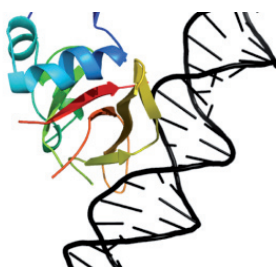


In this study, we present the X-ray structure of the NAC:DNA complex to 4.4 Å. The structure was solved with molecular replacement (MR) using as search models the apo-structure of NAC (1UT4) and a B-DNA model of the oligonucleotide (X.-J. Lu and W. K. Olsen (2003) *Nucleic Acids Res* 31(17):5108-5121). Refinement proved complicated due to the low resolution. The best strategy turned out to include NCS restraints on all atoms, reference-model restraints on protein atoms, and TLS. Phase restraints were available but did not improve refinement. Neither did simulated annealing.

The exact position of the individual DNA bases along the main DNA axis could not be determined by MR alone. Instead, the DNA sequence was assigned based on a uranyl photoprobing assay. The resulting model could be refined to $R_{\text{work}}=24.1\%$ and $R_{\text{free}}=34.4\%$.

The structure provides for the first time experimental evidence for the speculated evolutionary relationship between the plant-specific NAC proteins and other transcription factors with a surprising phylogenetic breath. The structure shows how the NAC domain inserts the edge of its core beta-sheet in the major groove (figure), while leaving the DNA largely un-distorted. Recognition of DNA with the edge of a beta-sheet is also believed to be a feature of the WRKY family of transcription factors (Rushton et al. (2010) *Trends Plant Sci* 15(5):247-258), which are found in early eukaryotes and plants. Further, the animal GCM transcription factors use the same binding motif (Cohen et al. (2003) *EMBO J* 22(8):1835-1845). In addition, these three transcription factors share a core beta-sheet with a very similar topology.

The presented NAC:DNA complex structure provides a framework for studying the effects of single amino acids as well as structural features on DNA binding affinity and specificity. Further, we have evidence of limited flexibility of the NAC dimer arrangement, which could explain the limited tolerance in NAC binding site spacing that has been reported (Olsen et al. (2005) *Plant Sci* 169:785-797, Xue (2005) *Plant J* 41:638-649)



Keywords: transcription factor, NAC, low resolution

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Optimising low resolution structural biology techniques

Andrew A. McCarthy,^a Sandor Brockhauser,^a Sean McSweeney,^b and the EMBL-Grenoble/ESRF Joint Structural Biology Group, ^aEuropean Molecular Biology Laboratory, Grenoble Outstation, 6 rue Jules Horowitz, Grenoble 38042, (France).^bEuropean Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP 220 38043 Grenoble, (France). E-mail: andrewmc@embl.fr

The investment in modern equipment and the development of highly automated beamline control software on the public MX-beamlines at the ESRF now allows standard X-ray diffraction experiments, even multiple anomalous diffraction (MAD), to be easily and robustly performed. However the success of X-ray diffraction experiments is still dependent on the quality of the crystals obtained. Most modern structural biology projects have become ever more complex and their success is now often dependent on a combination of low resolution techniques such as EM, X-ray small angle scattering and macromolecular crystallography. Many large and complex macromolecular assemblies often fail to crystallise or at best form few poorly diffracting crystals that are radiation sensitive. Such projects require newly developed equipment and a much more careful approach for data collection [1, 2]. In Grenoble we are developing improved instruments and methods

for optimised low resolution data collection possibilities. Here I will present our current abilities and some future developments for new and challenging structural biology experiments.

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Keywords: macromolecular crystallography, small angle X-ray scattering

MS87.P01

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Preferential enrichment of cocrystals of amino acids and achiral dicarboxylic acid classified as racemic compound

Sekai Iwama, Rajesh Gonnade, Yuko Mori, Kazunori Kuyama, Hiroki Takahashi, Hirohito Tsue, Rui Tamura, *Graduate School of Human and Environmental Studies, Kyoto University, Kyoto (Japan).* 606-8501. E-mail: sekai.i@ax2.ecs.kyoto-u.ac.jp

Preferential enrichment is a symmetry-breaking chiral separation phenomenon that is initiated by the solvent-assisted solid-to-solid transformation of the first-formed metastable polymorphic form into a thermodynamically stable one during crystallization from the supersaturated solution of certain kinds of racemic mixed crystals (i.e., solid solutions or pseudoracemates) composed of two enantiomers in organic solvents without the aid of any external chiral element [1].

