C. Morin, J. Org. Chem. 59 (1994) 1205.
- [13] Rigaku and Rigaku/MSC, CrystalStructure, Crystal structure analysis package, ver.3.7.0, The Woodlands, TX, USA, 2000–2005.
- [14] M.C.Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. de Caro, C. Giacovazzo, G. Polidori, R. Apagna, J. Appl. Cryst. 38 (2005) 381.
- [15] G.M. Sheldrick, Acta Crystallogr., A 64 (2008) 112.
- [16] J.G. Leipoldt, P. Coppens, Inorg. Chem. 12 (1973) 2269.
- [17] T. Brennan, I. Bernal, Phys. Chem 73 (1969) 443.
- [18] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 5 (2002) 730.
- [19] G.L. Miessler, G. Stuk, T.P. Smith, K.W. Given, M.C. Palazzotto, L.H. Pognolet, Inorg. Chem. 15 (1976) 1982.
- [20] F. Bonati, R. Ugo, J. Organomet. Chem., 10 (1967) 257.

Chapter 3: Preparation and molecular structures of N,N-2,2'-dipicolyl- and N,N-3,3'dipicolyldithiocarbamato metal complexes

- [21] S. Singhal, C.L. Sharma, A.N. Garg, K. Chandra, Polyhedron 21 (2002) 2489.
- [22] P. Deplano, E. Trogu, Inorg. Chim. Acta. 68 (1983) 147.

Chapter 4

Control of cyclodextrins inclusion with surfactants by metal complex

The high negative charges of dithiocarbamato metal complexes with carboxyl group, as diacetatodithiocarbamato (Ac₂dtc^{3–}) metal complexes exhibits surface tension reduction which is studied by surface tension measurement at water interface at 25.0±0.1 °C. This result is due to the strong interactions between these high negative charges of metal complexes and the cationic surfactant (dodecyltrimethylammonium chloride: DTAC) in an aqueous solution which shows the surface tension reduction (STR). Moreover, Inclusion compounds of α -, β -, and γ -cyclodextrin (α -, β -, and γ -CD) with sodium dodecyl sulfate (SDS) or dodecyltrimethylammonium chloride (DTAC) in aqueous solutions and positive charged metal complex: hexaamminecobalt(III) perchlorate ([Co(NH₃)₆](ClO₄)₃) or negatively charged metal complex: tribarium tris(*N*,*N*-diacetato-dithiocarbamato)cobaltate(III) (Ba₃[Co(Ac₂dtc)₃]) are also studied by surface tension measurements at water interface. In fixed concentration of metal complexes of Ba₃[Co(Ac₂dtc)₃] or [Co(NH₃)₆](ClO₄)₃) the surface tension plateaus at higher concentration of α -, β -, and γ -CDs against the

higher concentration of DTAC or SDS. The phenomenon can be interpreted as showing that α -, β -, and γ -CDs well included with SDS thus the cationic metal complexes of cannot easily draw the DTA⁺ or DS⁻ ion from its inclusion compound.

4.1 Introduction

Many applications of surfactants such as foaming, coating flows and detergency are based on their abilities to decrease the surface or interfacial tensions, at equilibrium or dynamically. These abilities correlate with their solubility, the critical micelle concentration (CMS), their surface activity, and the transport and adsorption rates to the interface [1]. The Cyclodextrins are a family of macrocyclic oligosaccharides consisting of six (α -CD), seven (β -CD), or eight (γ -CD) D-(+)glucopyranose units linked by α -(1,4) interglucose bonds and arranged in a torus shaped molecular structure with an internal cavity that is relatively hydrophobic [2]. The hydrophobic internal cavities give CDs the ability to form inclusion complexes with a variety of organic and inorganic molecules depending on their size and polarity and on the size of the particular cyclodextrin [3-5]. In particular, surfactant molecules which have an ionic head group as well as a large hydrocarbon chain of varying hydrophobicity are expected to form complexes with cyclodextrins by the inclusion of the hydrophobic chain of the surfactant into the apolar cavity of the cyclodextrin, affecting the micellization process of the surfactant itself [6–8]. The associations between α -, β -, and γ -CDs, with an anionic surfactant such as sodium dodecyl sulfate (SDS), have already been studied [9, 10]. The association process involves an inclusion phenomena and the critical micelle concentration shifts to a higher concentration [11, 12]. Drastic surface tension reductions (STRs) of aqueous SDS solution were observed by the addition of various metal complexes, such as $[Co(NH_3)_6]X_3$, $[Co(en)_3]X_3$, $[Co(bpy)_3]X_3$, $[Co(phen)_3]X_3$, (en = ethylenediamine, bpy = 2,2'dipyridine, phen = 1,10-phenanthroline, $X = Cl^{-}$, Br^{-} , I^{-} , and ClO_{4}^{-}). This STR involves interesting interactions between anionic surfactants and metal complex cations [13]. Moreover, drastic surface tension reduction (STR) of aqueous solutions containing anionic surfactants such as sodium dodecyl sulfate (SDS) and sodium dodecylbenzenesulfonate (SBS) is observed by the addition of various

