

CONTENTS

		Preface	
		Acknowledgement	
			Page
Chapter 1		General Introduction and Scope of the Thesis	
	1.1	General introduction	1
	1.2	Multicomponent Crystals – Salts, Cocrystals and Salt Cocrystals	2
	1.3	Inclusion Compounds	11
	1.4	Metal Complexes Derived from Acyclic Schiff Base Ligands	17
	1.4.1	Mononuclear Complexes Derived from Single Compartmental and Double Compartmental Ligands	20
	1.4.2	Homo/Heteronuclear Compounds Derived from Single/Double Compartmental Acyclic Schiff Base Ligands	30
	1.4.3	Copper(II)/Nickel(II)–s Block Metal Ion Complexes	30
	1.4.4	Copper(II)/Nickel(II)–p Block Metal Ion Complexes	33
	1.4.5	Copper(II)/Nickel(II)–3d metal ion complexes	35
	1.4.6	Copper(II)/Nickel(II)–d ¹⁰ Complexes	40
	1.4.7	Copper(II)/Nickel(II)–4f Metal Ion Complexes	43
	1.4.8	Copper(II)/Nickel(II)–Uranyl(VI) Complexes	47
	1.5	Catecholase Activity	49
	1.5.1	Definition and Proposed Mechanisms of Catechol Oxidase Activity	49
	1.5.2	Model Systems of Cathechol Oxidase	52
	1.6	Azide Bridged Metal Complexes	61
	1.7	Objective and scope of the Thesis	68
		References	73
Chapter 2		Heterometallic Copper(II)-Tin(II/IV) Salts, Cocrystals and Salt Cocrystals: Selectivity and Structural Diversity Depending on Ligand Substitution and Metal Oxidation State	
	2.1	Introduction	86
	2.2	Experimental Section	89
	2.2.1	Materials and Physical Methods	89
	2.2.2	Syntheses	89
	2.2.3	Analytical and FT-IR Data	91
	2.2.4	Crystal Structure Determination	92
	2.3	Results and Discussion	96
	2.3.1	Syntheses and Characterization	96
	2.3.2	Description of Crystal Structures	98

	2.3.3	Comparison of 1–10 with Previously Published Related Systems	118
	2.3.4	Brief Discussion on the Remarkable Difference of Some Metal Complexes Derived from Two Closely Similar Ligands, H ₂ L ¹ and H ₂ L ²	121
	2.4	Conclusions	124
		References	126
Chapter 3			
Chapter 3		Surprising Difference Between Two Closely Similar O(phenoxo)₂O(ether)₂ Compartments as Hosts for an Aquated Proton and a Novel Type of Host–Guest System	
	3.1	Introduction	134
	3.2	Experimental Section	136
	3.2.1	Materials and Physical Measurements	136
	3.2.2	Syntheses	136
	3.2.3	Analytical and FT-IR Data	137
	3.2.4	Crystal Structure Determination of 11–16	137
	3.3	Results and Discussion	140
	3.3.1	Description of Structures of 11–16	140
	3.3.2	FT-IR and Electronic Spectra	158
	3.3.3	Comparison of the Composition/Structures: Significant Aspects	161
	3.4	Conclusions	165
		References	166
Chapter 4			
Chapter 4		Syntheses, Structures, Catecholase Activity, Spectroscopy and Electrochemistry of a Series of Manganese(III) Complexes: Role of Auxiliary Anionic Ligand on Catecholase Activity	
	4.1	Introduction	171
	4.2	Experimental Section	173
	4.2.1	Materials and Physical Measurements	173
	4.2.2	Syntheses	174
	4.2.3	Analytical and FT-IR Data	175
	4.2.4	Crystal Structure Determination of 17–21	175
	4.3	Results and Discussion	178
	4.3.1	Syntheses and Characterization	178
	4.3.2	Description of Structures of 17–21	183
	4.3.3	Electrochemical Measurements	197
	4.3.4	Catecholase Activity	204
	4.4	Conclusions	218
		References	220

