

04.2-7 EVOLUTION OF BaC_2O_4 , $H_2C_2O_4$, xH_2O STRUCTURE IN RELATION WITH x . By O. Chaix-Pluchery, J. Bouilliot, Institut Laue-Langevin, 156X, 38042 Grenoble Cedex, France and J.C. Mutin, J.C. Niepce, Laboratoire de Réactivité des Solides, Fac. Sciences Mirande, Dijon, France

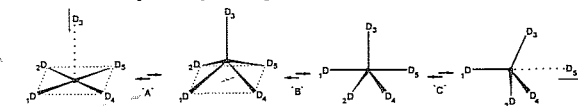
In the framework of the study of the precursor states preceding the crystalline structure transformation associated with a decomposition reaction of the type Solid 1 \rightarrow Solid 2 + Gas, we have studied the dehydration reaction of $BaC_2O_4 \cdot xH_2O$ into β - BaC_2O_4 , $H_2C_2O_4$ (or 1/1/2 into β 1/1/0). Precursor states of the structural transformation associated with a modification of the chemical composition of the initial material have been observed. 1/1/2 progressively loses water without any transformation of its crystalline structure into β 1/1/0. It happens for various amounts of water lost depending on the water vapour pressure. If this pressure is sufficiently low, 1/1/2 can lose all its 2 water molecules and becomes anhydrous (α 1/1/0). The main framework of the crystalline structure of 1/1/2 is preserved during the loss of water. Neutron diffraction experiments show how the hydrogens behave during the dehydration.

04.2-8 SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF MAGNETIC INTERACTING BIMETALLIC CDTA COMPLEXES. By A. Fuertes, C. Miravittles, E. Escrivá, D. Beltran. Instituto "Jaime Almera" del CSIC, Barcelona y Departamento de Química Inorgánica Facultad de Ciencias Químicas, Valencia. Spain.

Solid bimetallic ethylenedinitrilotetraacetic acid (EDTA) complexes of bivalent transition metal ions, $M(H_2O)_4 M'(EDTA) \cdot 2H_2O$, constituted by alternating ordered chain-forming paramagnetic metal complex ions, were the first example of "ferrimagnetic-like one-dimensional systems". EDTA-like polycarboxylic ligands are good candidates to form similar compounds. CDTA(1,2-trans cyclohexylenedinitrilotetraacetic acid) is a more rigid ligand than EDTA and forms hexadentate $M^{II}CDTA^{2-}$ complexes in solution that are however very inert versus metal displacement reactions due to hindering on the chelate rings from the repulsions with the cyclohexane moiety. Because that, non-equilibrium systems like $M'CDTA^{2-}(aq) + M^{2+}(aq)$ (where the formation constants are $K(M) \gg K(M')$) can exist indefinitely in solution. This allows us to design synthetic paths of "metastable crystalline bimetallic complexes", $M(H_2O)_x M'CDTA \cdot yH_2O$ that are compositional isomers of the "stable" ones $M'(H_2O)_x MCDTA \cdot yH_2O$. Various crystalline structures have been distinguished by X-ray diffraction: (I) $Cu_2CDTA \cdot 4H_2O$ (isolated $S=1/2$ chains); (II) $M'CDTA \cdot 6H_2O$ ($M = Ni, Zn, Co, Mn; M' = Cu, Ni$)—that behave as magnetic dimers at $T < 10K$; (III) $CuNiCDTA \cdot 6H_2O$, that is an 1/2-1 alternating spin ordered chain; (IV) $Zn_2CDTA \cdot 9H_2O$. The study of compounds $MZnCDTA, MCoCDTA$ and $MMnCDTA$ is in progress.

04.3-1 CHEMICAL REACTION PATHWAYS FROM CRYSTALLINE STRUCTURES: SUBSTITUTION REACTIONS AT TETRAHEDRAL ZINC AND SQUARE-PLANAR NICKEL COMPLEXES. By T.P.E. Auf der Heyde, University of the Western Cape, Bellville, South Africa and L.R. Nassimbeni, University of Cape Town, Cape Town, South Africa.

The structure correlation principle (Bürgi, H.B.; Dunitz, J.D.; *Acc. Chem. Res.* 1983, 16, 153-161) has been applied to five-coordinate zinc and nickel complexes in order to map the mechanism for a bimolecular ligand substitution reaction at typical tetrahedral and square-planar centres. Evidence for the following mechanistic pathways is presented:



Tetrahedral zinc complexes are shown to undergo a reversible ligand association reaction (C), yielding a trigonal bipyramidal (TBP) intermediate, which can then either dissociate (C) or pseudorotate via the Berry mechanism (B) into a square-pyramidal (SQP) conformation. This latter step is shown to lead into a "cul-de-sac" in terms of dissociation of the intermediate, since TBP conformation seems to be a prerequisite for axial departure of the leaving group. Square planar nickel complexes are shown to undergo a reversible ligand association reaction (A) leading to a SQP intermediate, which may pseudorotate via the Berry mechanism (B) into a TBP. Dissociation of the five-coordinate intermediate may proceed either via apical departure from the SQP (A), or via axial departure from the TBP (C). The reaction coordinates thus derived are compared with theoretically predicted ones, and are supported by a large amount of experimental observations.

04.3-2 Simultaneous Double N-Inversion Pathway

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The pathway for simultaneous double N-inversion has been derived from geometric data given by crystal structure determinations of various compounds containing the 1,2,4-triazolidinedione ring. Bond lengths and angles in this fragment are functions of the degree of flattening at the two mutually-bonded N atoms.

Two parameters were used to define the flattening at the N atoms; the out-of-plane displacement of the N-N bond (Δ) and the average of the valence angles at the N atoms (α_{av}). Bond lengths and angles are linearly related to α_{av} and logarithmically to Δ .

Extrapolation of the internal parameters according to their dependence on the degree of planarity, provides the fragment's geometry at the transition state of the inversion. The results also show pronounced effect of the different substituents at the triazolidinedione ring.

Statistical treatment suggests that only three independent factors concerning three molecular centres dominate the changes in the geometry of the molecular fragment during the inversion.