

**04.4-08** EVIDENCE FOR A TRAPPED REACTION INTERMEDIATE IN THE CRYSTAL OF p-n-PROPOXY-CINNAMIC ACID. By R.F. Bryan, Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, U.S.A.

The crystal structure of the monoclinic form of p-n-propoxycinnamic acid has been determined, and shown to be of the  $\alpha$ -type with the double bonds of adjacent parallel dimers disposed about crystallographic centers of symmetry to yield non-bonded distances between the atoms in these bonds of 3.56 and 3.72 Å.

Conventional least-squares refinement of the structure gave  $R = 0.053$ . A final difference electron-density map was quite featureless, except for two well-defined peaks of height 0.30 and 0.35 e/Å<sup>3</sup> adjacent to the atoms of the double bond and in the plane formed by the double bonds of two centrosymmetrically related molecules. The peaks therefore correspond to a centrosymmetric four-membered ring with inter-peak distances of 1.25 and 1.74 Å. One peak is 1.63 Å from C(4) of the phenyl ring, and the other is 1.96 Å from the carboxy carbon of the cinnamic acid. This geometry, and the total absence of peaks suggesting any migration of the phenyl rings or carboxy groups, suggests formation of an intermediate in the expected photodimerization of the cinnamic acid to the corresponding  $\alpha$ -truxillic acid, which is then trapped in the crystal.

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**04.4-09** CRYSTALLINE-STATE RACEMIZATION OF COBALOXIME COMPLEXES BY X-RAY EXPOSURE. IV. [(S)-1-CYANOETHYL][PYRIDINE]COBALOXIME. By Y. Ohashi, K. Yanagi, Y. Sasada, and Y. Ohgo,\* Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Yokohama 227, Japan and \*Niigata College of Pharmacy, Niigata 950-21, Japan

We have found that the crystal of [(R)-1-cyanoethyl][(S)(-)- $\alpha$ -methylbenzylamine]cobaloxime changes its unit-cell dimensions by X-ray exposure without degradation of a single crystal form, and have proved from the electron density calculation that the change reflects the racemization of the cyanoethyl group (Ohashi et al., Nature (1977) 267, 142).

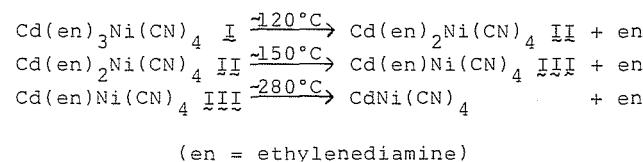
In searching another example of the crystalline state reaction, we found that the crystal of title complex also changes its unit-cell dimensions by X-ray exposure. However, the change was different from that of the above crystal since the volume of the unit-cell gradually decreased and the space group changed from  $P2_1$  to  $P2_1/n$ . The crystal structure at the initial, intermediate and final stages revealed that two crystallographically independent complexes are contained in the crystal at the initial stage and the cyanoethyl group of one complex is changed from the S configuration to R, another one remaining unaltered. The two complexes approach each other and the inversion center appears between them at the final stage. This means that the ordered enantiomeric structure is transformed to the ordered racemic one. The mechanism of such an unusual transformation is explained by the packing mode of each complex in the crystal.

**04.4-10** CRYSTALLINE-STATE RACEMIZATION OF COBALOXIME COMPLEXES BY X-RAY EXPOSURE. V. EXPERIMENTS AT HIGH TEMPERATURES AND A NEW TYPE OF RACEMIZATION. By Y. Ohashi, T. Kurihara, Y. Sasada, and Y. Ohgo,\* Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Yokohama 227, Japan and \*Niigata College of Pharmacy, Niigata 950-21, Japan

We have found that the cyanoethyl group of some cobaloxime complex crystals is racemized by X-rays without degradation of a single crystal form. When the crystals were cooled below 173 K, the racemization was no longer detectable. From the structure analyses at 173 K, it was proved that the void space around the cyanoethyl group is essential for the racemization (Ohashi et al., Chem. Lett., 1978, 457; *ibid.*, 1978, 743). These results suggested that the experiments at high temperatures should give further interesting information. The following three complexes were examined. (1) For the crystal of [(R)-1-cyanoethyl][(S)(-)- $\alpha$ -methylbenzylamine]cobaloxime described above, the rate of the racemization at 343 K became faster than that at 293 K, but the change of the cell dimensions was smaller than that at 293 K. (2) The crystal of [(R)-1-methoxycarbonylethyl][pyridine]cobaloxime also revealed the crystalline-state racemization by X-rays. The rate of the racemization was very slow at 293 K but accelerated at 343 K. The space group changed from  $P2_1$  to  $P2_1/n$ . The racemization occurs from a disordered enantiomeric structure to a disordered racemic one. (3) The crystal of [(R)-1-methoxycarbonylethyl][(R)(+)- $\alpha$ -methylbenzylamine]cobaloxime did not show the racemization even at 343 K.

