

P.07.06.2*Acta Cryst.* (2005). A61, C311**Polynuclear Coordination Polymer with Glutarate Ligand: $\text{Sr}(\text{C}_5\text{H}_7\text{O}_4)_2(\text{H}_2\text{O})_2$** Achoura Guehria-Laidoudi, K. Aliouane, Assia Djeghri, Kamel Taïbi, *Laobratoire de Cristallographie - Thermodynamique, Faculté de Chimie, USTHB, BP 32 El-Alia, BEZ, Alger, Algérie.* E-mail: guehria_laidoudi@yahoo.fr

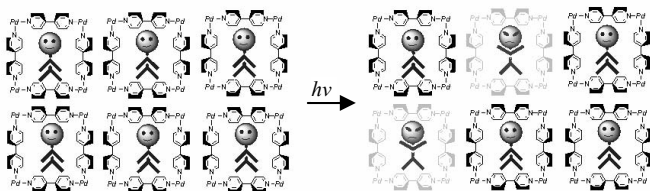
In our course of obtaining new organic-inorganic complexes built up of flexible dicarboxylate ligands, we have noticed the peculiar behavior of the ligands derived from glutaric acid. Linked to rare-earth or alkaline-earth metals, they lead to a wide variety of structural types: catena polynuclear complex [1], uncommon cage feature [2], isolated polyhedra [3] involving completely or partially deprotonated unities. The new strontium biglutarate has been obtained on single crystal form via silica medium synthetic route. It is different from barium biglutarate in that it completes its coordination sphere by two coordinated water molecules, and crystallizes in space group $P\bar{1}$. The metal is nine coordinated forming infinite chains of one-antiprism $\text{SrO}_7(\text{H}_2\text{O})_2$ within which the distance between two neighbouring Sr^{2+} ions are 4.272(6)Å. These chains are cross-linked, leading to a layered structure.

[1] Benmerad B., Guehria-Laïdoudi A., Balegrone F., Birkedal H., Chapuis G., *Acta Cryst.*, 2000, **C56**, 789. [2] Benmerad B., Guehria-Laïdoudi A., Dahaoui S., Lecomte C., *Acta Cryst.*, 2004, **C60**, m119. [3] Aliouane K., Djeghri A., Guehria-Laidoudi A., Dahaoui S., Lecomte C., *ECM-22*, Budapest, 2004.

Keywords: biglutarate, alkaline-earth complexes, organic-inorganic polymers

P.07.06.3*Acta Cryst.* (2005). A61, C311**Direct Observation of Photochemical Reactions by X-ray Crystallography – Supramolecular Approach**Masaki Kawano^a, Yasuhiro Kobayashi^a, Kanji Takaoka^a, Makoto Fujita^{a,b}, ^a*Department of Applied Chemistry, The University of Tokyo.* ^b*CREST (JST), Japan.* E-mail: mkawano@appchem.t.u-tokyo.ac.jp

Kawano and coworkers crystallographically studied photo-induced reactive species such as radicals, carbenes, and nitrenes cryo-trapped in a crystal [1,2,3]. Here we propose a supramolecular approach for *in situ* observation to overcome practical problem of crystal deterioration by photo-irradiation as shown in scheme. We used a void in a self-assembled giant cage complex to control the reaction cavity. In this talk, we would like to introduce *in situ* observation of a photo-induced unsaturated transition metal complex and a crystalline state [2+2] reaction of acenaphthylene in a M6L4 cage [4].



[1] Kawano M., Sano T., Abe J., Ohashi Y., *J. Am. Chem. Soc.*, 1999, **121**, 8106. [2] Kawano M., Hirai K., Tomioka H., Ohashi Y., *J. Am. Chem. Soc.*, 2001, **123**, 6904. [3] Kawano M., Takayama T., Uekusa H., Ohashi Y., Ozawa Y., Matsubara K., Imabayashi H., Mitsumi M., Toriumi K., *Chem. Lett.*, 2003, 922. [4] Yoshizawa M., Takeyama Y., Kusukawa T., Fujita M., *Angew. Chem. Int. Ed.*, 2002, **41**, 1347.

