allows us to determine the relevance of several structural parameters in the process of complexation, thus adding to the rational building of more efficient ligands. The initial state of the simulations is taken from X-ray diffraction results[1] which are also used to verify that the simulations predictions are in agreement with experimental data.

[1] de Namor A.F.D., Chahine S., Kowalska D., Castellano E.E., Piro O.E., *J. Am. Chem. Soc.*, 2002, **124**, 12824-12836.

Keywords: molecular dynamics, calixarene complexes, small molecules

P.03.04.3

Acta Cryst. (2005). A**61**, C166

Structural Properties of Pt-based Anti-cancer Drugs; Computational Studies

Sofia S. M. C. Godinho[a,b], Leif A. Eriksson[a], [a]*Department of Natural Sciences and Örebro Life Science Center University of Örebro, 701 82 Örebro, Sweden.* [b]*Grupo de Física Matemática, Universidade de Lisboa, Lisboa, Portugal.* E-mail: sofia.godinho@nat.oru.se

It is generally accepted that *cis*-[$PtCl_2Pyr_2$] is cytotoxic while *trans*-[$PtCl_2Pyr_2$] is not. Although original empirical structural-activity studies indicated *trans* Pt complexes as being inactive as anti-cancer drugs, it has subsequently been found that *trans*-[$PtCl_2Pyr_2$] is in fact active, both *in vitro* and *in vivo*, and that for the latter the compound is even more active than the corresponding *cis* form. A more likely explanation for the lack of antitumour activity is instead that the *trans* isomer is kinetically more reactive and more susceptible to deactivation than the corresponding *cis* form [1].

We have in the current work investigated both isomers and their corresponding step-wise activation (aquation) processes in order to provide more detailed insights into their mechanisms. The results are also compared to corresponding data for the parent compounds *cis* and *trans*-platin [$PtCl_2(NH_3)_2$]. Implicit as well as explicit solvent effects have previously been shown to be important for these types of reactions [2,3], and thus included in the study.

[1] Wong E., Giandomenico M., *Chem. Rev.*, 1999, **99**, 2451. [2] Raber J., Zhu C., Eriksson L.A., *Mol. Phys.*, 2004, **102**, 2537. [3] Zhu C., Raber J., Eriksson L.A., *J. Phys. Chem. B*, 2005, *in press*.

Keywords: anticancer compounds, DFT, platinum antitumour agents

P.03.05.1

Acta Cryst. (2005). A**61**, C166

Effect of Nanoscale Surface Modification on Interfacial Adhesion: a Theoretical Modelling Study

Irene Yarovsky[†], David J. Henry[†], Evan Evans[§], [†]*Applied Physics, RMIT University, GPO Box 2476V, Victoria, 3001, Australia.* [§]*BlueScope Steel Research Laboratories, Port Kembla, Australia.* E-mail: irene.yarovsky@rmit.edu.au

The effects of modification of polyester surfaces on adhesion to carbonaceous solids are investigated using theoretical techniques. Fully atomistic models are constructed of cross-linked polyester and glassy carbon surfaces. Polyester surface modifiers of both the hydrophilic and hydrophobic nature are introduced and simulations are then performed to obtain qualitative and quantitative measures of interfacial strength between the polyester and carbon thin layers [1].

Our studies indicate that Van der Waals forces contribute significantly to the interfacial strength between the thin layers while atomic scale surface roughness is found to significantly reduce adhesion. Interfaces formed from rigid surface models provide general information on structural and chemical effects but such rigid models tend to overestimate the magnitude of these effects. Relaxed interfacial models provide more realistic representations on interactions between the layers. Flexible chain-based modifiers on the surface of the polyester films tend to migrate away from the interface and flatten the surface thereby decreasing the roughness effects on interfacial strength. Both hydrophilic and hydrophobic surface modifications resulted in reduced adhesion at the interface.

[1] Henry D. J., Lukey C. A., Evans E., Yarovsky I., *Mol. Sim*., *in press.*

Keywords: adhesion, surface modification, molecular modelling

P.03.05.2

Acta Cryst. (2005). A**61**, C166

Modeling of Crystal Structures of Materials: Which Goals can be Achieved?

Tatiana V. Timofeeva[a], Boris B. Averkiev[a], Tiffany L. Kinnibrugh[a], Mikhail Yu. Antipin[a,b], [a]*Department of Natural Sciences, New Mexico Highlands University, Las Vegas, NM 87701, USA.* [b]*Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia.* E-mail: tvtimofeeva@nmhu.edu

Ability to predict structures of crystalline materials is important in many cases for practical applications. For instance, second harmonic generation by crystalline nonlinear optical materials necessarily require acentric structure of their crystals. Crystal structure is also important for high-energy materials, where molecular packing defines crystal density. Some other properties such as fluorescence, conductivity and even potency of drags are also related to their crystal structure.

We analyzed effectiveness of different force fields for crystal structure prediction for group of organic nonlinear optical, high-energy and conductive materials. It was shown that for non-planar molecules improvement of a force field could bring to a significant improvement of results. On the other hand crystal structure of planar molecules is difficult to predict, and in this case some new approaches for instance implementation of "stacking forces" should be introduced.

