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SYNTHESIS AND STRUCTURE OF A POLYNUCLEAR COMPLEX WITH A FRAMEWORK CONSISTING OF GERMANIUM, BISMUTH AND PLATINUM ATOMS

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Summary

The structure of the product of the interaction of $(C_6F_5)_2GeH_2$ with Et_3Bi has been defined more precisely by X-ray analysis. The heteroelemental framework of this compound is found to be a trigonal bipyramid in which the two apical Bi atoms are bonded by three bis(pentafluorophenyl)germyl bridges. The symmetry of the framework is D_{3h}. The average value of the Ge—Bi bond length is 2.739(1) Å. The average values of the Ge—Bi—Ge and Bi—Ge—Bi angles are equal to 72.11(4) and 93.94(4)°, respectively.

Reaction of the compound with $Pt(PPh_3)_3$ yields the unusual 6-nuclear complex $[(C_6F_5)_2Ge]_3Bi_2Pt(PPh_3)_2$. It was shown by an X-ray study that the two Ge, two Bi and Pt atoms form a nonplanar cycle in this complex. Moreover, the Bi atoms are bonded by the $(C_6F_5)_2Ge$ bridged group. The symmetry of the heavy atom framework is somewhat disordered from C_s. The Pt atom has a square-planar coordination. The Ge—Pt and Bi—Pt bond lengths are equal to 2.466(3) and 2.759(3) Å, respectively. The Ge—Bi bond lengths are changed in the range from 2.695(5) to 2.774(6) Å depending on their positions in the molecule. The GeBiGe angles in the 4-member GeBiGeBi cycle are 87.6(2) and 70.9(2)°, and the BiGeBi angles are 98.3(2) and 98.5(2)°. The GeBiGe angle in the 5-member PtGeBiGeBi cycle is equal to 87.6(2)°, and the GeBiPt angle is 100.8(1)°. The pentafluorophenyl and triphenylphosphine ligands have the usual geometry.

Introduction

Recently, we have shown that reaction of $(C_6F_5)_2GeH_2$ with triethylbismuth in the absence of solvent gives a light orange crystalline product, I, with dec.

>160°C [1]. This compound was found to contain 27.00% of C, 0.79% of H and 32.94% of Bi; its molecular weight (cryoscopy in benzene) is equal to 1340. In the IR spectrum of the product, together with the absorption bands characteristic of C_6F_5—Ge groups, there is a weak absorption at 630 cm^{-1} which may be assigned to the ν(C—Bi) stretching frequency. In view of these data the $[(C_6F_5)_2GeBiEt]_2$ formula was suggested for product I, which contains a $\overline{GeBiGeBi}$ heterocycle. The calculated composition of C, H, Bi and the calculated molecular weight for this formula (26.08, 0.78, 32.41% and 1289 mol.w.) correspond to found values of those elements. As it was shown, the reaction of I with bromine proceeds with formation of $(C_6F_5)_2GeBr_2$, $BiBr_3$ and EtBr (the last was identified qualitatively). Such a composition of products confirmed the proposed formula. But in the reaction of I with hydrogen chloride no derivatives containing ethyl groups were found which does not agree with this formulation.

To solve this problem we carried out an X-ray structural analysis of the product I. The results are given in this paper. In addition we report here on the interaction of germylbismuth compounds with triphenylphosphine complexes of zero-valent platinum and the structure of one of the products of these reactions.

Results and discussion

It was shown by X-ray study that the compound I, formed in the reaction of Et_3Bi with $(C_6F_5)_2GeH_2$, does not have ethyl substituents and that its structure is more interesting than that assumed before. Its heteroelemental framework consists of three Ge and two Bi atoms and has the trigonal-bipyramidal structure. The two apical Bi atoms are bonded by the three bis(pentafluorophenyl)-germyl bridges, so that the Ge atoms are situated in the equatorial positions (Fig. 1). The symmetry of the framework is D_{3h}. The Bi—C bond lengths are in the range 2.733(2)—2.751(2) Å, so that they are close to the sum of Pauling's covalent radii, 2.73 Å [2], i.e. the atoms form the normal covalent bonds with the Ge atoms. The Bi atoms have the usual pyramidal and the Ge atoms the usual tetrahedral coordination. However the values of the GeBiGe (71.71—73.58°) and BiGeBi (93.80—93.96°) angles differ significantly from the ideal values, 90 and 109.5°, respectively. The pentafluorophenyl fragments have the usual geometry.

