



UNIVERSITAT DE
BARCELONA

Spin crossover supramolecular coordination compounds: design, synthesis and properties

Mohanad D .Darawsheh

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Appendix

Appendix I: Chapter 2. Design of Host-Guest Triple Stranded Helicates

Table A.1: Crystallographic data and for **i**

Compound	i
Formula	C72 H48 Fe2 O15
Mr	1264.80
Wavelength	0.71073
<i>T</i> (K)	100
Crystal system	Triclinic
Space group	P-1
<i>Z</i>	2
<i>a</i> [Å]	14.469
<i>b</i> [Å]	14.499
<i>c</i> [Å]	17.100
α [°]	109.593
β [°]	106.773
γ [°]	105.195
<i>V</i> [Å ³]	2968.8
ρ_{calc} (gcm ⁻³)	1.415
μ (mm ⁻¹)	0.561
Independent reflections	1304
Restraints/parameters	174/5231
Goodness of fit on <i>F</i> ²	1.016
Final <i>R</i> 1/ <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.1128/0.2902
Final <i>R</i> 1/ <i>wR</i> 2 [all data]	0.1741/0.3265
Largest diff. peak and hole (eÅ ³)	0.807/-0.421

Table A.2: Selected interatomic distances [Å] and angles (°) found in **i**.

Fe1-O2	1.97(1)	Fe1-O3	1.98(1)
Fe1-O4	1.968(7)	Fe1-O7	1.99(1)
Fe1-O13	1.992(8)	Fe1-O15	1.98(1)
Fe2-O1	1.95(1)	Fe2-O6	1.993(8)
Fe2-O8	1.98(1)	Fe2-O12	1.984(9)
Fe2-O14	1.95(1)	Fe2-O17	1.96(1)
O2-Fe1-O15	88.8(5)	O2-Fe1-O13	96.8(5)
O2-Fe1-O3	86.1(4)	O2-Fe1-O4	89.3(4)
O7-Fe1-O4	85.8(5)	O7-Fe1-O15	100.2(5)
O7-Fe1-O13	89.3(5)	O7-Fe1-O3	85.5(5)
O4-Fe1-O15	88.2(4)	O15-Fe1-O13	84.0(5)
O13-Fe1-O3	90.3(5)	O3-Fe1-O4	98.0(4)
O14 Fe2 O8	89.1(5)	O14 Fe2 O12	100.5(5)
O14 Fe2 O1	85.6(5)	O14 Fe2 O6	85.8(5)
O17 Fe2 O6	85.9(4)	O6 Fe2 O8	88.5(4)
O8 Fe2 O12	86.2(4)	O12 Fe2 O1	87.7(5)
O1 Fe2 O6	98.3(4)	O17 Fe2 O1	89.6(4)
O17 Fe2 O12	88.4(4)	O17 Fe2 O8	96.7(4)