Chapter 5		Syntheses, Structures and Catecholase Activity of Two Cobalt(III) Complexes Derived from <i>N,N'</i>-ethylenebis(3-ethoxysalicylaldiimine): A Special Host-Guest System from a Special Ligand	
	5.1	Introduction	225
	5.2	Experimental Section	227
	5.2.1	Materials and Physical Measurements	227
	5.2.2	Syntheses	227
	5.2.3	Analytical and FT-IR Data	228
	5.2.4	Crystal Structure Determination	228
	5.3	Results and Discussion	230
	5.3.1	Synthesis and Characterization	230
	5.3.2	Description of Crystal Structures of 22 and 23	233
	5.3.3	Catecholase Activity	242
	5.3.4	Electrospray Ionization Mass Spectral Study	247
	5.4	Conclusions	254
		References	255
Chapter 6		Mononuclear and Heterometallic Dinuclear, Trinuclear and Dimer-of-Dinuclear Complexes Derived from Single- and Double-Compartment Schiff base Ligands Having a Less Utilized Diamine	
	6.1	Introduction	259
	6.2.	Experimental Section	260
	6.2.1	Materials and Physical Measurements	260
	6.2.2	Syntheses	261
	6.2.3	Analytical and FT-IR Data	262
	6.2.4	Crystal Structure Determination of 24–30	263
	6.3	Results and Discussion	266
	6.3.1	Description of Structures of $[\text{Cu}^{\text{II}}\text{L}^5]\cdot\text{MeOH}$ (24) and 25–30	266
	6.3.2	Diffuse Reflectance Spectra	286
	6.4	Conclusions	291
		References	292
Chapter 7		Syntheses, Crystal Structures, Lone Pair Functionality and Electrospray Ionization Mass Spectral Properties of Trinuclear, Dimer of Trinuclear and Trinuclear-Based One-Dimensional Systems of Copper(II) and Lead(II)	
	7.1.	Introduction	298
	7.2.	Experimental Section	300
	7.2.1	Materials and Physical Measurements	300
	7.2.2	Syntheses	300

	7.2.3	Analytical and FT-IR Data	301
	7.2.4	Crystal Structure Determination of 31–34	301
	7.3	Results and Discussion	303
	7.3.1	Syntheses and Characterization of $[(\text{Cu}^{\text{II}}\text{L}^8)_2\text{Pb}^{\text{II}}(\text{ClO}_4)_2]$ (31), $[(\text{Cu}^{\text{II}}\text{L}^6)_2\text{Pb}^{\text{II}}(\text{NO}_3)_2]$ (32) $[\{(\text{Cu}^{\text{II}}\text{L}^6)_2\text{Pb}^{\text{II}}\}_2(\mu\text{-adipate})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (33) and $[(\text{Cu}^{\text{II}}\text{L}^6)_2\text{Pb}^{\text{II}}(\mu_{1,5}\text{-dicyanamide})_2]_n$ (34)	303
	7.3.2	Description of Structures of 31–34	308
	7.3.3	Lone Pair Functionality of Pb^{II} in 31–34	318
	7.3.4	Comparison of the Compositions of 31–34 with Related Systems	321
	7.3.5	Electrospray Ionization Mass Spectral Study	322
	7.3.6	Interesting Aspect in the ESI-MS Study	336
	7.4	Conclusions	336
		References	338
Chapter 8		Crystal Structure and Magnetic Properties of a Hexacopper(II)-Based Azide-Bridged One-Dimensional Coordination Polymer: A New Pattern of Azide-Bridged Network	
	8.1	Introduction	343
	8.2	Experimental Section	344
	8.2.1	Materials and Physical Methods	344
	8.2.2	Synthesis	344
	8.2.3	Analytical and FT–IR Data	345
	8.2.4	Crystal Structure Determination of $[\text{Cu}^{\text{II}}_6(\text{N,N}\text{-diEten})_2(\mu_{1,1}\text{-N}_3)_8(\mu_{1,1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]_n$ (35)	345
	8.3	Results and Discussion	347
	8.3.1	Description of the Structure of $[\text{Cu}^{\text{II}}_6(\text{N,N}\text{-diEten})_2(\mu_{1,1}\text{-N}_3)_8(\mu_{1,1,1}\text{-N}_3)_2(\mu_{1,3}\text{-N}_3)_2]_n$ (35)	347
	8.3.2	Comparison of Composition/Structure of 35 with Related Systems	351
	8.3.3	Magnetic Properties	352
	8.4	Conclusions	355
		References	356
		List of Publications	
		Supporting Information	
	1	CCDC Numbers of 35 crystal structures included in this thesis	
	2	Reprints of seven published articles included in this thesis.	