

ORGANOPLATINUM SUPERMOLECULES FOR GAS-TRIGGERED CRYSTALLINE SWITCHES

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Our approach to crystal engineering (1) involves square-planar platinum (II) complexes containing terdentate coordinating pincer-type ligands. These complexes reversibly absorb gaseous SO₂ in the solid state by Pt-S bond formation (2). When the starting material is crystalline, exposure to SO₂ gas leads to quantitative adduct formation with the unique feature that the product is also crystalline, although the crystal structures of the adduct and the SO₂ free complex are significantly different from each other. Remarkably, the release of SO₂ gas does modify but not destroy the crystalline ordering in the arylplatinum assemblies. These crystalline transformations include repetitive expansion and reduction of the crystal lattice without detectable loss of crystallinity of the material (3). The potential of this class of supermolecules as crystalline switches with 'on' and 'off' positions which are a direct response on the gaseous environment will be discussed.

References

- (1) a) Desiraju, G. R. (ed.) *The Crystal as a Supramolecular Entity*, Wiley: Chichester, 1996; b) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* 1998, 98, 1375.
 (2) A) Albrecht, M.; Van Koten G. *Adv. Mater.* 1999, 11, 171; B) Albrecht, M.; Gossage, R. A.; Lutz, M.; Spek, A. L.; Van Koten, G. *Chem. Eur. J.* 2000, 6, 1431. (3) Albrecht, M.; Lutz, M.; Spek, A. L.; Van Koten, G. *Nature.* 2000, 406, 970-974.

Keywords: ORGANOMETALLIC SWITCHES SO₂-ABSORPTION**THE COORDINATION AND CATALYTIC PROPERTIES OF THE 1,1'-DIPHENYL-3,3',4,4'-TETRAMETHYL-2,2'-BIPHOSPHOLE**

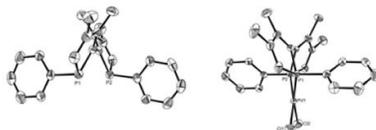
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Chiral diphosphine ligands, in particular those belonging to C₂-symmetry class, have been proved to be powerful auxiliaries in catalytic asymmetric processes. Since 1994, we are interested in the possibilities offered by the 1,1'-diphenyl-3,3',4,4'-tetramethyl-2,2'-biphosphole 1 (BIPHOS), first synthesized by F. Mathey et al.¹. This diphosphine which combines the axial chirality generated by the biphosphole framework with the central chiralities of the phosphorus atoms is stereolabile in solution and six stereoisomers are in fast equilibrium at room temperature². Among these three diastereoisomers, one has a favorable configuration for chelating metals (see figures). The synthesis and structures of numerous transition metal complexes are reported³. Their X-ray analysis proved that in each complex the 2,2'-biphosphole ligand have the expected configuration. The efficiency of some complexes as catalyst was demonstrated in racemic version. Then, we have investigated the preparation of enantiomerically pure complexes from enantiomerically pure BIPHOS ligand in order to explore the potential of these complexes in asymmetric catalysis⁴.

References

- 1- F. Mercier; S. Holand; F. Mathey *J. Organomet. Chem.* 1986, 316, 271.
 2- O. Tissot; M. Gouygou; J-C. Daran, G.G.A. Balavoine *J. Chem. Soc., Chem. Comm.* 1996, 2287.
 3- O. Tissot, J. Hydrio, M. Gouygou, F. Dallemer, J-C. Daran, G. G. A. Balavoine, *Tetrahedron*, 2000, 56, 85.
 4- a) O. Tissot, M. Gouygou, F. Dallemer, J-C. Daran, G. G. A. Balavoine, *Angew. Chem. Int. Ed. Engl.* 2001, 40, 1076; b) O. Tissot, M. Gouygou, F. Dallemer, J-C. Daran, G. G. A. Balavoine, *Eur. J. Inorg. Chem.* 2001, 2385-2389.

**Keywords: BIPHOSPHOLE CHIRAL DIPHOSPHINE ASYMMETRIC CATALYSIS****DNA-PLANAR COPPER COMPLEXES INTERACTION, π - π STACKING VS H BOND**R. Moreno-Esparza¹ S. Escalante-Tovar¹ L. Ruiz-Ramirez¹

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Biological structures are the most important examples of supramolecular chemistry. Undeniably, interactions such as π - π stacking, hydrogen bonds and host-guest play an important role in the formation of supramolecules. While π -stacking is an old argument for conformational stability, progress in understanding its molecular origins has been recent. Considering this, phenanthroline is an excellent rigid ligand liable to have intermolecular interactions such as hydrogen bonding and π - π stacking with other molecules. A series of mixed chelate copper (II) complexes of general formulae [Cu(N-N)(O-O)]NO₃ or [Cu(N-N)(O-N)]NO₃ have been registered as anticancer agents under the name of CASIOPEINAS [Were: N-N=Substituted 1,10-phenanthrolines or 2,2'-Bipyridines, N-O= aminoacidates, O-O=acetylacetonate or salicylaldehyde]. These compounds have shown cytotoxic and antineoplastic activity in vitro and in vivo, and also show SOD like activity. They also shown mutagenic activity in *Drosophila melanogaster* and induce apoptosis, which may indicate direct interaction between DNA and the complexes. We also found, that many crystal structures with phenanthroline or bipyridine show antiparallel ring-stacking with distances among planes less than 3.5 Å. Additionally our study of the interaction between DNA and these complexes, show they are able to associate with the DNA molecule. The association constant value, correspond to an intercalation process. This led us study the host-guest interaction of a small DNA chain with several of these complexes using a docking program to find the site were these complexes can accommodate in the DNA structure, and compare the energetics of the π - π stacking interaction with the H-bond on the selected moiety.

Keywords: STACKING, π - π INTERACTIONS, METAL COMPLEXES**WATER SOLUBLE CATALYSIS - LIGANDS AND COMPLEXES**

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Water-soluble complex catalyzed reactions have been gaining significant importance recently, because of the environmental friendly nature of the solvent (water) and interesting chemistry as well as selectivity of catalytic systems. Selected applications include carbonylation, hydroformylation, hydrogenation, hydrogen transfer reaction, hydrodehalogenation, carbon dioxide reduction, biological membrane hydrogenation etc. In some cases industrial scale processes are working on the basis of this chemistry. The main method to make a platinum group metal complex catalyzed homogeneous system aqueous is to apply water-soluble ligands i.e. sulfonated phosphanes. However, review of CCDC database shows that only very limited number of such structures are available because of the difficulties to grow single crystals. Our results show that guanidine and melamine form readily hydrogen bonds with sulfonated phosphanes¹ as well as with their metal complexes and this crystallization trick made it possible to determine approx. a dozen of new structures of this class. These structures are important not only from the catalytic point of view but they show very extensive hydrogen bond network and interesting supramolecular assemblies.

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References

- 1 A. Katho, A. Benyei, F. Joo and M. Sagi, *Applied Synthesis and Catalysis*, in press

Keywords: PHOSPHANES CATALYSIS HYDROGEN BOND