

FA4-MS33-P12

Single-crystal diffraction investigation of the transition mechanism in a gradual spin-crossover molecular material. Sabine Lakhloufi^{a,c}, A Kaiba^a, Marie-Hélène Lemée-Cailleau^c, JF Létard^a, Philippe Guionneau^a, ^aCNRS, Université de Bordeaux, ICMCB, France, ^cInstitut Laue-Langevin, ILL, Grenoble, France
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The molecular spin-crossover, **SCO**, phenomenon, involving thermo-, photo- and piezo-chromic properties of a class of transition-metal complexes ($3d^4-3d^7$), is one of growing importance in the area of functional materials, especially for application as **molecular switches** and in the field of **information storage**. These complexes are known to display a molecular bistability of high-spin (**HS**) and low-spin (**LS**) electronic configurations, which are distinguished by different occupation of antibonding e_g and bonding t_{2g} d orbitals of the central metal ion. The course to the design of materials with adequate properties for industrial applications goes through the control of the physical - especially magnetic, optical and structural - properties modifications induced by the spin crossover.

In order to better understand the phase transition mechanism of very gradual complete thermal spin transition, we have collected a series of complete diffraction patterns by single crystal X-ray diffraction versus the temperature. Thanks to these investigations, we were able to follow not only the evolution of cell parameters but also every Fe-N₆ octahedron geometric parameters as a function of the temperature every 5K. The accurate monitoring of inter-atomic distances such as the Fe...N distances and angles have well pointed out the anisotropic behavior of these parameters during the transition. Moreover, this study has revealed the physical mechanism of the propagation of the spin crossover along the material during the transition. Surprisingly for a gradual spin crossover, this mechanism appears different in nature in the cooling and in the warming modes.

Keywords: X-ray single crystal diffraction, gradual spin crossover mechanism

FA4-MS33-P13

Synthesis and Structural Resolution of C₂₁H₁₉NO, a new Alpha-aminoketone. Rafael Mendoza-Meroño^a, Laura Menéndez-Taboada^a, Santiago García-Granda^a and Félix Nápoles-Esculapio^b, ^aDepartment of Physical and Analytical Chemistry, University of Oviedo, Spain, ^bDepartment of Chemistry, University of Oriente, Cuba.
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The structure of the alpha-aminoketones family have been extensively studied [1]. These compounds can be used as intermediates to synthesize other biological activity compounds like thiosemicarbazones. Alpha-aminoketones also present a biological activity but in less extent than thiosemicarbazones.

The synthesis, crystal structure and electron density topological properties for title compound C₂₁H₁₉NO are reported here. According to the dihedral angle values between benzene rings planes, two benzene rings are nearly coplanar whereas the central ring is nearly normal to them. Comparing

these values with the reported structure [2] with the methyl substituent in *para* position, there are not noticeable modifications, while the structure with the methyl substituent in *meta* position shows more coplanarity than the previous ones.

In the crystal structure, the molecular packing is made up of a network of weak hydrogen bonding interactions, favouring the formation of a centrosymmetric dimer of molecules. Such conformation brings the C=O and N—H bonds into a syn orientation. The intermolecular distances between the centroids of the parallel benzene rings in crystal packing is 3.766Å. This value suggests the absence of relevant π -stacking interactions.

[1] Batsanov, A., Au, O., Goeta, A. & Howard, J., *Acta Cryst.*, 2006, C62, o304 o306. [2] Au, O. & Tafeenko, V., *Rev. Cubana Quim.*, 1986, 2, 65-74.

Acknowledgements: Financial support given by Agencia Española de Cooperación Internacional y Desarrollo (AECID), FEDER funding, Spanish MICINN (MAT2006-01997 and Factoría de Cristalización Consolider Ingenio 2010) and Gobierno del Principado de Asturias (PCTI) is acknowledged. Special acknowledgment to Prof. José Manuel Concellón for his support and scientific advice.

Keywords: alpha-aminoketones, synthesis, structural determination, Electron Density Topology.