metal complexes, such as $[Co(NH_3)_6]X_3$, $[Co(en)_3]X_3$ (en = ethylenediamine), $[Co(bpy)_3]X_3$ (bpy = 2,2'-dipyridine), $[Co(phen)_3]X_3$ (phen = 1,10-phenanthroline) (X = Cl⁻, Br⁻, l⁻, and ClO₄⁻). This STR involves interesting interactions between anionic surfactants and metal complex cations [14]. In addition, novel counterion effects have been reported [15].

The strong interaction of metal complexes with surfactants has been investigated, especially the novel interaction of metal complexes into inclusion compounds of surfactants and α -, β -, and γ -CDs have been explored in this study.

4.2 Experimental procedure

4.2.1 Materials

Dodecyltrimethylammonium chloride (DTAC), Sodium dodecyl sulfate (SDS) and α -, β -, and γ -cyclodextrins, were purchased from Tokyo Chemical Industry and Nacalaitesqueinc. All of the chemicals were of reagent grade and were used without further purification.

4.2.2 Surface tension measurement

Surface tension was measured by using the Wilhelmy plate technique at a temperature of 25.0 ± 0.1 °C by a Kyowa CBVP-Z tensiometer with an EYELA NCB-1200 temperature controller. Concentrations were 0.312–5.00 mM for α -cyclodextrin, 0.312–10.0 for mM β -cyclodextrin, 0.312–20.0 mM for γ -cyclodextrin, 1.0 mM tribarium tris(*N*,*N*-diacetato-dithiocarbamato)cobaltate(III) (Ba₃[Co(Ac₂dtc)₃]), 1.00 mM for hexaamminecobalt(III) perchlorate ([Co(NH₃)₆]Cl₃, 0.01 2.00 mM for dodecyltrimethylammonium chloride (DTAC) and 0.01–0.50 mM for sodium dodecyl sulfate (SDS).

4.2.3 Methods

The properties of α -, β -, and γ -CDs in solution are supported by a large number of crystal structure studies (figure 4.1) [16]. The effect of metal complex on the inclusion of DTAC or SDS

and α -, β -, and γ -CDs was conducted by mixing of various concentration of these cyclodextrins (10.0 mL), and DTAC or SDS (10.0 mL) and kept for five minutes, then 5.00 mL of $[Co(Ac_2dtc)_3]^{6-}$ or $[Co(NH_3)_6]^{3+}$ was added. The surface tension of all mixtures that became turbid was not measured.







Property	a-Cyclodextrin	β-Cyclodextrin	γ-Cyclodextrin
Number of glucopyranose units	6	7	8
Outer diameter (Å)	14.6	15.4	17.5
Cavity diameter (Å)	4.7–5.3	6.0–6.5	7.5-8.3
Height of torus (Å)	7.9	7.9	7.9
Cavity volume (Å ³)	174	262	427

Figure 4.1.	Construction	of Cyclodextrin
-------------	--------------	-----------------

4.3 Results and discussion



4.3.1 Surface tension of aqueous solution of Ac₂dtc³⁻ metal complexes

Figure 4.2 Surface tension of Na₆[Co(Ac₂dtc)₃] (\bullet), Ba₃[Co(Ac₂dtc)₃] (\blacksquare), Na₄[Ni(Ac₂dtc)₂] (\bullet), Ba₂[Ni(Ac₂dtc)₂] (Δ), Na₄[Cu(Ac₂dtc)₂] (\blacktriangledown), and Ba₂[Cu(Ac₂dtc)₂] (\blacktriangle), in water.

The surface tension results for aqueous solutions of *N*,*N*-diacetatodithiocarbamato metal complexes are shown in figure 4.2. These results demonstrate limited variation in surface tension values. Nevertheless, among these metal complexes, the results suggest that the cobalt complex provide the largest surface tension reduction, presumably because it has a larger negative charge of -6.

