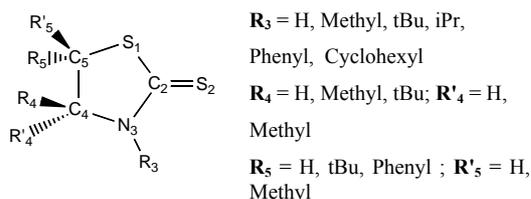


Keywords: Thiazolidine 2-thione, conformation, Heterocycle

In the prospect to study the heterocyclic thiazolidin-2-thione and its derivatives variously substituted (see figure below), our investigation in the solid state will be completed by *AMI* and *ab-initio* calculations.[5,6].

Both of the two theoretical methods leads us to preferential conformations and the comparison between the most stable molecular conformations of the different molecules investigated, helps us to estimate the "weight" of each effect in the real structure of the compound. Our interest has essentially been carried on the conformational behaviour of the heterocycle th-2-th studied and more exactly on the

Csp3-Csp3 part which is the soft part of cycle.



The detailed analysis of the conformations in the solid state [1,2,3,4] shows the flexibility of the heterocycle pentagonal form S1C2N3C4C5 and reveals a relationship between the flexibility of the cycle which is defined by the twisting angle S1C5C4N3 and the distance C4-C5. The quasi-planar and planar conformations are associated together with very short distances C4-C5 (up to 1.40 Å).

The study of the heterocycle by the semi-empirical methods [6] shows that the evolution towards the planar state entails a stabilization of the molecule by covering of *s* and *p* orbitals and particularly in part C4-C5.

At the end, it's possible to envisage that the combination of steric effects and electronic effects could lead to an efficient model in the treatment of the heterocyclic systems.

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MS16 P16

Coumarin 120 - crystallization experiments leading to a new type of polymorphism. Zofia Urbanczyk-Lipkowska, Dorota Niedziałek, *Institute of Organic Chemistry, Polish Academy of Sciences*. 01-224 Warsaw, Poland. E-mail: ocryst@icho.edu.pl

Keywords: coumarins, new polymorph, electronic structure

Coumarins are natural or synthetic compounds used as pharmaceuticals and herbicides. They exhibit fluorescent

properties (due to presence of benzopyrone moiety) and therefore, are used as high quantum yield laser dyes (e.g. coumarin 4, coumarin 120, etc). Their frequent use as a model compounds in photophysical studies prompted us to look for their polymorphs.

Crystallization experiments involved recrystallization from polar and non-polar solvents and their mixtures, co-crystallization with 5 % or equimolar amount of another coumarin derivative. We also investigated the influence of the crystallization solvent and additives on crystal habit. The transition behavior of the crystalline forms of coumarin 120, its melting point, and enthalpy were investigated by DSC, FTIR and X-ray crystallography.

These experiments allowed to obtain a new crystalline form of 7-amino-4-methyl-coumarin (coumarin 120) with unprecedented crystal structure, containing two types of molecules – nonpolar and polar. These crystals exhibit also a new type of polymorphism – where molecules of two different electronic structures co-exist in the same crystal. Both types of molecules are bound by the same hydrogen bonding pattern, similar to that found in first polymorph [1]. Although, polar molecules are bound slightly tighter (m.p. of a new form higher by 3 °C) during melting new polymorph transforms irreversibly into the first form. These studies confirm that fluorescence quenching observed for coumarin 120 [2] is due to the presence of equilibrium of various electronic structures in solution.

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MS21 P08

Crystal structure of the new titanium phosphate Na₃CaTi(PO₄)₃

S. Krimi^a, A. El Jazouli^b, A. Lachgar^c,

^aLPCMI, Faculté des Sciences Ain Chock, Casablanca, Maroc.

^bLCMS, Faculté des Sciences Ben M'Sik-UH2M, Casablanca, Maroc.

^cDepartment of Chemistry, Wake Forest University, Winston-Salem, North Carolina, USA.

Key Word : Titanium phosphate, Nasicon – type

Titanium phosphates are currently of interest for their chemical and physical properties as catalysts, non-linear materials and ionic conductors. In this context the new titanium phosphate Na₃CaTi(PO₄)₃ has been synthesized and structurally characterized. Single crystals were obtained by melting a mixture of Na₂CO₃, CaCO₃, TiO₂ and (NH₄)₂HPO₄ in stoichiometric proportion, at 900°C, followed by slow cooling (3°C/hr).

Na₃CaTi(PO₄)₃ crystallizes in the space group R32 with a = 8.985(1)Å, c = 21.920(3)Å, V = 1532.6(3)Å³, and Z = 6. The refinement factors are R₁ = 0.0365 and wR₂ = 0.0944. The structure of Na₃CaTi(PO₄)₃ belongs to the Nasicon-type family. It consists of a three dimensional network of PO₄ tetrahedra and AO₆ (A = Ti, Ca) octahedra sharing corners. A 2-2 ordered distribution of titanium and calcium occurs along the c axis giving rise to two different units [Ti₂(PO₄)₃] and [Ca₂(PO₄)₃]. Within this covalent framework exist two additional cationic sites usually labeled M1 and M2 where the sodium ions are located.

