07-Crystallography of Organometallic and Coordination Compounds

PS-07.04.20 STRONG INTRAMOLECULAR DONOR-ACCEPTOR Si-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=3 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-diethylthiacarbamoylmethyldifluorosilane (I) the coordinative Si-S(=C) bond enthalpy has an ordinary value of ca. 5 kJ/mole (Scorokh M.S., Stoevchenko S.G., Chipanina N.N., Frolov Yu.L., Lur'm M.F., Voronkov M.G., Metalloorganicheskiye Khimia (Russian 1. Organomet.), 1990, 3, N2, 419). The Si-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 larger than the value obtained for molecule I in solution by Scorokh et al. Therefore, it can be supposed that the Si-S bond is strengthened in crystal I, as compared with solution, due, most probably, to intramolecular 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-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-S interaction in such a structure is due to much greater diffuseness of the S atom lone electron pair as compared with the O atom.

PS-07.04.21 STRUCTURE OF NEW ORGANOSILICON o-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 titanocarbaboranes for the first time the crystal structure of tri-coordinated Ti(III) o-complex Ti(N(SiMe3))3-I (I) is determined. The molecule is situated on the 3 symmetry axis and the Ti atom coordination is planar with Ti-N of 1.550(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 HSMeO, or even LiSiMe3. The tetra-coordinated Ti(IV) complex (Et2NH)2Ti(Si(SiMe3))4-I (II) crystallizes in the chiral space group P4121/2 (Z=8). As the molecule II is itself chiral (with rather accurate own C3 symmetry and propeller-like conformation), the crystal is built of enantiomers of only one type. This is confirmed by the Hamilton test and n-refinement. An interesting feature of the molecule II structure is a significant (up to 15%) inequality of the Ti-Si angles is the Ti(IV) complex fragments. This structural feature is observed also in some other Ti(IV) o-complexes. On the contrary, in molecule I all bond angles at the N atoms are equal to 129°.

PS-07.04.22 CRYSTAL AND MOLECULAR STRUCTURES OF NEW METALLOBICYCLOPHALOCYANIN. By Jan Jacek and Ryszard Kubalek Institute for Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wroclaw, POLAND