Chapter 4: Control of cyclodextrins inclusion with surfactants by metal complex



4.3.2 Surface tension reduction of SDS with Ac₂dtc^{3–} metal complexes

Figure 4.3 Surface tension of an aqueous solution of the anionic surfactant SDS with Ac_2dtc^{3-} metal complexes (1.0 mM). SDS only (\bullet), $Na_6[Co(Ac_2dtc)_3]$ (\bullet), $Ba_3[Co(Ac_2dtc)_3]$ (\bullet), $Na_4[Ni(Ac_2dtc)_2]$ (\bigtriangledown), $Ba_2[Ni(Ac_2dtc)_2]$ (\blacklozenge), $Na_4[Cu(Ac_2dtc)_2]$ (\checkmark), and $Ba_2[Cu(Ac_2dtc)_2]$ (\triangleleft).

Figure 4.3 shows STR of an aqueous solution of SDS on addition of Ac_2dtc^{3-} complex (1.0 mM) which is due to the counter ions effects. STRs of aqueous solution of SDS and effect of counterions on SDS have been reported by Sovanna et al. [15]. As shown in Figure 4.2, Ba complexes have a greater propensity for STRs than the corresponding Na complexes $(Ba_3[Co(Ac_2dtc)_3] > Na_6[Co(Ac_2dtc)_3], Ba_2[Ni(Ac_2dtc)_2] > Na_4[Ni(Ac_2dtc)_2], and Ba_2[Cu(Ac_2dtc)_2] > Na_4[Cu(Ac_2dtc)_2])$ indicating that Ba^{2+} interacts with dodecyl sulfate ion (DS⁻) more strongly than Na⁺ because Ba^{2+} has a greater positive charge. Furthermore, a larger STR of $[Co(Ac_2dtc)_3]^{6-}$

compare with those of Ni(II) and Cu(II) analogs confirms that $[Co(Ac_2dtc)_3]^{6-}$ has a large negative charge such that it is completely hydrated in water and adsorbed on the water surface.



4.3.3 Surface tension reduction of DTAC with Ac₂dtc³⁻ metal complexes

Figure 4.4 Surface tension of an aqueous solution of the cationic surfactant DTAC with metal complexes (1.0 mM). DTAC only (\bullet), Na₆[Co(Ac₂dtc)₃] (\Box), Ba₃[Co(Ac₂dtc)₃] (\bullet), Na₄[Ni(Ac₂dtc)₂] (\blacktriangle), Ba₂[Ni(Ac₂dtc)₂] (\checkmark), Na₄[Cu(Ac₂dtc)₂] (\triangleleft), and Ba₂[Cu(Ac₂dtc)₂] (\triangleright).

The case of an aqueous solution containing a mixture of cationic surfactant DTAC and anionic Ac_2dtc^{3-} metal complex shows STR (figure 4.4), which is similar to the interaction of an aqueous solution containing mixture of a cationic surfactant and anionic polyelectrolyte reported by Merta et al. [17]. The surface tension curve for a cationic surfactant solution shows a reduction at ca. 28 mN

 m^{-1} for aqueous solution of DTAC without the Ac₂dtc³⁻ metal complexes. At high concentration of DTAC as 1.50–2.00 mM shows not too decreased which due to the state of critical micelle concentration (CMC) of the surfactant micelle formed. Adding of high negative charges' metal complexes to DTAC shows drastically decrease owing to the strong interaction of the opposite charge in the mixtures at certain concentration lower than 1.00 mM of DTAC at higher concentration resulting as turbid forms. The mixed solution containing [Ni(Ac₂dtc)₂]⁴⁻ and [Cu(Ac₂dtc)₂]⁴⁻ with DTA⁺ show the reduction at ca. 18 mN m⁻¹ which is higher than the mixed solution containing [Co(Ac₂dtc)₃]⁶⁻ with DTAC shows the reduction at ca. 10 mN m⁻¹. This result suggests that Ac₂dtc³⁻ metal complexes strongly interact with DTA⁺. In addition [Co(Ac₂dtc)₂]⁴⁻ ions because of a strong hydrophilic interaction between the anionic carboxyl group and cationic ammonium of DTA⁺. Thus, the existence of six negative charges in the complex enables a stronger association between the cationic surfactant and anionic complexes than the presence of four negative charges.

4.3.4 Effect of [Co(Ac₂dtc)₃]⁶⁻ on inclusion compounds

The large negative charges of $[Co(Ac_2dtc)_3]^{6-}$ were added to the mixture of the aqueous DTAC solutions and α -, β -, and γ -CDs, their results are shown in figures 4.5–4.7. Without the presence of α -, β -, and γ -CDs, surface tension decreased with the increasing of DTAC concentration which are due to the strong interaction of DTAC with $[Co(Ac_2dtc)_3]^{6-}$. When metal complex was added into the inclusion compound of α -, β -, and γ -CDs and DTAC, the surface tension was similarly stable at low concentration of DTAC. In contrast, the surface tension decreases while the concentration of DTAC increases owing to the possibility of $[Co(Ac_2dtc)_3]^6$ draws DTAC from its inclusion compound. The plateau region corresponds to the concentration of cyclodextrins at 5.0 mM for α -CD, 10.0 mM for β -CD or 20.0 mM for γ -CD which prevents the easiness of drawing from its inclusion compound.