Keywords: crystal structure modeling, force fields, crystalline materials

P.03.05.3

Acta Cryst. (2005). A**61**, C166

A Global Search for the Optimal Bandstructure for Thermoelectric Applications

Lars Lykke[a], Jorge Sofo[b], Bo B. Iversen[a], Georg K. H. Madsen[a], [a]*Department of Chemistry, Aarhus University.* [b]*Materials Research Institute, Penn State University.* E-mail: lykke@chem.au.dk

The best thermoelectric (TE) materials over the last 30 years has been Bi2Te3 and it's alloys. However recent discoveries have renewed the interest in finding a better TE material. We've decided to use a global search genetic algorithm to try and determine the optimal bandstructure for materials with TE applications. This project involves bandstructure analysis and transport property calculations of known materials with interesting TE properties. We want to employ a genetic algorithm to try and locate general features in a bandstructure which have importance for the TE effect of the material.

Keywords: density functional theory, band structure, transport properties

P.03.06.1

Acta Cryst. (2005). A**61**, C166-C167

Computer Modeling of Local Structure and Properties of Oxide Solid Solutions with NaCl Type Structure

Tatiana G. Petrova, Vadim S. Uruosv, Nikolai N.Eremin, *Department of Geology, Moscow State University, Russia.* E-mail: t_petr@mail.ru

Atomistic semi-empirical potentials were applied to calculate the structural, thermodynamic, elastic properties and phase equilibrium of MgO-CaO, MgO-MnO, MnO-CaO, CaO-SrO, BaO-SrO disodered solid solutions by using of the GULP code [1]. The calculations were performed with partially covalent approximations for 7:1, 3:1, 1:1, 1:3, 1:7 randomly mixed cation compositions. It was used 256-ion primitive supercell with quadrupled parameters of the unit cell for all compositions. It was demonstrated that such supercell allows to imitate random distribution of cations.

On the basis of the calculated values of free energy the component fields of stability, mixing limits and critical temperature were predicted. The values are in a good agreement within the temperature range 298 – 1800 K with the available data and results of other theoretical investigation. For 1:1 composition the analyses of the local

structure (interatomic distances and atomic displacements) from regular positions structure was perfomed. In particular, the insignificant shifts of cations and the essential shifts of anions from the initial ideal positions of the supercell were established [2], [3].

[1] Gale J., *GULP user manual*, Royal institution and Imperial College, London, 1992. [2] Urusov V.S., Petrova T.G., Eremin N.N., *D. Akad. Nauk*, 2002, **47**, 811. [3] Urusov V.S., Petrova T.G., Eremin N.N., *D. Akad. Nauk*, 2003, **392**, 469.

Keywords: solid solution, computer modeling, mixing properties

P.03.06.2

Acta Cryst. (2005). A**61**, C167

The Vibrational Properties of Katoite $Ca_3Al_2[(OH)_4]_3$: A Periodic *Ab-initio* Study

Roberto Dovesi[a], Roberto Orlando[b], Fabien Pascale[c], Javier Torres[a], [a]*Dipartimento di Chimica IFM, Università di Torino.* [b]*Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale.* [c]*Laboratoire de Pétrologie, Modélisation des Matériaux et Processus, Université Pierre et Marie Curie.* E-mail: roberto.dovesi@unito.it

The vibrational spectrum of katoite was simulated by using the periodic *ab initio* CRYSTAL program [1].

In spite of the structural similarities with garnets [2], katoite presents a quite different spectrum, due to the presence of hydrogen atoms and lack of connectivity among the $Al(OH)_6$ octahedra. A deep analysis of the dynamical-matrix eigenvectors, including isotopic substitutions and modes visualization, was performed in order to assign the 345 modes. Hydrogen related modes, namely OH strectching, AlOH bending and H rotation with respect to the Al-O axis can be identified as nearly pure modes, although only the former form a separated band.

For the OH strectching, anharmonicity effects, that are as large as 150 cm^{-1}, have been taken into account. The calculated values are in very good agreement with available experimental data. [3]

[1] Saunders V.R., Dovesi R., Roetti C., Orlando R., Zicovich-Wilson C., Harison N.H., Doll K., Civalleri B., Bush I.J., D'Arco Ph., Llunell M., *CRYSTAL2003 user's manual*, University of Torino, Torino, 2003. [2] Pascale F., Zicovich-Wilson C., Orlando R., Dovesi R., 2005, *in press*. [3] Rossman G.R., Aines R.D., *Am. Mineral.*, 1991, **76**, 1153.