We anticipated that the preferential enrichment phenomenon might be observed even for a so-called 'racemic compound', if the following three requirements are satisfied: i) The solubility of the enantiopure sample is higher than that of the corresponding racemic sample. ii) Upon recrystallization of racemic or nearly racemic sample from organic solvents under kinetic conditions, a solid-to-solid polymorphic transition of the initially-formed metastable mixed crystals composed of the heterochiral 1D *R* and *S* chains into the stable mixed crystals mainly comprising heterochiral (*R,S*) chains occurs. iii) In the resulting deposited crystals, the fairly random arrangement of two enantiomers can be retained, without undergoing further solvent-mediated polymorphic transition to give exact racemic compound crystals.

Recently, we reported that other racemic crystals having a regular packing of a pair of *R* and *S* enantiomers in their crystal could also display the 'preferential enrichment' phenomenon. We have found that neutral amino acids, alanine and leucine, exhibited a very similar phenomenon to 'preferential enrichment' [2]. Here we report the successful enantiomeric resolution of other amino acids, such as phenylalanine, histidine, and cysteine with a racemic compound structure, which could be spontaneously resolved into its enantiomeric components by co-crystallization with achiral dicarboxylic acid. For example, repeated recrystallization of the cocrystals of DL-phenylalanine and fumaric acid from the 6-fold supersaturated aqueous solution led to a remarkable alternating enrichment of the two enantiomers up to 85% *ee* in the mother liquor, together with slight enrichment (< 6% *ee*) of the opposite enantiomer in the deposited crystals [3]. The mechanism of preferential enrichment is proposed on the basis of i) the observation of polymorphic transition during crystallization by in situ ATR-FTIR and Raman spectroscopy, ii) the characterization of deposited crystals by X-ray crystallographic analysis and powder XRD measurement, and iii) the optical microscopic and AFM observations of the crystal shape and surface, respectively.

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Keywords: preferential enrichment, enantiomer resolution, complexity

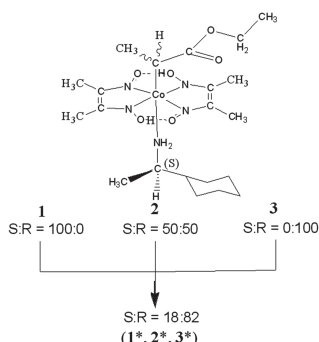
MS87.P02

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Direct observation of chirality inversion only by photo-irradiation in a crystal

Yuji Ohashi, Takeshi Nitami, Akiko Sekine, Hidehiro Uekusa
Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo, (Japan). E-mail: yujihashi@cms.titech.ac.jp

When the crystal of ((S)-1-cyclohexylethylamine)bis-(dimethylglyoximate)((S)-1-(ethoxycarbonyl)ethyl)cobalt(III), (**1**) was irradiated with a halogen lamp, the absolute configuration of the 1-(ethoxycarbonyl)ethyl (ece) group gradually changed from S to R with retention of the single crystal form. After 24 h exposure, the change became within the experimental error and the S:R ratio was found to be 18:82 by X-ray crystal structure analysis. The crystals with the (racemic)- and (R)- ece groups instead of the (S)-enantiomer, (**2**) and (**3**) have the isomorphous structures to the crystal with the (S)-enantiomer. Both of the crystals were also changed to the same structure as that with the (S)-enantiomer on exposure to the halogen lamp. This marvelous ratio of 18:82 was clearly explained with the shape of the reaction cavity for the photo-reactive ece group in each crystal structure. A pseudo isomorphous crystal of the complex with the (S)-enantiomer was obtained containing a water molecule as solvate. The (S)-ece group in the crystal gradually changed to the disordered racemate with retention of the single crystal form. The different reaction pathway between the pseudo isomorphous crystals was explained with the size and shape of the reaction cavity for the photo-reactive ece group.