**04.4-11** TOPOTACTICALLY RELATED Cd(en)<sub>x</sub>Ni(CN)<sub>4</sub> COMPLEXES. By Geoffrey B. Jameson, Wilhelm Bachmann, Hans Rudolf Oswald and Erich Dubler, Institute of Inorganic Chemistry, University of Zürich, Winterthurerstr. 190, 8057 Zürich, Switzerland.

In a topotactic process reaction and rearrangement of atoms in the crystalline state occur in geometrically specific ways (Günter and Oswald, J. Solid State Chem. (1977) 21, 211). The following sequence of reactions (as evidenced by thermogravimetry-mass spectrometry) have been shown to occur topotactically by single-crystal X-ray diffraction methods:



The crystal structures of II and III have been determined. Relevant crystal and refinement data for III are: orthorhombic, space group  $Pbcn$ ;  $a = 9.067(3)$ ,  $b = 10.203(2)$ ,  $c = 11.267(3)$  Å;  $Z = 4$ ;  $\rho_{\text{obs}} = 2.14(1)$ ,  $\rho_{\text{calc}} = 2.14$  gm cm<sup>-3</sup>;  $R = 0.038$ ,  $R_w = 0.027$  for 1327 unique observed reflections in the range  $3.5 < 2\theta < 60^\circ$  for Mo K $\alpha$  radiation. The structure is a three dimensional network with CN ligands bridging Cd and Ni atoms. The Ni coordination is square planar with four C-bonded CN ligands. The Cd coordination is distorted octahedral with one bidentate en ligand and four N-bonded CN ligands; the two CN ligands trans to the en ligand are substantially bent ( $152.5^\circ$ ) at the N atom.

Relevant crystal and refinement data for **II** are: monoclinic, space group  $P2_1/n$ ;  $a = 11.654(3)$ ,  $b = 9.270(3)$ ,  $c = 13.951(5)$  Å,  $\beta = 106.26(1)^\circ$ ;  $Z = 4$ ;  $\rho_{\text{obs}} = 1.82(1)$ ,  $\rho_{\text{calc}} = 1.83$  gm/cm<sup>3</sup>; 3744 reflections in the range  $3.5 < 2\theta < 70^\circ$  for Mo  $K\alpha$  radiation. Two CN ligands, bridging Cd to Ni, are N-bonded in cis configuration around Cd; octahedral coordination is completed by two en ligands. Two non-bridging CN ligands complete a square-planar geometry of C-bonded CN ligands around Ni. This series of complexes provides an unusual opportunity to study geometrically specific bond-breaking and formation processes in the crystalline state.

#### 04.4-13 DEHYDRATION REACTION MECHANISMS IN SOME LAYERED MINERAL CALCIUM ARSENATES.

By M. Catti and G. Ivaldi, Istituto di Mineralogia, Cristallografia e Geochimica, Università di Torino, via S. Massimo 22, 10123 Torino, Italy.

Paths of reaction were determined by structural methods for two solid-state single-crystal transformations:  $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 9\text{H}_2\text{O}$  (ferrarisite)  $\rightarrow$   $\text{Ca}_5(\text{HAsO}_4)_2(\text{AsO}_4)_2 \cdot 5\text{H}_2\text{O}$  (dimorph of vladimirite), and  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 11\text{H}_2\text{O}$  (new mineral)  $\rightarrow$   $\text{Ca}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$  (rauenthalite). Crystal data of these triclinic phases (space group  $P\bar{1}$ ), numbered as (1), (2), (3), (4) are shown below:

	a(Å)	b(Å)	c(Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	Z
(1)	8.294	6.722	11.198	106.16	92.94	99.20	1
(2)	8.286	6.673	9.743	86.58	111.10	99.74	1
(3)	12.563	12.181	6.205	88.94	91.67	113.44	2
(4)	12.564	12.169	6.195	89.09	79.69	118.58	2

Structural data were previously reported for ferrarisite (Catti et al., Bull. Minéral. (1980) 103, 541) and the new mineral (3) (Catti et al., ECM-6 Coll. Abstr. (1980), 120); the structures of phases (2) and (4) were solved by direct methods and refined to  $R=0.088$  and  $0.062$  on the basis of 1200 and 1003 counter reflections (Mo $K\alpha$  radiation), respectively. The dehydration reaction (1)  $\rightarrow$  (2) occurs at 60 °C preserving the single-crystal integrity; both phases show structures built up by isostructural (001) layers of As and Ca coordination polyhedra, which sandwich Ca octahedra lying on symmetry centres in (1) and disordered over centrosymmetrically-related positions in (2). Layers are shifted and differently spaced in the two structures, as is shown by the different c,  $\alpha$  and  $\beta$  cell constants. During the dehydration process, four inter-layer H<sub>2</sub>O molecules per unit-cell are lost, three of which come statistically from either set of centrosymmetrically-related Ca-coordinated molecules. This random mechanism of the reaction causes the inter-layer Ca atoms to get disordered, while facing layers slide and approach each other in order to fill the empty coordination sites of Ca octahedra.