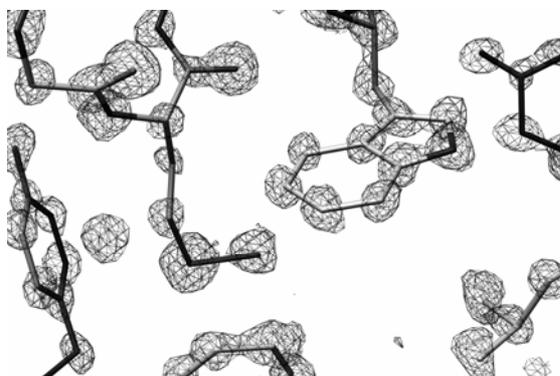
The M1 site is an antiprism sharing faces with two AO₆ octahedra. The M2 site is a large cage bounded by 8 oxygens.

MS33 P01

Atomic resolution structure of HEWL in complex with tris-dipicolinate lanthanide Guillaume Pompidor^a, Olivier Maury^b, Jean Vicat^a, Richard Kahn^a, ^a*Institut de Biologie Structurale, CEA-CNRS-UJF, UMR 5075, Grenoble, France.* ^b*Laboratoire de Chimie, UMR 5182, ENS-Lyon, France.*
E-mail: richard.kahn@ibs.fr

Keywords: macromolecular phase determination, atomic resolution crystallography, lanthanide

Tris-dipicolinate lanthanide complex, Na₃[Ln(DPA)₃], where DPA stands for pyridine-2,6 dicarboxylate, was used to obtain derivative crystals of hen egg-white lysozyme (HEWL). Derivative crystals were prepared by co-crystallization using conditions close to those leading to the native tetragonal HEWL crystals by adding in the crystallization drops solutions of Ce or Lu complexes to a final concentration of 50-100 mM. The crystals, belonging to a new monoclinic form of lysozyme, space group C2, were diffracting to a resolution never achieved with lysozyme crystals. Diffraction data for the Ce and Lu derivative crystals were recorded to resolutions of 0.80 and 0.85 Å, respectively. Taking advantage of the anomalous signal of Lu ($f'' = 7.8 e^-$ at $\lambda = 0.85 \text{ \AA}$), experimental phases were determined by the SAD method using the program *SHARP* [1]. Most of the atoms in the structure could be individually observed in the experimental electron-density map, similar in quality to the final 2Fo-Fc map.



Experimental electron-density map of lysozyme at 0.85 Å resolution (contours at 2.0 σ)

The structures were refined against anomalous diffraction data using the program *SHELX* [2]. Among 5 sites found for the lanthanide complexes, 2 sites turned out to be almost fully occupied. The tris-dipicolinate lanthanide complexes, located at the interface between protein molecules are involved in the crystal packing. Strong interactions between each lanthanide complex and different lysozyme molecules strengthen the packing thus enhancing the diffracting power of the crystals.

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MS35 P06

A comparative study of natural and synthetic calcium sulphates F. Karim^a, M. Waqif^a and L. Saadi^a, ^a*Laboratory of Condensed Matter and Nanostructures, Team of Study and Valorization of Mineral Resources and Synthetic Materials Evar-mimas, Department of Chemistry, Faculty of Science and Technology Guéliz, Marrakech, Morocco.*
e-mail: la.saadi@yahoo.fr

Keywords : Gypsum, calcium sulphate, medical plasters, mineralogy , chemistry.

In the past, plaster obtained by calcination of gypsum, has been used as biomaterial. However, there has been limited research on the Moroccan gypsum, although the Moroccan gypsum reserves are very significant.

Our study respectively refers to a physicochemical characterization of gypsum samples from three different areas of Morocco: Midelte (GMB), Immentanoute (GIB) and Safi (GRST). These samples were compared with medical plaster (PMC).

The mineralogy and chemistry of all samples were studied by X-ray Diffraction (XRD), IR X-ray fluorescence, DTA and TGA. The morphology of gypsum was studied by Scanning Electron Microscopy (SEM).

The chemical analyses revealed that the three natural gypsum samples GMB, GIB, GRST and PMC, are made up mainly by calcium sulphate and calcium oxide. These natural samples are characterized by a high purity comparable to sample PMC. SiO₂, Al₂O₃ and MgO, are present in very small abundances, in mineral impurities such as traces of clays and carbonates as was confirmed by XRD on bulk samples.

From thermal behavior point of view, samples GMB, GIB, GRST and PMC show almost the same thermal phenomena with increasing temperature. Using XRD it was possible to assign modifications in gypsum during calcination to the following gradual dehydration reactions:



In conclusion the Moroccan natural samples studied consist mainly of gypsum associated with traces of clay and carbonates. They raw materials are characterized by high purity and their mineralogy and chemistry are comparable to those of the medical plaster.

MS41 P28

Crystal structures of the K_{1,125}Rb_{1,875}La(VO₄)₂ and Rb_{1,435}Cs_{1,565}La(VO₄)₂ vanadates . L. Rghioui^{a,b}, L. Benarafa^a, S. Zaydoun^a and L. El Ammari^c. ^aLaboratoire de Spectroscopie infrarouge, Département de Chimie, Faculté des Sciences, B.P. 1014, Rabat, Maroc. ^bEquipe Physico-chimie de la matière condensée, Département de Chimie, Faculté des Sciences, B.P. 4010 Beni M'hamed, Meknès, Maroc. ^cLaboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, B.P. 1014, Rabat, Maroc
E-mail : lrgghioui@hotmail.com

Keywords : analysis of disordered structures, infrared spectroscopy, single-crystal structure

The new vanadates K_{1,125}Rb_{1,875}La(VO₄)₂ and Rb_{1,435}Cs_{1,565}La(VO₄)₂ have been synthesized by the reactive flux method. Their crystal structures were determined by single crystal X-ray diffraction. Both