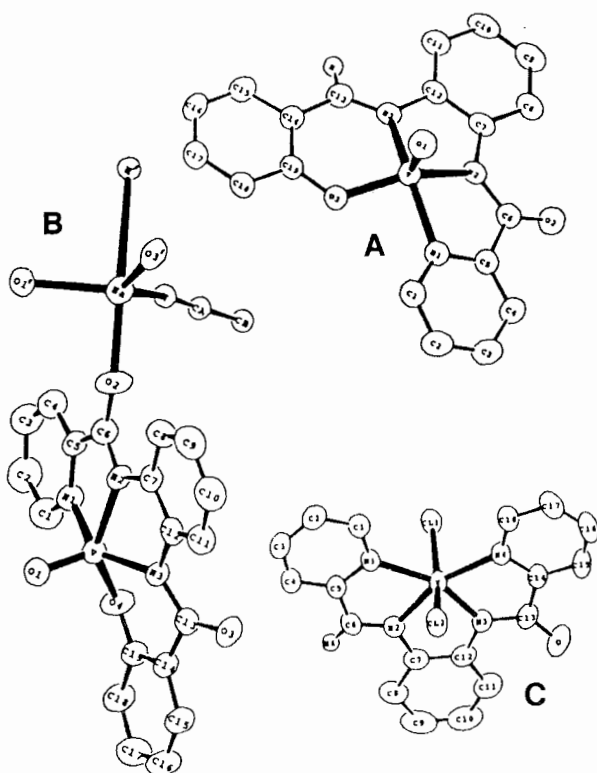


## 07-Crystallography of Organometallic and Coordination Compounds

225



PS-07.04.17

## 1,4-BENZODIAZEPINE COMPLEXES INVESTIGATION. CRYSTAL AND MOLECULAR STRUCTURE OF NIMETAZEPAM COPPER DERIVATIVE

F.Corradini, G.C.Franchini, A.Marchetti, C.Preti, M.Tagliazucchi, Department of Chemistry, University of Modena, via G.Campi 183, 41100 Modena, Italy

Following our studies in the chemical behaviour of 1,4-benzodiazepines as ligands owing to their biological applications, we report the preparation, the spectroscopic characterization, crystal and molecular structure of the copper(II) chloride derivative of nimetazepam,

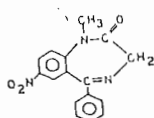
nimetazepam  
(nmz)

Figure 1

7-nitro-1,3-dihydro-5-phenyl-1-methyl-2H-1,4-benzodiazepin-2-one as shown in Figure 1.

The copper(II) derivative, of the type  $\text{Cu}(\text{nmz})_2\text{Cl}_2 \cdot 2\text{nmz}$ , belongs to the triclinic space group  $\bar{P}1$  with  $a = 9.860(2)$ ,  $b = 10.670(2)$  and  $c = 16.115(3)$  Å,  $\alpha = 91.46(2)$ ,  $\beta = 102.26(2)$ ,  $\gamma = 115.54(2)$  deg, and  $z = 2$ . The structure was solved by the heavy-atom method and refined by full-matrix least square techniques to a final  $R = 0.049$  ( $R_w = 0.052$ ) for 5051 collected reflections.

A stereoview of the molecule is shown in Figure 2. The copper ion is in a planar environment by conditions of crystallographic symmetry. This unusual perfect planarity could be explained taking into account the perturbation which could be induced by the proximity of the hydrogen atoms on the C(15) and its centrosymmetric which are close enough to warrant special attention,  $\text{Cu} \cdots \text{H} = 2.64(2)$  Å. The crystal packing consists of  $\pi - \pi$  interactions, involving also the two other non-bonded molecules of ligands present in the lattice.