#### 04.4-12 COPPER SPECIES WITHIN ZEOLITE A. Han Sik Lee and Karl Seff, Chemistry Department, University of Hawaii, Honolulu, Hawaii 96822, U.S.A.

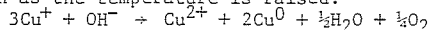
An intrazeolitic reduction product of Cu<sup>2+</sup> catalyzes the partial oxidation of small hydrocarbons and the oxidation of NO and CO. This work was initiated to learn more about the intrazeolitic chemistry of Cu.

Cu<sup>2+</sup> in dilute aqueous solution destroys zeolite A. From aqueous ammoniacal solution, two Cu<sup>2+</sup> ions can be introduced per unit cell at 25°C. They occupy non-equivalent sites, both far from the zeolite framework, which suggests the stoichiometry  $(\text{CuOH}^+)_2(\text{NH}_4^+)_{10}\text{-A}$  or  $(\text{HOCuOH})_2(\text{NH}_4^+)_{12}\text{-A}$ . ( $\bar{a}$  in  $Pm\bar{3}m = 12.369(2)$  Å;  $\bar{R}$  ca 0.06; A is the zeolite framework,  $\text{Si}_{12}\text{Al}_{12}\text{O}_{48}^{12-}$ .) Upon evacuation at 25°C,  $(\text{CuOH}^+)_2(\text{NH}_4^+)_{10}\text{-A}$ , in which Cu<sup>2+</sup> is trigonal pyramidal, forms. ( $\bar{a} = 12.280(2)$  Å;  $\bar{R}$  ca 0.06) Upon evacuation at elevated temperatures, the NH<sub>4</sub><sup>+</sup> ions decompose, as do, in turn, the crystals.

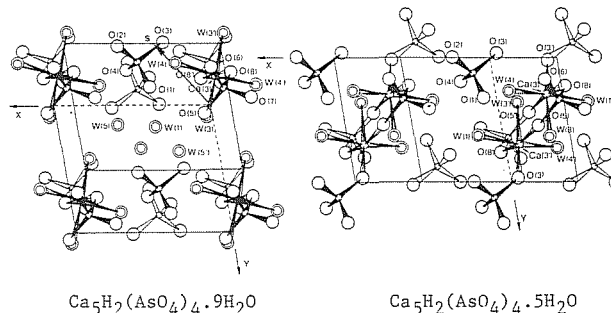
Cu<sup>2+</sup> exchange from aqueous ammonia solution in a bomb at 100°C yielded good crystals with 8 Cu ions per unit cell. Because only 6 Cu<sup>2+</sup> ions are needed to balance the negative charge of the zeolite framework, it is clear that either some Cu<sup>2+</sup> has been reduced or some OH<sup>-</sup> ions have entered the zeolite. Evacuation yields

- $(\text{Cu}^{2+})_5\text{Cu}^+(\text{Cu}^+-\text{OH}^--\text{Cu}^+)\text{-A}$ . ( $T = 350^\circ\text{C}$ ,  $\bar{a} = 12.146(5)$  Å,  $\bar{R} = 0.073$ )
- $(\text{Cu}^{2+})_5(\text{Cu}^+)_{1.25}(\text{Cu}_3^+)_{0.25}(\text{Cu}^+-\text{OH}^--\text{Cu}^+)_{0.5}\text{-A}$ . ( $T = 450^\circ\text{C}$ ,  $\bar{a} = 12.192(2)$  Å,  $\bar{R} = 0.078$ )
- $(\text{Cu}^{2+})_6\text{-A}$ . ( $T = 500^\circ\text{C}$ ,  $\bar{a} = 12.208(15)$  Å,  $\bar{R} = 0.065$ )

(The above formulas are relatively careful surmises.) All Cu<sup>2+</sup> ions in the activated structures lie in 6-ring planes and some are 3-coordinate. O<sub>2</sub>, H<sub>2</sub>O, and Cu leave the zeolite according to the following net reaction as the temperature is raised:



This work was sponsored by NSF Grant No. CHE77-12495.



The dehydration reaction (3)  $\rightarrow$  (4) occurs very slowly in dry air at room temperature, and most natural crystals of the higher hydrate (3) are actually oriented intergrowths of both phases. The two structures are formed by isostructural (100) layers of As and Ca coordination polyhedra, which sandwich three and two Ca which are not coordinated by water molecules per unit-formula, respectively. A relative shift of layers in the two minerals is shown by the different values of the  $\beta$  and  $\gamma$  angles. In the dehydration process one inter-layer water molecule is lost, and hydrogen bonds are rearranged through a relative sliding of adjacent layers.