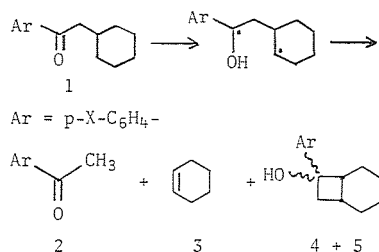


04.4-4 MULTI-STEP CRYSTALLINE-STATE RACEMIZATION OF CYANOETHYL GROUP IN SOME COBALOXIME COMPLEXES. By Yasuko Tomotake, Yuji Ohashi and Yoshio Sasada, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama, Japan.

It has been found that the crystals of [(R)-1-cyanoethyl](3-methylpyridine)- and [(R)-1-cyanoethyl](piperidine)cobaloxime, 1 and 2 respectively, reveal crystalline-state racemization with a new characteristic mode. Crystals of 1 are orthorhombic,  $P2_12_12_1$ ,  $a=11.689(3)$ ,  $b=38.35(2)$ ,  $c=9.212(2)$  Å at 293 K and  $Z=8$ . The unit cell was changed gradually by X-ray exposure;  $a=11.732$ ,  $b=38.63$  and  $c=9.352$  Å after 115 h, the space group being unaltered. X-ray analysis of every stage showed that only one independent molecule in an asymmetric unit, B, undergoes racemization. At 343 K, the cell dimensions of unreacted crystals are:  $a=11.758$ ,  $b=38.52$  and  $c=9.198$  Å. X-ray irradiation at this temperature results in racemization of both of the independent molecules. Change of the occupancy factors of newly developed enantiomers indicated that the rate of inversion of the A molecule is far slower than that of B, and that of B at room temperature is faster than at high temperature. Crystals of 2 are orthorhombic,  $P2_12_12_1$ ,  $a=11.733(2)$ ,  $b=31.026(5)$ ,  $c=11.311(2)$  Å and  $Z=8$ . No crystalline-state reaction was observed at 293 K. At 363 K, only one of the two independent molecules was racemized, but the change of the cell dimensions is very small. Although a reaction similar to 1 was expected, the crystals were broken at higher temperatures. Cavities calculated for the reactive groups in the above cases well explain such complicated behaviour of reactions in these crystals.

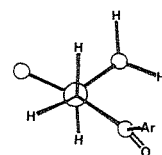
04.4-5 SOLID-STATE PHOTOCHEMISTRY OF  $\alpha$ -CYCLOHEXYL-ACETOPHENONES. By Sara Ariel, V. Ramamurthy, John R. Scheffer and James Trotter, Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6

Photolysis in solution or in the solid state of  $\alpha$ -cyclohexylacetophenones (1) yields a mixture of the corresponding acetophenones (2) and cyclohexene (3) [formed by bond cleavage] and the cyclobutanols 4 and 5 [formed by cyclization].



In solution the cyclobutanols are the major products; in the solid state much less cyclobutanol formation is observed. To obtain quantitative information on the mechanism of these processes, the crystal structures of 1a-e have been determined. All five molecules crystallize with a common conformation in which the carbonyl-containing side chain is equatorial with respect to the chair-shaped cyclohexane ring. In this

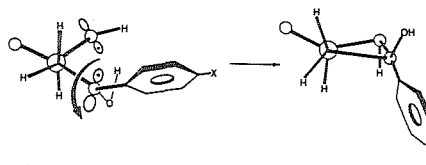
conformation the equatorial hydrogen atom H<sub>e</sub> is favourably oriented for abstraction by oxygen via a boat-like six-atom geometry:



The O...H<sub>e</sub> distances ( $\sim 2.6$  Å) are within the suggested upper limit of 2.72 Å (van der Waals radii sum) for this type of process. The angle  $\tau$ , a measure of the displacement of the O...H<sub>e</sub> vector from the carbonyl plane, is in the range 42-50°.