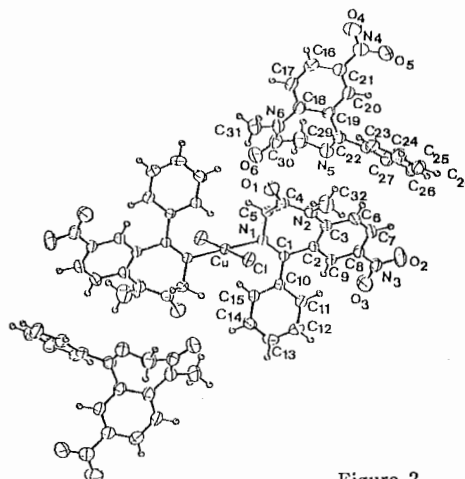


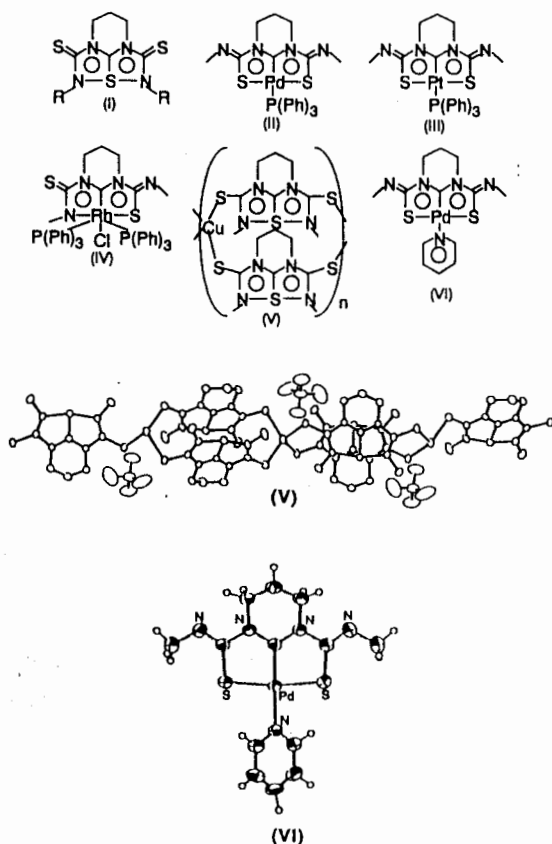
Figure 2

PS-07.04.18 STRUCTURES OF METAL COMPLEXES DERIVED FROM THE TETRAAZATHIAPENTALENE DERIVATIVE. By N. Manabe\*, M. Yasui, S. Yoshida, S. Shimamoto and F. Iwasaki, Dept. of Applied Physics and Chemistry, The Univ. of Electro-Communications, Chofu, Tokyo 182, Japan.

6 $\alpha$ -Thiatetraazapentalene derivative (I) which contains a hypervalent sulfur atom (Iwasaki, F., et al. (1991) Acta Cryst. C47, 998-1003) was found to give some novel metal complexes (II-IV) with metalpentalene frameworks by treating with metal triphenylphosphines (Yasui, M., et al. (1992) AsCA Inaugural Conference, 15U-57). In this paper we describe structures of a new type copper complex (V) and a palladium complex with a pyridine ligand (VI). The Cu complex (V) was synthesized by the reaction of (I) with  $\text{Cu}(\text{ClO}_4)_2$ . X-Ray study has revealed that four S atoms of the thiocarbonyl group from four molecules of (I) coordinate to the Cu atom and that the rest of the thiocarbonyl S atoms coordinate to another Cu atom. Thus the Cu atom is four-coordinated with tetrahedral arrangement and the molecular chain extends over the whole unit cell. In this complex, two pairs of pentalene frameworks are facing parallel to each other. The Pd complex (II) was treated with 18% HCl aq. to give the complex without triphenylphosphine, and then treated with pyridine to give complex (VI). The metalpentalene framework still remains in complex (VI). The Pd atom is consequently four coordinated square-planar as in (II). The two molecules in the asymmetric unit are chemically equivalent. Bond lengths are Pd-S 2.28 Å and Pd-C 1.944 Å that are slightly shorter than the sum of covalent radii. The length of Pd-N (2.106 Å) is longer than the sum of covalent radii.

	(V)	(VI)
Color	Yellow	Yellow
Fw	683.77	414.9
Crystal System	monoclinic	monoclinic
Space group	P2/n	P2/n
a/Å	17.693(2)	16.155(2)
b	9.848(1)	23.092(3)
c	16.085(2)	8.901(1)
$\beta$ /°	11.82(1)	105.72(1)
Z	4	8
measured	6377	7820
observed	4696	5627
R	0.039	0.035

## 07-Crystallography of Organometallic and Coordination Compounds

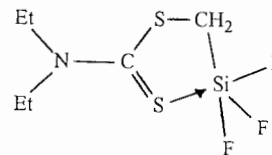


**PS-07.04.19** ACTINIDE(IV) COMPLEXES OF THE INDENYL LIGAND: SYNTHESIS AND CRYSTAL STRUCTURES OF THREE NOVEL COMPOUNDS. By M.R. SPIRLET\* Physique Expérimentale, University of Liège, Belgium, J. Rebizant, Karlsruhe, Germany, S. Beltonville and J. Goffart, Chimie Analytique et Radiochimie, University 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  $15^\circ$ ) 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  $120^\circ$ .

**PS-07.04.22**  
CRYSTAL AND MOLECULAR STRUCTURES  
OF NEW METALLOBICYCLOPHthalocyanines

Jan Janczak and Ryszard Kubiak

Institute for Low Temperature and Structure Research,  
Polish Academy of Sciences, 50-950 Wrocław, POLAND