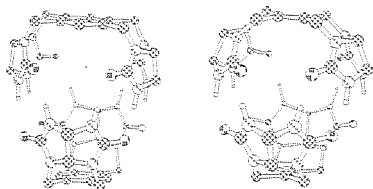


**MS06.00.04 SELF-ASSEMBLY THROUGH HYDROGEN BONDING. CRYSTAL STRUCTURES OF PSEUDO-SPHERICAL CAPSULES.** Leticia M. Toledo, Carlos Valdés, Urs Spitz, Julius Rebek Jr. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139 USA

Complementarity of shape, size and chemical surface drives molecular recognition processes and self-complementarity is the singular feature of biological molecules capable of assembly. We have described a series of compounds, whose structures are self-complementary and, thus contain the code for self-assembly.<sup>1</sup> These new entities are composed of identical monomeric units held together by intermolecular interactions, in the fashion of palindromic nucleic acid and viral capsids.

The monomers, symmetrical bisglycoluril molecules, are interlocked into pseudo-spherical dimers by hydrogen bonds in the same way that stitches along the seam hold together a tennis ball. Upon self-association in solution, internal cavities are generated and guest of appropriate sizes can be encapsulated within them.



The crystal structures of two of these capsules have been determined. These crystallize in  $\bar{P}1$  and  $C2/c$  space groups, respectively. Both capsules share similar packing arrangements in the solid and both contain disordered guests in their internal cavities.

1. C. Valdés, U. P. Spitz, L. M. Toledo, S. W. Kubik, J. Rebek Jr., *J. Am. Chem. Soc.* **1995**, *117*, 12733, and references within.

**MS06.00.05 HYDROGEN BONDING IN METAL COMPLEXES: EMPIRICAL AND COMPUTATIONAL COMPARISONS WITH ORGANIC ANALOGUES** A. Guy Orpen, Dena Bellamy, School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

The ability of organic moieties to participate in hydrogen bonding is fundamental to life and to the burgeoning field of solid state engineering. Similar functionalities are frequently present in metal complexes albeit in different electronic and steric environments. In this paper we report comparative studies of hydrogen bonding for a series of metal-bound ligands and their organic analogues. Systems studied include: M-Cl, Cl<sup>-</sup> and C-Cl; M-CN and C-CN; M<sub>2</sub>CO and C<sub>2</sub>CO. In each case the relative frequency and geometries of hydrogen bonds involving these fragments were established from the Cambridge Structural Database (CSD).<sup>1</sup> These provide structural indicators of the strength of the various units as hydrogen bond acceptors. To provide an alternative measure of these interactions, *ab initio* molecular orbital (MO) calculations were performed on representative examples of each system. Atomic charges (calculated by a variety of algorithms) electrostatic potentials and energies and geometries of interaction with a water molecule were computed. General conclusions from the CSD study may be summarised as follows: metal-bound chloride is a stronger H-bond acceptor than is C-Cl (although both are weaker than Cl<sup>-</sup>); metal-bound carbonyl and cyanide groups are weaker hydrogen bond acceptors than their organic analogues. These observations will be discussed and shown to be in accord with the results of the MO studies.

1. F.H. Allen *et al.*, *Acc. Chem. Res.*, 1983, **16**, 146; F.H. Allen *et al.*, *J. Chem. Inf. Comput. Sci.*, 1987, **31**, 187.

**MS06.00.06 SELF-ASSEMBLY VIA HYDROGEN BONDING AND METALLATION REACTIONS** Paul R. Raithby, Department of Chemistry, Cambridge University, U.K.

Our studies on multi-functional organic molecules have shown that they may self-aggregate via hydrogen bonding or the assembly may be induced via metallation reactions involving the intermediacy of neutral Lewis base molecules. Both types of interaction have been confirmed by X-ray crystallographic studies on the reaction products.

