

P.08.09.11*Acta Cryst.* (2005). A61, C335**Au(I)-arene Interactions**

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Gold(I) chloride complexes catalyze a wide range of reactions, in the presence of different silver(I) salts. In particular alkoxy cyclization and skeletal rearrangement of 1,6-enynes proceed at room temperature with [Au(PPh₃)Cl]/AgSbF₆.^[1] In addition, dienynes and 1,6-enynes with an aryl ring at the alkyne, give [4+2] products in a reaction catalyzed by gold(I) complexes with bulky phosphines.^[2]

In order to avoid the use of silver salts, we have synthesized new cationic complexes with bulky phosphines. The preparation of this new type of gold(I) compounds involves the reaction with AgSbF₆ in different coordinating solvents. When aromatic solvents are used, a new type of complexes are formed, which show an interaction between the arene and the electrophilic metal center. The structures of these new gold(I) complexes have been studied by X-ray diffraction.

[1] Nieto-Oberhuber C., Muñoz M. P., Buñuel E., Nevado C., Cárdenas D.J., Echavarren A.M., *Angew. Chem. Int. Ed.*, 2004, **43**, 2402-2406. [2] Nieto-Oberhuber C., López S., Echavarren A.M., *J. Am. Chem. Soc.*, 2005, **127**, ja04225t.

Keywords: gold catalysis, 1,6-enynes, π -interactions

P.08.09.12*Acta Cryst.* (2005). A61, C335**Comparative Study of Structural Aspects of Monocyclopentadienyl Niobium and Tantalum Complexes. Synthesis and Reactivity**

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Cyclopentadienyl complexes of early transition metals are well established as important types of olefin polymerization catalysts. Recently a spectacular development of a new generation "non-metallocene" catalysts have been designed and several systems capable of catalyzing the living polymerization of olefins was made. Alternatively, this kind of compounds also provided convenient routes to synthetic applications by unsaturated organic derivatives coupling reactions, via metallacyclic intermediates.

The broad success of early transition metal based organic synthesis is due in part to the unique ability of the metal to activate ligands to which it is directly bound through organometallic transformations than are often highly chemo-, regio- and stereoselective processes. In the group 5, niobium and tantalum alkynes complexes, via metallacyclic compounds, have provided good examples of that behaviour [1].

We report herein the synthesis and the structural study of monocyclopentadienyl alkyl and chloro azatantalacyclo-propane-, pentane and -pentene derivatives, their reactivity in the insertion of isocyanides and the intramolecular rearrangements processes observed in the resulting complexes. Comparative studies with the alkyl Niobium complexes will be presented.

[1] Galakhov M., Gómez M., Gómez-Sal P., Velasco P., *Organometallics*, 2005, **24**, 848.

Keywords: organometallic reactivity, group 5 metals, catalysis

P.08.09.13*Acta Cryst.* (2005). A61, C335**Synthesis of cis,cis-1,2,3,4-tetrakis(diphenylphosphino)butadiene Exploiting the "Template Effect"**

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In 1999 we reported the synthesis of cis,trans,cis-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane, which was obtained by an

intramolecular [2+2] photocycloaddition reaction.^[1] A similar template effect has been exploited in a Pd(II) complex, promoting an asymmetric [4+2] Diels-Alder reaction.^[2]

In order to synthesize cis,cis-1,2,3,4-tetrakis(diphenylphosphino)butadiene (dppbd), a bis-bidentate tetraphosphine ligand with a conjugated backbone, we designed a synthesis, which comprises three steps. The first step is the synthesis of the mixed bridged Pt(II) compound [Pt₂Cl₂(dppa)(t-dppen)] containing trans-1,2-bis(diphenylphosphino)ethene (t-dppen) and bis(diphenylphosphino)acetylene (dppa). In the second step a [2+2] photocycloaddition reaction takes place, where a phosphine substituted cyclobutene is formed, which is not stable under these reaction conditions. A conrotatory ring opening of the cyclobutene leads to the formation of [Pt₂Cl₂(dppbd)]. Finally in the third step the free ligand is obtained by a cyanolysis reaction.

[1] Oberhauser W., Bachmann C., Stampfl T., Haid R., Langes C., Kopacka H., Rieder A., Brueggeller P., *Inorg. Chim. Acta*, 1999, **290**, 167. [2] Leung P.-H., Siah S.-Y., White A.J.P., Williams D.J., *J. Chem. Soc., Dalton Trans.*, 1998, 893.

