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Keywords: preferential enrichment, enantiomer resolution, complexity

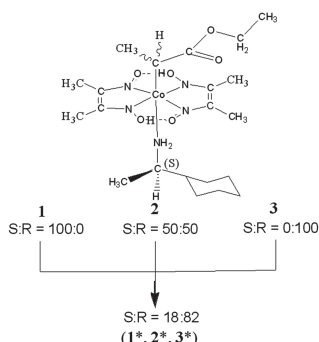
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Direct observation of chirality inversion only by photo-irradiation in a crystal

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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

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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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Crystal handedness and spin chirality of transition metal monosilicides

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The X-ray and polarized neutron diffraction are used to determine the crystal handedness and magnetic chirality of the series of high-purity MnSi single crystals and mixed compounds crystals of $Mn_{1-x}Fe_xSi$ and $Fe_{1-x}Co_xSi$ grown by Czochralski methods [1,2]. To test the possibility to control the crystal handedness of the single crystals we have performed the following experiments with the crystal growth using Czochralski technique. (i) Using as a seed the right-handed crystal $Fe_{1-x}Co_xSi$ with $x = 0.10$ we have grown one series of $Fe_{1-x}Co_xSi$ samples with $x = 0.10, 0.15, 0.20, 0.25, 0.30, 0.50$. (ii) Using as a seed the left-handed crystal with $x = 0.50$ we have grown another series of $Fe_{1-x}Co_xSi$ samples again of different concentrations. The result of these experiments aimed to demonstrate whether handedness of these crystals depends on the concentration of Co, or, it is solely determined by the seed used for this synthesis. The third option could be if the handedness would not depend on a seed and/or concentration x .

In 90% cases the grown sample has been found to be enantiopure and to inherit the crystallographic chirality of its seed crystal. In 10% cases undefined circumstances flip the chirality over for the next progeny or produce a racemic sample. We demonstrate that (i) left and right forms of all transition metal monosilicides can be grown by the Czochralski method, (ii) the magnetic chirality of all $Mn_{1-x}Fe_xSi$ crystals follows its crystallographic counterpart [1], (iii) the opposite coupling between the crystal handedness and the spin chirality has been found for $Fe_{1-x}Co_xSi$ compounds [2].

Knowing the rigid coupling between the structural handedness and magnetic chirality we used the polarised neutron diffraction to indirectly determine the average handedness of six different polycrystalline samples of MnSi with large number of crystallites (100 crystals per cm^3). The average chirality of these polycrystals deviates unexpectedly high from zero. This net chirality is maybe related to the yet poor statistics in the numbers of the left or right crystallites inside the polycrystals.

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Non-centrosymmetric molecules - centrosymmetric structure?

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It is recognized that macroscopically centrosymmetric crystal structures can still give rise to NLO phenomena, due to growth-induced polarization [1]. We can take this one step further, and look at molecules which conformationally, due to their synthesis, inherently are a mixture of centrosymmetric and non-centrosymmetric forms. If the conformational differences are very small, one would in such a case normally come to expect a completely disordered, centrosymmetric crystal structure.

The compound being discussed in this contribution, a double

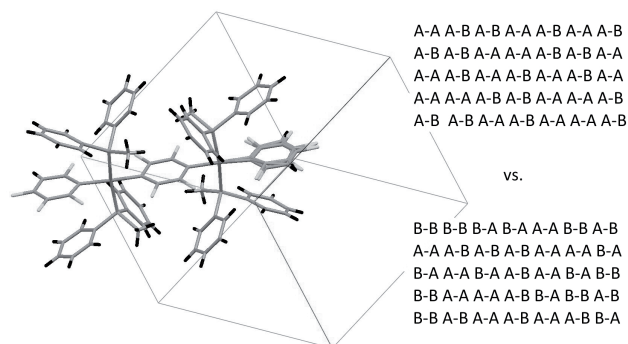
square planar Ni-phenylene complex [2] with 2,3,4,6-F-substituted phenyl rings that are unable to rotate once they bind to the complex, is ideally suited for this kind of study.

At first sight the compound indeed crystallizes in the space group P-1. We will explore the possibilities for experimentally exposing by x-ray crystallography the presence or absence of additional ordering within the crystal by way of growth-induced polarization, as well as the crystallization possibilities that such a substance really has.

These crystallization options for an A-A/A-B type compound consist of either a homogeneous, centrosymmetric, completely disordered structure (see figure, bottom); a racemic twin (i.e. polarization) with a (slight) preference for a particular orientation of one of the two rings; or else what is in fact a completely ordered structure on the molecular level, only allowing for disorder due to the statistical distribution of the second fluorinated ring. This would lead to the existence of large, completely ordered racemic twin domains within the crystal (see figure, top).

The presence or absence of this latter phenomenon would provide details on the process of crystal growth in this particular case.

We will here present the results, which indicate that centrosymmetry is not always what it appears to be at first sight. We have been able to deduce perfect ordering in the growth direction by re-examining different fragments of the same crystal, thus demonstrating that the resulting twin components are different in different regions of the same crystal, and that one ring is in fact completely ordered in domains that are macroscopic.



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Influencing absolute structure determination

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It is well established that the different enantiomers of a chiral material can have significantly different physiological properties. There are many well known, often quoted examples including the terpenes limonene & carvone [1], and the pharmaceuticals ibuprofen, naproxen and thalidomide [2]. As a consequence of this, drug manufacturers and drug authorisation authorities are increasingly concerned about the absolute configuration of active pharmaceutical ingredients. There are a number of "sporting" techniques, but one of the most relied upon is X-ray structure analysis [3], which in appropriate cases can give very reliable results.

The first absolute structure determination, of sodium rubidium