



Advanced Study of Switchable Spin Crossover Compounds

Gavin Craig

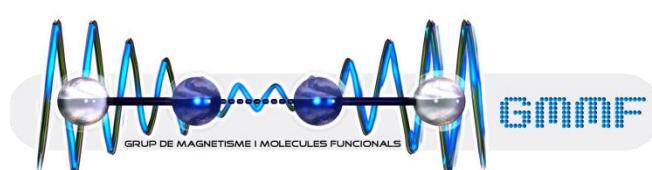
ADVERTIMENT. La consulta d'aquesta tesi queda condicionada a l'acceptació de les següents condicions d'ús: La difusió d'aquesta tesi per mitjà del servei TDX (www.tdx.cat) i a través del Dipòsit Digital de la UB (deposit.ub.edu) ha estat autoritzada pels titulars dels drets de propietat intel·lectual únicament per a usos privats emmarcats en activitats d'investigació i docència. No s'autoritza la seva reproducció amb finalitats de lucre ni la seva difusió i posada a disposició des d'un lloc aliè al servei TDX ni al Dipòsit Digital de la UB. No s'autoritza la presentació del seu contingut en una finestra o marc aliè a TDX o al Dipòsit Digital de la UB (framing). Aquesta reserva de drets afecta tant al resum de presentació de la tesi com als seus continguts. En la utilització o cita de parts de la tesi és obligat indicar el nom de la persona autora.

ADVERTENCIA. La consulta de esta tesis queda condicionada a la aceptación de las siguientes condiciones de uso: La difusión de esta tesis por medio del servicio TDR (www.tdx.cat) y a través del Repositorio Digital de la UB (deposit.ub.edu) ha sido autorizada por los titulares de los derechos de propiedad intelectual únicamente para usos privados enmarcados en actividades de investigación y docencia. No se autoriza su reproducción con finalidades de lucro ni su difusión y puesta a disposición desde un sitio ajeno al servicio TDR o al Repositorio Digital de la UB. No se autoriza la presentación de su contenido en una ventana o marco ajeno a TDR o al Repositorio Digital de la UB (framing). Esta reserva de derechos afecta tanto al resumen de presentación de la tesis como a sus contenidos. En la utilización o cita de partes de la tesis es obligado indicar el nombre de la persona autora.

WARNING. On having consulted this thesis you're accepting the following use conditions: Spreading this thesis by the TDX (www.tdx.cat) service and by the UB Digital Repository (deposit.ub.edu) has been authorized by the titular of the intellectual property rights only for private uses placed in investigation and teaching activities. Reproduction with lucrative aims is not authorized nor its spreading and availability from a site foreign to the TDX service or to the UB Digital Repository. Introducing its content in a window or frame foreign to the TDX service or to the UB Digital Repository is not authorized (framing). Those rights affect to the presentation summary of the thesis as well as to its contents. In the using or citation of parts of the thesis it's obliged to indicate the name of the author.

ADVANCED STUDY OF SWITCHABLE SPIN CROSSOVER COMPOUNDS

Universitat de Barcelona
Facultat de Química
Departament de Química Inorgànica
Programa de Doctorat: Química Inorgànica Molecular
Grup de Magnetisme i Molècules Funcionals



Gavin Craig

Director: Dr. Guillem Aromí Bedmar, Departament de Química Inorgànica

Tutor: Dr. Santiago Alvarez Reverter, Departament de Química Inorgànica

Guillem Aromí Bedmar, Professor del Departament de Química Inorgànica de la Facultat de Química de la Universitat de Barcelona,

CERTIFICA: que el treball titulat *Advanced Study of Switchable Spin Crossover Compounds* que presenta el Gavin Craig per optar al grau de Doctor per la Universitat de Barcelona, ha estat realitzat sota la seva direcció al Departament de Química Inorgànica d'aquesta Facultat.

Barcelona, abril de 2013

Dr. Guillem Aromí Bedmar

Santiago Alvarez Reverter, Catedràtic del Departament de Química Inorgànica de la Facultat de Química de la Universitat de Barcelona,

CERTIFICA: que ha estat el tutor responsable dels estudis de Doctorat realitzats dins del programa de Doctorat de Química Inorgànica Molecular pel Gavin Craig.

Barcelona, abril de 2013

Dr. Santiago Alvarez Reverter

For my Mum

Contents

Abbreviations and Symbols

Chapter 1: Introduction	1
1.0 Introduction to Spin Crossover (SCO)	1
1.1 Methods of measurement.....	4
1.1.1 SQUID Magnetometry	4
1.1.2 Single crystal X-ray diffraction	5
1.1.3 Differential Scanning Calorimetry (DSC)	6
1.1.4 Raman spectroscopy.....	6
1.2 Thermodynamic considerations	7
1.3 Trapping of meta-stable high spin states.....	8
1.4 Latest advances and applications.....	11
1.4.1 Beyond bi-stability.....	12
1.4.2 Physical control of domains	13
1.4.3 Size reduction	15
1.4.4 Detection of SCO on increasingly small scales.....	17
1.4.5 SCO materials as fluorescent thermometers.....	18
1.5 2,6-Bis(pyrazol-3-yl)pyridine	20
1.6 Aim and scope of the thesis	28
1.7 References.....	30
Chapter 2: Synthetic and Experimental Procedures.....	39
2.1 Synthesis	39
2.1.1 Ligands	39
2.1.2 Coordination compounds containing iron	41
2.2 Physical Techniques.....	47
2.2.1 Infrared Spectroscopy.....	47
2.2.2 Elemental Analysis.....	47
2.2.3 SQUID Magnetometry	48
2.2.4 Differential Scanning Calorimetry.....	48