Keywords: *in situ* observations, unstable compounds, photochemistry

P.07.07.1*Acta Cryst.* (2005). A61, C311**Metal-Ligand and Metal-Metal Bonding Characterization from X-ray Diffraction**Nouzha Bouhmaid¹, B. Fraisse², A. Perez-Benitez³, M.A. Méndez-Rojas⁴, N.E. Ghermani^{2,5}, ¹*LSM, Université Cadi Ayyad, Faculté des*

Sciences Semlalia, Boulevard Moulay Abdallah, BP 2390, 40000 Marrakech, Morocco. ²*Ecole Centrale Paris, SPMS UMR CNRS 8580 1, Grande Voie des Vignes, 92295 Châtenay-Malabry, France.* ³*Facultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla, Puebla 72000, México.* ⁴*Departamento de Química y Biología, Universidad de las Américas-Puebla, Ex-Hacienda Sta. Catarina Mártir, Cholula, 72820 Puebla, Pue., Mexico.* ⁵*PPB UMR CNRS 8612, Faculté de Pharmacie 5, Rue Jean-Baptiste Clément, 92296 Châtenay-Malabry, France.* E-mail: nouzha@ucam.ac.ma

The metal complex of a non-steroidal anti-inflammatory drug (NSAID), di- μ -aspirinato-copper(II), crystallizes in its biochemical active form [1]. The electron density and electrostatic potential calculations are useful for the understanding of the metal-ligand bonding and its connection with the biochemical activity of such molecule. The compound also offers the opportunity to characterize the occurring copper-copper bond ($\text{Cu} - \text{Cu} = 2.604 \text{ \AA}$).

X-ray diffraction measurements were performed on a smart CCD diffractometer at 100 K with the $\text{MoK}\alpha$ radiation. up to $\sin \theta/\lambda = 1.11 \text{ \AA}^{-1}$. The compound crystallizes in the $P2_1/c$ group and reveals a one dimensional polymeric structure. The copper is in an irregular octahedral coordination corresponding to five oxygen atoms and one copper.

Electron density refinements are carried out using the Hansen-Coppens model [2]. The Cu-O, Cu-Cu electron density bonds are discussed according to the copper d-orbital populations. Electrostatic potential and active sites of the molecule are also shown.

[1] Garcia F., Méndez-Rojas M.A., González-Veraga E., Bernes S., Quiroz M.A., *Acta Cryst.*, 2003, **E59**, m1171-m1173. [2] Hansen N., Coppens P., *Acta Cryst.*, 1978, **A34**, 909.

Keywords: electron density, electrostatic potential, metal-metal bonds

P.07.07.2*Acta Cryst.* (2005). A61, C311**Scanning Texture Analysis of Lamellar Bone using Microbeam Synchrotron Radiation**Wolfgang Wagermaier^a, Himadri S. Gupta^a, Aurelien Gourrier^a, Paul Roschger^b, Manfred Burghammer^c, Oskar Paris^a, Christian Riekel^c, Peter Fratzl^a, ^a*Max Planck Institute of Colloids and Interfaces, Potsdam, Germany.* ^b*L. Boltzmann-Inst. of Osteology at Hanusch Hospital of WGKK and at AUVA Trauma Center Meidling, Vienna, Austria.* ^c*ESRF, Grenoble, France.* E-mail: wagermaier@mpikg.mpg.de

Bone consists of mineral particle reinforced collagen and is structurally optimized for its biological functions. The 3D mineral nanostructure is still not fully understood. Specifically, little is known about the lamellar and sublamellar structure of the osteon, the fundamental unit of compact bone. The combination of microbeam (one micrometer) synchrotron scanning SAXS (small angle x-ray scattering) and WAXD (wide angle x-ray diffraction) allows us to reconstruct the full 3D mineral particle distribution at different positions within single osteonal lamellae. The WAXD data was used to calculate pole figures (stereographic projections), which delivers information on the mean orientation and texture of the principal axes of the mineral crystallites (which have a hexagonal cubic structure).

We scanned several osteons from a human femoral midshaft which were cut into slices of 3 micrometers. Our results show that the mineral crystal orientation has a fibre texture within single lamellae and shows intralamellar variation. The direction of mineral crystals rotates within the plane of each lamella.