Keywords: photoreaction, chirality inversion, cobalt complex

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On mixed crystals of chiral organic substances

Nikolay Taratin,^a Arkady Glikin,^a Elena Kotelnikova,^a Heike Lorenz,^b Andreas Seidel-Morgenstern,^b ^aDepartment of Crystallography, Saint-Petersburg State University, Saint-Petersburg (Russia). ^bMax Planck Institute for Dynamics of Complex Technical Systems, Magdeburg (Germany). E-mail: taratin@rambler.ru

Crystallogenic grounds of isomorphism were established

using mainly inorganic model substances [1]. We are extending this concept to chiral organic series. They require special experimental approaches due to some peculiarities in molecular features and phase relations. Detailed examination of phase diagrams and related features of crystal structure and morphology is the necessary basis for further understanding of mixed crystal (solid solution) formation. The results could be useful for pharmacology and agrochemistry.

The system of (S)-(R) enantiomers of an ethanolamine salt of 3-chloromandelic acid (E3CIMA) was investigated. The crystal structure of the pure (R)-E3CIMA was solved in the widespread orthorhombic $P2_12_12_1$ space group. The main feature of the crystal structure of (R)-E3CIMA is a set of hydrogen bonds, a part of these bonds belongs to the chiral center. Changing the lattice parameters versus isomorphous mixture composition was investigated by means of XRPD method. The significant shift of lattice parameters ($\Delta a \sim 0.03 \text{ \AA}$, $\Delta b \sim 0.06 \text{ \AA}$, $\Delta c \sim 0.1 \text{ \AA}$) versus mixture composition was detected. The phase diagram for the (S)-E3CIMA-(R)-E3CIMA system was constructed [2] by means of DSC measurements. The miscibility gap in solid state was detected between 20 and 80 wt.% of (R)-E3CIMA. Mutual solubility in ethanol was measured by means of polythermal method. The solubility increases in a non-linear way from the pure enantiomer to the racemic composition. The width of metastable zone does not change within the mixed crystal region but the pure enantiomers reveal its smallest values. Crystals were grown by evaporation. Their morphology and inhomogeneity were investigated by means of optical microscopy and X-ray microtomography. Crystals of the pure (R)-E3CIMA are well shaped. Crystal morphology depends significantly on the presence of (S)-enantiomer in the (R)-E3CIMA solution. Addition of 10% (S)-E3CIMA changes crystal habit to needle-like and causes defects, such as splitting. More (S)-E3CIMA causes a strong splitting up to formation of spherulites in the racemic solution.

Unlike E3CIMA, molecule of threonine has two chiral centers. Therefore, two enantiomeric (L-Thr-D-Thr, L-alloThr-D-alloThr) and four diastereomeric systems should be considered. The enantiomeric system L-Thr-D-Thr demonstrates the classical conglomerate [3]. Nowadays, the diastereomeric system of L-threonine (L-Thr) and L-allothreonine (L-alloThr) has been examined. Slight differences between XRPD patterns of pure diastereomers and their mixtures were detected. Pattern indexing shows that all the mixtures belong to the orthorhombic $P2_12_12_1$ space group. Cell parameters a and c decrease from the pure substances to mixture compositions ($\Delta a \sim 0.1 \text{ \AA}$, $\Delta c \sim 0.05 \text{ \AA}$) but b increases simultaneously ($\Delta b \sim 0.1 \text{ \AA}$). Changes of lattice parameters versus mixture compositions proved the formation of solid solutions between L-Thr-L-alloThr.

Growth features of mixed crystals appear to be similar for enantiomers and inorganic substances; this is the principal subject for our future investigations.

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Keywords: mixed crystals, isomorphism, enantiomers

MS87.P04

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Crystal handedness and spin chirality of transition metal monosilicides

S. V. Grigoriev,^a D. Chernyshov,^b V.A. Dyadkin,^a D. Menzel,^c V. Dmitriev,^b E.V. Moskvina,^a N.M. Potapova,^a H. Eckerlebe,^d S.V. Maleyev,^a ^aPetersburg Nuclear Physics Institute, Gatchina, 188300