2.2.5 Nuclear Magnetic Resonance Spectroscopy	48
2.2.6 X-ray Crystallography.....	48
2.2.7 Raman Spectroscopy.....	51
2.3 References	52

Chapter 3: Towards novel polypyrazolyl ligands for SCO systems57

3.0 Introduction.....	57
3.1 Synthesis.....	59
3.2 Definitions of the structural parameters ϑ, Φ, Σ, Θ.....	59
3.3 Single crystal X-ray diffraction study	61
3.4 Magnetic properties.....	65
3.5 Differential Scanning Calorimetry	66
3.6 Development of polypyrazolyl derivatives	67
3.7 Cluster coordination chemistry of the polypyrazolyl ligands	68
3.8 Crystal structure of H₄L	71
3.9 Concluding remarks.....	72
3.10 References	74

Chapter 4: Magneto-structural study of the compound
[Fe(H₄L)₂](ClO₄)₂·H₂O·2(CH₃)₂CO81

4.0 Introduction.....	81
4.1 Synthesis.....	82
4.2 Single crystal X-ray diffraction study (I)	82
4.3 Magnetic properties (I)	87
4.4 Differential Scanning Calorimetry (DSC).....	88
4.5 Magnetic properties (II): Thermally Induced Excited Spin State Trapping.....	89
4.6 Single crystal X-ray diffraction study (II): Thermally trapped structure, and hysteresis of the unit cell parameters.....	92
4.7 Magnetic properties (III): Thermal relaxation within the hysteresis loop	96
4.8 Single crystal X-ray diffraction study (III): Thermal relaxation within the bi-stable regime	97
4.9 Concluding remarks.....	98
4.10 References	100

Chapter 5: Photo-physical properties of the compound [Fe(H ₄ L) ₂](ClO ₄) ₂ ·H ₂ O·2(CH ₃) ₂ CO	105
5.0 Introduction	105
5.1 Photo-magnetic properties of 1 (I): LIESST experiments	107
5.2 LIESST versus TIESST: An unexpected discrepancy	110
5.3 Single crystal X-ray diffraction study: Under irradiation	113
5.4 Photo-magnetic properties of 1 (II): Light Induced Thermal Hysteresis	118
5.5 Raman spectroscopy	120
5.6 Excitation within the hysteresis loop on selecting the wavelength of light	123
5.7 Following the pressure-induced SCO by Raman spectroscopy	124
5.8 Concluding remarks	125
5.9 References	127
 Chapter 6: The effect of solvent and anion variation on [Fe(H ₄ L) ₂](ClO ₄) ₂ ·H ₂ O·2(CH ₃) ₂ CO	133
6.0 Introduction	133
6.1 Synthesis	134
6.2 Single crystal X-ray diffraction study of [Fe₂(H₄L)₂(ox)(NCS)₄]	136
6.3 Magnetic properties (I)	137
6.4 Single crystal X-ray diffraction study of compounds 2 and 3	140
6.5 Magnetic properties of compounds 2 and 3	142
6.6 Single crystal X-ray diffraction study of compounds 4, 5, 6, 8, and 9	143
6.7 Magnetic properties of compounds 4, 5, 6, 8, and 9	152
6.8 Concluding remarks	153
6.9 References	155
 Chapter 7: Magneto-structural properties of [Fe(H ₄ L) ₂](ClO ₄) ₂ ·2THF·H ₂ O: The effect of ageing	161
7.0 Introduction	161
7.1 Synthesis	162
7.2 Single crystal X-ray diffraction study	162
7.3 Magnetic properties	165
7.4 Differential Scanning Calorimetry	168

7.5 Concluding remarks.....	168
7.6 References	170
Chapter 8: Mononuclear Fe(II) compounds containing the ligand 2,6-Bis(5-(2-methoxyphenyl)-pyrazol-3-yl)pyridine.....	175
 8.0 Introduction.....	175
 8.1 Synthesis.....	176
 8.2 Single crystal X-ray diffraction study	176
 8.3 Magnetic properties.....	187
 8.4 Concluding remarks.....	187
 8.5 References	189
Chapter 9: Magneto-structural correlations	193
 9.0 Introduction.....	193
 9.1 Definition of the parameters employed.....	194
 9.2 Compounds obtained in this thesis	195
 9.3 Extension to the family of 3-bpp derivatives in the literature	196
 9.4 Continuous Symmetry Measures (CSMs)	203
 9.5 Hirshfeld Surface analysis	204
 9.6 Concluding remarks.....	212
 9.7 References	214
Chapter 10: Conclusions	217
Appendix A: List of Publications 221	
Acknowledgements	

Abbreviations and Symbols

CSD	Cambridge Structural Database
CSM	Continuous Symmetry Measures
χ	Magnetic susceptibility
DSC	Differential Scanning Calorimetry
E_a	Activation energy
g	Landé g-factor
G	Gibbs free energy
γ_{HS}	Normalised high spin fraction
H	Enthalpy
HS	High spin
IR	Infra-red
k_B	Boltzmann constant
k_{HL}	Relaxation rate at a given temperature
k_∞	Relaxation rate as the temperature tends to infinity
LIESST	Light Induced Excited Spin State Trapping
LITH	Light Induced Thermal Hysteresis
LS	Low spin
N_A	Avogadro's number
NMR	Nuclear Magnetic Resonance
R	Gas constant
RT	Room temperature
S	Entropy
SCO	Spin CrossOver
SQUID	Superconducting Quantum Interference Device
TIESST	Thermally Induced Excited Spin State Trapping