Figure 4.5 Surface tension of an aqueous solution of DTAC in 1.0 mM



Figure 4.6 Surface tension of an aqueous solution of DTAC in 1.0 mM $[Co(Ac_2dtc)_3]^{6-}$ with or without the presence of β -CD.



Figure 4.7 Surface tension of an aqueous solution of DTAC in 1.0 mM $[Co(Ac_2dtc)_3]^{6-}$ with, and without the presence of γ -CD.



4.3.5 Inclusion compounds of SDS with α -, β -, and γ -CDs

Figure 4.8 Surface tension of an aqueous solution of SDS with, and without α -CD.



Figure 4.9 Surface tension of an aqueous solution of SDS with, and without β -CD.

The formation of an inclusion compound effects on the surface activity of some surfactants by the addition of CDs in the order α -CD > β -CD > γ -CD as reported by Saito et al. [18]. Figures 4.8– 4.10 show the surface tension aqueous SDS solution in the presence of aqueous α -, β - and γ cyclodextrins solution which illustrates that the surface tension of mixture is higher than its original value is due to the formation of an inclusion compound. The surface tension of aqueous SDS solution decreases with increasing the SDS concentration, but at its higher concentration shows not too decreased which is due to the state of critical micelle concentration (CMC) of the surfactant micelle formed. In the presence of α -, β - and γ -CDs; the surface tension of aqueous SDS solution is not shown, due to the plateau slop which is close to the surface tension of water (72.5 mN/m), because the α -, β - and γ -CD molecules include the SDS molecule, and adsorbed on the interface of aqueous solution. The result could mainly be attributed to the hydrophobic interaction between the alkyl chain and the inner wall of CD molecules, and partly to release water molecules from the alkyl end of the detergent and the cavity of the CD during the penetration process into the cavity. On the other hand, at higher concentration of SDS at 1.25 mM, 2.00 mM and 5.00 mM with 1.25 mM, 2.50 mM, and 5.00 mM of α -, β - and γ -CDs, respectively. The SDS surface tension shows drastically decrease which is due to its excess amount in the mixture to form the inclusion compounds. The distinction between SDS and α -, β - and γ -CDs of inclusion compounds is illustrated in Figure 4.11 shows the inclusion compound formation that has an effect on interface area which causes an increase in the surface tension. Table 4.1 lists a ratio of SDS with α -, β - and γ -CDs which confirms that the inclusion compound can form in ratio SDS / 2: α -, β - or γ -CDs.



Figure 4.10 Surface tension of an aqueous solution of SDS with, and without γ -CD.

Table 4.1

α -, β -, and γ -	α -, β -, and γ -	SDS	Ratio of α -, β -, and γ -	Averaged ratio
CDs	CDs		CDs/SDS	
α-CD	1.25	0.62	2.02	
α-CD	2.50	1.25	2.00	2.01
α-CD	5.00	2.50	2.00	
β-CD	1.25	0.62	2.02	
β-CD	2.50	1.25	2.00	2.01
β-CD	5.00	2.50	2.00	
γ-CD	1.25	0.56	2.23	
γ-CD	2.50	1.23	2.03	2.16
γ-CD	5.00	2.25	2.22	

Molar ratio of α -, β -, γ -CDs and surfactant (SDS) as inclusion compound.



SDS molecule α -, β - and γ -CD molecules Inclusion complex formation

4.3.6 Effect of [Co(NH₃)₆](ClO₄)₃ on inclusion compound of SDS and α-, β-, and γ-CDs

The surface tension of aqueous SDS solution with $[Co(NH_3)_6](ClO_4)_3$ solution decreased with the increasing SDS concentration as reported by Sovanna et al. [14]. Mixtures of SDS and α -CD were added to a fixed concentration of aqueous $[Co(NH_3)_6]^{3+}$ solution (1.00 mM), and surface tension of this mixture plotted against SDS concentration are shown in figure 4.12. There are two

