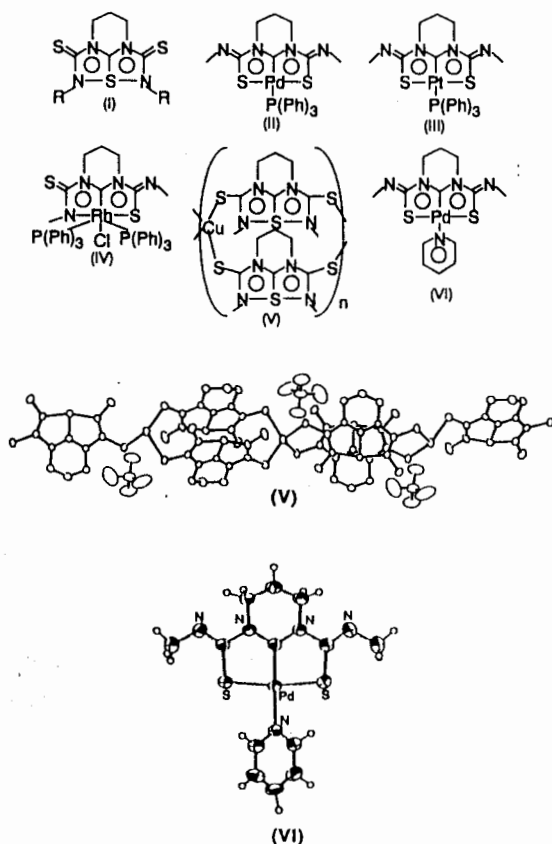


## 07-Crystallography of Organometallic and Coordination Compounds

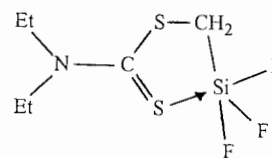


**PS-07.04.19** ACTINIDE(IV) COMPLEXES OF THE INDENYL LIGAND: SYNTHESIS AND CRYSTAL STRUCTURES OF THREE NOVEL COMPOUNDS. By M.R. SPIRLET\* Physique Expérimentale, University of Liège, Belgium, J. Rebizant, Karlsruhe, Germany, S. Beltonville and J. Goffart, Chimie Analytique et Radiochimie, University 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  $\sigma$ -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)  $\sigma$ -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  $\eta$ -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)  $\sigma$ -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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## 07-Crystallography of Organometallic and Coordination Compounds

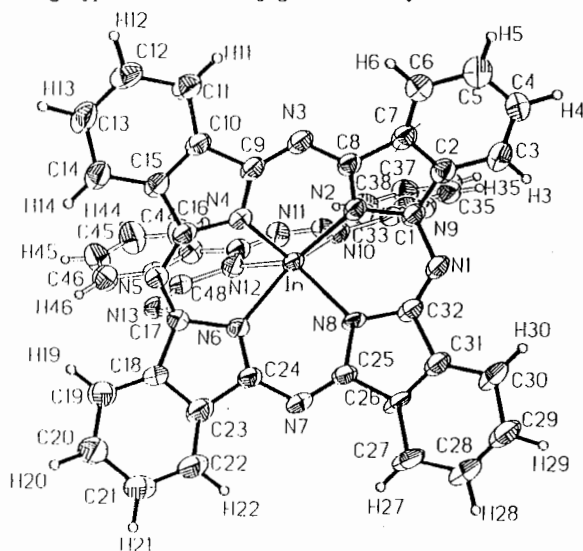
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Two new complexes of bicyclophtalocyanines have been obtained in the crystalline form. Here we present the crystal structures determination of (I)  $\text{GdC}_{48}\text{H}_{24}\text{N}_{12}$  and (II)  $\text{InC}_{48}\text{H}_{24}\text{N}_{12}$ .

Crystal Data: (I)  $M_r = 939.3$ , triclinic system, space group  $P\bar{1}$ ,  $a = 12.388(2)$ ,  $b = 15.978(3)$ ,  $c = 11.683(2)$  Å,  $\alpha = 86.00(2)$ ,  $\beta = 65.12(2)$ ,  $\gamma = 75.62(2)^\circ$ ,  $V = 2030.5(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_0(\text{floatation}) = 1.53$  gcm<sup>-3</sup>,  $D_c = 1.537$  gcm<sup>-3</sup>,  $\lambda(\text{MoK}\alpha) = 0.71073$  Å,  $\mu = 16.9$  cm<sup>-1</sup>,  $T = 300$  K,  $F(000) = 934$ . Final  $R = 0.047$ ,  $R_w = 0.050$  and  $S = 1.31$  for 4749 independent reflections ( $I > 4\sigma$ ) and 655 refined parameters.

