



Contents

1 Introduction	1
1.1 Lanthanides.....	1
1.1.1 Oxidation states	1
1.1.2 Lanthanide contraction	1
1.1.3 Optical properties	1
1.1.4 Luminescence	2
1.2 Magnetism	4
1.2.1 Diamagnetism.....	4
1.2.2 Paramagnetism	5
1.2.3 Ferromagnetism.....	6
1.2.4 Antiferromagnetism.....	6
1.2.5 Ferrimagnetism.....	7
1.2.6 Canted Antiferromagnetism	7
1.3 Magnetic behaviour	8
1.4 Single Molecule Magnets (SMM)	9
1.4.1 4f-based SMM.....	11
1.4.2 3d-4f-based SMM.....	13
1.4.3 SMM Applications	14
1.5 Metal Organic Frameworks (MOFs)	14
1.5.1 History of MOF based catalysis	15
1.5.2 Basic Catalytic Requirements of CMOFs	18
1.5.3 Enantioselective Sulfoxidation	19
2 Research Objectives	21
3 Results and Discussion	23
3.1 Mononuclear and Tetranuclear Compounds of Yttrium and Dysprosium: Synthesis, Photoluminescence and Magnetism	23
3.1.1 Synthesis and Structures.....	23
3.1.2 Photoluminescence (PL) properties.....	27
3.1.3 Magnetic Properties of Compounds	31
3.2 Mononuclear dysprosium compound	35
3.3 Synthesis and Characterization of Binuclear (Ni-Ln) and Trinuclear (Ni-Ln-Ni) Complexes	37
3.3.1 Synthesis and Structures.....	37
3.4 Tetranuclear and Pentanuclear Clusters of Lanthanides: Synthesis and Magnetic Studies.....	41



3.4.1 Synthesis and structures.....	42
3.4.2 Magnetic Properties.....	46
3.5 See-Saw and Square Planar Shaped Tetranuclear and Pentagonal prism Shaped Pentanuclear Complexes of Lanthanides: Synthesis and Magnetic study	50
3.5.1 Synthesis and Structures.....	50
3.5.2 Magnetic Properties.....	55
3.6 Mononuclear, Pentanuclear and Hepatanuclear Complexes of Lanthanides: Synthesis and Magnetism.....	58
3.6.1 Synthesis and Structures.....	58
3.6.2 Magnetic Properties.....	63
3.7 Binuclear and Trinuclear complexes of Dysprosium: Synthesis	71
3.7.1 Synthesis and Structures.....	71
3.8 Salen-Based 1-D Coordination Polymers of Manganese and lanthanides: Synthesis and Catalytic sulfoxidation	76
3.8.1 Synthesis and Structures.....	76
3.8.2 Catalysis	79
4 Experimental sections.....	83
4.1 General considerations:	83
4.2 Photoluminescence (PL) Measurements.....	83
4.3 Magnetic Measurements.....	83
4.4 Synthesis of Compounds	84
4.4.1 Synthesis of $\{[\text{Ln}(\text{HL})_4][\text{ETAH}]\}$ (1,2).....	84
4.4.2 Synthesis of $\{[\text{Y}_4(\text{HL})_2(\text{L})_4(\mu_3\text{-OH})_2]\cdot 4(\text{MeOH})\cdot 4(\text{H}_2\text{O})\}$ (3).....	84
4.4.3 Synthesis of $\{[\text{Dy}_4(\text{HL})_2(\text{L})_4(\mu_3\text{-OH})_2]\cdot 5(\text{MeOH})\cdot 7(\text{H}_2\text{O})\}$ (4).....	85
