

Preface

The research work described in this thesis entitled “Structural, Magnetic, Catalytic And Spectroscopic Properties Of Metal Complexes Of Varying Nuclearity” was commenced in January, 2012.

This thesis includes the contents of seven published articles: (i) *Cryst. Growth. Des.* **2016**, *16*, 3777–3790; (ii) *Polyhedron* **2014**, *77*, 39–46; (iii) *Inorg. Chim. Acta* **2015**, *435*, 38–45; (iv) *Inorg. Chim. Acta* **2014**, *410*, 65–75; (v) *Polyhedron* **2015**, *87*, 98–108; (vi) *Inorg. Chim. Acta* **2017**, *455*, 70–80; (vii) *Polyhedron* **2014**, *73*, 67–71.

This thesis is comprised of eight chapters. Brief reviews of the relevant topics and objective and scope of the thesis are discussed in **Chapter 1**.

Chapter 2 deals with syntheses, characterization and molecular and supramolecular structures of eight Cu^{II}Sn^{IV} salt cocrystals / cocrystals of composition [CuL¹]₂·[SnMe₂Cl₄]²⁻·(H₂ED)²⁺ (**1**), [CuL¹]₂·[SnEt₂Cl₄]²⁻·(H₂ED)²⁺·0.5H₂O (**2**), [CuL¹]₂·[Sn(*n*-Bu)₂Cl₄]²⁻·(H₂ED)²⁺ (**3**), [CuL¹]₂·[SnPh₂Cl₄]²⁻·(H₂ED)²⁺ (**4**), [CuL¹]₂·[SnPh₂Cl₄]²⁻·(H₂ED)²⁺·2MeOH (**5**), [CuL²]₂·[SnMe₂Cl₂(H₂O)₂]·0.2H₂O (**6**), [CuL²]₂·[Sn(*n*-Bu)₂Cl₂(H₂O)] (**7**), and [CuL²]₂·[SnPh₂Cl₄]²⁻·(H₂ED)²⁺ (**8**) and two Cu^{II}Sn^{II} salts [CuL¹SnCl]⁺·[SnCl₃]⁻ (**9**) and [CuL²SnCl]⁺·[SnCl₃]⁻ (**10**) (ED = 1,2-ethylenediamine), where H₂L¹ = *N,N'*-ethylenedis(3-methoxysalicylaldimine) and H₂L² = *N,N'*-ethylenedis(3-ethoxysalicylaldimine). All the compounds have been characterized by single crystal X-ray crystal structure determination. Some interesting features on multicomponent crystals of metal complexes have been observed in this series of complexes. This study also reveals that the two closely similar ligands are very different in stabilizing the type of heterometallic systems.

Chapter 3 This chapter deals with syntheses, characterization, crystal structures and diffuse reflectance spectra of the products obtained from the reactions of three mononuclear copper(II) compounds derived from three 3-methoxysalicylaldehyde–diamine ligands, H₂L¹ (diamine = ethylenediamine), H₂L³ (diamine = *o*-phenylenediamine), and H₂L⁴ (diamine = *trans*-1,2-diaminocyclohexane), with perchloric acid in DMF, MeOH and MeOH–MeCN. The objective of this work has been to explore whether such ligands can trap aquated proton. However, no aquated proton is trapped in any case, revealing that this type of ligands is not potential to interact with aquated proton. The six compounds isolated

from the above mentioned reactions are: $[\{\text{Cu}^{\text{II}}\text{L}^1\}(\text{Me}_2\text{NH}_2)](\text{ClO}_4)$ (**11**); $[\{\text{Cu}^{\text{II}}\text{L}^3\}(\text{Me}_2\text{NH}_2)](\text{ClO}_4)$ (**12**); $[\{\text{Cu}^{\text{II}}\text{L}^4\}(\text{Me}_2\text{NH}_2)](\text{ClO}_4)$ (**13**); $[\{\text{Cu}^{\text{II}}\text{L}^1\}_2(\text{enH}_2)](\text{ClO}_4)_2$ (**14**; enH₂ means diprotonated ethylenediamine); $[\{\text{Cu}^{\text{II}}\text{L}^3\}_2(\text{opdaH}_2)](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**15**; opdaH₂ means diprotonated *o*-phenylenediamine); $[\{\text{Cu}^{\text{II}}\text{L}^4\}(\text{MeOH}_2)](\text{ClO}_4)$ (**16**). The individual units in **11–16** are self-assembled by noncovalent interactions to generate one-/two-/three-dimensional self-assemblies. A spectroscopic correlation has been enlightened.