FA4-MS33-P14

Crystal structure of butyl and propyl N-(3-chloropropyl)-(2S)-alaninate. Laura Menéndez-Taboada^a, Santiago García-Granda^a, Dejana Dimitrijević^b, Gordana Vasić^b, Niko Radulović^c, Mirjana Vukićević^d, Rastko D. Vukićević^b and Srećko R. Trifunović^b, ^aPhysical and Analytical Chemistry Department, Faculty of Chemistry, University of Oviedo, Spain ^bDepartment of Chemistry, Faculty of Science, University of Kragujevac, Serbia, ^cDepartment of Chemistry, Faculty of Science and Mathematics, University of Niš, Višegradaska, Serbia, ^dDepartment of Pharmacy, Medical Faculty, University of Kragujevac, Serbia
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N-(ω-Halogenoalkyl)alanines are suitable precursors for synthesis of polydentate ligands, since the halogen atom can be easily substituted with certain nucleophile. The title compounds we synthesized by refluxing the mixture of dry alcohols saturated with gaseous HCl and (2S)-2-(2-oxo-1,3-oxazinan-3-yl)propanoic acid [1].

Suitable crystals for an X-ray crystal structure determination were collected after recrystallization of both compounds from water. The synthesis, crystal structure and electron density topological properties for both compounds are reported here.

The butyl N-(3-chloropropyl)-(2S)-alaninate hydrochloride (compound 1) crystallizes in the space group $P2_12_12$ with $a = 7.2650(4)$, $b = 14.8864(7)$, $c = 13.3082(10)$ Å, and $Z = 4$. Two significant hydrogen bonds have been observed, that, in fact, are responsible for the observed crystal packing, namely the interaction between the chloride ion and two hydrogen atoms of the two neighboring ammonium groups. The tridimensional crystallographic structure shows helix type propagation along a axis. That helix is formed by parallel molecules, along ac plane. Compound 2 crystallizes in the space group $P2_1$ with a

$a = 5.4456(3)$, $b = 10.0655(5)$, $c = 12.2423(8)$ Å, $\beta = 96.997(6)$ and $Z = 2$. The molecular structure shows also helix type propagation along b axis. The helical structure is supported by H bonds involving N and Cl, forming an infinite zig-zag chain along ab plane.

Relevant structural parameters are the C=O and CO-C bond lengths on the ester group. They are somewhat shorter than those previously reported for the ethyl esters of some β -alanine and glycine derivatives, whereas the O2-C2 bond (the C-O bond of the butoxy group) is almost the same as the one of the mentioned derivatives [2, 3, 4, 5, 6].

[1] S. Trifunović, D. Dimitrijević, G. Vasić, N. Radulović, M. Vukićević, F. W. Heinemann, R. D. Vukićević, *Synthesis*, 6 (2010) 943; [2] R. S. Herrick, K. L. Houde, J. S. McDowell, L. P. Kiczek, G. Bonavia, *J. Organomet. Chem.*, 589 (1999) 29-37; [3] D. Savage, J. F. Gallagher, Y. Ida, P. T. M. Kenny, *J. Organomet. Chem.*, 5 (2002) 1034; [4] D. Savage, G. Malone, J. F. Gallagher, Y. Ida, P. T. M. Kenny, *J. Organomet. Chem.*, 690 (2005) 383; [5] D. Savage, G. Malone, S. R. Alley, J. F. Gallagher, A. Goel, P. N. Kelly, H. Mueller-Bunz, P. T. M. Kenny, *J. Organomet. Chem.*, 691 (2006) 463; [6] V. V. Glodjović, F. W. Heinemann, S. R. Trifunović, *J. Chem. Crystallogr.*, 38 (2008) 883-889

Acknowledgements: Financial support given by Spanish MICINN (MAT2006-01997 and Factoría de Cristalización Consolider Ingenio 2010), grant PCTI- FICYT (BP09060) and FEDER founding, is acknowledged.

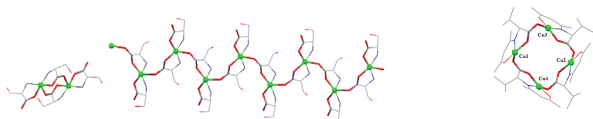
Keywords: Alaninate, Electron Density Topology, Helix propagation.