	X	O...H <sub>e</sub>	$\tau_e$
1a	CH <sub>3</sub>	2.60 Å	49.6°
1b	Cl	2.60	42.0
1c	CH <sub>3</sub> O	2.61	42.5
1d	COOH	2.60	43.7
1e	CN	2.65	42.1

While a coplanar arrangement ( $\tau = 0^\circ$ ) is most favourable, a  $\cos^2\tau$  dependence for abstraction has been suggested, which in the present examples would reduce the relative reactivity by a factor of only two. The reduced amount of cyclization in the solid state can be ascribed to the fact that the formation of cyclobutanols requires extensive atomic movement, most notably large displacements of the bulky aryl groups from their original positions, a process which is topochemically unfavourable in the solid state:



04.4-6

"X-Ray Study of Some Solid State Reactions in Sn-Pb Alloys"

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(Fac. of Science, Suez Canal and Minia Univ)

Tin alloys with 0.01, 0.05 and 0.1 Pb% were prepared and homogenised by solution heat treatment in one phase region ( $\beta$ -phase) for 24 hours. The alloys were plastically deformed (90%) by rolling. They were then isothermally heat treated at 170°C and 190°C in silicon oil bath for different times from 0.5 to 60 min. Both hardness and X-ray diffraction measurements were used to follow the characteristics changes. It was found that at any heating time, as the Pb% increases the hardness increases due to solid solution hardening. The relation between hardening and heating time showed softening and hardening associated with different solid state reactions. Firstly, softening was observed and the hardness value reaching a minimum in less than three minutes. This is due to recrystallisation of the highly

deformed specimens. As heating time increases the alloys were hardened and then softening again. This phenomena was explained by age-hardening and over aging. Lattice distortion, which is associated with hardening, were confirmed by X-ray diffraction analysis. The  $\Delta a$  values were calculated taken the lattice parameter,  $a$ , at 3 minutes as origin. The measurement of lattice parameters showed a good correlaton with the hardness results. Lattice distortion was firstly decreased in the recrystallisation stage and then was increased as the age-hardening process began. Over aging leads to decrease in lattice distortion due to disappearance of the coherent strains. It can be concluded that during heat treatment of highly deformed Sn-Pb alloys the following processes take place : (a) softening (recrystallisation), (b) hardening (age-hardening) and (c) softening (over aging). Therefore, high plastic deformation instead of quenching may influence the mutual interaction between the solid-state reactions during the subsequent heat treatment.

**04.5-1 INTERMOLECULAR TRANSITION DIPOLE-DIPOLE COUPLING BETWEEN THE NON-CYANIDE LIGANDS IN SOME CRYSTALLINE PENTACYANO-L-METALLATES.** By O.E. Piro and, in part, S.R. González and P.J. Aymonino, Depts of Physics and Chemistry, Faculty of Exact Sciences, National Univ. of La Plata, C.C.67, 1900 La Plata, R. Argentina.

The nature and magnitude of intermolecular vibrational coupling of NO groups in  $\text{Sr}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 4\text{H}_2\text{O}$  and  $\text{Ba}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  and of the antisymmetric stretching mode of  $\text{N}_3$  ligands in  $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]\cdot 2\text{H}_2\text{O}$  were studied on the basis of reported crystallographic and spectroscopic data. In all three compounds, the non-cyanide ligands of the complex ions are piled up in an antiparallel quasi-eclipsed fashion at distances of about  $4 \text{ \AA}$ , forming linear chains in the crystals. The fine structure of the NO stretching band in the IR spectra of polycrystalline  $\text{Sr}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 4\text{H}_2\text{O}$  isotopic mixtures and of single crystals of  $\text{Ba}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  can be interpreted in terms of a linear-chain model of  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  ions coupled through their NO ligands via transition dipole-dipole forces. By this model, the value  $|(\partial\mu/\partial S)_0| = 13 \text{ Debye/\AA}$  is obtained for the NO dipole-moment derivative and  $f_1 = 0.172$  and the average  $\bar{f}_1 = 0.189 \text{ mdyne/\AA}$  values for the force constants that respectively couple the NO stretching vibration in the barium and strontium salts. Similar calculations for  $\text{K}_3[\text{Co}(\text{CN})_5\text{N}_3]\cdot 2\text{H}_2\text{O}$  (S.G. $P\bar{1}$ ) explain the Davydov splitting of  $25 \pm 2 \text{ cm}^{-1}$  observed in the frequencies of the IR- and Raman-active vibrations associated with the  $\text{N}_3$  antisymmetric stretching mode. The value  $|(\partial\mu/\partial Q_3)_0| = 263 \text{ (esu)/gr}^{1/2}$  was obtained for the dipole-moment derivative of this mode, and the value  $f_3 = 0.071 \text{ mdyne/\AA}$  for the force constant that couples such vibrations in the crystal.