Chapter 4 deals with the syntheses, characterization, catechol oxidase activity, electrochemistry and electrospray ionization mass spectroscopy (ESI-MS positive) of five mononuclear manganese(III) compounds of composition $[\text{Mn}^{\text{III}}\text{L}^2(\text{OAc})(\text{H}_2\text{O})] \cdot \text{DMF}$ (**17**), $[\text{Mn}^{\text{III}}\text{L}^2(\text{Cl})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**18**), $[\text{Mn}^{\text{III}}\text{L}^2(\text{N}_3)(\text{H}_2\text{O})]$ (**19**), $[\text{Mn}^{\text{III}}\text{L}^2(\text{NCS})(\text{H}_2\text{O})]$ (**20**), and $[\text{Mn}^{\text{III}}\text{L}^2(\text{NCSe})(\text{H}_2\text{O})] \cdot \text{MeCN}$ (**21**), derived from the Schiff base compartmental ligand *N,N'*-ethylenebis(3-ethoxysalicylaldehyde) (H_2L^2). Major outcomes of this chapter are (i) The title compounds are among a few examples of mononuclear manganese compounds showing catechol oxidase activity; (ii) Dependency of K_{cat} values with different auxiliary anionic ligands and also solvent have been explored.

Chapter 5 presents, syntheses, crystal structures, catechol oxidase activity and ESI-MS (positive) studies of two mononuclear cobalt(III) compounds of composition $[\text{Co}^{\text{III}}\text{L}^2(\text{N}_3)_2 \rhd (\text{H}_3\text{O}^+)] \cdot 2\text{MeOH}$ (**22**) and $[\text{Co}^{\text{III}}\text{L}^2(\text{NCS})(\text{H}_2\text{O})] \cdot \text{DMF} \cdot \text{H}_2\text{O}$ (**23**), where H_2L^2 is *N,N'*-ethylenebis(3-ethoxysalicylaldehyde). Both the compounds show catechol oxidase activity (**22** in MeCN, **23** in DMF) as monitored by the UV–Vis spectroscopy of the aerial oxidation of 3,5-DTBCH₂ to 3,5-DTBQ. The kinetic parameters have been determined using Michaelis–Menten approach. The K_{cat} values for **22** in MeCN and **23** in DMF are 10.0 and 11.2 h⁻¹, respectively. ESI-MS (positive) of **22** and the mixture of **22** and 3,5-DTBCH₂ have been recorded and the positive ions have been well assigned. Interestingly, a 1:2 adduct of composition $[\text{Co}^{\text{II}}\text{L}^2(3,5\text{-DTBQ})_2 + \text{H}^+]^+$ has been identified from the spectrum of the mixture of **22** and 3,5-DTBCH₂. Unique features of **22** and **23** in terms of showing catechol oxidase activity and, more importantly, unique structural features of compound **22** have been discussed.

Chapter 6 deals with the syntheses, characterization, crystal structures and diffuse reflectance spectra of two mononuclear compounds of composition