Figure 4.11 Inclusion formation of α -, β - and γ -CDs with SDS

phenomena in the slop (figure 4.12) after the metal complex ($[Co(NH_3)_6]^{3+}$ is added into the mixture of SDS and α -CD. First phenomenon is a characterization of plateau slop at concentrations of α -CD; 1.25 mM, 2.50 mM and 5.00 mM, with concentration of SDS; 0.25 mM, 0.50 mM and 1.00 mM, respectively. These results confirm an ability of α -CD can either include or surround the SDS from the penetration metal complex to attract SD⁻ ion from its inclusion compound. The second phenomenon shows drastically decrease in surface tension of concentration SDS; 0.80 mM, 1.25 mM and 3.00 mM with α -CD at 1.25 mM, 2.50 mM and 5.00 mM, respectively, which confirm the penetration of metal complex to draw SD⁻ anion. In addition, at higher concentrations of SDS are not shown (figure 4.12) which is due to the turbidity forms which illustrate that metal complex interacts completely with SDS solution to [Co(NH₃)₆](DS)₃. The results confirm that these higher concentrations of SDS, the α -CD cannot prevent the penetration of [Co(NH₃)₆]³⁺ to react with the surfactant. Table 4.2 lists the suitable ratio of SDS with α -CD as inclusion compounds to inhibit the entering of [Co(NH₃)₆]³⁺ to interact with SD⁻.

Table 4.2

α-, β-, and	α-, β-,		Ratio of α-, β-, Ave	eraged ratio	Free CD/
γ-CDs	and γ-	SDS	and γ-CDs/SDS		including CD
	CDs				
α-CD	1.25	0.25	5.00		
α-CD	2.50	0.51	4.90	4.94	2.94/2.01
α-CD	5.00	1.02	4.90		
β-CD	2.50	0.26	9.61		
β-CD	5.00	0.51	9.80	9.80	7.80/2.01
β-CD	10.0	1.00	10.0		
γ-CD	5.00	0.25	20.0		
γ-CD	10.0	0.49	20.41	20.2	18.0/2.16
γ-CD	20.0	0.99	20.2		

Molar ratio of α -, β -, γ -CDs and SDS as inclusion formation after adding of metal complex.



Figure 4.12 Surface tension of an aqueous solution of SDS with and without the presence of α -CD with 1.00 mM $[Co(NH_3)_6]^{3+}$ solution.



Figure 4.13 Surface tension of an aqueous solution of SDS with or without the presence of β -CD in 1.00 mM $[Co(NH_3)_6]^{3+}$

In the case of surface tension of aqueous solutions of SDS with β -CD and [Co(NH₃)₆](ClO₄)₃ solution plotted against SDS concentrations are shown in figure 4.13 which distinguishes almost similar phenomenon to the α -CD. But in the presence of β -CD; 2.50 mM, 5.00 mM and 10.0 mM with concentration of SDS at 0.25 mM, 0.50 mM and 1.00 mM, respectively, exhibit plateau slop which is due to the inclusion of β -CD with SDS can penetrate of [Co(NH₃)₆]³⁺ to interact with SD⁻ anion. On the other hand, the surface tension of SDS concentration; 0.80 mM, 1.25 mM and 3.00 mM with β -CD at 2.50 mM, 5.00 mM and 10.0 mM, respectively, show drastically decrease which confirm the penetration of metal complex to interact with SD⁻ anion. At higher of SDS concentration from these concentrations' range are not shown in the figure 4.13 owing to the turbidity forms which illustrate that metal complex penetrate to interact completely with SDS solution. Thus, the results confirm that these higher concentrations of SDS, the β -CD cannot prevent the penetration of [Co(NH₃)₆]³⁺ to interact with surfactant. Table 4.2 lists the suitable ration of SDS with β -CD as inclusion compounds to inhibit the entering of [Co(NH₃)₆]³⁺ to interact with SD⁻.



Figure 4.14 Surface tension of an aqueous solution of SDS with or without the presence of γ -CD in 1.00 mM $[Co(NH_3)_6]^{3+}$ solution.

For the surface tension of aqueous solutions of SDS with γ -CD and [Co(NH₃)₆](ClO₄)₃ solution plotted against SDS concentrations are shown in figure 4.14 which is almost similar properties to the β -CD. The presence of γ -CD at 5.00 mM, 10.0 mM, 20.0 mM with concentration of SDS at 0.25 mM, 0.50 mM, 1.00 mM, respectively, which exhibited the plateau slop due to the inclusion of γ -CD with SDS can forbid the penetration of [Co(NH₃)₆]³⁺ to interact with SD⁻ anion. Moreover, the surface tension of concentration SDS; 0.80 mM, 1.25 mM and 3.00 mM with γ -CD at 5.00 mM, 10.0 mM and 20.0 mM, respectively show drastically decrease which confirm the entering of metal complex to interact with SD⁻ anion. At higher of γ -CD and SDS concentration from these concentrations' range are not shown in the figure 4.14 which is due to the turbidity forms which illustrates that metal complex penetrate to interact completely with SDS solution. The results confirm that these higher concentrations of SDS, the γ -CD cannot prevent the penetration of [Co(NH₃)₆]³⁺ to the surfactant. Table 4.2 lists the suitable ration of SDS with γ -CD as inclusion compounds to inhibit the entering of [Co(NH₃)₆]³⁺ to interact with SD⁻.

