

09.3-1 TETRAPHENYLANTIMONY(V) COMPOUNDS; STRUCTURES OF TETRAPHENYLANTIMONY(V) BROMIDE, PERCHLORATE, & TETRAPHENYLBORATE. By G. Ferguson, Department of Chemistry & Biochemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1 and C. Glidewell, D. Lloyd and S. Metcalfe, Chemistry Department, University of St. Andrews, Fife, KY16 9ST, Scotland.

The structure of  $\text{Ph}_4\text{SbBr}$  consists of discrete molecules which have trigonal-bipyramidal geometry; the Sb-Br bond is very long (2.965(1) Å), the apical Sb-C bond (2.151(9) Å) is longer than the mean equatorial distance (2.102(9) Å), and the mean C(eq)-Sb-C(ap) angle is 95.8°. These data are consistent with both salt and stiborane forms making significant contributions to the ground state structure, but with the stiborane form predominating.

Crystals of  $\text{Ph}_4\text{Sb}^+\cdot\text{ClO}_4^-$  contain discrete cations and anions each of which has crystallographic  $\bar{4}$  symmetry. The  $\text{SbC}_4$  core has  $\bar{4}3m$  symmetry within experimental error and the unique Sb-C bond length is 2.095(2) Å. Work is in progress on the structure of  $\text{Ph}_4\text{Sb}^+\cdot\text{Ph}_4\text{B}^-$ . The material crystallizes in a body-centred tetragonal lattice with  $4/mmm$  Laue symmetry. Both cation and anion appear to be scrambled in the unit cell, with the tetrahedral ions disordered about various sets of special positions.

**Crystal Data:**  $\text{Ph}_4\text{SbBr}$ ,  $a = 16.293(3)$ ,  $b = 10.616(3)$ ,  $c = 12.507(3)$  Å,  $\beta = 105.60(1)^\circ$ ,  $Z = 4$ ,  $P2_1/n$ . Data to two theta (Mo)  $54^\circ$ ,  $R = 0.044$  for 1660 observed reflections.

$\text{Ph}_4\text{Sb}^+\cdot\text{ClO}_4^-$ ,  $a = 12.670(2)$ ,  $c = 6.711(2)$  Å,  $Z = 2$ , Space group  $I4$ . Data to two-theta (Mo)  $80^\circ$ ,  $R = 0.025$  for 1647 observed reflections.

$\text{Ph}_4\text{Sb}^+\cdot\text{Ph}_4\text{B}^-$ ,  $a = 16.272(3)$ ,  $c = 13.703(4)$  Å,  $Z = 4$ . Body-centred  $I$ -lattice, various space groups possible. Data to two-theta (Mo)  $54^\circ$ .

09.3-2 STRUCTURE OF A HETEROBIMETALLIC COBALT/PLATINUM COMPLEX WITH UNUSUAL COBALT GEOMETRY

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Bis[(N,N-diisopropylidithiocarbamato)bis(diphenylthio-phosphinito)platinate-0,0']cobalt(II) is one of a series of heterobimetallic complexes of sulphur ligands prepared in order to study the coordination geometry at the metal atoms (e.g. J.R. Allan, J. Halfpenny, G.H.W. Milburn, T.A. Stephenson and P.M. Veitch, J.Chem.Res.(S) 1986, 270; J.Chem.Res.(M) 1986, 2601). As in similar compounds of this type, each of the two platinum atoms is surrounded by two sulphur and two phosphorus atoms in an approximate square plane. The central cobalt(II) atom however does not have the expected tetrahedral geometry but instead has an unusual Y-shaped coordination to three sulphur atoms with two long and one short Co-S bonds. Comparison will be made with the structures of related cobalt(II) complexes.

09.3-3 EXPERIMENTAL MODELLING OF THE STRUCTURE OF CYCLOLINEAR CARBOSILOXANES. By Yu. E. Ovchinnikov, V.E. Shklover and Yu. T. Struchkov, Institute of Organoelement Compounds of the USSR Academy of Sciences, Moscow, Vavilov St.28.

The method of experimental modelling of the polymer structures based on structural studies of corresponding low oligomers was used for interpretation of a poor diffraction pattern of polyhexamethylcyclotetrasiloxanylene (PHMCTSOE). According to monocrystal data the dimeric (I) and trimeric (II) oligomers of this polymer are isostructural (Table) with the c axis being elongated on the chain growth. Therefore it became possible to determine the sub-unit cell of crystalline PHMCTSOE (Fig.). The obtained model of the polymer crystal structure was compared with its diffractogram, which had three main well-resolved peaks. The corresponding experimental interplanar distances are in good agreement with the values calculated from the model sub-unit cell parameters based on oligomer structures. This testifies to validity of this model approach, which has been applied to other organosilicon polymers.

Table	PHMCTSOE		
	Sub-unit cell		
a, Å	6.345(4)	6.357(3)	6.36
b	8.104(4)	8.111(4)	8.11
c	15.939(8)	23.394(8)	7.77
$\alpha$ , deg.	92.54(4)	90.72(3)	95.4
$\beta$	96.67(4)	95.88(3)	105.3
$\gamma$	105.16(4)	104.87(4)	104.9

Angle between the long molecule axis and axis, deg

a	74.4	74.7
b	84.4	84.7
c	16.6	16.3

Distances between axes of adjacent molecules, Å

	6.112	6.130
	8.065	8.076

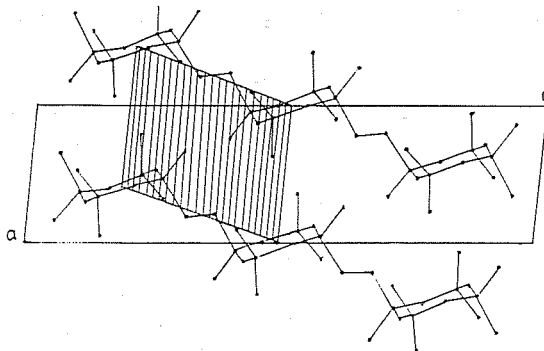


Fig. Sub-unit cell of PHMCTSOE in the crystal structure II