

**P.07.01.5***Acta Cryst.* (2005). A61, C296**Mn- and Cr-highly Electrophilic Carbenes: Calculated vs Experimental Parameters**

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The experimental geometry obtained from single-crystal X-ray diffraction data for  $[\text{Mn}(\text{CO})_4(\text{PH}_2)_2\text{C}]^+$  [1] is compared with the results of theoretical calculations made in the singlet ground state at the *ab initio* level by using HF and DFT methods, following similar procedures than those used for other organometallic complexes [2,3]. In addition to the structural computations, in order to theoretically quantify the highly electrophilic character showed experimentally by the carbene, further calculations were carried out involving the doublet ground state resulting from the addition of one electron to the cation. Electron affinities (EA) were found to be between 6.24 eV and 6.97 eV for the Mn complex, which confirmed the expectations.

The effect of the ligands on EAs has been analyzed by replacing P-bonded H atoms by  $\text{NH}_2$  ligands, whereas the effect of the metal fragment has been studied by replacing  $\text{Mn}^+$  by Cr and also comparing with our previous results with  $\text{Ru}^{2+}$  complexes, from which it seems clear that the effect of the positive charge on the metal dominates over the effect of changing the ligands to more  $\pi$ -accepting ones.

[1] Ruiz J., Arauz R., Riera V., Vivanco M., García-Granda S., Menéndez-Velázquez A., *Organometallics*, 1994, **13**, 4162. [2] Ruiz J., Mosquera M. E. G., García G., Patrón E., Riera V., García-Granda S., Van der Maelen J. F., *Angew. Chem. Int. Ed.*, 2003, **42**, 4767. [3] Van der Maelen J. F., Ruiz J., García-Granda S., *J. Appl. Cryst.*, 2003, **36**, 1050.

**Keywords:** *ab initio* and DFT calculations, organometallic compounds, electron-affinity computations

**P.07.01.6***Acta Cryst.* (2005). A61, C296**Structure of New Different-ligand Uranyl Complexes**

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Synthesis and structure investigation were performed for new uranyl complexes including three different acid ligands: sulfate or selenate ions, thiocyanate, and oxalate ions. As is known, thiocyanate ions are at the end of the row of mutual replacement in uranyl complexes, that means lower donor ability of thiocyanate nitrogen or sulfur atoms in comparison with oxygen atoms of prior oxygen-containing ligands, in particular, of oxalate, sulfate, and selenate ions. A special synthetic method allowed us to obtain the compounds of this group considering the essential differences in complexing abilities of the ligands. According to X-ray analysis data the crystal structure of  $(\text{NH}_4)_4[(\text{UO}_2)_2(\text{C}_2\text{O}_4)(\text{XO}_4)_2(\text{NCS})_2] \cdot 6\text{H}_2\text{O}$  [ $\text{X} = \text{S}$  (I) or  $\text{Se}$  (II)] is formed by ribbons  $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)(\text{XO}_4)_2(\text{NCS})_2]^{4z-}$  connected to 3D framework by ammonium ions and water molecules. In relation to uranium atoms oxalate groups are quadridentate-bridging, selenate ions are bidentate-bridging, and iso-thiocyanate ions are monodentate. The compounds I and II are related to the crystallochemical group  $\text{A}_2\text{B}_2\text{K}^{02}\text{M}_1^2$  ( $\text{A} = \text{UO}_2^{2+}$ ). The compounds are characterized by the methods of derivatography, IR and Raman spectroscopy. The results of the analysis of I and II vibrational spectra are in a good correlation with the data of the X-ray experiment.

**Keywords:** uranyl compounds, crystal structure research, X-ray analysis

**P.07.01.7***Acta Cryst.* (2005). A61, C296**Polymorphism of Yttrium Threemethylacetate**

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Rare-earth threemethylacetates are of interest to inorganic chemistry because of molecular type of structure and ability to sublime under heating.

First modification of yttrium threemethylacetate with  $P2_1/n$ ,  $a=16.401(8)$ ,  $b=11.906(5)$ ,  $c=20.220(9)$  Å,  $\beta=108.73(4)$ ,  $Z=4$ ,  $R=0.1367$  was synthesized according to the reaction of yttrium carbonate and excess of threemethylacetic acid. Second one with  $P2_1/c$ ,  $a=21.617(4)$ ,  $b=36.559(4)$ ,  $c=29.930(4)$  Å,  $\beta=104.40(2)$ ,  $Z=12$ ,  $R=0.0501$  was obtained as a result of co-crystallization of calcium and yttrium threemethylacetate mixture ( $\text{Ca}:\text{Y} = 4:1$  mol) from threemethylacetic acid solution. The two molecular type modifications differ in the packing of centrosymmetric dimers  $\text{Y}_2[(\text{CH}_3)_3\text{CCOO}]_6 \cdot 6(\text{CH}_3)_3\text{CCOOH}$ . Within the dimers two yttrium atoms are linked by four bridging anions  $(\text{CH}_3)_3\text{CCOO}^-$ . The other anions and neutral acid molecules are unidentate mode ligands (coordination number of yttrium atoms is eight).