Keywords: photochemistry coordination compounds, phosphorous compounds, platinum compounds

P.08.10.1*Acta Cryst.* (2005). A61, C335**Yellow and Violet Polymorphs of (2Z)-2-(Nitromethylene)-2H-1,4-benzothiazine-3(4H)-one**

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The title compound, (2Z)-2-(nitromethylene)-2H-1,4-benzothiazine-3(4H)-one, C₉H₆N₂O₃S, was obtained in the reaction of bromonitroacrylate and o-aminothiophenol [1]. In the solid state, two crystalline polymorphic modifications of the title compound were found - monoclinic, (**I**), and triclinic, (**II**). Single-crystal structure determination of **I** and **II** revealed the closeness of molecular conformations in both polymorphs. Moreover, the molecules in **I** and **II** form centrosymmetric dimers via N-H...O hydrogen bonds. The dimers are further linked into the identical ribbons by the weak intermolecular C-H...O interactions. The distinctions in crystal structures and colours, yellow for **I** and violet for **II**, are provided by different packing of the ribbons in both polymorphs.

[1] Berestovitskaya V.M., Tafeenko V.A., Makarenko S.V., Sadikov K.D., Chernyshev I.V., *Russ. Zh. Obshchey Khimii*, 2005, submitted.

Keywords: polymorphs, polymorphic structures, organic molecular packing

P.08.10.2*Acta Cryst.* (2005). A61, C335-C336**Isostructurality of Analogues Triarylsilanol and -Methanol Inclusion Compounds**

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Developing strategies for host design require synthesis and structural comparison of enormous variety of crystalline inclusion compounds. The vast quantities of host molecules are organic while others containing inorganic elements, such as silicon, are relatively rare.

Single crystal X-ray structures of 22 inclusion compounds [1] of triphenylsilanol (**1**), triphenylmethanol (**2**), trinaphthylsilanol (**3**) and trinaphthylmethanol (**4**) hosts, respectively, with various guest molecules are compared. Half of them are newly prepared inclusion compounds. Cell similarity indices (π), isostructurality indices (I_s) and molecular isometricity indices for the host molecules (I_m) are

calculated in order to describe the effect of the small guest molecules on the crystal structure. Also the influence of the replacement of the phenyl substituent to naphthyl and the exchange of the carbinol C to Si on the inclusion properties and on the geometry of the host molecules has been studied.

[1] Csöregi I., Weber E., Skobridis K., Bombicz P., Seichter W., *Silicon Analogues of Triarylmethanol Hosts. Inclusion Properties and Host-Guest Structures – A Comparative Study., in preparation, and references therein.*

Keywords: isostructurality, host isometricity, inclusion compounds

P.08.10.3

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The Many Crystal Forms of $[M(15\text{-crown-5})(\text{H}_2\text{O})_2](\text{NO}_3)_2$

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Five structure types have been found between 90 and 320 K for crystals grown near 295 K from aqueous solutions equimolar in 15-crown-5 and $M(\text{NO}_3)_2$, $M = \text{Mg, Mn, Fe, Co, Cu, or Zn}$ (12 structures). In the tetragonal form ($P4_1$, $Z'=2$; Mn and Co) water ligands and nitrate ions form a 3-D network of H bonds. The other four structure types have 2-D patterns of H bonds and are best understood as modulated variants of a basic structure. Two 2-D phases have been seen for each metal except Co; the phase pairs are all linked by reversible transitions during which the crystals remain single. The 2-D phases all have $Z' > 1$: $P2_1/c$, $Z'=3$ (Mg, Mn, Fe, Zn); $P2_1/n$, $Z'=5$ (Cu), $P2_1$, $Z'=8$ (Mg, Fe, Zn), and $P-1$, $Z'=2$ (Mn, Cu).

In the 2-D phases, cations adjacent along the direction of the modulation are either essentially superimposable or enantiomeric. In the five transitions, which relate three different pairs of the four phases, the phase found at the higher temperature always has a larger value of V/Z and a more perfect pattern of enantiomeric alternation.

The values of $Z' > 1$ are a consequence of a conflict between the spacings of the M and nitrate ions most favorable for the formation of H bonds and the spacings most favorable for the close packing of the crown ligands. The reversible phase transitions are possible because inversion of the crown ligand does not require large atomic displacements. Analyses of the crystal packings show why 15-crown-5 ligands increase the probability that a structure will be disordered or modulated.