Table A.3: Crystallographic data and for **ii**

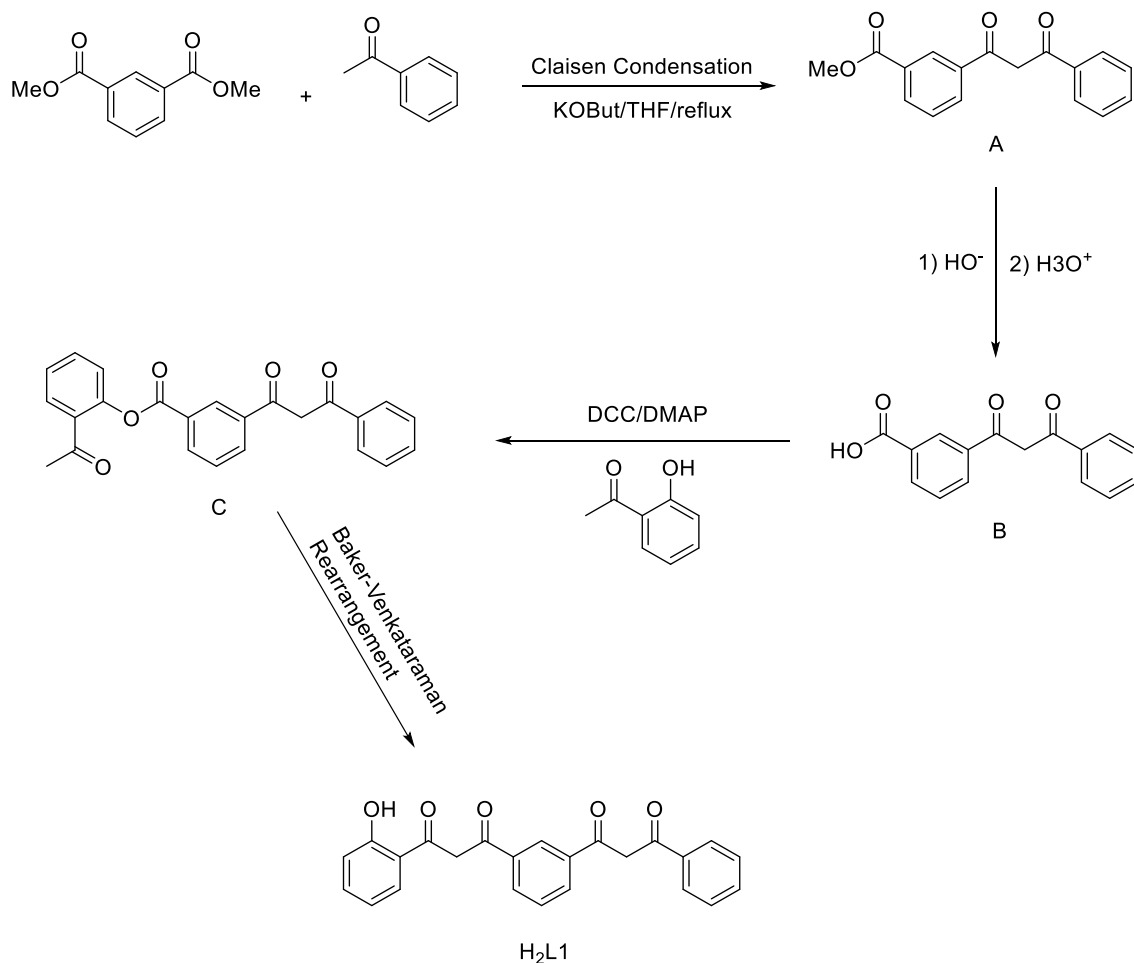
Compound	ii
Formula	Fe ₃ KC ₇ H ₅ N ₃ O ₁₈ Cl ₄
Mr	1634.01
Wavelength	0.71073
<i>T</i> (K)	100
Crystal system	Triclinic
Space group	P-1
<i>Z</i>	4
<i>a</i> [Å]	15.3021(9)
<i>b</i> [Å]	17.4308(9)
<i>c</i> [Å]	18.8562(10)
α [°]	89.465(3)
β [°]	83.270(3)
γ [°]	66.923(2)
<i>V</i> [Å ³]	4591.44
<i>R</i> 1	0.1827
<i>wR</i> 2	0.5342
<i>S</i>	2.134

Table A.4: Selected interatomic distances [Å] found in **ii**.

Fe1-O3	1.9967	Fe1-O1	1.9574
Fe1-O4	1.9589	Fe1-O2	1.9993
Fe1-O7	2.0125	Fe1-O5	1.9582
Fe1-O8	1.9839	Fe2-O6	1.9968
Fe1-O11	2.0135	Fe2-O9	1.9602
Fe1-O12	1.9788	Fe2-O10	1.9983
K3-O2	2.8267	K3-O3	2.847
K3-O6	2.8250	K3-O7	2.810
K3-O10	2.7681	K3-O11	2.7667
K3-N1	2.8034	K3-N2	2.8101
K3-N3	2.8382		

Synthesis of 1-(2-hydroxyphenyl)-3-(3-(3-oxo-3-phenylpropanoyl)phenyl)propane-1,3-dione **H₂L1**

H₂L1 was prepared according to the procedure described in the Master thesis {Sadurní. A. (2014). L'Aplicació de la transposició de Baker-Venkataraman a la síntesi de lligands 1,3-dicarbonílics per a la complexació de lantànides: utilització en computació quàntica, University of Barcelona, Barcelona, Spain}. The steps of the preparation are illustrated in the following scheme:



And following the details of the synthesis:

Synthesis of Methyl-3-(3-oxo-3-phenylpropanoyl)benzoate(A). Dimethylisophthalate (2.5 g, 12.9 mmol) was dissolved in 50 ml anhydrous THF. To this solution, KOtBu (1.73 g, 15.44 mmol) in 25 ml THF and acetophenone (1.55 g, 12.9 mmol) were added and the mixture left for refluxing overnight under inert atmosphere. The solution was cool down to room temperature and the pH was adjusted to 1 using 2 N HCl. The resulting mixture was extracted with CH₂Cl₂ (2x25 ml). The organic layer was washed with 10% NaHCO₃ (3x15 ml), water (3x15 ml) and brine (3x15 ml). The organic layer was dried and the solvent was removed. Yellow solid was obtained which purified by flash column chromatography [silica gel, Hexane/EtOAc 70:30] yielding compound **A** as off-white solid. The yield was 1.88g (52 %).