The metal complex of 1.0 mM $[Co(NH_3)_6]^{3+}$ was added to 1.25, 2.50, and 5.00 mM α -CDs, the plateau regions of the surface tension were lower concentration than 0.25, 0.51 and 1.02 mM SDS, respectively, as shown in figure 4.12. For 2.50, 5.00, 10.0 mM β -CD, the plateau regions were lower concentration than 0.26, 0.51, and 1.00 mM SDS, respectively, as shown in figure 4.13. For 5.00, 10.0, and 20.0 mM γ -CDs, the plateau regions were lower concentration than 0.25, 0.49, 0.99 mM SDS, respectively, as shown in figure 4.14.

In these conditions, the inclusion compound must be still 2:1 and a competition between CD and $[Co(NH_3)_6]^{3+}$ cation must be occurring to associate with DS⁻ anion. Table 4.2 also suggests the ratio of free CD against including CD as 2:1 CD/SDS inclusion compound after adding of metal complex, 2.94/2.01, 7.80/2.01, and 18.0/2.16 for α -, β -, and γ -CDs, respectively. The ratio of free CD/including CD clearly shows that free CD increase in the order, α -, β -, γ -CD, indicating that strength of the inclusion complex formation with SDS. It is in the reverse order of the easiness of drawing of SDS from the inclusion compound by Co(III) complex is in the increasing order α -, β -, γ -CD. This order is corresponded to the cavity diameter, 4.7–5.4, 6.0–6.5, 7.5–8.3 Å, respectively.

4.4 Conclusion

The interaction of metal complexes into the inclusion compounds of surfactants (DTAC and SDS) and α -, β -, and γ -CDs has been revealed. There are two possibilities in this interaction due to the strong interaction of opposite charges of metal complexes and surfactants. Firstly, at low concentration of α -, β -, and γ -CDs, metal complexes attract easily to surfactants which can form precipitate. At high concentration of α -, β -, and γ -CDs, metal complexes cannot draw surfactants easily. To prevent the penetration of metal complexes which draw surfactant from its inclusion compound, the ratios of surfactants and α -, β -, and γ -CDs were increased to 5, 10, and 20 for α -, β -, and γ -CDs. Thus, this novel interaction shows that molecular assembly/ inclusion interaction of surfactants and CDs are highly sensitive to the metal ions.

References

- [1] X. Wen, K.C. McGinnis, E.I. Franses, Colloids Surf. A 143 (1998) 371.
- [2] W. Saenger, Chem. Int. Ed. Engl. 19 (1980) 344.
- [3] C. Merino, E. Junquera, J. Barbera, E. Aicart, Langmuir 16 (2000) 1557.
- [4] E. Junquera, L. Pena, E. Aicart, J. Pharm. Scie. 87 (1998) 86.
- [5] E. Stefansson, T. Loftsson, J. Inclusion Phenom. Macro. Chem. 44 (2002) 23.
- [6] E.S. Aman, D. Serve, J. Colloid Interface. Sci. 138 (1990) 365.
- [7] A. Harada, J. Li, M. Kamachi, Macromolecules. 26 (1993) 5698.
- [8] T. Cserhati, E. Forgacs, J. Szejtli, Int. J. Pharm. 141 (1996) 1.
- [9] J. Andreaus, J. Draxler, R. Marr, A. Hermetter, J. Colloid Interface. Sci. 193 (1997) 8.
- [10] M.D. Veiga, F. Ahsan, J. Pharm. Sci. 9 (2000) 291.
- [11] M.S. Bakshi, J. Colloid Interface Sci. 227 (2000) 78.
- [12] E. Junquera, G. Tardajos, E. Aicart, Langmuir 9 (1993) 1213.
- [13] J.W. Park, H.J. Song, J. Phys. Chem. 93 (1985) 6454.
- [14] S. Sovanna, T. Suzuki, M. Kojima, S. Tachiyashiki, M. Kita, J. Colloid Interface. Sci. 332 (2009) 194.