(II)  $M_r = 896.8$ , triclinic system, space group  $P\bar{1}$ ,  $a = 12.408(2)$ ,  $b = 15.998(3)$ ,  $c = 11.693(2)$  Å,  $\alpha = 85.63(2)$ ,  $\beta = 64.92(2)$ ,  $\gamma = 75.56(2)^\circ$ ,  $V = 2034.7(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_0(\text{floatation}) = 1.46$  gcm<sup>-3</sup>,  $D_c = 1.465$  gcm<sup>-3</sup>,  $\lambda(\text{CuK}\alpha) = 1.54056$  Å,  $\mu = 51.5$  cm<sup>-1</sup>,  $T = 300$  K,  $F(000) = 904$ . Final  $R = 0.069$ ,  $R_w = 0.073$  and  $S = 1.65$  for 7194 independent reflections ( $I > 4\sigma$ ) and 655 refined parameters.

The molecular geometry and numbering of the atoms is illustrated on Fig.1. The bicyclophtalocyaninato ligand consists of the phtalocyaninato skeleton of four isoindole units bridged by two additional isoindole moieties (see Fig.1). The ligand can also be described as two phtalocyaninato anions having one common half. It can be assumed that the ligand is less stable than phtalocyaninato anion as the conjugation  $\pi$ -electron system of the inner 16-membered C-N ring is interrupted at the two  $sp^3$ -hybridized atoms C1 and C17 of the ring linkage to a bicyclo system. The C-N distances reflect the interruption of the  $\pi$ -electron delocalization system. The bonds at the atoms C1 and C17 average 1.520 Å, and this is close to the expected value for a single bond between  $sp^3$ - and  $sp^2$ - hybridized C atoms. They adjoin shorter bonds of about 1.281 Å which represent double bonds. The other C-N bond distances ranging from 1.315 to 1.440 Å, being typical for a conjugated C-N system.



The six N-isoindole donor atoms of the whole bicyclophtalocyaninato ligand which are coordinated to the central atom (Gd or In) form an irregular octahedron.

PS-07.04.23 THREE CRYSTAL STRUCTURES OF Cu(II) COMPLEXES OF THE DEPROTONATED ANION WITH THE LIGANDS OF DIAZADIAMIDES. By Chung-Sun Chung\* and Kelun Shu, Department of Chemistry; Tahir. H. Tahirov, and Tian-huey Lu, Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, China

The solution chemistry of diazadiamides and Cu(II) ions forming binuclear and monomer complexes has been extensively studied by potentiometric and spectrophotometric methods (Bai & Martell, J. Amer. Chem. Soc., 1969, 91, 4412-4420; Muir & Rechani, Inorg. Chim. Acta. 1974, 11, 127-136; Armani, Marchelli, Dossena, Casasti & Dallavalle, Helv. Chim. Acta, 1986, 69, 1916-1922). However, in solid state, these complexes containing alkyl groups on carbon or nitrogen have received very little attention. In order to study the steric effect of the N-alkyl or C-alkyl groups on the structure of the C(II) complexes, we have prepared and studied the structures of the three Cu(II) complexes which were determined by X-ray diffraction. Their ligands and crystal data at room temperature are: (A), N,N'-diglycylethylenediamine,  $[\text{Cu}_2(\text{C}_6\text{H}_{13}\text{N}_4\text{O}_2)_2(\text{H}_2\text{O})_2][(\text{ClO}_4)_2] \cdot 4(\text{H}_2\text{O})$ ,  $M_r = 780.47$ , monoclinic,  $P2_1/n$ ,  $a = 7.321(1)$ ,  $b = 9.786(1)$ ,  $c = 20.803(2)$  Å,  $R = 0.038$ ,  $wR = 0.038$  for 1424 observed reflections; (B), N,N'-bis(N-propylglycyl)ethylenediamine,  $[\text{Cu}_2(\text{C}_{12}\text{H}_{25}\text{N}_4\text{O}_2)_2(\text{H}_2\text{O})_2][(\text{ClO}_4)_2]$ ,  $M_r = 820.708$ , monoclinic,  $P2_1/n$ ,  $a = 9.454(1)$ ,  $b = 27.61(1)$ ,  $c = 14.762(3)$  Å,  $R = 0.058$ ,  $wR = 0.061$  for 7012 observed reflections; (C), (2R, 10R)-N,N'-dialanyethylenediamine,  $[\text{Cu}(\text{C}_9\text{H}_{18}\text{N}_4\text{O}_2)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.656(3)$ ,  $b = 12.020(2)$ ,  $c = 15.890(1)$  Å,  $R = 0.043$  for 1615 observed reflections. The first two complexes are binuclear. Both Cu(II) ions are five-coordinated, and the geometry about Cu(II) is a distorted square pyramid. Two donor N atoms of one tetradentate ligand and one O atom of the other ligand form a slightly distorted plane and a water O atom occupies the axial position. The last complex is monomeric. The coordination geometry about the Cu(II) ion is distorted square pyramidal with a water O atom in the axial position, and two amine and two deprotonated amide N atoms in equatorial positions. The water molecules, amino groups and carbonyl O atoms participate in forming H-bonds. [Work was supported by National Science Council, Taiwan, China].