Synthesis of 3-(3-Oxo-3-phenylpropanoyl)benzoic acid (B). Methyl-3-(3-oxo-3-phenylpropanoyl)benzoate (A) (1g, 3.55 mmol) was added to a solution of 1M NaOH (10 eq.) mixed with THF (5 ml). The mixture was stirred until the starting material was

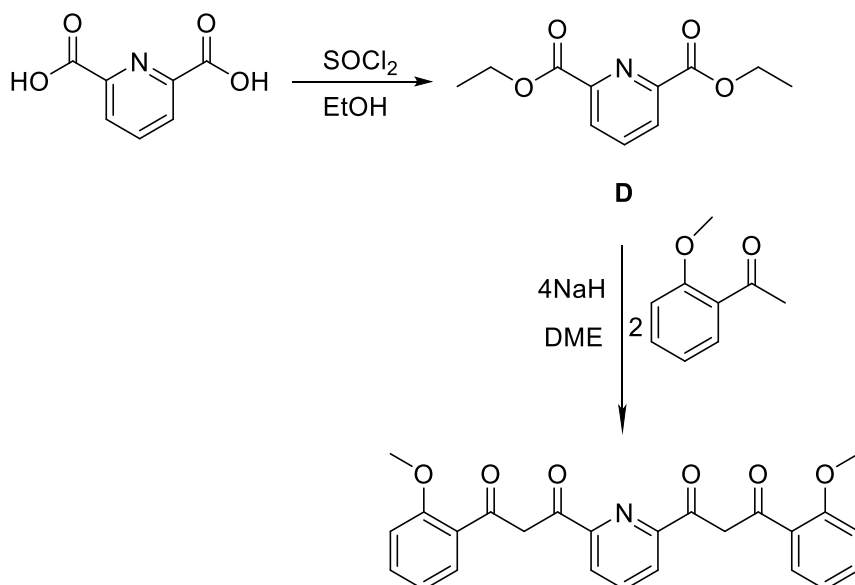
consumed which monitored by TLC. The pH of the solution was adjusted to 1 using 2N HCl. The mixture was extracted with CH₂Cl₂ (3x20 ml). The combined organic layers were washed with 10% NaHCO₃ (3x20 ml), water (3x20 ml) and brine (3x20 ml). The organic layer was dried and the solvent was removed yielding compound **B** as a white solid. The yield was 0.80 g (80 %).

Synthesis of 2-acetylphenyl-3-(3-oxo-3-phenylpropanoyl)benzoate (C). 3-(3-Oxo-3-phenylpropanoyl)benzoic acid (**B**) (0.50 g, 1.87 mmol), a spatula tip of DMAP were mixed in anhydrous CH₂Cl₂ (15 ml) and the mixture was stirred at 0 °C. Then DCC (0.46 g, 2.25 mmol) and 2'-hydroxyacetophenone (0.30 g, 2.25 mmol) were added. The mixture was allowed to warm to room temperature and then stirred for 12 hour. The mixture was filtered off and the filtrate was washed with 10% NaHCO₃ (3x10 ml), water (3x10 ml) and brine (3x10 ml). The organic layer was dried and the solvent was removed yielding a yellow solid that was purified by flash column chromatography [silica gel, Hexane/EtOAc (4:1)] affording compound **C** as yellow solid. The yield was 0.56 g (78 %).