The calculated carbon content in $[(C_6F_5)_2Ge]_3Bi_2$ is closer to the found value (27.00%) than that of $[(C_6F_5)_2GeBiEt]_2$ is. However, the H and Bi contents and the molecular weight (0%, 25.52%, 1638) differ noticeably from the found values (0.79%, 32.94%, 1340) [1]. This discrepancy is obviously explained by insufficient purity of the samples of I used for analysis and determination of the molecular weight. The presence in the samples of even a small amount of intermediates or by-products (for example $(C_6F_5)_2Ge(BiEt_2)_2$) could lead to the results obtained. Repeated investigation of the compound I has shown that the absorption band at 630 cm^{-1} in the IR spectrum mentioned above does not relate to the stretching modes of ethyl groups or C—Bi bonds because this band remains in the spectrum of sample of I purified thoroughly by repeated recrystallization from toluene. Assignment of this band and also of the previously

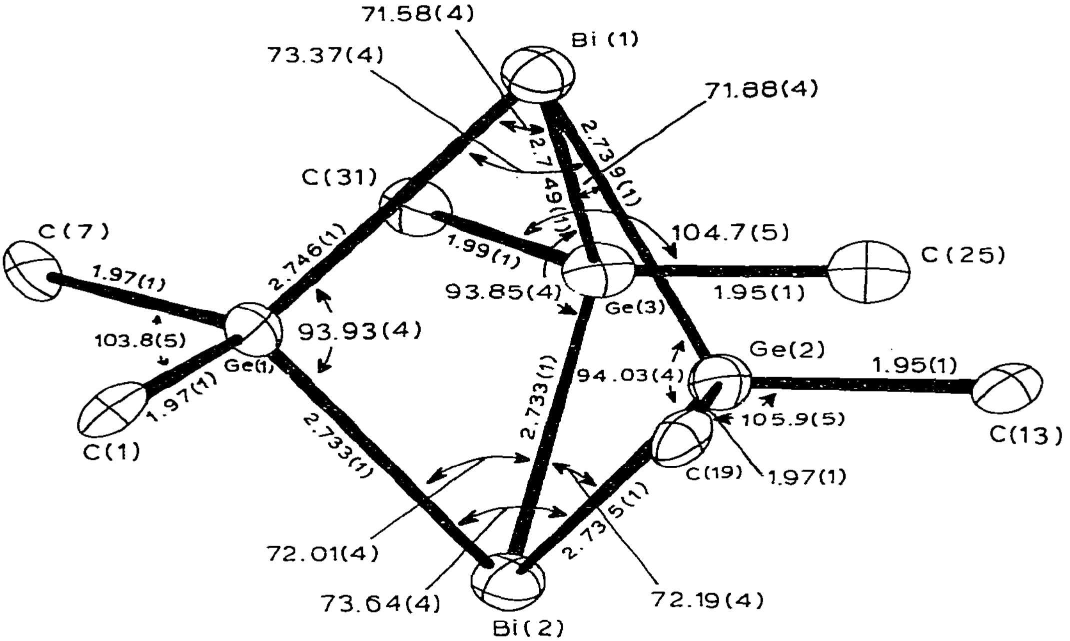
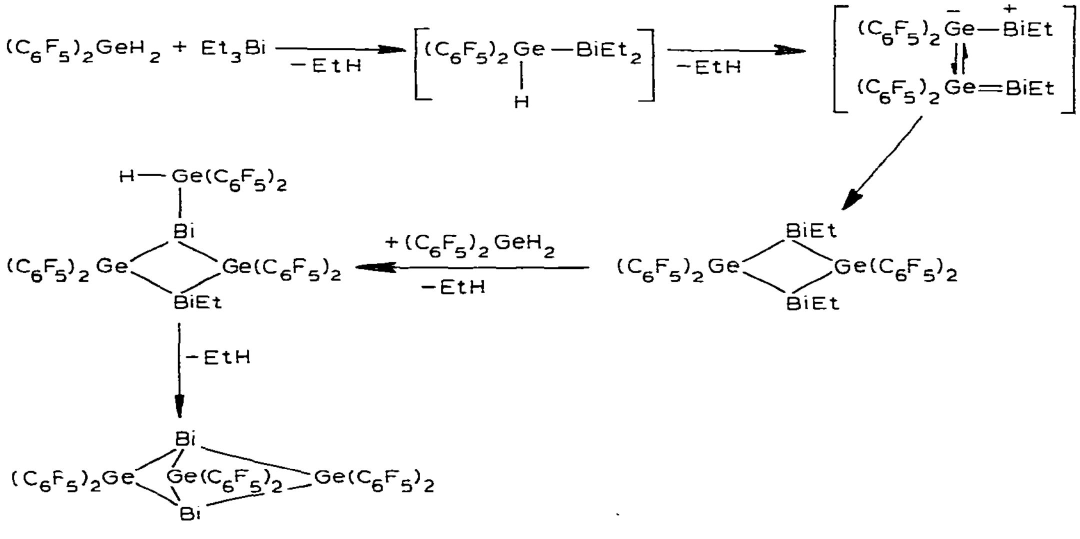


