

**PS05.07.10 THE CRYSTAL STRUCTURES OF SOME BENZODIAZEPINES AND BENZAZEPINES AS NONPEPTIDE CHOLECYSTOKININ RECEPTOR LIGANDS.** Nancy N. Tsou, Karst Hoogsteen, James P. Springer, and Richard G. Ball, Merck Research Laboratories, P. O. Box 2000, Rahway, New Jersey 07065-0900, USA

A series of 1,4-benzodiazepine and novel benzazepine derivatives are reported as high affinity cholecystokinin (CCK) antagonists. The gastrointestinal hormone cholecystokinin<sup>1</sup> is found both in the gut and in the central nervous system. Two principle CCK receptor subtypes have been identified: CCK-A (alimentary canal) and CCK-B (brain). The CCK-A antagonists are believed to provide a new therapeutic agent for the treatment of irritable bowel syndrome and the CCK-B antagonists as a palliative for anxiety disorders.

Thirteen structures determined in our laboratory by single crystal X-ray diffraction studies are discussed here. All thirteen structures are either 1-methyl-2-oxo-1,4-benzodiazepines or 1-methyl-2-oxo-1 benzazepines and can be classified into three different groups: 1,3,5-trisubstituted benzazepines, 1,5-disubstituted benzodiazepines, and 1,3,5-trisubstituted benzodiazepines. Discussion of these structures will encompass structure motifs common to the structures, conformation of substituents and the relationship of structure and biological activity. These types of compounds are poorly represented in the structural literature with only a single similar compound in the Cambridge database.

<sup>1</sup>Dethloff L. A. and De La Iglesia F. A., Cholecystokinin Antagonists - a Toxicologic Perspective, *Drug Metab. Rev.*, 24(2), 267 (1992).

**PS06.05.17 STUDIES OF HYDROGEN BONDING IN CRYSTALLINE SOLIDS OF CYCLIC DIPEPTIDES.** G. Tayhas, R. Palmore, Mary T. McBride, Department of Chemistry; University of California, Davis; Davis, CA 95616

Understanding how molecules influence the structure of crystalline solids is essential to the design of new solid-state materials. Researchers have only recently begun to exploit the strength, directionality and selectivity of hydrogen bonds to control the orientation of molecules in the solid state. Although the manipulation of individual molecules into large aggregates with well-defined shapes is masterfully demonstrated in nature, the deliberate control of molecular orientation by researchers is still in its infancy. One promising strategy is to examine the hydrogen-bonding interactions present in crystals of related molecules; such studies define the strengths and weaknesses of a common functional group in controlling the architecture of the solid. Once the organizational properties of a functional group are established, other intermolecular interactions can be systematically introduced and evaluated. We will describe the solid-state packing patterns of cyclic dipeptides that contain hydrogen-bonding functional groups at the 3,6-positions of the diketopiperazine ring. Diketopiperazines contain two amide functional groups within the piperazine ring itself that enable these molecules to self-assemble into hydrogen-bonded "tapes". We will discuss how functional groups at the 3,6-positions of the diketopiperazine ring influence the integrity of these hydrogen-bonded tapes.

**PS10.05.26 DISPLACEMENTS OF THE PLANAR-Cu AND APICAL-O ATOMS AT INTERVALS OF THE COHERENCE LENGTH IN  $YBa_2Cu_3O_{7-\delta}$  DECREASE WITH OXYGEN CONTENT.** J. Etheridge, Dept. Of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK

It has recently been observed<sup>1</sup> that the copper-oxygen planes of  $YBa_2Cu_3O_{7-\delta}$  ( $\delta < 0.1$ ) are partitioned into cells by displacements of the planar-copper and apical oxygen atoms at the boundaries of these cells. The dimensions of the cells is comparable to the superconducting coherence length in the copper-oxygen planes ( $\sim 10\text{\AA}$ ) and the directions in which the atoms are displaced are  $\langle 28\ 0\ 3 \rangle$  and  $\langle 0\ 9\ 1 \rangle$ . These displacements perturb the bonding in the planes that carry the principal superconducting current and may thus play a role in the superconducting properties of this material. In an effort to understand both the origin of these displacements and their role, if any, in the superconducting properties of  $YBa_2Cu_3O_{7-\delta}$  ( $\delta < 0.1$ ), their dependence on oxygen content is being investigated using a combination of electron diffraction and microscopy techniques. Results so far suggest that the displaced planar-copper and apical-oxygen atoms relax towards their periodic lattice sites as oxygen from the chain-oxygen site is removed. Once the oxygen-stoichiometry has been reduced to as little as  $\sim 6.55$ , the displacements parallel to  $\langle 28\ 0\ 3 \rangle$  disappear whilst those parallel to  $\langle 0\ 9\ 1 \rangle$  become extremely small. In other words, those displacements in a direction with a component perpendicular to the alternately full-empty copper-oxygen chains disappear, whilst those with a component parallel to these chains reduce in magnitude. Details of observations at a range of stoichiometries and their relevance to understanding the origin and role of the displacements will be discussed.

<sup>1</sup>I. Etheridge, J. (1996), *Phil. Mag.* A73, 643-668.

**PS10.05.27 MODULAR CRYSTAL CHEMISTRY OF OXIDE SUPERCONDUCTORS REVISITED: POLYSOMATISM IN BISMUTH CUPRATES.** M. O. Figueiredo, Crystallography and Mineralogy Center, IICT, Alameda D. Afonso Henriques, 41-4°, P-1000 Lisbon, Portugal

*Modular crystal chemistry* stands on two fundamental concepts that have required successive refinements: i) *polytypism*, which is strictly concerned with layered arrangements, either imposing chemical identity to the planar modules in *polytypes* or allowing for slight chemical variations in *polytypoids*; ii) *polysomatism*, which releases the chemical constraint but restricts the structural affinity to the presence of identical modules, planar (layers) or columnar (beams). These concepts tie up crystallographic and chemographic relationships through a unified approach.

The basic square syngony of the atomic arrays in superconducting and allied oxide phases hinders true polytypism. Indeed, these layered arrays are based on coherent stackings of square-type anionic layers (labeled Q), either of a single metrics - in closest ( $Q_f$ ) and simple ( $Q_s$ ) stackings or in mixed sequences involving both stacking modes ( $Q_{f/s}$ ) - or in composite arrays with layers of two distinct but coherent metrics ( $Q_1/Q_2$ ). Relationships with mineral structure types other than perovskite - namely, fluorite and diabolite - have already been established (Figueiredo, 1993, *Phase Trans.* 43, 129).

An approach to polysomatic features parallel to those recognized in pyrolusite and affine oxide minerals is now considered. Polysomes in these minerals are generated by cutting out slabs of varied thickness from closepacked octahedral layers and interlinking these octahedral bands into columnar arrays with square or rectangular cross section.

A description is presented of identical structural processes relating the prototype structures of  $La_2CuO_4$ ,  $Y_2BaCu_3O_{7-\delta}$  and  $Tl/HgBa_2CuO_5$  with the series of bismuth strontium/barium cuprates, where examples of both commensurate (polysomatic interconnections) and incommensurate (modulated) adjustments may be found.