Synthesis of 1-(2-hydroxyphenyl)-3-(3-oxo-3-phenylpropanoyl)phenyl)propane-1,3-dione (H₂L1). 2-acetylphenyl-3-(3-oxo-3-phenylpropanoyl)benzoate (**C**) (0.20 g, 0.52 mmol) was dissolved in anhydrous THF (15 ml). KOtBu (0.14 g, 1.29 mmol) in THF (4 ml) was added and the mixture was refluxed overnight under inert atmosphere. The solution was cool down to room temperature and the pH was adjusted to 1 using 2 N HCl. The mixture was extracted with CH₂Cl₂ (1x20ml) and the organic layer was washed with 10% NaHCO₃ (3x10 ml), water (3x10 ml) and brine (3x10 ml). The organic layer was dried and the solvent was removed yielding a yellow solid which purified by column chromatography [silica gel, CH₂Cl₂] affording **H₂L1** as yellow solid. The yield was 90 mg (45 %).

Synthesis of 1,3-bis-(3-oxo-3-(2-methoxyphenyl)-propionyl)-pyridine H₂L2

The ligand was synthesized previously in our group according to the following scheme:



And following the details of the synthesis:

Synthesis of diethyl pyridine-2,6-dicarboxylate **D.** Pyridine-2,6-dicarboxylic acid (10.0 g, 60 mmol) was dissolved in ethanol (100 ml). Thionyl chloride (8.8 ml, 120 mmol) was added drop by drop and the mixture refluxed for 2 hours. The solution was filtered off and the solvent was evaporated to dryness which yielded oily product. The product was placed under vacuum to get a solid product with high yield (12.31 g, 92 %).

Synthesis of 1,3-bis-(3-oxo-3-(2-methoxyphenyl)-propionyl)-pyridine **H₂L2.** To a suspension of 60% NaH oil dispersion (14.8 g, 127mmol) in 150 ml DME was added 2-methoxy-acetphenone (8.8 ml, 64mmol) and the mixture was stirred for 15 minutes. Then diethyl pyridine-2,6-dicarboxylate (**D**)(7.1 g, 32mmol) in 50 ml DME was added dropwise, and the mixture brought and left to reflux overnight. A yellow suspension was formed after that, which was quenched with 5 ml EtOH and the resulting solid was then collected by filtration. The solid was suspended in 350 ml H₂O, the pH was adjusted to 5 using 12% HCl and the mixture was left 30 minutes under stirring. The yellow solid was collected by filtration, washed with water and dried under vacuum. The yield was 11.62 g (84.7 %).

Appendix II: Chapter 3. Spin Crossover in Iron (II) Dinuclear Triple-Stranded Helicates

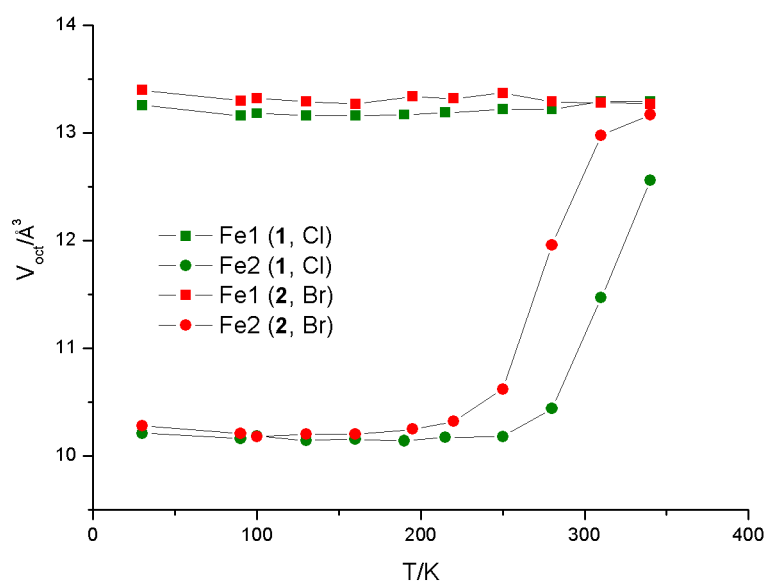


Figure AII.1: Temperature dependence of octahedral volume for compounds **1** and **2** drawn for both Fe(II) centers.

