Preface

The research work described in this thesis entitled “Syntheses, Molecular and Supramolecular Structures, and Properties of Some Coordination Compounds of s, p, d, and f Block Metal Ions” was commenced in December 2006.


New type of hydrate isomerism, structural diversity, and cocrystals of s-block and f-block metal ions derived from acyclic compartmental ligand, variable-temperature magnetic properties of rare heterobridged nickel(II) compounds derived from acyclic ligands, hydrogen bonded interesting topologies of macrocyclic complexes and of uranium complexes, spectroscopic (absorption and emission) and electrochemical aspects have been described in this thesis.

This thesis is comprised of six chapters. A brief review and scope of the thesis is discussed in Chapter 1. Chapter 2 deals with three mononuclear copper(II) compounds derived from the acyclic compartmental Schiff base ligand \(N, N'-\text{ethylenedibio(3-ethoxyxsalicylaldimine)} \ (\text{H}_2\text{L}^1)\). One among these is the previously reported compound \([\text{Cu}^{II}\text{L}^1\subset(\text{H}_2\text{O})] \ (\text{1} \ (\text{Inorg. Chem. 2006, 45, 10764–10773}))\), while other two are \([\text{Cu}^{II}\text{L}^1(\text{H}_2\text{O})] \ (\text{2}) \) and \([\text{Cu}^{II}\text{L}^1] \ (\text{3})\). Crystal structures of 2 and 3, a comparison of the structures, thermogravimetric analyses, \(^1\text{H}\) NMR and infrared spectroscopic properties, and interconversion behaviour of 1–3, are described in this Chapter. Interestingly, compounds 1 and 2 represent a new type of hydrate isomerism in coordination chemistry.

Syntheses and crystal structures a dinuclear compound \([\text{Cu}^{II}\text{L}^1\text{Bi}^{III}(\text{NO}_3)_3] \ (\text{4})\), a trimuclear sandwich type compound \([\text{(Cu}^{II}\text{L}^1\text{)}_2\text{Ba}^{II}(\text{NO}_3)_2\cdot0.2\text{H}_2\text{O}] \ (\text{5})\), a tetranuclear compound \([\text{Cu}^{II}\text{L}^1\text{Pb}^{II}(\mu-\text{NO}_3)(\text{NO}_3)]_2 \ (\text{6})\), a tetrametallic \([2\times1+1\times2]\) cocrystal \([\text{Cu}^{III}\text{L}^1\text{Na}^1(\text{H}_2\text{O})_2] \{\text{Cu}^{II}\text{L}^1\}_2(\text{NO}_3) \ (\text{7})\), a hexametallic \([2\times1+1\times4]\) cocrystal \([\text{(U}^{IV}\text{O}_2)_2(\mu-\text{H}_2\text{O})_2(\text{NO}_3)_4\cdot4[\text{Cu}^{III}\text{L}^1\subset(\text{H}_2\text{O})] \ (\text{8})\), and a octametallic \([3\times1+5\times1]\) double-decker-triple-decker cocrystal \([\{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^4(\text{NO}_3)_5\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_5\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-\text{H})_4(\text{NO}_3)_3\} \cdot \{\text{(Cu}^{II}\text{L}^1\}_2\text{K}^2(\mu-}\)
Unprecedented structural resemblance of sodium(I) with 3d metal ions and bismuth(III) with 4f metal ions, and structural diversity of coordination compounds derived from H$_2$L are described in this Chapter.

Syntheses, structures, and magnetic properties of a heterobridged $\mu$-phenoxo-$\mu_{1,1}$-azide dinickel(II) compound [Ni$^{II}_2$(HL)$_3$(μ$_{1,1}$-N$_3$)]-3H$_2$O (10), a heterobridged $\mu$-phenoxo-$\mu_{1,1}$-NCO dinickel(II) compound [Ni$^{II}_2$(HL)$_3$(μ-NCO)]-2H$_2$O (11), and a heterobridged bis($\mu_1$-phenoxo)bis($\mu_1$-alkoxo) cubane type tetranickel(II) system [Ni$^{II}_4$(L)$_2$(HL)$_3$(SeCN)$_2$(H$_2$O)$_2$]-C$_3$H$_7$NO-4H$_2$O (12) derived from the acyclic Schiff base ligand N-(2-hydroxyethyl)-3-methoxysalicylaldimine (H$_2$L) are described in Chapter 4. Interestingly, comparison of the exchange integral of 10 with that of the previously reported only $\mu$-phenoxo-$\mu_{1,1}$-azide dinickel(II) compound results in the emergence of a unique example of the dependence of strength of magnetic exchange interaction on the metal–ligand bridge distance. As evidenced from variable field magnetization studies, complex 12 exhibits an unusual $S_f = 3$ spin ground state.

Chapter 5 deals with the diprotonated perchlorate salt, [H$_4$L$_3$](ClO$_4$)$_2$ (13), of a Robson type macrocyclic ligand (H$_2$L), and five dinuclear complexes of composition [Pb$^{II}_2$L$_3$(NO$_3$)$_2$] (14), [Zn$^{II}_2$L$_3$(NO$_3$)(H$_2$O)](ClO$_4$) (15), [Zn$^{II}_2$L$_3$(H$_2$O)$_2$](ClO$_4$)$_2$ (16), [Cu$^{II}_2$L$_3$(H$_2$O)(ClO$_4$)](ClO$_4$)-2H$_2$O (17), and [Cu$^{II}_2$L$_3$(N$_3$)$_2$]-2H$_2$O (18). The single crystal X-ray structures of compounds 13, 15, 17, and 18 have been determined. Absorption and emission properties of 13, 15, and 17, and magnetic and electrochemical properties of 17 and 18 have been investigated.

A [1×1+1×1] cocrystal [(UO$_2$)(L)$_4$(H$_2$O)=C(H$_2$O)]•[(UO$_2$)(L)$_4$(H$_2$O)] (19), derived from $N,N'$-o-phenylenebis(3-ethoxysalicylaldimine) (H$_2$L), and two dialkoxo-bridged diuranyl(VI) compounds, [(UO$_2$)$_2$(L)$_2$(dmf)$_2$] (20) and [(UO$_2$)$_2$(L)$_2$(dmf)$_2$] (21), derived from N-(2-hydroxyethyl)-3-ethoxysalicylaldimine (H$_2$L) and N-(2-hydroxyethyl)-3-methoxysalicylaldimine (H$_2$L), respectively, have been described in Chapter 6. Syntheses, molecular and supramolecular structures, and electrochemical properties of these complexes (19–21) have been described in this Chapter.