Keywords: ab-initio calculations, hydrogernet, vibration

P.03.07.1

Acta Cryst. (2005). A**61**, C167

3D Model of Ternary Complex of Human 3β-HSD type I. Rational Mutagenesis

Vladimir Pletnev[b], James Thomas[b], William Duax[c], [a]*Inst. Bioorg. Chem. RAS, Moscow, Russia*. [b]*Mercer Univ., School. of Medicine, Macon, GA, USA*. [c]*HW Med. Res. Inst., Buffalo, NY, USA*. E-mail: pletnev@hwi.buffalo.edu

Mammalian 3β-Hydroxysteroid Dehydrogenase/Isomerase (3β-HSD) catalyzes conversion of dehydroepiandrosterone and pregnenolone to active hormones, progesterone and androstenedione. A 3D model of ternary complex of human 3β-HSD type I complexed with NAD cofactor and androstenedione product has been developed based upon two X-ray structures, the UDP-galactose 4-epimerase (UDPGE) complexed with an NAD cofactor and substrate, and the 17β-hydroxysteroid dehydrogenase (17β-HSD) complexed with an NADP cofactor and the androstenedione substrate. These enzymes share 21% and 15% sequence identity with 3β-HSD_1 enzyme in the overlapping regions. The cofactor and substrate binding sites in 3β-HSD_1 resemble the corresponding sites in UDPGE and 17β-HSD structures. A dimer structure of 3β-HSD_1 with a stereochemically optimal interface was built by respective 3D superposition with both subunits of dimeric structure of DTDP-D-glucose 4,6-dehydratase with which 3β-HSD shares 19% sequence identity. The 3D structure of 3β-HSD enzyme is in good agreement with existing biochemical data and is being used to design rational mutations to elucidate key substrate binding residues in the active site and the basis for enzyme dual oxidoreductase and isomerase functions. As predicted by the 3D model, mutagenic data have confirmed a role for H232 in recognizing the 17-keto group of the bound substrate. The H232A mutant lacks the oxidoreductase activity but retains the isomerase activity.

Supported by NIH Grants DK026546 (WD, VP) and CA114717 (JT)

Keywords: 3D model, structure/function relation, mutagenesis

P.03.07.2

Acta Cryst. (2005). A**61**, C167

Force Field Parameters for the Photosystem II Reaction Center

Michal Kuty[a,c], Peter Palencar[a,c], Frantisek Vacha[b,c], [a]*Institute of Landscape Ecology, ASCR, Nove Hrady, Czech R.* [b]*Institute of Plant Molecular Biology, ASCR, Ceske Budejovice, Czech R.* [c]*Institute of Physical Biology, University of South Bohemia, Nove Hrady, Czech R.* E-mail: kuty@ufb.jcu.cz

Our recent experimental results [1] led to the hypothesis that at a room temperature the reduced pigment pheophytin *a* (PHO) induces conformational changes of the photosystem II reaction center (PSII RC) pigment-protein complex. The conformational changes affect excitonic interaction of the RC chlorophylls, which was observed in absorption and CD spectra. In order to better interpret our experiments, theoretical approach such as molecular dynamics simulation is useful tool through the use of dynamic conformational analysis of PSII RC. At present the complete force field (FF) parameters applied in MD are not available for the photosynthetic pigments of PSII RC, namely partial atomic charges and force constants of chlorophyll *a*, plastoquinone and both neutral and reduced form of PHO. From that reason we have developed new FF parameters calculated by quantum chemical method on the pigments with known experimental 3D structure. New FF parameters were successfully applied in preliminary MD simulations on the pigment-protein complex PSII RC (experimental structure pdbID 1S5L). This work is supported by MSMT (MSM6007665808, GACR206/02/D177) and by AVCR (AVOZ60870520).

[1] Vacha F., Durchan M., Siffel P., *Biochim Biophys Acta*, 2002, **147** 1554.

Keywords: force field, molecular dynamics simulations, photosystem

P.03.08.1

Acta Cryst. (2005). A**61**, C167

MAIN 2004: Model Building beyond 100 Residues per Minute

Dusan Turk, *Department of Biochemistry and molecular biology, Structural biology group, Jozef Stefan Institute, Ljubljana, Slovenia.* E-mail: Dusan.Turk@ijs.si

Model building of macromolecular structures at moderate resolution (around 2.8A and below) still requires user intervention to resolve the potential chain trace ambiguities, however, the classical approach by which amino acids are edited manually on one by one basis is becoming history. After an electron density map has been converted to a skeleton, the skeleton is used for recognition of secondary structure and main chain trace directly. Two consecutive screw turns are recognized as a helical structure, whereas beta structures are recognized from straight stretches of skeleton corresponding to at least five amino acids and their arrangements in pairs or sheets. After the secondary structure elements are established a combinatorial search of possible connectivities is used to further reduce the main chain ambiguities. The remaining ambiguities can be further resolved interactively by manual editing of the skeleton. The resolved skeleton then serves for building of the first main chain trace based on sp3 fragments positioned at the potential CA positions. If the resulting model looks satisfactory, it is converted to amino acid residues and enters refinement. Otherwise the resulting models can at any stage continue along the classical path of automated and manual model rebuilding, still using the same program with the same interactive 3D graphical user interface. (See http://www-bmb.ijs.si/)

Keywords: computational methods, crystallographic software, macromolecular crystallography