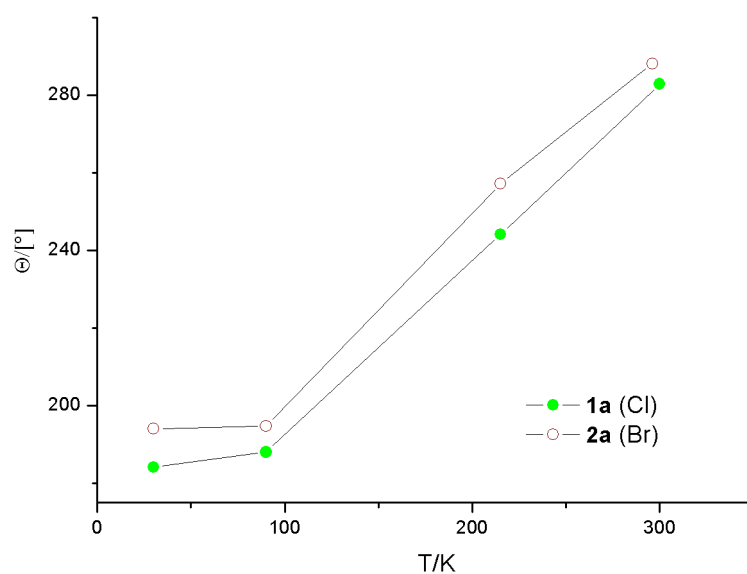


Figure AII.2: Temperature dependence of octahedral distortion parameter Θ for compounds **1a** and **2a**.

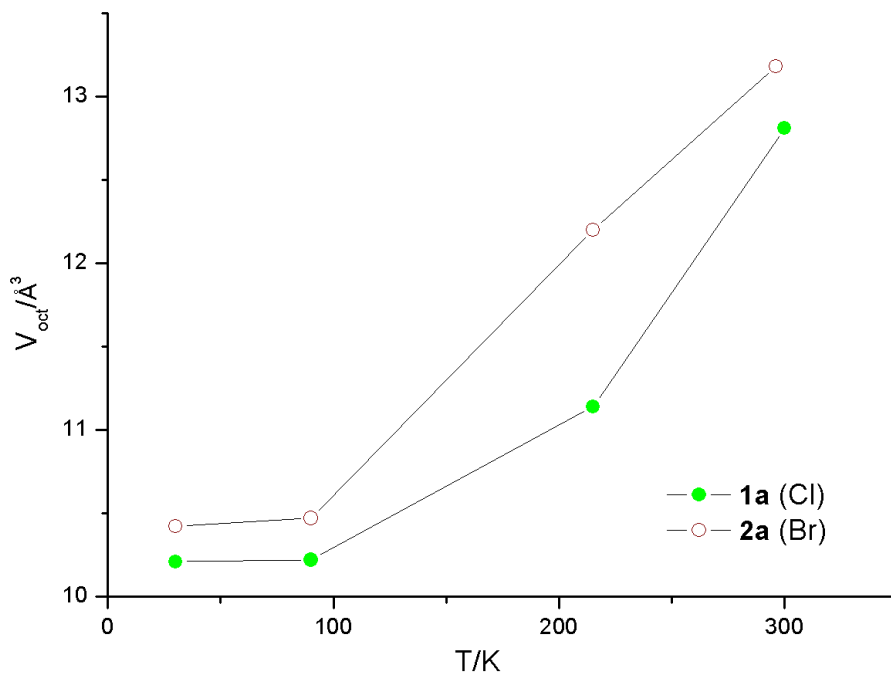


Figure AII.3: Temperature dependence of octahedral volume for compounds **1a** and **2a**.

Appendix III: Chapter 5. Spin Crossover and Single Ion Magnet Behavior in Host-Guest Fe(II) Helicates

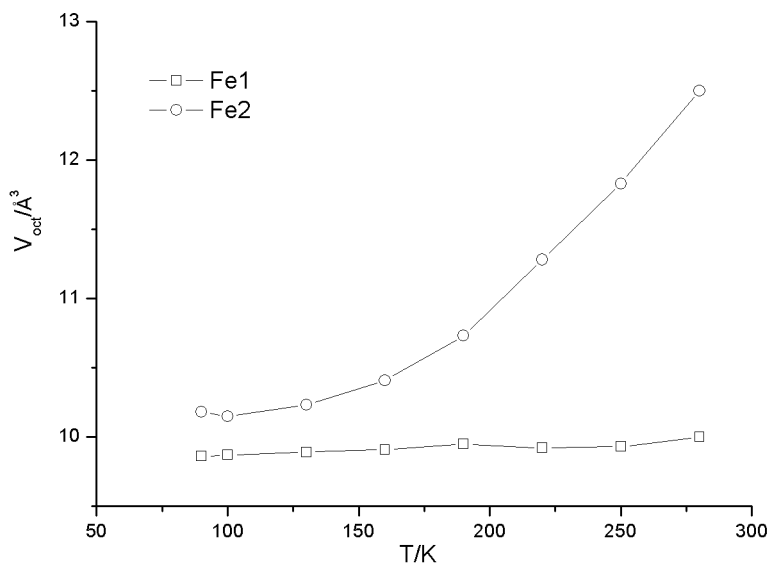


Figure AIII.1: Temperature dependence of octahedral volume for compound **11** drawn for both Fe(II) centers.

