PS11.08.07 GENERALISING THE CONCEPT OF OPTICAL RESOLUTION THROUGH CO-CRYSTALLISATION. K. Simon, Zs. Böcskei, K. Takács, Chinoin Pharmaceuticals, Budapest, Hungary; A. Mravik, D. Kozma, E. Fogassy, Technical University of Budapest, Hungary.

Diastereomeric salt formation is perhaps the most widely used technique for chiral resolution. Here we present a dozen crystal structures in which the principles of this classical method has been extended by utilising the intermolecular interactions between compounds which are not necessarily corresponding acid-base partners.

In our first example chiral acid was applied instead of a chiral base to separate a racemic acid by the mediation of a metal ion. Another case involves the resolution of an alcohol type compound with a chiral acid. A third example presents the investigation of small modifications of the resolving agent versus the efficiency of the resolution. Dramatically different resolving power of tartaric acid derivatives can be rationalised based on hydrogen bonding networks. In the last example we provide a structural explanation for an unsuccessful resolution experiment via camphorsulphonicacid. Due to the relative flexibility of the middle part of the base to be resolved both enantiomer base was found in the crystal structure in an approximate 1:2 ratio.

In conclusion the above examples clearly demonstrate the importance of investigating the entire crystal structure including minor interactions rather than just considering the most obvious salt forming hydrogen bonds.

Structure & Chemical Reactivity

PS11.09.01 SOLID STATE CHEMISTRY OF O-ETHOXY-TRANS-CINNAMIC ACID. Manuel A. Fernandes, C.B. de Koning and D.C. Levendis. Centre for Molecular Design, Chemistry Department, University of the Witwatersrand, Private Bag 3, Wits, 2050, South Africa

o-Ethoxy-trans-cinnamic acid has been found in three polymorphic forms, alpha, beta and gamma , with the form obtained depending on the solvent used to grow the crystal [1, 2 & 3]. The alpha and beta forms react in UV light to form a dimer product unique to the crystal form, 2,2'-diethoxy-alpha-truxillic acid and 2,2'-diethoxy-beta-truxinic acid respectively. No other product is obtained for either crystal form. The gamma form is light stable. This selectivity in the reaction products is due to lattice control over reaction pathways with the reacting double bonds needing to be between 3.6 and 4.1Å apart in order for the reaction to occur. In order to provide information on the ability of the molecular packing to control these reactions, comparisons in the molecular packing between the various crystal types and products of o-Ethoxy-trans-cinnamic acid are to be presented.

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PS11.09.02 SOLID STATE PHOTOISOMERIZATION OF COBALOXIME COMPLEX IN DIFFERENT CLATHRATE CRYSTALS. Daisuke Hashizume and Yuji Ohashi, Department of Chemistry, Tokyo Institute of Technology, Japan

The reactivity in the solid state can be controlled by the environment of the reactive group. The 2-cyanoethyl group bonded to the cobalt atom in some cobaloxime complexes is isomerized to the 1-cyanoethyl group on exposure to visible light in the solid state. For the solid state reaction, the void space, which is called cavity, around the reactive group is an important factor for the rate and the selectivity of the reaction as well as the conformation of the reactive group. As the cavity is made by the surrounding atoms of the reactive group, the reaction can be controlled by the crystal environment.

Recently, we have been found that the (2-cyanoethyl)(isonicotinic acid) cobaloxime complex forms clathrate complexes, (**1, 2**), with dicyclohexylamine and diphenylamine when the cobaloxime complex crystallizes from the methanol solutions containing respective amines.

The crystal structure analyses for **1, 2** and the crystal of the guest molecules, **3**, were performed. The conformation and the cavity of the reactive group are different among the crystals. The reaction rates are clearly found to be controlled by making the clathrate crystals.

Table 1. Crystal Data

	1	2	3
a/Å	17.537(2)	12.440(1)	8.329(2)
b/Å	16.113(7)	12.893(2)	15.209(3)
c/Å	23.487(5)	9.4376(9)	32.055(4)
α/°	–	92.26(1)	–
β/°	94.81(1)	96.081(7)	–
γ/°	–	82.55(1)	–
V/Å^3	6613(3)	1492.0(3)	4060(3)
Z	8	2	8
Space Group	$P2_1/n$	$P\bar{1}$	$Pbcn$

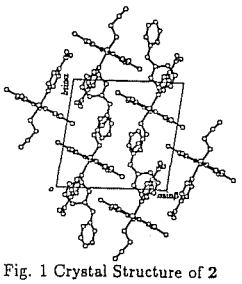

Fig. 1 Crystal Structure of **2**

PS11.09.03 SOLID-STATE PHOTOISOMERIZATION OF 4-BUTEN-1-YL COBALOXIME COMPLEXES. Taro Yamada and Yuji Ohashi Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

We have found that trans-2-buten-1-yl cobaloxime complexes isomerize to *cis* isomer without degradation of the single crystal form on exposure to visible light. Recently we prepared several 4-buten-1-yl cobaloxime complexes with different axial base ligands. ^{1}H-NMR measurement showed the complex isomerized to the 2-buten- 1-yl cobaloxime complex when it was irradiated with a Xe-lamp for a day. This means allylic migration of the methylenic hydrogen atom occurred in the solid-state. In order to examine the reason why the migration can occur, the crystal structures of the 4-buten-1-yl complexes with triphenylphosphine, 3-chloropyridine, aniline, and water as axial base ligands were analyzed by X-rays. The space group of the 3chloropyridine complex crystal is P2/a and two 4-butenyl groups related by a 2-fold axis face each other in the crystal structure (Fig. 1). The molecular structure (Fig. 2) showed disordered 4-butenyl group. Such disordered structures were also observed in the other crystals. The structural change from 4-buten-1-yl to 2-buten-1-yl may easily occur because of the disordered structure with large void space.

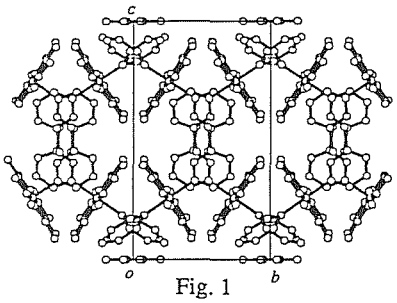

Fig. 1

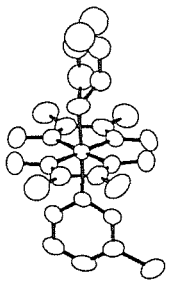

Fig. 2