**04.5-2 CRYSTAL STRUCTURES OF PERMETHYLATED  $\alpha$ -CYCLODEXTRIN COMPLEXES WITH L- AND D-MANDELIC ACIDS**

By K. Harata, Research Institute for Polymers and Textiles, 1-1-4 Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan; K. Uekama, M. Otagiri, and F. Hirayama, Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-honmachi Kumamoto 862, Japan.

Cyclodextrins form diastereoisomers by including optically active guests within the cavity of the macrocyclic ring. Permethylated cyclodextrins are expected to have higher stereo-selectivity in the complex formation with chiral guests because of the distorted conformation of the macrocyclic ring. The crystal structures of permethylated  $\alpha$ -cyclodextrin (methyl- $\alpha$ -CDx) complexes with L- and D-mandelic acids (L-MA and D-MA, respectively) are reported, and the chiral recognition in the crystalline state is demonstrated.

The methyl- $\alpha$ -CDx complexes with L- and D-mandelic acids crystallized in the space group  $P2_1$  with the following crystal data: (1) L-MA complex,  $\text{C}_{54}\text{H}_{96}\text{O}_{30} \cdot \text{C}_8\text{H}_8\text{O}_3 \cdot 3\text{H}_2\text{O}$ , F.W.=1431.5,  $a=13.123(2)$ ,  $b=23.187(4)$ ,  $c=13.113(2) \text{ \AA}$ ,  $\beta=107.19(1)^\circ$ ,  $D_x=1.247 \text{ g}\cdot\text{cm}^{-3}$ ; (2) D-MA complex,  $\text{C}_{54}\text{H}_{96}\text{O}_{30} \cdot \text{C}_8\text{H}_8\text{O}_3 \cdot 2\text{H}_2\text{O}$ , F.W.=1413.5,  $a=11.624(2)$ ,  $b=23.739(4)$ ,  $c=13.786(2) \text{ \AA}$ ,  $\beta=106.56(1)^\circ$ ,  $D_x=1.289 \text{ g}\cdot\text{cm}^{-3}$ . The structures of the above complexes were solved by the trial-and-error method combined with the rigid-body least-squares technique and refined by the block-diagonal least-squares method to the R-values of 0.087 for 4837 reflections (L-MA complex) and 0.055 for 4925 reflections (D-MA complex).

As shown in Fig. 1A, the methyl- $\alpha$ -CDx molecule of the L-MA complex has a pseudo two-fold symmetry. A water molecule is included at the O(6) side of the cavity, and links two glucose residues facing each other by the O(6)  $\cdots$  water  $\cdots$  O(6) hydrogen-bond bridge. The phenyl group of L-MA is partly included at the O(2), O(3) side of the methyl- $\alpha$ -CDx ring, while the hydroxyl and carboxyl groups, protruding outside the cavity, form hydrogen bonds with water molecules. The methyl- $\alpha$ -CDx molecule of the D-MA complex is distorted so as to include tightly the phenyl group of D-MA (Fig. 1B). The O(6) side of the cavity is capped by an O(6)CH<sub>3</sub> methoxyl group. The hydroxyl group of D-MA is hydrogen-bonded to an O(2) oxygen atom of methyl- $\alpha$ -CDx, while the carboxyl group forms the hydrogen bond with an O(6) oxygen atom of the adjacent methyl- $\alpha$ -CDx molecule. Therefore, methyl- $\alpha$ -CDx binds the D-MA molecule more strongly through the induced-fit type conformational change and the host-guest hydrogen bond.

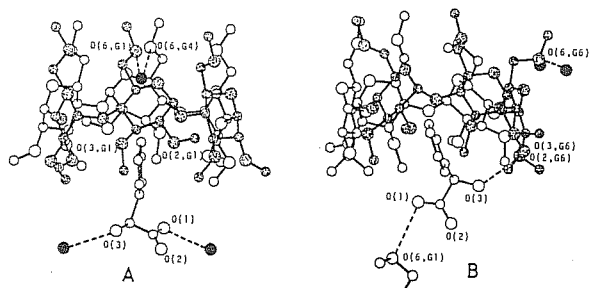


Fig. 1. The inclusion feature of the methyl- $\alpha$ -CDx complexes with L-MA (A) and D-MA (B). Water molecules are shown by full circles.