

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)Cl<sub>2</sub>, Pt(II)Cl<sub>2</sub> and (cod)Pt(II)Cl<sub>2</sub> to form complexes of general formula [η<sup>3</sup>(L)M(II)X]. Furthermore, these complexes undergo substitution reactions with monodentate phosphines, PR<sub>3</sub>, to yield complexes of the general formula [η<sup>3</sup>(L)M(II)PR<sub>3</sub>]ClO<sub>4</sub>. 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 [η<sup>3</sup>(L<sup>3</sup>)Pd(II)Cl], [η<sup>3</sup>(L<sup>2</sup>)Pt(II)Cl] and [η<sup>3</sup>(L<sup>2</sup>)Pt(II)I] and phosphine derivatives, [η<sup>3</sup>(L<sup>3</sup>)Pd(II)PPh<sub>3</sub>]ClO<sub>4</sub>, [η<sup>3</sup>(L<sup>4</sup>)Pd(II)P(tolyl)<sub>3</sub>]ClO<sub>4</sub>, [η<sup>3</sup>(L<sup>4</sup>)Pt(II)P(tolyl)<sub>3</sub>]ClO<sub>4</sub>. 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

#### P.07.07.4

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##### Modelling Copper-Protein Backbone Binding

Sara Furlan<sup>a</sup>, Giovanni La Penna<sup>b</sup>, Silvia Morante<sup>c</sup>, <sup>a</sup>ICCOM-CNR, Florence. <sup>b</sup>ISMac-CNR, Section of Genova. <sup>c</sup>Physics 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 Cu<sup>2+</sup> 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 Cu<sup>2+</sup>.

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

#### P.07.08.2

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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 Fe<sup>2+</sup>Fe<sup>3+</sup><sub>2</sub>S<sub>4</sub> 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

#### P.07.10.1

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##### Design of New Mn Precursors for Single-molecule Magnet

María Hernández Molina<sup>a</sup>, Fabien Tuyeras<sup>b</sup>, Valérie Marvaud<sup>b</sup>, <sup>a</sup>Lab. de Rayos X y Materiales Moleculares. Dpto de Edafología y Geología Universidad de La Laguna. Spain. <sup>b</sup>Laboratoire 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

role in determining the blocking temperature of the magnetic moment. The synthesis of high-spin molecules has been considered as one possible route to the preparation of molecular-based ferromagnets.

Three new inorganic-organic compounds of formulae  $[\text{Mn}(\text{AcAc})_2(\text{py})_2]_2(\text{ClO}_4)_2$ ,  $[\text{Mn}(\text{AcAc})_3]$  and  $[\text{Mn}(\text{acacen})_2](\text{ClO}_4)$ , were AcAc = acetylacetonato, acacenH<sub>2</sub> = N,N'-ethylenebis(acetylacetonato) imine and py = pyridine. They might be viewed as new precursors for the design of single molecule or single chain magnets.

[1] Solari E., Latronico M., Blech P., Floriani C., *Inorg. Chem.*, 1996, **35**, 4526. [2] Marvaud V., Decroix C., Scullier A., Tuyéras F., Guyard-Duhayon C., Vaissermann J., Marrot J., Gonnet F., Verdaguer M., *Chem. Eur. J.*, 2003, **9**, 1692-1705.

**Keywords:** molecular magnetism, crystal engineering, coordination complexes

#### P.07.11.1

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#### Synthesis and Characterization by Diffraction of X-rays of a new Hybrid Compound Based on Tin

Sofiane Bouacida, H. Merazig, A. Beghidja, C. Rihane, *Laboratoire de chimie moléculaire, du contrôle de l'environnement et de mesures physico-chimique. Université Mentouri Constantine, Route Ain el Bey 25000, Algérie.* E-mail: Bouacida\_sofiane@yahoo.fr

Organic-inorganic hybrid materials have attracted a great deal of attention during the past few decades because of their ionic, electrical, magnetic and optical properties [1-3]. Only one crystal structure of an arylammonium hexachlorostannate(IV) compound has been reported previously [4]. In this study we present a new organic-inorganic hybrid compound with the formula  $(\text{R-NH}_3)_2\text{SnX}_6$ , it promises both the superior carrier mobility of inorganic semiconductors and the processability of organic materials.

The title compound,  $(\text{C}_7\text{H}_8\text{NO}_2)_2(\text{SnF}_6)$ , crystallized in the C2/c space group of the monoclinic system, was prepared from aminobenzoic acid and tin(II) fluoride in hydrofluoric acid. The structure can be described by alternating layers of  $\text{SnF}_6^{2-}$  and  $\text{C}_7\text{H}_8\text{NO}_2^+$  ions along the *a* axis. The cations and anions are linked to each other through strong hydrogen bonds, formed by all H atoms covalently bonded to the N and O atoms. This three-dimensional complex network of hydrogen bonds reinforces the cohesion of the ionic structure.

[1] Hill C.L., *Chem. Rev.*, 1998, **98**, 1-2. [2] Kagan C.R., Mitzi D.B., Dimitrakopoulos C.D., *Science*, 1999, **286**, 945-947. [3] Raptopoulou C.P., Terzis A., Mousdis G.A., Papavassiliou G.C., *Z.Naturforsch. Teil B*, 2002, **57**, 645-650. [4] Rademeyer M., *Acta Cryst.*, 2004, **C60**, m55-m56.