Fig. 1. The heteroelement framework of $[(C_6F_5)_2Ge]_3Bi_2$.

unmentioned additional band at 1150 cm^{-1} is difficult without a special investigation.

Thus, the scheme of the interaction of $(C_6F_5)_2GeH_2$ with Et_3Bi can be represented in the following way:

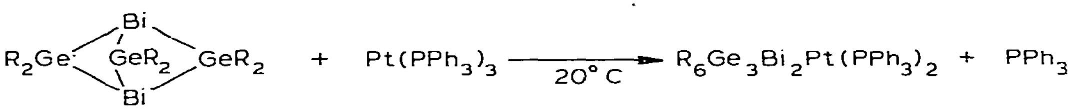
SCHEME 1



(I)

The determination of the exact structure of product I allowed use of the correct ratio of starting reagents in its synthesis. Besides, we found that the synthesis of I in toluene proceeds more calmly than the synthesis in the absence of solvent proposed before.

Continuing the investigation of the properties of germylbismuth derivatives we made an attempt to obtain novel polynuclear compounds via insertion of a complex of zero-valent platinum into the Ge—Bi bond. Earlier we had found that $Pt(PPh_3)_2$ carbenoid readily inserts into Ge—Hg, Ge—Cd, Ge—Zn and Sn—Hg bonds [4—6]. It was found that tris(triphenylphosphine)platinum does not react with $(C_6F_5)_2GeBiEt_2$ on heating at 50°C in benzene solution. Interaction of the platinum complex with ethyl{bis[tris(pentafluorophenyl)germyl]}bismuth, $[(C_6F_5)_3Ge]_2BiEt$, proceeds slowly at room temperature according to liquid adsorption chromatography, but we failed to isolate an individual compound from the complex mixture of products. On the contrary, tricyclic dibismuth derivative I readily adds one equivalent of $Pt(PPh_3)_2$ to form a stable six-nuclear product of a general formula $(C_6F_5)_6Ge_3Bi_2Pt(PPh_3)_2$ (II).



(I) (II)

$R = C_6F_5$

On addition of a benzene solution of $Pt(PPh_3)_3$ to a benzene solution of $[(C_6F_5)_2Ge]_3Bi_2$ (I) the reaction mixture immediately turns dark cherry. During the process of benzene evaporation in vacuo the complex II is precipitated in the form of dark cherry crystals containing an equimolar amount of solvating benzene. It melts with decomposition at 158—160°C. In the crystalline state the compound II does not oxidize in air; it is well soluble in THF, aromatic solvents and insoluble in alkanes. The IR spectrum of II in the region 4000—400 cm^{-1} contains absorption bands of coordinatively linked PPh_3 groups (in the region 650—550 cm^{-1}) and of benzene (680 cm^{-1}) in addition to the bands of starting compound I.