$[\text{Cu}^{\text{II}}\text{L}^5]\cdot\text{MeOH}$ (**24**) and $[\text{Ni}^{\text{II}}\text{L}^5]$ and six heteronuclear complexes of composition $[\text{Cu}^{\text{II}}(\text{acetone})\text{L}^5(\text{U}^{\text{VI}}\text{O}_2)(\text{NO}_3)_2]\cdot 1.5\text{CH}_3\text{COCH}_3$ (**25**), $[\text{Cu}^{\text{II}}(\text{H}_2\text{O})\text{L}^7(\text{U}^{\text{VI}}\text{O}_2)(\text{NO}_3)_2]\cdot\text{MeCN}$ (**26**), $[\text{Ni}^{\text{II}}\text{L}^5(\text{U}^{\text{VI}}\text{O}_2)(\text{NO}_3)_2]\cdot\text{CH}_3\text{COCH}_3$ (**27**), $[\{\text{Cu}^{\text{II}}\text{L}^5\text{Ag}^{\text{I}}(\text{NO}_3)\}_2]$ (**28**), $[\{\text{Cu}^{\text{II}}\text{L}^6\text{Ag}^{\text{I}}(\text{NO}_3)\}_2]$ (**29**), and $[(\text{Cu}^{\text{II}}\text{L}^6)_2\text{Cd}^{\text{II}}(\text{ClO}_4)_2]$ (**30**), where H_2L^5 , H_2L^6 and H_2L^7 are the [1+2] condensation products of 2,2-dimethyl-1,3-diaminopropane and, respectively, 2-hydroxyacetophenone (for H_2L^5), salicylaldehyde (for H_2L^6) and 3-ethoxysalicylaldehyde (for H_2L^7). The major outcomes of this chapter can be summarized as (i) Six heterometallic compounds described in this chapter are among only a few examples where the diamine part is 2,2-dimethyl-1,3-diaminopropane; (ii) Compounds **25–27** are among only a few examples of dinuclear 3d–uranyl compounds and **27** is the only example of discrete dinuclear $\text{Ni}^{\text{II}}\text{–U}^{\text{VI}}\text{O}_2$ compound; (iii) In one (**28**) of the six heterometallic compounds, discussed in above chapter, the two dinuclear units are bridged by $\text{Ag}^{\text{I}}\text{–C}$ bonds and also silver(I)⋯silver(I) interactions.

Chapter 7 deals with the syntheses, crystal structures, lone pair functionality and electrospray ionization spectra in positive mode (ESI–MS positive) of two trinuclear $\text{Cu}^{\text{II}}\text{Pb}^{\text{II}}\text{Cu}^{\text{II}}$ compounds of composition $[(\text{Cu}^{\text{II}}\text{L}^8)_2\text{Pb}^{\text{II}}(\text{ClO}_4)_2]$ (**31**) and $[(\text{Cu}^{\text{II}}\text{L}^6)_2\text{Pb}^{\text{II}}(\text{NO}_3)_2]$ (**32**), one dimer of trinuclear $(\text{Cu}^{\text{II}}\text{Pb}^{\text{II}}\text{Cu}^{\text{II}})_2$ compound of composition $[\{(\text{Cu}^{\text{II}}\text{L}^6)_2\text{Pb}^{\text{II}}\}_2(\mu\text{-adipate})](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ (**33**) and one trinuclear $\text{Cu}^{\text{II}}\text{Pb}^{\text{II}}\text{Cu}^{\text{II}}$ -based one-dimensional (1D) compound of composition $[(\text{Cu}^{\text{II}}\text{L}^6)_2\text{Pb}^{\text{II}}(\mu_{1,5}\text{-dicyanamide})_2]_n$ (**34**), where H_2L^8 and H_2L^6 are the [2+1] condensation products of salicylaldehyde and respectively, 1,3-diaminopropane and 2,2-dimethyl-1,3-diaminopropane. ESI-MS positive spectra reveal the existence of mono / di / trinuclear and even unusual tetranuclear star type gaseous positive ions; the observed and simulated isotopic distribution patterns are nicely matched. The existence of stereochemically active / inactive lone pair of electrons of lead(II) has been explored. Salient and interesting features in the structures and ESI-MS have been discussed.

Chapter 8 present, synthesis, crystal structure and magnetic properties of an azide-bridged one-dimensional tape-type coordination polymer of copper(II) of composition $[\text{Cu}^{\text{II}}_6(\text{N,N-diEten})_2(\mu_{1,1}\text{-N}_3)_8(\mu_{1,1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]_n$ (**35**), where N,N-diEten is N,N-diethylethylenediamine. Variable-temperature and variable-field magnetic properties of **35** have been studied, revealing overall ferromagnetic

interaction. The major outcomes of this chapter are (i) The network-topology in **35** is new among a few previously reported hexacopper(II)-based coordination polymers and also among the metallo-azide systems; (ii) Some special structural aspects in **35** has been described.

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