**Keywords:** yttrium threemethylacetate, polymorphism, molecular structure

**P.07.01.8***Acta Cryst.* (2005). A61, C296**Unconventional Distribution of Hydrides in Hydrido Rhenium Carbonyl Clusters**

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We have recently shown that coupling stereochemical considerations to potential energy (PE) calculations it is possible to retrieve hydrides locations in hydrido carbonyl clusters as large as  $[\text{H}_6\text{-}_x\text{Os}_{10}(\text{CO})_{24}]^{x-}$  ( $x = 1, 2$ ). [1] However, when the ratio between the number of hydrides and that of carbonyls increases, such as in  $[\text{H}_7\text{-}_x\text{Re}_5(\text{CO})_{15}]^{x-}$  ( $x = 1, 2$ ) and  $[\text{H}_7\text{Re}_5(\text{CO})_{15}]^{2-}$ , the 'empty' space to be 'filled' with the hydrides becomes more evenly distributed about the cluster surface and the localisation of the hydrido ligands becomes more elusive thus requiring additional theoretical tools.

[1] Beringhelli T., Cariati E., Dragonetti C., Galli S., Lucenti E., Roberto D., Sironi A., Ugo R., *Inorg. Chim. Acta*, 2003, **354**, 79-89.

**Keywords:** clusters, hydrides, structural computing

**P.07.01.9***Acta Cryst.* (2005). A61, C296-C297**C-H... $\pi$  Interactions in the Novel Ni(II) Complex with Tetradentate Thiosemicarbazide Based Ligand**

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$[\text{4}-(2\text{-diphenylphosphino-}\alpha\text{-ethoxy-benzyl-P)-3\text{-methyl-1-acetylacetonone-isothiosemicarbazido-N1,N4,O}]\text{nickel(II)}$ ,  $[\text{Ni}(\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_2\text{SP})]$ , represents one of the rare examples of transition metal complexes with S-alkylisothiosemicarbazide-derived ligands where a phosphorus atom is involved in the coordination sphere of the metal atom. The Ni(II) atom in the  $[\text{Ni}(\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_2\text{SP})]$  complex has a distorted square-planar configuration formed by a thiosemicarbazide-based tetradentate ligand with ONNP donor atoms. This complex molecule contains three condensed chelate rings. The six-membered chelate ring containing the P atom adopts an unusual boat conformation, while the other two chelate rings are planar.

The crystal structure has been determined by a single-crystal X-ray analysis and refined to a final  $R = 0.044$  for 10824 reflections and 657 parameters. Two independent molecules with the same composition exist in the asymmetric unit. There are no hydrogen

bonds in the crystal structure but crystal packing is stabilized by eight C-H $\cdots\pi$  and four  $\pi\cdots\pi$  interactions. Some of the C-H $\cdots\pi$  interactions are with the H $\cdots$ Cg distance shorter than 2.70Å (Cg is the centroid of five- or six-membered ring with delocalized  $\pi$  bonds). Two of the C-H $\cdots\pi$  interactions are intramolecular and play a very significant role in the orientation of phenyl rings and -OCH<sub>2</sub>CH<sub>3</sub> fragments.

**Keywords:** C-H $\cdots\pi$  interaction, Ni(II) complex, thiosemicarbazide

#### P.07.01.10

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#### Isolation and Characterization of a Ferromagnetic Gadolinium(III) Citrate Chain

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Novel lanthanide citrate chains have been hydrothermally synthesized from Ln<sub>2</sub>O<sub>3</sub> (Ln = Gd, Nd) and citric acid at pH = 2 and 120 °C. Their structure, crystal packing, network topology, hydrogen bonds, metal ligand interactions, TG and DTA measurements and magnetic susceptibility properties are examined. Two new isostructural compounds are described in detail: [Ln(Hcit)(H<sub>2</sub>O)<sub>2</sub>.H<sub>2</sub>O]<sub>n</sub> (Ln: Gd (1), Nd (2), Hcit = C(OH)(COO-)(CH<sub>2</sub>COO)<sub>2</sub>). They are monoclinic, P2<sub>1</sub>/n, and crystallize as linear polymers. The multidentate citrate anion coordinates through six out of its seven oxygen atoms, five of them acting as simple donors and the remaining one in a bridging mode. Two aqua molecules complete a LnO<sub>9</sub> coordination environment. Each citrate links to 3 lanthanide metal centers leading to the formation of "ladder like" chains parallel to [100] where the steps are defined by the Ln-O-Ln bridges (Ln...Ln: 4.321(4)/4.389(2)Å, for Gd/Nd respectively), connected to each other by longer citrate-based "linkers" (Ln...Ln : 6.145(4)/6.230(2)Å).

