MS.06.08.04 HYDROGEN-BOND PATTERN FUNCTIONALITY AND GRAPH SETS. J. Bernstein, Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, Israel 84965, and R. E. Davis, Department of Chemistry, University of Texas, Austin,TX 78712, U.S.A.

One of the most promising approaches for defining and understanding hydrogenbond patterns in crystals and multimolecular arrays was developed by the late M.C. Etter (1990), who applied a shorthand graph theory to recognize, summarize and then to utilize patterns of hydrogen bonding. There has been an increasing use and recognition of the power of the method, and the very formalism of the procedure has led to new insights about characterizing and classifying arrays of molecules (Bernstein et al, 1995). This efficient shorthand notation for describing hydrogenbonded networks makes the patterns easy to describe, compare and recall, and a new language describing the structures of micro- and macromolecular ensembles is emerging.

In the course of developing and refining this new language we have come to recognize the existence of *hydrogen-bond pattern functionality* that is based on properties of molecular recognition dictated by the characteristics of hydrogen bonding but that cuts across traditional lines of chemical functionality. For instance, the ring pattern commonly associated with by carboxylic acids, I, has been found for eighty different combinations (i.e. chemical functional groups, II(AA = any atom, D= hydrogen bond donor, A = hydrogen bond acceptor), thus demonstrating how this *hydrogen-bond pattern functionality* crosses the boundaries of traditional chemical group functionality.

We will review the basics tenets of the use of graph sets to characterize hydrogen-bond networks, and will provide examples demonstrating the recognition and potential use of hydrogen-bond pattern functionality.

ETTER, M.C. (1990). *Acc. Chem. Res.* **23**, 120.
BERNSTEIN, J., DAVIS, R.E., SHIMONI, L., CHANG, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555-1573.

MS06.08.05 INTERMOLECULAR INTERACTIONS IN *CHIRAL-AT-METAL* **COMPLEXES - CHIRALITY CHANGES AT THE CRYSTALLIZATION PROCESS** F.J. Lahoz and R. Atencio. Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias, Universidad de Zaragoza, 50009 Zaragoza, Spain.

In the course of our studies on transition metal complexes with *chiral metal centers* we have been surprised by the occurrence of epimerization processes (chirality changes at the metal center) associated to the crystallization process. Furthermore, in some cases, the ratio between diastereoisomers observed in solution is dramatically altered upon crystallization, with the unique presence, in the solid state, of the minor-in-solution diastereoisomer. Here we present a detailed analysis of the intra and inter-molecular interactions of these *chiral-at-metal* complexes in a search of the factors that control the different stability of diastereoisomers in solution and in the solid state.

The studied complexes are new mononuclear neutral or monocationic species of the type [Cp*M(aa)L], containing Rh or Ir as *chiral metal centers*. They all present a bonded C_5Me_5 group (Cp*) as a fixed ligand to restrict the synthetic processes. The asymmetry of the complexes is related to the *N,O*-quelate coordination of a chiral a-aminoacidate (aa = L-prolinate, L-valinate, etc.). The third ligand L varies among different neutral or anionic N, P or C-donor groups.

The crystal structures have been investigated by means of empirical packing potential calculations, van der Waals volume analysis and computer graphics. In general, the packing of these complexes seems to be fundamentally controlled by the steric effects associated to the C_5Me_5 groups. In most of the cases, a columnar arrangement of the molecules around an helical axis has been observed, always with an external and

parallel-to-the-axis disposition of the Cp* rings. No significant hydrogen bonding has been detected.

Additionally, the influence of the different metal center has been considered and a comparison between two analogous complexes [Cp*M(L-valinate)(PPh₃)] (M = Rh or Ir), only differing at the metal, has been carried out. Interestingly, both crystalline organizations show a peculiar packing based on layers formed by an intercrossing of the phenyl groups of the PPh₃ ligands, surprisingly in an analogous way to those observed in the free ligand or in its oxide.

MS06.08.06 THE SCOPE AND THE LIMITS OF VSEPR-THEORY AS MIRRORED BY THE STEREOCHEMISTRY OF Xe (VI). Arkady Ellern[1], Konrad Seppelt, Ben-Gurion University of the Negev, Chemistry Dept., P.O.B. 653, Beer Sheva, Israel and Institute of Inorganic and Analytical Chemistry, FU-Berlin, Germany.

Even the first reports of the molecular structure of Xe-containing compounds in the highest oxidation state, in particular XeF6, exhibited some interesting features, which could not be explained on a basis of Valence Shell Electron Pair Repulsion theory, which serves as a reliable model for predicting molecular geometry, if the coordination number 6 is not exceeded. The general question of this theory is whether to consider electron lone pairs (LP) as additional ligands.

The precise low-temperature X-ray analysis of single crystals of a variety of exotic Xe (VI) derivatives $NO^+XeOF_5^-$, $Cs^+XeF_7^-$, $(NO)_2^+XeF_8^{2-}$, $Cs_2^+XeF_8^{2-}$ 4BrF₅ has been performed. The LP is stereochemically active only in the case of $XeOF_5^-$ (pentagonal pyramidal configuration C_{5v}). The anion XeF7- possesses C_{3v} symmetry with a Xe atom in the center of a capped octahedron. No suitable space for LP has been found. However, the bond length and angles are in accord with VSEPR.

Our redetermination of the structure of $(NO)_2^+XeF_8^{2-}$ has shown, that the bonds in a square antiprismatic anion are not regular in contrast to the isostructural Re and W derivatives. This mystery of this anomaly was solved only after obtaining the structure of $Cs_2^+XeF_8^{2-}$ 4BrF₅ which shed light on the reliability of VSEPR for different coordination numbers.

MS06.08.07 STRUCTURE AND REACTIVITY OF HOST-GUEST INCLUSION COMPOUNDS. Anita Coetzee, Mino R. Caira and Luigi R. Nassimbeni, Department of Chemistry, University of Cape Town, Rondebosch, 7700,South Africa, Edwin Weber and Andreas Wierig, Institut fur Organische Chemie, Technische Universitat Bergakademie Freiberg, Leipziger Strasse 29 D-09596 Freiberg, Germany

The reactivity of a host-guest system can often be related to the crystallographic structure of the host-guest inclusion compound. The rate of guest uptake or release is of interest in the study of inclusion compounds between solid hosts and volatile guest molecules. Guest molecules are most commonly either entrapped in cavities formed by the host compound, or along channels, running through the host network. Molecules which contain the fluorene moiety have proved to be successful hosts, capable of forming inclusion compounds with a wide variety of guests[1]. Inclusion compounds of 2,2'-bis (9-hydroxy-9-fluorenyl) biphenyl have been studied extensively[2]. Substituting the fluorene moieties at the 2- and 7-positions with bulky groups such as halogens or *p-tert*-butyl, also yields successful compounds, which are often stabilised by hydrogen bonding between host and guest. The structures of the inclusion compounds of related host molecules with acetone have been elucidated and the kinetics of desolvation have been studied, using isothermal thermogravimetry.

1. I. Csöregh, E. Weber, L. R. Nassimbeni, O. Gallardo, N. Dörpinghaus, A. Ertan and S. A. Bourne, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1775.
2. L. J. Barbour, S. A. Bourne, M. R. Caira, L. R. Nassimbeni, E. Weber, K. Skobridis and A. Wierig, *Supramolecular Chem.* 1993, 1, 331.