Appendix IV: Physical Techniques:

Elemental analysis was performed with an Elemental Microanalyzer (A5), model Flash 1112 at the Servei de Microanàlisi of CSIC, Barcelona, Spain.

Positive ion ESI TOF mass spectrometry experiments were performed on a LC/MSD-TOF (Agilent Technologies) at the Unitat d'Espectrometria de Masses de Caracterització Molecular (CCiT) of the University of Barcelona.

Variable-temperature magnetic susceptibility data were obtained with either:

- Quantum Design MPMS-XL SQUID magnetometer at the “Unitat de Mesures Magnetiques” of the Universitat de Barcelona
- MPMS5 or MPMS-XL SQUID magnetometers through the Physical Measurements unit of the Servicio de Apoyo a la Investigación-SAI, Universidad de Zaragoza. For the irradiation studies the commercial FOSH set-up was used in combination with a Xe arc lamp and short-pass and long-pass interference filters. The samples were in the form of small pieces of very thin pellets, to minimize the effect of the attenuation of the propagation of light through the sample. The data were corrected for the sample holder contributions, determined empirically as well as for the intrinsic diamagnetism of the samples, estimated using Pascal constants.

Differential Scanning Calorimetry (DSC) measurements were done with a Q1000 calorimeter from TA Instruments equipped with the LNCS accessory, using aluminium pans crimped mechanically and an empty pan as reference. The temperature and enthalpy scales were calibrated with a standard sample of indium, using its melting transition (156.6 °C, 3296 Jmol⁻¹). The zero-heat-flow procedure described by TA Instruments was followed to derive heat capacities, using a synthetic sapphire as reference compound. An overall accuracy of about 0.2 K and up to 10% was estimated respectively for the temperature and heat capacity over the whole temperature range. The lattice contributions to the heat capacity were estimated from the data above and below the observed anomalies. Excess enthalpy and entropy were derived by integration of the excess heat capacity with respect to T and $\ln T$, respectively.

NMR Spectra were recorded on Bruker AVQ Spectrometer (400 MHz) or Varian Mercury Spectrometer (400 MHz) at the Unitat de RMN at the Universitat de Barcelona.

X-ray data were collected:

- Beamline 11.3.1 at the Advanced Light Source, at Lawrence Berkeley National Laboratory on a Bruker D8 diffractometer equipped with a PHOTON 100 CCD detector and using silicon 111 monochromated synchrotron radiation ($\lambda = 0.7749 \text{ \AA}$). The crystals were mounted on a MiTegenkapton loop and placed in the N₂ stream of an Oxford CryosystemsCryostream Plus or for the lowest temperature (30 K) in the He stream from a Cryoindustries of America LT-HE Cool cryosystem. Data reduction and absorption corrections were performed with SAINT

-Bruker APEX II QUIZAR diffractometer with Mo_{k α} radiation ($\lambda = 0.71037 \text{ \AA}$) and equipped with microfocus multilayer monochromator. Data reduction and absorption corrections were performed with SADABS. All structures were solved by intrinsic phasing with SHELXT and refined by full-matrix least-squares on F² with SHELXL-2014.

Appendix V: List of Publications

-M.D. Darawsheh, L.A. Barrios, O. Roubeau, S.J. Teat, Guillem Aromí. Guest-, Light- and Thermally-Modulated Spin Crossover in $[\text{Fe}^{\text{II}}_2]$ Supramolecular Helicates. Chemistry, A European Journal 22 (2016) 8635-8645

-H. Abu Ali, S.N. Omar, M.D. Darawsheh, H. Fares. Synthesis, Characterization and Antimicrobial Activity of Zinc (II) Ibuprofen Complexes with Nitrogen-Based Ligands. Journal of Coordination chemistry 69 (2016) 1110-1122

-H. Abu Ali, H. Fares, M.D. Darawsheh, E. Rappocciolo, M. Akkawi c, S. Jaber. Synthesis, Characterization and Biological Activity of New Mixed Ligand Complexes of Zn(II) Naproxen with Nitrogen Based Ligands. European Journal of Medicinal Chemistry 89 (2015) 67-76