The inter-linkage of chains is achieved through H-bonding to which the three water molecules provide five donor hydrogens.

Magnetic susceptibility measurements in (1) show that ferromagnetic interactions are operative between the Gd(III) centers below 10 K.

**Keywords:** lanthanides, structures, ferromagnetism

#### P.07.01.11

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#### Novel Water-soluble Peroxo Complexes of Nb(V) and Ta(V)

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In recent years, multimetallic Nb-based oxides have generated considerable interest in many fields: these oxides are mainly described as ferroelectrics, ion conductors and oxidation catalysts. In the frame of research aimed at developing new synthetic procedures of these Nb-containing oxides, water-soluble peroxo complexes of niobium(V) and tantalum(V) have been prepared and investigated spectroscopically and structurally.

The compounds studied are of two types: peroxo-carboxylato and peroxo-polyaminocarboxylato (PAC) complexes, the latter ones will be described. The peroxo-PAC complexes were synthesized in the presence excess hydrogen peroxide. These conditions led to the oxidation *in situ* of the nitrogen atoms of the ligands into N-oxides. Two PAC ligands were selected: ethylenediaminetetraacetic acid (H<sub>4</sub>edta) and propylenediaminetetraacetic acid (H<sub>4</sub>pdta).

The crystal structures of the guanidinium derivatives of the (edta)- and (pdta) Nb and also of the (edta)-Ta complexes have been determined at 100K. In all the three compounds, the metal exhibits an eightfold coordination by two bidentate peroxo ligands and a tetradentate bis(N-oxido) PAC ligand resulting in a distorted dodecahedral geometry. The coordination Nb-O and Ta-O bond

lengths are very similar.

**Keywords:** niobium complexes, peroxo compounds, polyaminocarboxylate acids

#### P.07.01.12

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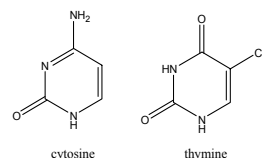
#### Studies in the Structural Chemistry of Complexes between Nucleobases and s-Block Metals

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In the past years, it has been found that interaction of biomolecules with metal ions are of interest in studies of biological functions of metal ions, especially alkali and alkaline earth metals, because they have abundant distribution in the human body. In addition it is known that s-block metal ions interact with the negatively charged phosphate group of nucleic acids and thus stabilise the DNA and RNA structures.

The study of the structural chemistry of nucleobases with transition metals is well known and many complexes have been synthesized and characterised. By contrast, the literature does not show many structures containing nucleobases and s-block metals and only little information is provided on the subject [1].

To rectify this imbalance, part of our research concentrates on the synthesis and crystallographic characterisation of complexes of the five nucleobases (cytosine and thymine for example) with the Group I metal ions lithium, sodium, potassium, rubidium and caesium. We will present some examples of these new complexes and discuss the structural features observed in each case (coordination, hydrogen bonding etc.).



[1] Lippert B., *Coordination Chemistry Reviews*, 2000, **200-202**, 487-516.

**Keywords:** nucleobases, s-block metals, coordination

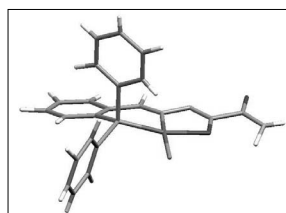
#### P.07.01.13

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#### Structure of Pd(II) Complex with a 2-(diphenylphosphino)benzaldehyde Derivative

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A Pd(II) complex with 2-{{(2E)-2-[2-(diphenylphosphino)benzylidene]hydrazino}-2-oxoacetamide was obtained from K<sub>2</sub>[PdCl<sub>4</sub>] and the ligand in ethanol.



The complex crystallizes in the monoclinic P2<sub>1</sub>/n space group. The chelate ligand is monodeprotonated at the hydrazonic nitrogen, and behaves as a PNO tridentate, generating a six-membered and a five-membered ring upon coordination. A chloride atom completes the square planar coordination geometry, which is slightly distorted, with the P atom deviating from the N, O, Pd, Cl best plane, due to the puckering of the six-membered chelation ring. Despite the presence of several hydrogen bond donors and acceptors on the complex molecule, the only evident directional interaction in the crystal packing is a very weak intermolecular contact N-H...N (N...N=3.405(6)Å, N-H...N=150(6)°).

**Keywords:** Pd(II) complex, hydrazone, PNO tridentate