4.4.4 Synthesis of $\{[\text{Dy}_4(\text{HL})_8(\text{L})_2]\cdot 4(\text{MeOH})\cdot 2(\text{H}_2\text{O})\}$ (5).....	85
4.4.5 Synthesis of $\{[\text{Dy}(\text{HL}^1)_2(\text{H}_2\text{O})_3]\cdot (\text{NO}_3)\}$ (6).....	85
4.4.6 Synthesis of $[\text{NiLnL}(\text{acac})_2]$ (7-9).....	86
4.4.7 Synthesis of $\{[\text{NiDyL}(\text{Ph}_2\text{acac})_2]_2\cdot 4(\text{CH}_2\text{Cl}_2)\cdot (\text{MeOH})\}$ (10).....	87
4.4.8 Synthesis of $[\text{Ni}_2\text{Ln}(\text{L}1)_2]$ (11- 13).....	87
4.4.9 Synthesis of $\{[\text{Dy}_4(\text{L}^2)_3(\text{Ph}_2\text{acac})_4]\cdot (\text{Et}_3\text{NH})\cdot 4(\text{MeOH})\cdot (\text{MeCN})\cdot (\text{H}_2\text{O})\}$ (14).....	88
4.4.10 Synthesis of $\{[\text{Ln}_5(\mu_3\text{-OH})_2(\text{L}^2)_2(\text{Ph}_2\text{acac})_7(\text{Ph}_2\text{acacH})]\cdot 7(\text{PhMe})\}$ (15,16).....	89
4.4.11 Synthesis of $\{[\text{Ln}_4(\mu_3\text{-OH})_2(\text{L}^2)(\text{HL}^2)(\text{acac})_5(\text{H}_2\text{O})]\cdot (\text{NO}_3)\cdot (\text{HNEt}_3)\cdot 2(\text{Et}_2\text{O})\}$ (17-21).....	89
4.4.12 Synthesis of $\{[\text{Dy}_4(\mu_4\text{-OH})(\text{L}^2)_2(\text{acac})_4(\text{MeOH})_2(\text{EtOH})(\text{H}_2\text{O})]\cdot (\text{NO}_3)\cdot 2(\text{MeOH})\cdot 3(\text{EtOH})\}$ (22).....	91
4.4.13 Synthesis of $\{[\text{Dy}_5(\mu_5\text{-NO}_3)(\text{L}^2)(\text{L}^{2a})_2(\text{acac})_6(\text{iPrOH})_2(\text{HO})(\text{H}_2\text{O})]\cdot 4(\text{H}_2\text{O})\}$ (23).....	91
4.4.14 Synthesis of $\{[\text{Ln}(\text{Ph}_2\text{acac})_4](\text{Et}_3\text{NH})\}$ (24, 25).....	92
4.4.15 Synthesis of $\{[\text{Dy}_5(\mu_3\text{-OH})_2(\text{L}^2)_3(\text{Ph}_2\text{acac})_4(\text{MeOH})_4]\cdot 4(\text{MeOH})\}$ (26).....	92
4.4.16 Synthesis of $\{[\text{Tb}_7(\mu_3\text{-OH})_2(\mu_5\text{-}(\text{NO}_3)(\mu_3\text{-NO}_3)(\text{L}^2)_3(\text{Ph}_2\text{acac})_5(\text{H}_2\text{N-Ph-O})(\text{MeO})_2(\text{MeOH})_3]\cdot (\text{MeOH})_3\cdot (\text{MeCN})\cdot 15(\text{H}_2\text{O})\}$ (27).....	93



4.4.17 Synthesis of $\{[\text{Dy}_2\text{L}_3] \cdot 3(\text{OH}) \cdot 6(\text{H}_2\text{O}) \cdot (\text{C}_6\text{H}_{12})\}$ (28).....	93
4.4.18 Synthesis of $\{[\text{Dy}_2\text{L}_3(\text{OH})] \cdot [\text{Dy}(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot 3(\text{Py}) \cdot 2(\text{HO}) \cdot 7(\text{H}_2\text{O}) \cdot 6(\text{MeOH}) \cdot (\text{CHCl}_3)\}$ (29)....	93
