

**s9.m3.p25** **Anionic-Cationic Interactions in Dinuclear Cyclic Complexes of Cu(I), Ag(I) and Hg(II) with Phosphines Containing an Imidazole Ring.** F. Bachechi<sup>1</sup>, A. Burini<sup>2</sup>, R. Galassi<sup>2</sup>, B. R. Pietroni<sup>2</sup>. <sup>1</sup>*Istituto di Strutturistica Chimica, C.N.R., Area della Ricerca di Roma, C.P. 10, 00016 Monterotondo St. (Roma), Italy. E-mail: fior@isc.cnr.mlib.it.* <sup>2</sup>*Dipartimento di Scienze Chimiche, Università di Camerino, 62032 Camerino, Italy.*  
 Keywords: Cu, Ag, Hg complexes; hybrid P,N-ligand; crystal structures.

Recently a new ligand containing an imidazole ring has been used in a series of coinage metal complexes. The unsymmetrical ligand (1-benzyl-2-imidazolyl) diphenyl phosphine, (BzIm)Ph<sub>2</sub>P, can act either as a P-bound monodentate or as a bidentate ligand with P and N as donor atoms, giving both mononuclear and binuclear complexes. The soft character of the imidazole ring allows a good stabilisation of complexes with metals of group 11 in low oxidation states.

Dinuclear cyclic compounds with [M<sub>2</sub>{μ-(Bzim)Ph<sub>2</sub>P}<sub>2</sub>]<sup>2+</sup> units (M = Ag(I); Hg(II)), and with [M<sub>2</sub>{μ-(Bzim)Ph<sub>2</sub>P}<sub>3</sub>]<sup>2+</sup> units (M = Cu(I); Ag(I)) were obtained. The coordinations of the metal centres are strongly affected by the counterion used. In the silver complexes the nuclearity changes according to the coordination modes of the anions. When bridging two metal centres infinite chains of dinuclear cyclic units can also form.

The crystal structures of [Cu<sub>2</sub>{μ-(Bzim)Ph<sub>2</sub>P}<sub>3</sub>] [BF<sub>4</sub>]<sub>2</sub>, [Ag<sub>2</sub>{μ-(Bzim)Ph<sub>2</sub>P}<sub>3</sub>] [F<sub>3</sub>CSO<sub>3</sub>]<sub>2</sub> and [Hg<sub>2</sub>{μ-(Bzim)Ph<sub>2</sub>P}<sub>2</sub>] [ClO<sub>4</sub>]<sub>4</sub>, will be presented and discussed together with the (Bzim)Ph<sub>2</sub>P polynuclear complexes of silver having BF<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> as counterions.

**s9.m3.p26** **Hydrogen-Bonded Networks and Porous Crystals of Metalloporphyrins.** Y. Diskin-Posner, S. Dahal and I. Goldberg, *School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, 69978 Tel-Aviv, Israel.*

Keywords: molecular interactions, supramolecular assemblies, metalloporphyrins

New tetra [4-(3',5'-diaminotriazino)-phenyl] porphyrin building block was synthesized, and applied successfully to the formulation of a uniquely structured solid which consists of flat multiporphyrin networks with very large voids, 2.2x2.2 nm.<sup>1</sup> These assemblies mutually interpenetrate each other, yielding a concatenated arrangement in three-dimensions by cooperative hydrogen bonding. The resulting multiporphyrin architecture resembles a molecular sieve material, having 0.6 nm wide channels, which propagate through the crystal and are accessible to other species.

Zinc-tetra(4-carboxyphenyl)porphyrin, along with 4,4'-bipyridyl bridging ligand and sodium ions, are used to form a spectacular and remarkably stable molecular-sieve structure with channels of nanometric dimensions.<sup>2</sup> The crystal structure represents an open three-dimensional framework wherein the individual metalloporphyrin units are cross-linked both axially as well as equatorially by ion-pairing interactions, metal-ligand coordinations, and hydrogen bonding. It has a striking resemblance to porous architectures of common zeolites.

Aquazinc tetra(4-carboxyphenyl)porphyrin has been used to form a unique supramolecular assembly with very wide channels (~1.5 nm).<sup>3</sup> The open porphyrin lattice is sustained by cooperative hydrogen-bonding and characteristic π-π stacking interactions. It comprises only about 39% of the crystal volume, and preserves its crystallinity up to 360K.

[1] Dahal, S.; Goldberg, I. *J. Phys. Org. Chem.* **2000**, in the press.

[2] Diskin-Posner, Y.; Dahal, S.; Goldberg, I. *Angew. Chem. Int. Ed.* **2000**, 39, 1288-1292.

[3] Diskin-Posner, Y.; Goldberg, I. *Chem. Commun.*, **1999**, 1961-1962.