The structure of the heteroelemental framework in the molecule of II, determined by X-ray analysis, is shown in Fig. 2. The two Bi atoms in the molecule of II are bonded by the two $(C_6F_5)_2Ge<$ and one $(C_6F_5)_2Ge—Pt(PPh_3)_2$ bridge, i.e. the framework has two 5-member and one 4-member metallocycles. The symmetry of the framework is somewhat distorted from the ideal C_s (the deviations of the Pt, Bi(1), Bi(2) and Ge(1) atoms from their average plane are equal to 0.10, —0.05, 0.06 and —0.11 Å, respectively, and the Ge(2) and Ge(3) atoms are displaced from this plane by —1.62 and 1.55 Å). Thus, both the 5-member PtGe(1)Bi(2)Ge(3)Bi(1) and PtGe(1)Bi(2)Ge(2)Bi(1) metallocycles have the envelope conformation with bends of the Bi(1)Ge(3)Bi(2) and Bi(1)Ge(2)Bi(2) planes at 66.6 and 60.3°, respectively, from the middle, approximately planar, Bi(1)PtGe(1)Bi(2) fragment. The 4-member Bi(1)Ge(3)Bi(2)Ge(2) cycle is also nonplanar (bend on the Bi(1) ... Bi(2) line is equal to 53.1°).

The Pt—Bi and Pt—Ge bond lengths are equal to 2.759(3) and 2.466(3) Å,

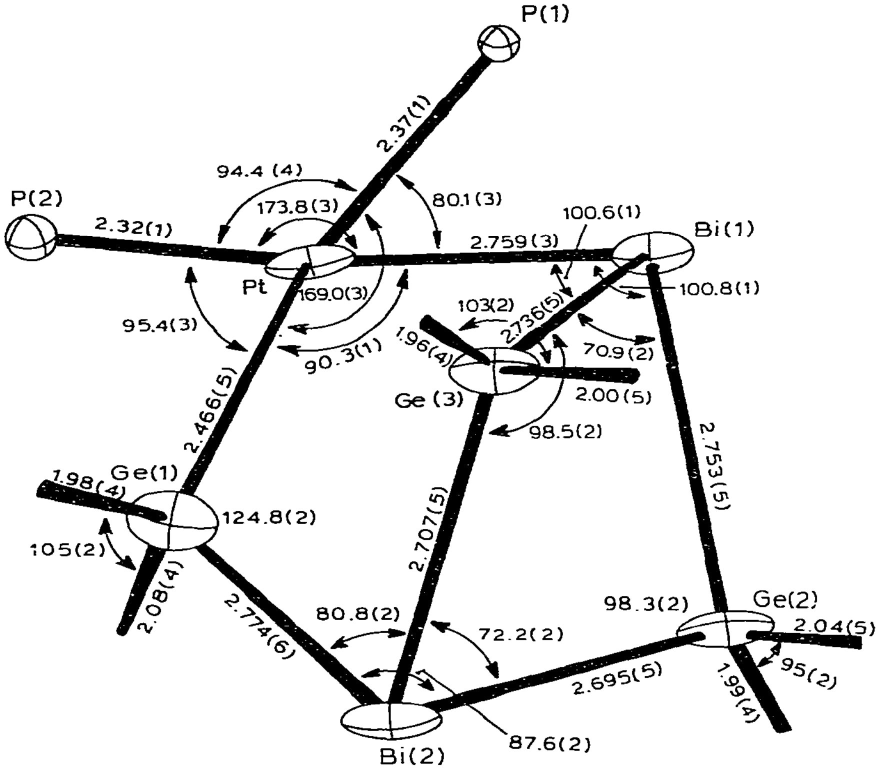


Fig. 2. The heteroelement framework of $[(C_6F_5)_2Ge]_3Bi_2Pt(PPh_3)_2$.

respectively, and the average value of the Bi—Ge bond length is 2.733(5) Å. The last value coincides with the average value of this bond distance (2.739(1) Å) in the molecule of I. The values of single-bonded covalent radii (SCR) calculated on the basis of M—M bond lengths in the molecule of II have the following values: r_{Bi} = 1.51, r_{Ge} = 1.22 and r_{Pt} = 1.25 Å. The first two values coincide with and the third value is close to the corresponding Pauling's covalent radii: r_{Bi} = 1.51, r_{Ge} = 1.22 and r_{Pt} = 1.30 Å [2], i.e. all the M—M bonds in the molecule of II are covalent as in the molecule of I.