4.4.19 Synthesis of $\{[\text{Dy}_2\text{L}_3(\text{H}_2\text{O})] \cdot [\text{Dy}(\text{NO}_3)(\text{H}_2\text{O})_7] \cdot 5(\text{NO}_3) \cdot 3(\text{MeOH}) \cdot 7(\text{H}_2\text{O})\}$ (30).....	94
4.4.20 General procedure for the synthesis of complexes (31- 34).....	94
4.4.21 General procedure for catalysis.....	95
4.4.22 NMR data of Sulfoxides.....	95
5 Crystal Structure Measurements.....	97
5.1 Data collection and refinement.....	97
5.1.1 $\{[\text{Y}(\text{HL})_4][\text{ETAH}] \cdot (\text{H}_2\text{O})\}$ (1).....	98
5.1.2 $\{[\text{Dy}(\text{HL})_4][\text{ETAH}] \cdot (3\text{MeOH}) \cdot (\text{H}_2\text{O})\}$ (2).....	98
5.1.3 $\{[\text{Y}_4(\text{HL})_2(\text{L})_4(\mu_3\text{-OH})_2] \cdot 4(\text{MeOH}) \cdot 4(\text{H}_2\text{O})\}$ (3).....	99
5.1.4 $\{[\text{Dy}_4(\text{HL})_2(\text{L})_4(\mu_3\text{-OH})_2] \cdot 5(\text{MeOH}) \cdot 7(\text{H}_2\text{O})\}$ (4).....	99
5.1.5 $\{[\text{Dy}_4(\text{HL})_8(\text{L})_2] \cdot 4(\text{MeOH}) \cdot 2(\text{H}_2\text{O})\}$ (5).....	100
5.1.6 $\{[\text{Dy}(\text{HL}^1)_2(\text{H}_2\text{O})_3](\text{NO}_3)\}$ (6).....	100
5.1.7 $\{\text{NiGdL}(\text{acac})_2\}$ (7).....	101
5.1.8 $\{\text{NiTbL}(\text{acac})_2\}$ (8).....	101
5.1.9 $\{[\text{NiDyL}(\text{acac})_2]_2 \cdot 7(\text{MeOH})\}$ (9).....	102
5.1.10 $\{[\text{NiDyL}(\text{Ph}_2\text{acac})_2]_2 \cdot 4(\text{CH}_2\text{Cl}_2) \cdot (\text{MeOH})\}$ (10).....	102
5.1.11 $\{[\text{Ni}_2\text{Gd}(\text{L}^1)_2] \cdot (\text{NO}_3) \cdot 2(\text{H}_2\text{O})\}$ (11).....	103
5.1.12 $\{[\text{Ni}_2\text{Tb}(\text{L}^1)_2]_4 \cdot 4(\text{NO}_3) \cdot 3(\text{MeCN}) \cdot 5(\text{MeOH}) \cdot (\text{H}_2\text{O})\}$ (12).....	103
5.1.13 $\{[\text{Ni}_2\text{Dy}(\text{L}^1)_2] \cdot (\text{NO}_3)(\text{MeOH}) \cdot (\text{H}_2\text{O})\}$ (13).....	104
5.1.14 $\{[\text{Dy}_4(\text{L}^2)_3(\text{Ph}_2\text{acac})_4](\text{Et}_3\text{NH}) \cdot 4(\text{MeOH}) \cdot (\text{MeCN}) \cdot (\text{H}_2\text{O})\}$ (14).....	104
5.1.15 $\{[\text{Tb}_5(\mu_3\text{-OH})_2(\text{L}^2)_2(\text{Ph}_2\text{acac})_7(\text{Ph}_2\text{acacH})] \cdot 7(\text{PhMe})\}$ (15).....	105
5.1.16 $\{[\text{Dy}_5(\mu_3\text{-OH})_2(\text{L}^2)_2((\text{Ph}_2\text{acac})_7(\text{Ph}_2\text{acacH}))] \cdot 7(\text{PhMe})\}$ (16).....	105
5.1.17 $\{[\text{Tb}_4(\mu_3\text{-OH})_2(\text{L}^2)(\text{HL}^2)(\text{acac})_5(\text{H}_2\text{O})] \cdot (\text{NO}_3) \cdot (\text{HNET}_3) \cdot 2(\text{Et}_2\text{O})\}$ (17).....	106
