Relevant crystal and refinement data for $\underline{II}$ are: monoclinic, space group $P2_1/n$; $a = 11.654(3)$, $b = 9.270(3)$, $c = 13.951(5)$ Å, $\beta = 106.26(1)°$; $Z = 4$; $\rho_{obs} = 1.82(1)$, $\rho_{calc} = 1.83$ gm/cm^3; 3744 reflections in the range $3.5 < 2\theta < 70°$ for Mo Kα 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.

04.4-12   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^{2+} 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^{2+} in dilute aqueous solution destroys zeolite A. From aqueous ammoniacal solution, two Cu^{2+} 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 $(CuOH^+)_2(NH_4^+)_{10}$-A or $(HOCuOH)_2(NH_4^+)_{12}$-A. ($\underline{a}$ in $\underline{Pm3m}$ = 12.369(2) Å, $\underline{R}$ $\underline{ca}$ 0.06; A is the zeolite framework, $Si_{12}Al_{12}O_{48}^{-12}$.) Upon evacuation at 25°C, $(CuOH^+)_2(NH_4^+)_{10}$-A, in which Cu^{2+} is trigonal pyramidal, forms. ($\underline{a}$ = 12.280(2) Å; $\underline{R}$ $\underline{ca}$ 0.06) Upon evacuation at elevated temperatures, the NH_4^+ ions decompose, as do, in turn, the crystals.

Cu^{2+} 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^{2+} ions are needed to balance the negative charge of the zeolite framework, it is clear that either some Cu^{2+} has been reduced or some OH$^-$ ions have entered the zeolite. Evacuation yields
a. $(Cu^{2+})_5Cu^+(Cu^+-OH^--Cu^+)$-A.
       (T = 350°C, $\underline{a}$ = 12.146(5) Å, $\underline{R}$ = 0.073)
b. $(Cu^{2+})_5(Cu^+)_{1.25}(Cu_3^+)_{0.25}(Cu^+-OH^--Cu^+)_{0.5}$-A.
       (T = 450°C, $\underline{a}$ = 12.192(2) Å, $\underline{R}$ = 0.078)
c. $(Cu^{2+})_6$-A. (T = 500°C, $\underline{a}$ = 12.208(15) Å, $\underline{R}$ = 0.065)
(The above formulas are relatively careful surmises.) All Cu^{2+} ions in the activated structures lie in 6-ring planes and some are 3-coordinate. O_2, H_2O, and Cu leave the zeolite according to the following net reaction as the temperature is raised:
$$3Cu^+ + OH^- \rightarrow Cu^{2+} + 2Cu^0 + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2$$

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: $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 9H_2O$ (ferrarisite) $\rightarrow Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 5H_2O$ (dimorph of vladimirite), and $Ca_3(AsO_4)_2 \cdot 11H_2O$ (new mineral) $\rightarrow Ca_3(AsO_4)_2 \cdot 10H_2O$ (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)	α(°)	β(°)	γ(°)	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 (MoKα 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, α and β cell constants. During the dehydration process, four inter-layer H_2O 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.

$Ca_5H_2(AsO_4)_4 \cdot 9H_2O$ $Ca_5H_2(AsO_4)_4 \cdot 5H_2O$

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 β and γ angles. In the dehydration process one inter-layer water molecule is lost, and hydrogen bonds are rearranged through a relative sliding of adjacent layers.