Keywords: bone, texture analysis, synchrotron X-ray diffraction

P.07.07.3*Acta Cryst.* (2005). A61, C311-C312**Palladium(II) and Platinum(II) Complexes with Tridentate Iminophosphine Ligands and their Phosphine Derivatives; Synthesis and Structural Studies**Joanne Lennon^a, O.M. Ni. Dhubhghail^a, Michael G.B. Drew^b, ^a*Department of Chemistry, University College Cork, College Rd., Cork.* ^b*Department of Chemistry, University of Reading, Whiteknights,*

Reading, RG6 6AD. E-mail: j.lennon@ucc.ie

Bidentate aminophosphines comprising hard and soft donor atoms continue to attract the attention of coordination chemists. These ligands exhibit partial lability where the coordination mode alters between bidentate and monodentate and back again, leading to coordinatively unsaturated metal centres. Late transition metal complexes of this type of ligand have been shown to mediate a range of catalytic transformations [1] and recently, have also shown potential as antitumour agents [2]. Expanding on this premise, we prepared tridentate ligands with P, N and O donor atoms by condensation of *o*-diphenylphosphinoaniline with substituted salicylaldehydes and explored their complexation behaviour towards group 10 metal centres. These were found to deprotonate readily upon reaction with Pd(II)Cl₂, Pt(II)Cl₂ and (cod)Pt(II)L₂ to form complexes of general formula [η³(L)M(II)X]. Furthermore, these complexes undergo substitution reactions with monodentate phosphines, PR₃, to yield complexes of the general formula [η³(L)M(II)PR₃]ClO₄. These were characterised by spectroscopic, microanalytical and crystallographic methods.

A series of crystal structures representative of the work is discussed in detail comparing and contrasting palladium complexes with their platinum counterparts [η³(L³)Pd(II)Cl], [η³(L²)Pt(II)Cl] and [η³(L²)Pt(II)I] and phosphine derivatives, [η³(L³)Pd(II)PPh₃]ClO₄, [η³(L⁴)Pd(II)P(tolyl)₃]ClO₄, [η³(L⁴)Pt(II)P(tolyl)₃]ClO₄. Crystal studies confirm tridentate [P,N,O] coordination of the deprotonated ligands to the metal centres and the formation of both five- and six-membered rings with both halide and phosphine derivatives.

[1] Zehnder M., Schaffner S., Neuberger M., Plattner D., *Inorganica Chimica Acta*, 2002, **337**, 287, and references therein. [2] Habtemariam A., Watchman B., Potter B.S., Palmer R., Parsons S., Parkin A., Sadler P.J., *Journal of the Chemical Society, Dalton Transactions*, 2001, 1306.

Keywords: coordination chemistry, crystallographic structure, bioinorganic compounds

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Modelling Copper-Protein Backbone Binding

Sara Furlan^a, Giovanni La Penna^b, Silvia Morante^c, ^aICCOM-CNR, Florence. ^bISMac-CNR, Section of Genova. ^cPhysics Department, University of Rome - Tor Vergata, Italy. E-mail: sara.furlan@iccom.cnr.it

The determination of the X-ray structure [1] of a complex formed by Cu²⁺ and the peptide with the (His-Gly-Gly-Gly-Trp) sequence, which is part of the prion protein octarepeat, opened a new perspective in the identification of possible copper binding sites. This structural information and that coming from further studies extended to peptides containing several octarepeat sequences and to the whole protein [2], confirmed the importance of the existence of bonds between copper and the N and O amide atoms of the peptide backbone. These bonds strongly contribute in modifying the secondary structure of the peptide and compete with the bonds between His side-chain and Cu²⁺.

The aim of this work is at understanding of the structure of the complex Cu-(HGGG), that was proposed in the literature, in the language of quantum chemistry. The coordination chemistry of this complex is coupled with the protonation state of the peptide as well as with the distortion of the protein backbone and intramolecular hydrogen bonds. These interactions can be reasonably well described within a density functional model for the electronic structure and Car-Parrinello ab-initio molecular dynamics can be carried out through recent advances in the field [3].

[1] Burns C.S. et al., *Biochemistry*, 2002, **41**, 3991. [2] Morante S. et al., *J. Biol. Chem.*, 2004, **279**, 11753. [3] Giannozzi P. et al., *J. Chem. Phys.*, 2004, **120**, 5903.