-M.D. Darawsheh, H. Abu Ali, A. Abuhijleh, E. Rappocciolo, M. Akkawi, S. Jaber, S. Maloul, Y. Hussein. New Mixed Ligand Zinc(II) Complexes Based on the Antiepileptic Drug Sodium Valproate and Bioactive Nitrogen-Donor Ligands. Synthesis, Structure and Biological Properties. European Journal of Medicinal Chemistry 82 (2014) 152-163

-H. Abu Ali, M.D. Darawsheh, E. Rappocciolo. Synthesis, Crystal Structure, Spectroscopic and Biological Properties of Mixed Ligand Complexes of Zinc(II) Valproate with 1,10-Phenanthroline and 2-Aminomethylpyridine. Polyhedron 61 (2013) 235-241

Appendix VI: List of Oral Communications in Conferences

M.D Darawsheh, L. Barrios, O. Roubeau, S.J. Teat, G. Aromí. A Spin Crossover [Fe^{II}₂] Supramolecular Helicate with an Encapsulated [Cr(oxalate)₃]³⁻ Single Ion Magnet. 42th International Conference on Coordination Chemistry, ICC2016 (Brest, France, July 3-8, 2016)

M.D Darawsheh, L. Barrios, O. Roubeau, S.J. Teat, G. Aromí. Guest, Light and Thermally Modulated Spin Crossover in [Fe(II)₂] Supramolecular Helicates. 5th European Conference on Molecular Magnetism, ECMM2015 (Zaragoza, Spain, September 6-10, 2015)

M.D. Darawsheh, L. Barrios, O. Roubeau, G. Aromí. Supramolecular Encapsulation of Coordination Complexes. 7th European School on Molecular Nanoscience (Gandia, Spain, October, 26-30, 2014).

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Most of the physical measurements would not have been possible without the work, support and patience of Dr. Olivier Roubeau. So I am extremely grateful to him. I thank Dr. Leoní Barrios for all the help and the guidance in the lab for three years and to be patient for answering my questions. It gives me great pleasure to thank all of the members of the GMMF group, Veronica, Raul, Ivana, Marta, Jorge, Carlos, Carolina, Albert, Lidia and Mariona, who have been extremely helpful throughout my study and I thank them for their support, feedback and friendship. I especially thank Jorge for his help in the correction of the Spanish summary of the thesis.

I have to mention Dr. Jordi Garcia and Dr. Paul Lloyd-Williams and the SMBioCom group in the Organic Chemistry Department in the University of Barcelona for their warm hospitality for two weeks and for the knowledge I gained with them. I thank Dr. Patrick Gamez and Dr. M. Salah el Fallah for their nice comments. I acknowledge the help and the the physical measurements done by Dr. Nuria Clos (magnetic measurements), Dr. Francisco Cárdenas (NMR), Dr. Irene Fernández and Laura Ortiz Vera (MS Spectrometry)

Last, but certainly not least, I would like to thank my parents, brothers, sister, family and friends for their support and encouragement throughout my study.

بسم الله الرحمن الرحيم

الحمد لله رب العالمين والصلاة والسلام على معلم البشرية وسيد المرسلين سيدنا محمد وعلى آله وصحبه أجمعين.

قال تعالى: (ولئن شكرتم لأزيدنكم) فالحمد والشكر لله عز وجل، شكرا يليق بجلال وجهه وعظيم سلطانه، على اتمام هذا العمل فله المنة والفضل والثناء الحسن.

تصديقا لقول الرسول صل الله عليه وسلم (من لا يشكر الناس لا يشكر الله)، أتقدم بالشكروالعرفان والإمتنان:

إلى أساتذتي الأفاضل على مر الوقت على ما قدموه من علم ونصح وعون.

إلى أمي وأبي العزيزين أطال الله في عمرهما وكساهما ثوب الصحة والعافية على ما قدموه لي من مساندة ومؤازرة على مر الوقت.

إلى أخوتي الأعمام والأخوات الذين وقفوا إلى جانبي دائما بالدعم والمؤازرة.

وكافة عائلتي وأسرتي وأصدقائي على ما قدموه من دعم وتشجيع مستمر.

وإلى كل من قدم لي يد العون والمساعدة من قريب أو بعيد من أجل انجاز هذا البحث.