Our work has been concerned with alkali or alkaline earth metallation of multi-functional organic molecules which contain acidic groups such as NH, NH<sub>2</sub> or OH along with heteroatoms such as S, O or N or with functional groups such as C=O or SO<sub>2</sub>. Metallation produces highly polar anionic organic residues in conjunction with the metal cations. It is electrostatically inevitable that such species will aggregate, the negative centres and the heteroatoms within the organic anion will interact with as many metal atoms as possible. The extent of the aggregation depends largely upon the steric constraints of the organic ligand and upon those of the neutral Lewis base usually present during metallation. The Lewis bases normally stabilise the metal cation in the metallated organic product by complexing with it, and often block metal coordination sites limiting the extent of the aggregation. However, we have found recently that having such Lewis bases in the system can prevent metallation of the organic acid. Instead, these Lewis bases form adducts with the intact organic molecules. The adducts assemble using hydrogen bonds, the cumulative strength of which appears to be sufficient to block metallation.

I. Cragg-Hine, M.G. Davidson, A.J. Edwards, E. Lamb, P.R. Raithby and R. Snaith, *Chem. Commun.* 1996, 153.

M.G. Davidson, C. Lambert, I. Lopez-Solera, P.R. Raithby and R. Snaith, *Inorg. Chem.*, 1995, **34**, 3765.

**PS06.00.07 INTRAMOLECULAR HYDROGEN BONDING IN SOME AZOENAMINONES.** Bernardo Lages Rodrigues and Maria Teresa do Prado Gambardella, Instituto de Química de São Carlos - Universidade de São Paulo - Brazil

Crystal Structures of four azoenaminones (Figure 1) were determined using X-ray diffraction. Intramolecular hydrogen bonds strengths are correlated to the differences in the aromatic ring and amino nitrogen electron densities produced by the presence of the different substituents. Data clearly show that the stronger the O1-H-N2 hydrogen bond, the weaker the N3-H-N1 resonance assisted hydrogen bond is.

Crystal data: (I): C<sub>13</sub>H<sub>16</sub>N<sub>4</sub>O<sub>5</sub>, P2<sub>1</sub>/n, a=7.345(1), b=9.937(1), c=19.725(2)Å, β=91.440(9)°, V=1419.9Å<sup>3</sup>, Z=4, R(F)=0.052, wR(F)=0.058; (II): C<sub>13</sub>H<sub>16</sub>N<sub>3</sub>O<sub>3</sub>Cl, P2<sub>1</sub>/n, a=7.566(2), b=9.823(1), c=19.111(2)Å, β=91.35(1)°, V=1439.3(3)Å<sup>3</sup>, Z=4, R(F)=0.047, wR(F)=0.069; (III): C<sub>16</sub>H<sub>21</sub>N<sub>4</sub>O<sub>5</sub>Cl, P2<sub>1</sub>/c, a=7.324(2), b=22.790(6), c=11.715(2)Å, β=106.59(1)°, V=1874.1(7)Å<sup>3</sup>, Z=4, R(F)=0.053; wR(F)=0.095; (IV): C<sub>12</sub>H<sub>13</sub>N<sub>4</sub>O<sub>5</sub>Cl P2<sub>1</sub>/c, a=9.238(2), b=14.388(3), c=11.763(2)Å, β=109.40(4)°, V=1474.8(5)Å<sup>3</sup>, Z=4, R(F)=0.045, wR(F)=0.040.

(I): R<sub>1</sub>=H, R<sub>2</sub>=NO<sub>2</sub>, R<sub>3</sub>=CH<sub>3</sub>  
 (II): R<sub>1</sub>=H, R<sub>2</sub>=Cl, R<sub>3</sub>=CH<sub>3</sub>  
 (III): R<sub>1</sub>=NO<sub>2</sub>, R<sub>2</sub>=Cl, R<sub>3</sub>=H  
 (IV): R<sub>1</sub>=NO<sub>2</sub>, R<sub>2</sub>=Cl, R<sub>3</sub>=C(CH<sub>3</sub>)<sub>3</sub>

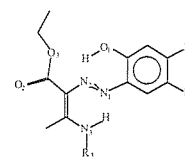


Figure 1-Structures determined