The Bi and Ge atoms have pyramidal and tetrahedral coordination, respectively, with the valence angles very distorted from the ideal values. The Ge(2)—Bi(1)—Ge(3) and Ge(2)—Bi(2)—Ge(3) angles in the 4-member metallocycle are equal to 70.9(2) and 72.2(2)° and they are close to the average value 72.11(4)° of the Ge—Bi—Ge angle in the molecule of I. On the contrary, the Ge(2)—Bi(1)—Pt, 100.8(1)°, Ge(3)—Bi(1)—Pt, 100.6(1)°, Ge(2)—Bi(2)—Ge(1), 87.6(2)°, and Ge(3)—Bi(2)—Ge(1), 80.8(2)°, angles in the 5-member metallocycles are significantly larger and close to the ideal value of 90°. The Bi(2)—Ge(2)—Bi(1), 98.3(2)°, and Bi(1)—Ge(3)—Bi(2), 98.5(2)°, angles both in the 4-member and in the 5-member cycles are larger than the average value, 93.94(4)°, of the Bi—Ge—Bi angle in molecule I and are closer to the ideal value of 109.5°. At the same time, the Pt—Ge(1)—Bi(2) angle in the 5-member cycle is increased to 124.8(2)° but it has a difference from the ideal value the same as (but with the opposite sign) the difference of the angles at the Ge atoms from the ideal value in the molecule of I. The Pt atom has square-planar coordination: the Pt, P(1), P(2), Ge(1) and Bi(1) atoms are situated almost in one plane (the maximum deviation from the average plane is 0.09 Å). The Ge(1)—Pt—P(2) and P(1)—Pt—P(2) angles are increased to 95.4(3) and 94.4(3)°, respectively, but the P(1)—Pt—Bi(1) angle, 80.1(3)°, is decreased in comparison with the ideal of 90° which is perhaps due to steric repulsion of the bulky C_6F_5 and PPh_3 groups. At the same time the Bi(1)—Pt—Ge(1) intracycle angle 90.3(1)° is close to the ideal value.

The C_6F_5 and PPh_3 groups have the usual geometry. The average value of the Ge—C bond length in the molecules of I and II is equal to 1.97(1) and 2.01(5) Å, respectively, and they somewhat exceed this bond length, 1.959(9) Å in $[(C_6F_5)_3Ge]_2Hg$ [6] and 1.956(4) Å in $(C_6F_5)_4Ge$ [7]. The average value, 2.31(1) Å, of the Pt—P bond length in molecule II also coincides with these bond lengths in phosphine complexes of platinum (for example 2.321(9) Å in the *cis*-F_3CHg—$Pt(PPh_3)_2CF_3$ [8]). Some decrease of the C—Ge—C valence angles in the molecules of I and II, respectively, to 103.8—105.9(5)° and 95—105(2)° is due to steric repulsion of the C_6F_5 groups at the neighbouring Ge atoms.

Thus, comparison of the geometry of molecules I and II shows that the insertion of the $Pt(PPh_3)_2$ carbenoid into the Bi(1)—Ge(1) bond in molecule I, leading to the formation of molecule II, practically does not change the Bi—Ge bond lengths but it significantly changes some valence angles at the Bi and Ge atoms in the polymetallic framework. The significant differences in the angles in the frameworks of molecules I and II evidence that the valence angles at the metal atoms in the polynuclear compound can be in a wide region of values (71—100° for pyramidal Bi and 94—124° for tetrahedral Ge).

The strain in the framework in the molecule of II is much less than the strain in the molecule of I. This can be explained by the fact that instead of two very strenuous 4-member cycles in the molecule of I two less strenuous 5-member cycles appear in II and the strain in the third maintained 4-member cycle is also decreased. Nevertheless, the framework of II remains very strained. The stability of such strained polymetallic frameworks testifies to the great strength of M—M bonds in molecules I and II, distances of which retain the standard values. Thus, as usual, the strain in polycyclic systems is revealed first in deformation of valence angles, while the bond lengths remain unchanged.

