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Keywords: preferential enrichment, enantiomer resolution, complexity

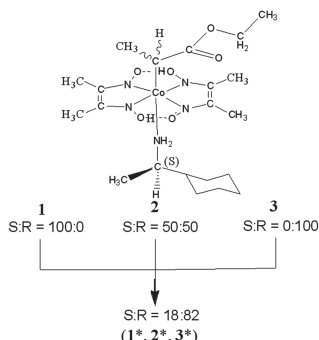
MS87.P02

Acta Cryst. (2011) A67, C748

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

MS87.P03

Acta Cryst. (2011) A67, C748

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.

The work is granted by RFBR (10-05-00891, 10-02-01303).

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Keywords: mixed crystals, isomorphism, enantiomers

MS87.P04

Acta Cryst. (2011) A67, C748-C749

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