Keywords: polymorphs, phase transition, crystal packing

P.08.10.4

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Polymorphs of 4,4-Diphenyl-2,5-cyclohexadienone

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4,4-Diphenyl-2,5-cyclohexadienone **1** exists as a cluster of four conformational polymorphs A, B, C and D [1]. X-ray crystal structures show 19 crystallographic distinct molecular conformations due to rotation of gem-diphenyl rings: form A ($P2_1$, $Z'=1$), form B ($P-1$, $Z'=4$), form C ($P-1$, $Z'=12$) and form D ($Pbca$, $Z'=2$). These crystal structures are analyzed in terms of having different C-H...O hydrogen bonds and phenyl ring conformations. Crystal lattice and molecular conformation energies (Cerius², DFT) suggest that forms A and D are more stable than triclinic forms B, C. The stable form A has molecule **1** in a lower energy conformation whereas molecular conformations in forms D, B and C having increasing Z' numbers are progressively higher in energy. Variable-temperature PXRD shows transformation of various forms present in the solid to the stable form A upon heating to ca. 70 °C. Further heating of A to 110-120 °C and cooling gives form B, implying that the melt phase is the kinetic form (ca. 2 kcal/mol less stable than form A, Dreding). The monoclinic form A is SHG active (ca. 2 x urea); this morph can be prepared in pure form by heating the mixture of polymorphs to ca. 70 °C. X-ray crystal structures, VT-PXRD measurements, energy computations and phenyl ring conformations of tetramorphic cluster **1** will be discussed.

[1] Kumar V.S.S., Addlagatta A., Nangia A., et al., *Angew. Chem. Int. Ed.*, 2002, **41**, 3848-3851.

Keywords: conformational flexibility, polymorphism, powder X-ray diffraction

P.08.10.5

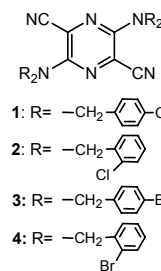
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A Series of Polymorphs with Different Colours in Diaminodicyanopyrazine Dyes

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2,5-Diamino-3,6-dicyanopyrazine dyes have been studied as a novel fluorescent dye because of their intense fluorescence in solution as well as in the solid state [1]. These dyes have also been found to have crystal polymorphs with different colours depending on the amino substituents. The colour difference, in the range from yellow through orange to red, of the polymorphs of dyes **1-4** were investigated in terms of intermolecular interactions.

The colour of these polymorphs were found to reflect different molecular conformation in the crystals. The amino nitrogen in the red and orange phases have a trigonal planar geometry; whereas a tetrahedral conformation of the amino groups was found in the yellow phase. Semi-empirical molecular orbital calculations revealed that this structural feature is well related to the calculated absorption band of a molecule in the crystals. Exciton interaction was also estimated and it was found to be about one order of magnitude smaller than the effect of conformational change. The colour difference is thus considered to be mainly attributed to the change in molecular conformation among the polymorphs.



[1] Matsuoka M., *Colorants for Non-textile Applications*, Freeman H.S. and Peters A.T. ed., Elsevier Science, 2000, 339.

Keywords: dyes, polymorphism, structure colour relationship

P.08.10.6

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A New Crystallographic Form of the Layered Weak-Ferromagnet $\text{Fe}[(\text{CH}_3\text{PO}_3)(\text{H}_2\text{O})]$

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A second form of the literature-known layered weak-ferromagnet $\text{Fe}[(\text{CH}_3\text{PO}_3)(\text{H}_2\text{O})]$ has been isolated. The X-ray single crystal structure of this new form, i.e. form (2), has been carried out at $T = 300, 200$ and 130 K [1]. The latter crystallizes as a needle-like crystals, in the orthorhombic space group $Pmn2_1$: $a = 5.717(1)$, $b = 8.809(2)$, $c = 4.815(1)$ Å, while form (1) crystallizes, as a platelet-like crystals, in the orthorhombic space group $Pna2_1$: $a = 17.58(2)$, $b = 4.814(1)$, $c = 5.719(1)$ Å [2]. The difference between the two forms lies in the ligand arrangement. In the form (2) the methyl groups above and below the inorganic layer are $\sim 12^\circ$ away from the normal axes of the inorganic layers, keeping the same orientation from layer to layer along the b -direction. In form (1) the a parameter is twice larger than the corresponding b parameter of form (2) due to the alternation of the inclination of the methyl groups in a zig-zag way. This is the first example of dimorphism observed in metal alkylphosphonates.

[1] Léone P., Palvadeau P., Boubekeur K., Meerschaut A., Bellitto C., Bauer E.M., Righini G., *J. Solid State Chem.*, in press. [2] Bellitto C., Federici F., Colapietro M., Portatone G., Caschera D., *Inorg. Chem.*, 2002, **41**, 709.

Keywords: polymorphism, organic inorganic hybrid materials, metal phosphonates