- [15] S. Sovanna, T. Suzuki, M. Kojima, S. Tachiyashiki, M. Kita, Chem. Lett. 39 (2010) 306.
- [16] E.M.M.D Valle, Process Biochem 39 (2004) 1033.
- [17] J. Merta, P. Stenius. Colloids Surf. A: Physicochem. Eng. Aspects 149 (1999) 36.
- [18] Y. Saito, M. Abe, T. Sato, J.F. Scamehorn, S.D. Christian, Coll. Surf. A 292 (2007) 196.

Chapter 5

Summary and Conclusion

The studies concentrate on the preparation and molecular structures of dithiocarbamato metal complexes bearing carboxyl or pyridine groups and the interaction of metal complexes on the inclusion compounds of surfactants and cyclodextrins. The preparation of *N*,*N*-diacetatodithiocarbamato complexes such as Na₆[Co(Ac₂dtc)₃], Ba₃[Co(Ac₂dtc)₃], Na₄[Ni(Ac₂dtc)₂], Ba₂[Ni(Ac₂dtc)₂], Na₄[Cu(Ac₂dtc)₂], and Ba₂[Cu(Ac₂dtc)₂] and molecular structure of Ba₃[Co(Ac₂dtc)₃] were described in chapter 2 which reveal that these metal complexes are synthesized in simply method to the previous one, and provided appropriate yields for all compounds. Moreover, the molecular structure of Ba₃[Co(Ac₂dtc)₃]·16H₂O exhibits two types of complex anion of [Co(Ac₂dtc)₃]⁶⁻ in the asymmetric unit of the monoclinic enantiomorphic space group *P*2₁, which correspond to the tris(chelate)-type CoS₆ octahedral coordination geometry with a Δ and Λ configuration. In addition, the variety of bond lengths between Ba²⁺ and O atoms of carboxyl groups is due to the bond angle of C–O–Ba and suggests that, the smaller the bond angle of C–O–Ba, the longer the bond length of O–Ba in carboxyl groups. Thus, the X-ray diffraction of Ba₃[Co(Ac₂dtc)₃]·16H₂O illustrates a well-organized and rigid network among carboxyl groups of the complex anions, barium cations, and water molecules. On the other hand, the

study of absorption and infrared spectra are also carried out by comparison with previous prepared dithiocarbamato metal complexes. By this comparison study, the novel of *N*,*N*-diacetatodithiocarbamato metal complexes are well coordinated in their compounds' bonding such as, the bonding of C–S and C–N.

In conclusion, the study in chapter 2 clearly introduces the synthesis of *N*,*N*-diacetatodithiocarbamato metal complexes which confirms that these metal complexes are large negative charges. Furthermore, The crystal structure of $Ba_3[Co(Ac_2dtc)_3] \cdot 16H_2O$ revealed that the complex anion capture Ba^{2+} cation very tightly.

The molecular structure of N,N-2,2'-, and N,N-3,3'-dipycolyldithiocarbamato complexes such as $[Fe(2,2'-dpdtc)_3]$, $[Fe(3,3'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$, and $[Co(3,3'-dpdtc)_3]$ were introduced in chapter 3, reveal that the structures of $[Fe(2,2'-dpdtc)_3]$, $[Co(2,2'-dpdtc)_3]$ and $[Co(3,3'-dpdtc)_3] \cdot H_2O$ crystallize in the triclinic space group $P_{\overline{1}}$ with Z = 2 and $[Fe(3,3)^2 - dpdtc)_3] \cdot H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with Z = 4. And the coordination arrangement of these metal complexes are normal tris(dithiocarbamate) MS_6 structures. The dipicolyl groups do not coordinate to any metal. Thus they are tetradentate complexes which can be used as a starting material for polynuclear complexes, resulting as $[Fe(2,2'-dpdtc)_3Ni_2]Cl_4$, $[Fe(2,2'-dpdtc)_3Cu_2]Cl_4$, $[Fe(3,3'-dpdtc)_3Ni_{0.5}]Cl_4$ $[Fe(3,3)^{-}dpdtc)_{3}Cu]Cl_{2}\cdot 2H_{2}O_{3}$ $[Co(2,2'-dpdtc)_3Ni]Cl_2 \cdot H_2O, [Co(2,2'-dpdtc)_3Cu_2]Cl_4,$ $[Co(3,3)^{-}]$ dpdtc)₃Ni₂]Cl₄, [Co(3,3'-dpdtc)₃Cu₃]Cl₆. These polynuclear properties were illustrated by magnetic moment and diffused reflection spectra with liquid paraffin because they are insoluble in water and other organic solvents. Even, the crystal structures of polynucleare complexes was not formed, it is revealed that the dithiocarbamato metal complexes with pyridine groups can be used to prepared the polynuclear complexes. On the other hand, the study of absorption and infrared spectra are also identified by comparison with previous prepared dithiocarbamato metal complexes. This comparison study, the novel of N,N-2,2'-, and N,N-3,3'-dipycolyldithiocarbamato metal complexes are well coordinated in their compounds such as, the bonding of C–S and C–N. Moreover, these metal complexes are soluble in the organic solvents but insoluble in water. Thus, the Beer Lamber's law method was used to conduct their solubilities in acidic media, reveal that metal complexes are soluble in acidic media, due to the protonation of the dipicolyl nitrogen atom in the acidic media and identified that pH 1 and pH 2 are good protonation for these *N*,*N*-2,2'-, and *N*,*N*-3,3'-dipycolyldithiocarbamato metal complexes.