5.1.18 $\{[\text{Dy}_4(\mu_3\text{-OH})_2(\text{L}^2)(\text{HL}^2)(\text{acac})_5(\text{H}_2\text{O})] \cdot (\text{NO}_3) \cdot (\text{HNET}_3) \cdot 2(\text{Et}_2\text{O})\}$ (18).....	106
5.1.19 $\{[\text{Ho}_4(\mu_3\text{-OH})_2(\text{L}^2)(\text{HL}^2)(\text{acac})_5(\text{H}_2\text{O})] \cdot (\text{NO}_3) \cdot (\text{HNET}_3) \cdot 2(\text{Et}_2\text{O})\}$ (19).....	107
5.1.20 $\{[\text{Er}_4(\mu_3\text{-OH})_2(\text{L}^2)(\text{HL}^2)(\text{acac})_5(\text{H}_2\text{O})] \cdot (\text{NO}_3) \cdot (\text{HNET}_3) \cdot 2(\text{Et}_2\text{O})\}$ (20).....	107
5.1.21 $\{[\text{Tm}_4(\mu_3\text{-OH})_2(\text{L}^2)(\text{HL}^2)(\text{acac})_5(\text{H}_2\text{O})] \cdot (\text{NO}_3) \cdot (\text{HNET}_3) \cdot 2(\text{Et}_2\text{O})\}$ (21).....	108
5.1.22 $\{[\text{Dy}_4(\mu_4\text{-OH})(\text{L}^2)_2(\text{acac})_4(\text{MeOH})_2(\text{EtOH})(\text{H}_2\text{O})] \cdot (\text{NO}_3) \cdot 2(\text{MeOH}) \cdot 3(\text{EtOH})\}$ (22).....	108
5.1.23 $\{[\text{Dy}_5(\mu_5\text{-NO}_3)(\text{L}^2)(\text{L}^{2a})_2(\text{acac})_6(\text{iPrOH})_2(\text{HO})(\text{H}_2\text{O})] \cdot 4(\text{H}_2\text{O})\}$ (23).....	109
5.1.24 $\{[\text{Tb}(\text{Ph}_2\text{acac})_4] \cdot (\text{Et}_3\text{NH})\}$ (24).....	109
5.1.25 $\{[\text{Dy}(\text{Ph}_2\text{acac})_4]_2 \cdot 2(\text{Et}_3\text{NH}) \cdot 3(\text{CH}_2\text{Cl}_2)\}$ (25).....	110
5.1.26 $\{[\text{Dy}_5(\mu_3\text{-OH})_2(\text{L}^2)_3(\text{Ph}_2\text{acac})_4(\text{MeOH})_4] \cdot 4(\text{MeOH})\}$ (26).....	110
5.1.2 $\{[\text{Tb}_7(\mu_3\text{-OH})_2(\mu_5\text{-NO}_3)(\mu_3\text{-NO}_3)(\text{L}^2)_3(\text{Ph}_2\text{acac})_5(\text{H}_2\text{N-PhO})(\text{MeO})_2(\text{MeOH})_3] \cdot 3(\text{MeOH}) \cdot (\text{MeCN}) \cdot 15(\text{H}_2\text{O})\}$ (27).....	111



5.1.28	{[Dy ₂ L ₃]·3(OH)·6(H ₂ O)·(C ₆ H ₁₂)}	(28)	111
5.1.29	{[Dy ₂ L ₃ (OH)]·[Dy(NO ₃) ₃ (H ₂ O) ₃]·3(Py)·2(HO)·7(H ₂ O)·6(MeOH)·(CHCl ₃)}	(29)	112
5.1.30	{[Dy ₂ L ₃ (H ₂ O)]·[Dy(NO ₃)(H ₂ O) ₇]·5(NO ₃)·3(MeOH)·7(H ₂ O)}	(30)	112
5.1.31	{[Pr ₂ (MnLCINO ₃) ₂ (dmf) ₆ (H ₂ O) ₂]·(H ₂ O)} _n	(31)	113
5.1.32	{[Nd ₂ (MnLCINO ₃) ₂ (dmf) ₆ (H ₂ O) ₂]·(H ₂ O)} _n	(32)	113
5.1.33	{[Sm ₂ (MnLCINO ₃) ₂ (dmf) ₆ (H ₂ O) ₂]·(H ₂ O)} _n	(33)	114
5.1.34	{[Gd ₂ (MnLCINO ₃) ₂ (dmf) ₆ (H ₂ O) ₂]·(H ₂ O)} _n	(34)	114
6	Summary/ Zusammenfassung		115
6.1	Summary		115
6.2	Zusammenfassung		119
7	References		123
8	Appendices		131
8.1	Directory of Abbreviations		131
8.1.1	NMR Abbreviations		132
8.1.2	IR Abbreviations		133
8.1.3	Magnetic Abbreviations		133
8.2	Directory of Compounds		134