**Keywords:** hybrid compound, X-ray, single crystal

#### P.07.11.2

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#### X-ray Structural Study of $\sigma$ -borane and Dihydridoborate Ruthenium Complexes

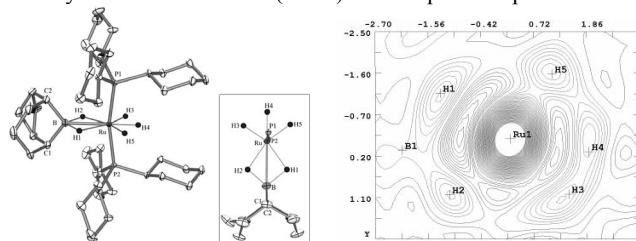
Laure Vendier, S. Lachaize, S. Sabo-Etienne, *Laboratoire de Chimie de coordination, Toulouse* E-mail: vendier@lcc-toulouse.fr

In this work, we present 3 X-ray structures of a new family of  $\sigma$ -borane and dihydridoborate complexes. Two  $\sigma$ -borane and one dihydridoborate complexes have been produced: respectively  $\text{RuH}_2(\eta^2\text{-HBpin})(\eta^2\text{-H}_2)(\text{PCy}_3)_2$  (2Bpin) and  $\text{RuH}_2(\eta^2\text{-HBcat})(\eta^2\text{-H}_2)(\text{PCy}_3)_2$  (2Bcat), and  $\text{RuH}[(\mu\text{-H})_2\text{BBN}](\eta^2\text{-H}_2)(\text{PCy}_3)_2$  (2BBN).

The formulation of each complex has been ascertained by an X-ray structural study. Each experiment was carried out at 100 °K, in order to prevent as much as possible dihydrogen rotation, and to help the localisation of all the hydrogen atoms around the ruthenium. These complexes have been studied as well by NMR spectroscopy and by DFT/B3LYP calculations.

In the case of 2-BBN, the highly delocalized electronic density precluded any good location in the region of the equatorial plane *trans* to the dihydridoborate, and the hydride positions should be considered as artefacts. To solve this problem, our X-ray structural study has been completed by calculating Fourier differences map of the electronic

density observed at small  $\theta$  ( $< 18^\circ$ ) in the equatorial plane.



**Keywords:** low temperature, hydride structures, Fourier maps

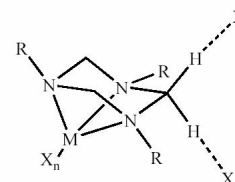
#### P.07.11.3

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#### C-H...X Intermolecular Interaction in Crystals of Triazacyclohexane Complexes

Gabriele I. Kociok-Köhn<sup>a</sup>, Randolf Köhn<sup>a</sup>, Zhida Pan<sup>b, a</sup> *Department of Chemistry, University of Bath, BA2 7AY, UK.* <sup>b</sup>*Department of Chemistry, Freie Universität Berlin, D-14195, Germany.* E-mail: g.kociok-kohn@bath.ac.uk

The ring C-H bonds in the triazacyclohexane of transition metal complexes tend to engage in C-H...X (X = Cl, F, O) dominating the intermolecular interaction [1]. These interactions lead to low solubility of many complexes. The comparative analysis of many neutral and cationic complexes is presented.



[1] Köhn R.D., Kampe P., Kociok-Köhn G., *Eur. J. Inorg. Chem.*, 2005, in press.

**Keywords:** hydrogen bonding, transition metal complexes, triazacyclohexane

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#### Chirality Inversion Process in Cobaloxime Complex Crystals by Photoirradiation

Akiko Sekine, Tsuyoshi Nitami, Kazutaka Sasaki, Hiraku Takeoka, Hidehiro Uekusa, Yuji Ohashi, *Department of Chemistry and Materials Science, Tokyo Institute of Technology, Japan.* E-mail: asekin@chem.titech.ac.jp

It was found that the racemic crystal of (1-cyanoethyl)-(piperidine)cobaloxime complex was transformed to a chiral one on exposure to visible light with retention of the single crystal form [1]. Although the crystal showed the optical rotation after photoirradiation, the molecule in the crystal was racemized. Recently we found that the chirality of the molecule was inverted to the opposite configuration when the crystal was irradiated with visible light.

The first example is the crystal of ((S)-1-ethoxycarbonyl)ethyl)-((S)-cyclohexylamine)cobaloxime. The (S)-1-ethoxycarbonyl group of the complex was inverted to the opposite configuration. The R:S ratio of the chiral group was changed from 0:100 to 76:24. The second example is the crystal of ((S)-chlorocyanomethyl)(pyridine)-cobaloxime. The R:S ratio was changed from 0:100 to 80:20. The third one, which did not show the chirality inversion, is ((R)-tert-butoxycarbonyl)ethyl)(phenylethylamine)cobaloxime. The R:S ratio of the chiral group became from 100:0 to 60:40 and was not changed to 50:50.

Such chirality changes were well explained by the cavity shape of the chiral group in the original crystals.

[1] a) Osano Y.T., et al., *Nature*, 1991, **352** 510; b) Nemoto T., et al., *Bull Chem Soc. Jpn.*, 1999, **72**, 1971.

**Keywords:** chirality, crystalline state reactions, photoreaction