

08.2-41 THE CRYSTAL AND MOLECULAR STRUCTURE OF GEM- $N_3P_3Cl_4(NPPh_3)_2$. CONFORMATION OF THE TRIPHENYLPHOSPHAZENYL GROUPS.

By M. Krishnalah and L. Ramamurthy, Department of Physics, Sri Venkateswara University, Tirupathi-517502, India and P. Ramabrahmam and H. Manohar, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India.

Triphenylphosphazencyclophosphazenes have recently attracted considerable interest in view of the dependence of the conformation of the exocyclic $-N=PPH_3$ group on the other substituent attached to the same phosphorus atom (Shaw, Phosphorus and Sulphur (1979) 5, 363). Basicity data (Biddlestone et al., J.C.S. Dalton (1975) 2634) and ^{31}P NMR spectroscopy (Biddlestone et al., Z. Naturforsch. (1976) 31b, 1001) have proved useful in these conformational studies and several predictions based on these measurements have been assessed in the light of X-ray crystallographic results. The $-NPPH_3$ substituent exhibits what is termed as Type I conformation in $N_3P_3Cl_5(NPPh_3)$ (Babu et al., Acta Cryst. (1979) B35, 1410) and Type II conformation in gem- $N_3P_3Cl_4Ph(NPPh_3)$ (Biddlestone et al., Chem. Comm. (1974) 56). A Type III conformation intermediate between Types I and II has been identified in $N_4P_4Cl_7(NPPh_3)$ (Babu et al., Acta Cryst. (1979) B35, 2363) and gem- $N_3P_3Cl_4(NEt_2)(NPPh_3)$ (Babu et al., J.C.S. Dalton (1981) 0000). The crystal structure of gem- $N_3P_3Cl_4(NPPh_3)_2$ has been investigated in order to assess the mutual effect of the two geminal $NPPH_3$ groups on their conformation, as well as on the conformation of the P-N ring.

The crystals are triclinic, space group $P\bar{1}$ with $a=10.723(1)$, $b=11.567(2)$, $c=17.454(6)$ Å, $\alpha=102.6(2)$, $\beta=87.1(2)$, $\gamma=114.6(1)^\circ$, $V=1918$ Å³, $Z=2$, $D_c=1.435$, $D_m=1.45$ g cm⁻³. Based on 3071 diffractometer data collected using MoK α radiation, the structure was solved by a combination of direct and Fourier methods and refined to $R=0.036$ with anisotropic temperature factors for non-hydrogen atoms.

The phosphazene ring exhibits three distinct pairs of P-N distances, whose variation can be correlated with the nature of the substituents. In the exocyclic $-NPPH_3$ groups, two sets of P-N bond lengths (mean values: 1.601 and 1.559 Å) are observed, consistent with chemical reasoning. Such differences are observed for the first time in cyclophosphazenes. Contrary to expectation on the basis of basicity values, both $NPPH_3$ groups exhibit virtually exact Type II conformation, where the N_{exo} - P_{exo} bond of one group is coplanar with P_{endo} - N_{exo} bond of the other (torsion angles: 7° and -177°). The phosphorus atom carrying the $NPPH_3$ groups deviates by 0.50 Å from the plane of the other atoms in the P-N ring. The $^4J(P-P)$ coupling constant for this compound in solution is close to zero, consistent with Type II conformation in the crystal.

08.2-42 STRUCTURAL CHEMISTRY OF TERNARY PHOSPHORUS

CHALCOGENIDES: THE CRYSTAL STRUCTURES OF TiP_2S_6 AND $Ti_4P_8S_{29}$. By M. Z. Jandali, G. Eulenberger and H. Hahn. Institute of Chemistry, Hohenheim University, Garbenstrasse 30, D-7000 Stuttgart 70, F. R. G.

TiP_2S_6 crystallizes in the orthorhombic system, space group Fdd2 with $a = 10.842(4)$, $b = 7.440(5)$, $c = 21.535(6)$ Å and $Z = 8$. The crystal structure of TiP_2S_6 contains anionic $(P_2S_6)^{4-}$ groups, thus the compound constitutes a titanium(IV) hexathiohypodiphosphate. The P atoms are tetrahedrally surrounded by three S atoms (mean distance P-S: 2.039 Å) and one further P atom at a distance of 2.207 Å. The P-P atom pairs are located within planes parallel to (001) and have parallel orientation in each of them. By Ti-S bonds the $(P_2S_6)^{4-}$ groups are linked into chains extending approximately in the direction of the P-P axes. By further Ti-S bonds a three-dimensional framework is formed. In this way the Ti atoms attain a distorted octahedral coordination with distances Ti-S ranging from 2.433 to 2.454 Å. TiP_2S_6 represents a new structural type unrelated to the known structural types of hexathiohypodiphosphates of divalent metals.

$Ti_4P_8S_{29}$ is monoclinic, space group C 2/c with $a = 19.724(4)$, $b = 17.050(5)$, $c = 12.608(3)$ Å, $\beta = 95.52(2)^\circ$ and $Z = 4$. According to its structure the compound constitutes a titanium(IV) thiophosphate(V) containing three types of anionic P-S groups. There are three crystallographically different $(PS_4)^{3-}$ groups, two of them situated at twofold axes (mean distance P-S for the $(PS_4)^{3-}$ groups: 2.028 Å). Furthermore, the $(P_2S_6)^{2-}$ group formed by two edge-sharing PS_4 tetrahedra is characterized by a planar four-membered ring of alternate P and S atoms. The novel $(P_2S_7)^{2-}$ group can be derived by replacement of one bridging S atom in the $(P_2S_6)^{2-}$ group by a pair of S atoms, thus containing a non-planar five-membered ring of P and S atoms. The $(P_2S_7)^{2-}$ group exhibits disorder corresponding to two possible orientations of the five-membered ring in the structure. The Ti atoms are octahedrally surrounded by six S atoms (mean distance Ti-S: 2.434 Å). In this way, the P-S structural units described above are linked into a complicated three-dimensional framework.