FA4-MS33-P15

Conformation effect in engineering a new magnetic materials. Amel Messai^a, Amani Direm^a, Nourredine Benali-Cherif^a, Dominique Luneau^b, ^a*Laboratoire des Structures, Propriétés et Interactions Inter Atomique (LASPI2A), Centre Universitaire de Khenchela 40000-Khenchela, Algérie.* ^b*Laboratoire de Mutlimatériaux et Interfaces (UMR 5615) Université Claude Bernard Lyon 1, Campus de la Doua 69622 Villeurbanne cedex, France*

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Among all the potentialities of coordination chemistry, molecular magnetism is very promising as magnetic information can be stored on one molecule. In that sense we developed in our group several strategies in order to obtain such molecular magnets. The idea was to use Schiff base ligands and copper to generate high nuclear complexes. Complexation of different conformation Schiff bases with copper (II) has been investigated. Tetranuclear complex with a cubane like core have been synthesised with conformation DL (Schiff base). With the same base D conformation we obtain a single magnetic chain



Chain of CuL

Cu₄L₄

In this poster, we report the effect of the conformation of the ligand to obtain a different structure and properties, also we report synthesis, crystal structure and magnetic properties of

the tetranuclear compound (Cu₄L₄), and a single chain of copper (CuL)

[1] B. Le Guennic ; S. Petit ; G. Chastanet ; G. Pilet ; D. Luneau ; N. Benamor ; V. Robert , Antiferromagnetic behavior Based on quasi-orthogonal Mos : Synthesis and characterization of Cu₃ oxidazone model. *Inorg. Chem.* 2008, 47, 572-577.

[2] S. Petit ; G. Pilet ; D. Luneau ; L. F. Chibotaru ; L. Ungur, A dinuclear cobalt (II) complex of calix [8] arenes exhibiting strong magnetic anisotropy. *Dalton trans*, 2007, 4582-4588.

Keywords: Cluster-assembled materials, magnetic compounds, absolute configuration.

FA4-MS33-P16

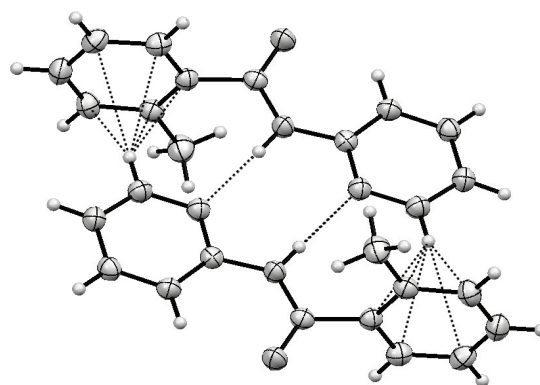
Structural and conformational analysis studies of a 3x3 isomer grid of Methyl-N-(pyridyl)benzamides.

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A 3x3 isomer grid of nine Methyl-N-(pyridyl)benzamides (C₁₃H₁₂N₂O) as **Mxx** ($x = para/meta/ortho$) was examined to evaluate structural relationships from both *ab initio* calculations (*gas-phase*, PCM-SMD solvation model) and the solid-state. The effect of methyl group (**Mx**) and pyridine N atom (**x**) substitution patterns on molecular conformations from calculations and in terms of molecular organization is evaluated. Eight isomers form N-H...N hydrogen bonds with only **Mpm** having N-H...O=C interactions. The N-H...N interactions form C(6) chains in the **Mxp** series, C(5) chains in **Mmm**, **Mom** and cyclic centrosymmetric rings in the **Mxo** series. In **Moo** (below) a short *intra-dimer* C-H... π (arene) interaction is observed.



The solid state structures and conformations from calculations are mismatched in four **Mxx** molecules, in which the solid state structures adopt *meta*-stable or unstable conformations relative to the optimized computational models. The solvation model has no effect on the conformational trends, but decreases the rotational barriers making a conformational transition more probable, especially in more polar solvents.

Keywords: benzamides, conformational analysis, *ab initio*