In conclusion, the study in chapter 3 clearly exhibits the synthesis of N,N-2,2'-, and N,N-3,3'dipycolyldithiocarbamato metal complexes. Furthermore, the 2,2'- and 3,3'-dpdtc ligands have four donor atoms, S, S', N, N'. These complexes are insoluble in water but they are soluble in acidic solution. Crystal structures of these metal complexes reveal that the central metal ions have MS₆ (M = Fe and Co) octahedral structures and all dipicolyl groups do not coordinate. And the mononuclear complexes were used to prepared polynuclear complexes.

Chapter 4 describes the interaction of metal complexes into inclusion compounds of surfactants and cyclodextrins, reveal that the surface tension of dodecyltrimethylammonium chloride (DTAC) and sodium dodecyl sulfate (SDS) aqueous solution reduces by an addition of α -, β -, or γ -cyclodextrin (CD) since the 1:2 inclusion compound, DTAC or SDS/2CD, is formed. The addition of Ba₃[Co(Ac₂dtc)₃] or [Co(NH₃)₆](ClO₄)₃ into the above inclusion compound aqueous solution shows the characteristic drawing of DTAC or SDS from CDs. The easiness of the drawing is shown as γ -CD > β -CD > α -CD due to the cavity size of CDs. The strong interaction of metal complexes with surfactants increases in ratio of CDs / DTAC or SDS up to 5, 10, and 20 for α -, β -, and γ -CDs, respectively. Within the interaction of high positive charges of metal complexes to inclusion compound suggests the ratio of free CD against including CD as 2:1 CD/SDS inclusion compound after adding of metal complex, 2.94/2.01, 7.80/2.01, and 18.0/2.16 for α -, β -, and γ -CD, indicating that strength of the inclusion complex formation with SDS. It is in the reverse order of the easiness of drawing of SDS
from the inclusion compound by Co(III) complex is in the increasing order α -, β -, or γ -CD. This order is corresponded to the cavity diameter, 4.7–5.4 , 6.0–6.5, 7.5–8.3 Å, respectively.

In conclusion, the study in chapter 4 clearly reveals that strong interaction of metal complexes with surfactants effect on the inclusion compounds of surfactant and cyclodextrins. Furthermore, it can be an example which shows that molecular assembly/inclusion interaction of surfactants and CDs are highly sensitive to a metal complex.

ACKNOWLEDGEMENTS

The accomplishment of this study could not be possible without the supports, guidance, and encouragement from a number of generous people.

First of all, I would like to express my sincere thanks to the Ministry of Education, Science, Sports and Culture of the Government of Japan for a financial support for my research study program.

My greatest gratitude must be offered to Prof. Dr. MASAKAZU KITA and my supervisor Prof. Dr. TAKAYOSHI SUZUKI for their most precious advices and tireless assistance throughout my research study program. Their valuable guidance and discussions are the big foundation of my achievement. Moreover, I would like to express my deep thanks to the involved professors in Division of Chemistry and Biochemistry and Japanese students in Graduate school of Natural Science and Technology and Graduate School of Science Education of Okayama University, for their assistances and encouragements.

I would like to thank to Mr. David Ford who works at Royal University of Phnom Penh for his supporting in the English correction. My faithfully thanks must be offered to my classmate Mr. Abukari Moses Abdullai and my colleagues for their encouragements, comment and assistance.

Finally, I would like to express my uncountable gratitude to my parents, Keo Tit and Van Sarin, my Parents in law, Eang Ny and Khim Vanna, My elder brother and sisters, and my beloved wife.

DEDICATION

I would like to dedicate this dissertation to my parents Keo TIT and Van SARIN, to my parents in law Eang NY and Khim VANNA, to my beloved wife Eang THARY VANTHOEUN, to my brother and sisters. Their precious love, encouragement and patience are uncountable to me and make me remember deeply in all my mind and heart. I wish they would be happy and satisfy with my graduation as well.