

**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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$[\text{4}-(2\text{-diphenylphosphino-}\alpha\text{-ethoxy-benzyl-P})\text{-3-methyl-1-acetylacetonate-isothiosemicarbazido-N1,N4,O}]\text{nickel(II)}$ ,  $[\text{Ni}(\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_2\text{SP})]$ , 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