Keywords: prion protein, copper complex, Car-Parrinello ab-initio molecular dynamics

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Oscillatory Biomineralization in Mollusc Shells

Ulli Bismayer, Melanie Bartels, Klaus Bandel, *Department of Earth Sciences, University of Hamburg, Germany.* E-mail: ubis@mineralogie.uni-hamburg.de

Impurity distribution in mollusc shells of the species *Patella crenata*, *Fissurella*, *Littorina*, *Nerita*, *Nucella* and *Concholepas* was studied using microprobe analysis (CAMECA-SX 100). In detail the Mg content and its spatial distribution in calcite as well as the Sr distribution in aragonite were investigated. The Sr distribution has been determined qualitatively, Mg and its distribution was measured quantitatively. Oscillatory growth and the corresponding modulation of Mg in the order of 0.2 - 1.65 weight percent was found. Patterns of distributed impurities were correlated with shell structures and growth directions. Nanoparticle orientations, growth directions and impurity patterns are analysed and show complex correlations.

Structural information was obtained via TEM, IR and Raman spectroscopy. The oscillatory pattern of the impurity distribution and related strain may lead to an increased thermodynamic stability of the systems which is supported by theory [1].

[1] Lee W.T., Salje E.K.H., *European Physical Journal B*, 2000, **13**, 395.

Keywords: zone structure, nanostructures, carbonates

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The Biomineralization of Iron Sulfides under Anoxic Conditions

Anton Preisinger, S. Aslanian, J. Wernisch, *Technical University of Vienna, Austria.* E-mail: apreisin@mail.zserv.tuwien.ac.at

For about 9500 years high salinity water has been flowing from the Marmara Sea over the Bosphorus to the Black Sea, increasing its salinity, anoxity and the amount of sulfate reducing bacteria (SRB). Authigenic biomineralization of framboidal greigites (FG) in the form of biologically controlled mineralization of ferrimagnetic iron sulfides led to the intracellular crystallisation of the greigite found in the magnetosomes of sulfate reducing bacteria (SRB) [1]. Since this time the FG have sizes of 2 to 13 μm in diameter and show rhythmical distribution in the sediment cores [2]. Under influence of oxygen the single crystals of greigites are changed partially to pyrite, without change of morphology. This pyritization may take place by transportation of framboidal greigites through oxidizing sea water or by influence of air on the sample. Transmission Electronic Microscopy (TEM) of an ultramicrotome section shows by electron diffraction and EDX analysis single crystals of a ferri -magnetic inverse thiospinel of a composition of Fe²⁺Fe³⁺₂S₄ and a cell edge of a = 9.868 Å. The micro - crystals of ~ 0.4 μm exhibit {111} as the dominant form accompanied by {100}, surrounded by a membrane [XL30ESEM/Philips]. Each cubo-octahedron crystal is tetrahedrally coordinated by 4 octahedra over {111} to form a 3-D array with cavities in form of 4 icosahedra. The 3-D array of the octahedra and the icosahedra form a super close package. The influence of oxygen was studied by TEM, ESEM and X-ray powder diffraction.

[1] Preisinger A., *ECM 22*, Budapest, Hungary, 2004, 45. [2] Preisinger A., Aslanian S., *GSA, Ann. Meet.*, Seattle, 2003.

Keywords: sediments, bacteria, sulfide minerals

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Design of New Mn Precursors for Single-molecule Magnet

María Hernández Molina^a, Fabien Tuyeras^b, Valérie Marvaud^b, ^aLab. de Rayos X y Materiales Moleculares. Dpto de Edafología y Geología Universidad de La Laguna. Spain. ^bLaboratoire de Chimie Inorganique et Matériaux Moléculaires, U.P.M.C. France. E-mail: hmolina@ccr.jussieu.fr

In the field of molecular magnetism, specific attention is devoted to polynuclear complexes with large-spin ground states and high anisotropy that exhibit original magnetic properties such as single-molecule magnet behaviour. The important feature of the rationale synthetic approach is the possibility that the chemist has to predict the nature of the ground state, the size of the molecule, its shape and the order of magnitude of the magnetic anisotropy that plays an crucial