Taking structural-coordination factors into consideration and also the presence of five Ge—Bi bonds (the potentional centres of carbenoid $Pt(PPh_3)_2$ attack) in II it might be expected that the product II would add one or more equivalents of platinum. However, our attempts in this direction were unsuccessful. After addition of an equimolar amount of $Pt(PPh_3)_3$ to a benzene solution of II at room temperature (3 h), compound II was isolated from mixture in an unchanged form. After heating the same mixture at 80°C for 2 h, 12 products were found by liquid-adsorption chromatography data but we failed to isolate or identify individual products. It should be noted that compounds R_3M—M'—MR_3 (M = Ge, Sn; M' = Zn, Cd, Hg) also add only one equivalent of platinum [4] but the 6-nuclear derivative $R_3GeHgGeR_2GeR_2HgGeR_3$, in which mercury atoms are separated by Ge—Ge groups, adds two $Pt(PPh_3)_2$ moieties [9].

Preliminary investigation shows that I adds a palladium complex $Pd(PPh_3)_3$ under similar conditions to give a dark green crystalline product. The investigation of the latter product and also data on the reactivity of II will be reported in a subsequent communication.

Experimental

Syntheses of I and II were carried out in evacuated sealed ampoules. Liquid-adsorption analyses were carried out on a Tsvet-304 liquid chromatograph with a detector of absorption in the UV region (254 nm). 25 × 0.1 and 30 × 0.4 cm columns packed with Silochrom C-80 was used; n-hexane/ether mixture (32 : 1) served as a mobile phase. IR spectra were recorded on a UR-20 spectrometer.

An X-ray experiment for the crystals of I and II was carried out with a Syntex $P2_1$ automatic diffractometer at —120°C (λ Mo-K_α, 4652 and 5226 independent reflections with $I > 2\sigma$ for I and II, respectively, $2\theta/\theta$ scan in range $1 \leqslant 2\theta \leqslant 47°$ (I) and $1 \leqslant 2\theta \leqslant 45°$ (II)). Absorption corrections were made taking into account the real crystal shape in both cases [10].

The crystals of I are monoclinic, at —120°C a = 41.561(7), b = 8.492(2), c = 23.320(8) Å, β = 102.61(2)°, V = 8031.8 Å^3, at 20°C D_m = 2.55, D_c = 2.63 g cm^{-3}, Z = 8, space group $C2/c$.

The crystals of II are monoclinic, at —120°C a = 16.918(8), b = 22.943(7), c = 20.116(8) Å, β = 109.55(3)°, V = 7357.9 Å^3, at 20°C D_m = 2.07, D_c = 2.15 g cm^{-3}, Z = 4, space group $P2_1/c$.

The structures of I and II were solved by the heavy atom method. Heavy atoms were found by the direct method using the MOLTAN programme. Other non-hydrogen atoms were revealed by subsequent electron density syntheses. Positions of the hydrogen atoms in the Ph groups of the triphenylphosphine ligands were calculated from geometrical conditions: C—H = 1.0 Å, C—C--H = 120°. Hydrogen atoms were included in the refinement with fixed positional and isotropic thermal parameters for these H atoms (B_{iso} = 4.0 Å^2). The structures of I and II were refined by a block-diagonal least-squares method with anisotropic (for the Bi, Ge and C atoms in the I and for the Bi, Ge and Pt atoms in the II) and isotropic parameters. Finally, the values of the discrepancy factors are: I, R = 0.042, R_g = 0.037; II, R = 0.087, R_g = 0.096. Atomic coordinates and thermal parameters are given in the Tables 1 and 2 for the structures of I and II, respectively.

Synthesis of $[(C_6F_5)_2Ge]_3Bi_2$ *(I)*

To a solution of 5.2 g (12.7 mmol) of bis(pentafluorophenyl)germane in 20 ml of toluene was added 2.5 g (8.5 mmol) of Et_3Bi. The temperature of the mixture was gradually increased during an hour to 110°C and the reaction mixture was kept at this temperature for 3 hours. Smooth ethane evolution was observed and the gas was collected in a gas burette. The yield of ethane is 470 ml (82%). The reaction solution was decanted from traces of metallic bismuth precipitated and the major part of toluene was removed by recondensation in vacuo. 15 ml of hexane was added to the residue. Orange crystals of I precipitated were washed by hexane to give 4.1 g (59%) of I. After recrystallization twice from

(Continued on p. 216)

TABLE 1

COORDINATES OF ATOMS (Bi,Ge × 10^5; C,F × 10^4) AND ANISOTROPIC (Bi,C) AND ISOTROPIC (F) THERMAL FACTORS (Å^2) $T = \exp[-1/4(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + ... + 2B_{23}b^*c^*kl)]$ IN THE STRUCTURE OF I

