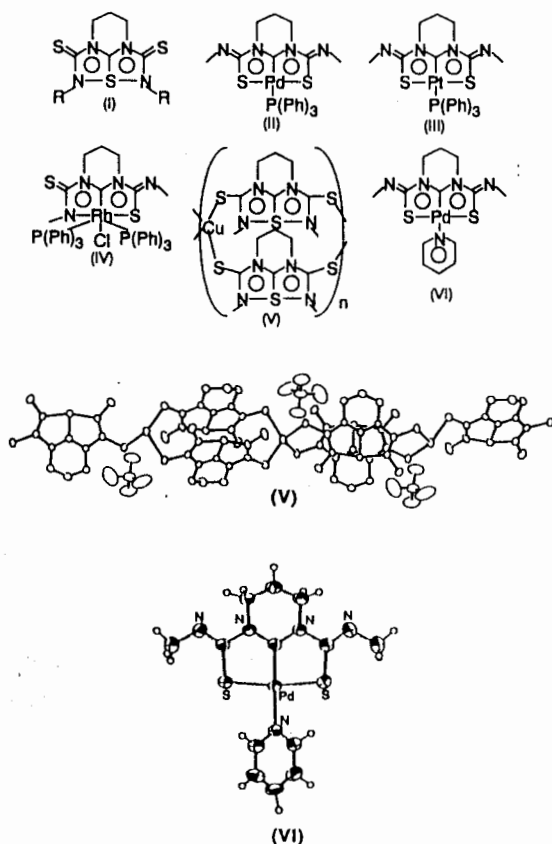


07-Crystallography of Organometallic and Coordination Compounds

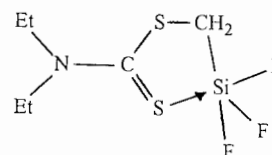


PS-07.04.19 ACTINIDE(IV) COMPLEXES OF THE INDENYL LIGAND: SYNTHESIS AND CRYSTAL STRUCTURES OF THREE NOVEL COMPOUNDS. By M.R. SPIRLET* Physique Expérimentale, University of Liège, Belgium, J. Rebizant, Karlsruhe, Germany, S. Beltonville and J. Goffart, Chimie Analytique et Radiochimie, University of Liège, Belgium.

As part of our structural investigations of actinide(IV) indenyl complexes, we report the preparation and crystal structure analysis of $U[C_9H-(CH_3)_6]_3Cl$ (I), $Th(C_9H_6-C_2H_5)_3CH_3$ (II) and $U(C_9H_7)_3OCH_2CF_3$ (III). Compound (I) crystallizes in space group $P-1$, $a=10.081(4)$, $b=13.339(4)$, $c=15.083(3)$ Å, $\alpha=85.24(4)$, $\beta=82.673(5)$, $\gamma=67.37(4)^\circ$, $Z=2$. The structure was refined to $R=0.027$ for 4364 reflections with $I>3\sigma(I)$. Compound (II) is monoclinic $P2_1/c$, $a=9.914(3)$, $b=30.95(1)$, $c=18.145(5)$ Å, $\beta=95.214(4)^\circ$, $Z=8$. The structure refined to $R=0.053$ for 3289 reflections with $I>3\sigma(I)$. Compound (III) is monoclinic $P2_1/c$ with $a=21.735(9)$, $b=9.339(4)$, $c=31.95(10)$ Å, $\beta=132.106(6)^\circ$, $Z=8$. The structure was refined to $R=0.056$ for 2917 reflections with $I>2\sigma(I)$. The stereochemistry about the U and Th atoms and the mode of bonding of the indenyl rings are discussed. A comparison is made with the structures of analogous actinide indenyl complexes previously reported.

PS-07.04.20 STRONG INTRAMOLECULAR DONOR-ACCEPTOR $Si\leftarrow S(=C)$ INTERACTION. By Yu.E.Ovchinnikov* and Yu.T.Struchkov, X-Ray Structural Centre, Russian Academy of Sciences, Vavilov St. 28, Moscow, 117813, Russia.

In the earlier known crystal structures the $Si\leftarrow S$ donor-acceptor bond length exceeds 3.4 Å (the Van der Waals radii sum is ca. 3.9 Å), i.e. its strength does not exceed that of a typical H-bond. By spectroscopic estimates in the molecule of recently prepared N,N-diethylthiocarbaminomethyltrifluorosilane (I) the coordinative $Si\leftarrow S(=C)$ bond enthalpy has an ordinary value of ca. 5 kJ/mol (Sorokin M.S., Shevchenko S.G., Chipanina N.N., Frolov Yu.L., Larin M.F., Voronkov M.G., *Metalloorganicheskaya Khimia* (Russian J. Organomet. Chem.), 1990, 3, N2, 419). The $Si\leftarrow S$ bond length in crystal I as obtained by our X-ray structural study is 2.697(1) Å. According to various indirect evaluations, the strength of bond with this length is ca. 10 times higher than the value obtained for molecule I in solution by Sorokin et al. Therefore, it can be supposed that the $Si\leftarrow S$ bond is shortened in crystal I, as compared with solution, due, most probably, to intermolecular dipole-dipole interactions. It should be stressed that in molecule I an additional coordination of the Si atom by the $>C=S$ group is observed for the first time. Contrary to analogs with a $Si\leftarrow O(=C)$ bond the 5-membered chelate cycle in I is strongly non-planar: the Si atom deviation from the rest four atoms plane is 1.17 Å. Probably, the retention of a relatively strong $Si\leftarrow S$ interaction in such conformation is due to much greater diffuseness of the S atom lone electron pairs as compared with the O atom.



PS-07.04.21 STRUCTURE OF NEW ORGANOSILICON σ -COMPLEXES OF TITANIUM. By Yu.E.Ovchinnikov* and Yu.T.Struchkov, X-Ray Structural Centre, Russian Academy of Sciences, Vavilov St. 28, Moscow, 117813, Russia.

In continuation of the systematic structural study of titanasilazanes for the first time the crystal structure of tri-coordinated Ti(III) σ -complex $Ti[N(SiMe_3)_2]_3$ (I) is determined. The molecule is situated on the 3 symmetry axis and the Ti atom coordination is planar with Ti-N of 1.956(4) and N-Si 1.746(3) Å. The extremely loose molecular packing in crystal leaves channels of ca. 8 Å in diameter filled with strongly disordered and hardly identifiable $HSiMe_3$ or/and $LiSiMe_3$. The tetra-coordinated Ti(IV) complex $(Et_2N)_3Ti-Si(SiMe_3)_3$ (II) crystallizes in the chiral space group $P4_12_12$ ($Z=8$). As the molecule II is itself chiral (with a rather accurate own C_3 symmetry and propeller-like conformation), the crystal is built of enantiomers of only one type. This is confirmed by the Hamilton test and η -refinement. An interesting feature of the molecule II structure is a significant (up to 15°) inequality of the TiNSi angles in the $Ti-N(SiMe_3)_2$ fragments. This structural feature is observed also in some other Ti(IV) σ -complexes. On the contrary, in molecule I all bond angles at the N atoms are equal to 120°.

PS-07.04.22
CRYSTAL AND MOLECULAR STRUCTURES
OF NEW METALLOBICYCLOPHthalocyanines

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