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Bi(1)	14 566(1)	10 625(6)	1909(2)	1.76(2)	1.50(2)	1.82(2)	0.30(2)	0.40(2)	−0.09(2)
Bi(2)	13 416(1)	47 138(2)	12 144(2)	1.84(2)	1.46(2)	1.87(2)	0.26(2)	0.46(2)	−0.12(2)
Ge(1)	16 088(3)	42 132(15)	2581(6)	1.25(6)	0.90(6)	1.28(6)	0.26(5)	0.28(5)	0.12(5)
Ge(2)	16 282(3)	18 001(16)	13 616(6)	1.07(5)	1.01(6)	1.22(6)	0.19(5)	0.18(5)	0.08(5)
Ge(3)	9404(3)	26 718(16)	4804(6)	0.95(6)	1.41(6)	1.30(6)	0.24(5)	0.14(5)	−0.16(5)
C(1)	2067(3)	4961(16)	404(5)	1.3(5)	2.3(7)	0.7(5)	0.5(5)	0.0(4)	0.0(5)
C(2)	2651(3)	−970(15)	4502(5)	2.3(6)	1.2(6)	1.1(5)	0.3(5)	0.7(5)	0.3(5)
C(3)	2336(3)	−373(16)	4336(5)	0.6(5)	2.8(7)	1.6(6)	0.8(5)	0.4(4)	0.3(5)
C(4)	2294(3)	1231(16)	4275(5)	1.6(6)	2.6(7)	1.5(6)	1.2(5)	0.0(5)	0.1(5)
C(5)	2559(3)	2207(14)	4370(5)	2.5(7)	0.5(6)	1.6(6)	−0.1(5)	0.5(5)	−0.5(5)
C(6)	2132(3)	6564(15)	479(5)	1.8(6)	1.4(6)	1.2(6)	−0.6(5)	0.5(5)	−0.6(5)
C(7)	1388(3)	5384(14)	−446(5)	1.5(5)	0.7(5)	2.0(6)	0.0(4)	0.0(4)	0.0(5)
C(8)	1167(3)	6586(16)	−449(6)	1.5(6)	1.7(7)	2.2(6)	0.6(5)	0.6(5)	0.5(5)
C(9)	997(3)	2710(14)	4034(6)	1.6(6)	0.6(6)	3.3(7)	−0.7(5)	0.2(5)	0.0(5)
C(10)	1057(3)	3157(15)	3520(5)	2.2(6)	2.1(6)	0.9(6)	0.2(5)	−0.6(5)	−0.9(5)
C(11)	1276(3)	4352(14)	3484(5)	1.6(6)	1.6(6)	0.9(5)	−0.4(5)	0.1(4)	−0.5(5)
C(12)	1435(3)	4963(15)	−1006(6)	2.1(6)	1.1(7)	2.9(5)	0.6(5)	1.1(5)	−0.1(5)
C(13)	1442(3)	407(15)	1870(5)	0.9(5)	1.4(6)	1.6(6)	1.1(5)	0.3(4)	−0.2(5)
C(14)	1232(3)	−852(15)	1684(5)	2.0(6)	0.8(6)	1.0(6)	−0.7(5)	0.1(5)	0.0(5)
C(15)	1080(3)	−1725(14)	2046(6)	1.0(5)	0.6(6)	3.2(7)	−0.1(5)	0.5(5)	0.0(5)
C(16)	1149(3)	−1379(15)	2643(6)	2.6(6)	1.6(6)	2.5(7)	−0.2(5)	1.8(5)	−1.2(5)
C(17)	1365(3)	−179(16)	2856(5)	1.5(6)	2.3(7)	1.4(6)	0.1(5)	0.5(5)	0.4(5)
C(18)	1502(3)	681(14)	2481(5)	1.0(5)	0.8(6)	2.4(6)	0.4(4)	0.0(5)	0.2(5)
C(19)	2109(3)	1787(14)	1676(5)	1.6(6)	1.2(6)	0.9(5)	0.5(5)	0.3(4)	0.2(4)
C(20)	2300(3)	3136(15)	1808(5)	1.6(6)	1.8(6)	0.9(5)	0.7(5)	0.0(5)	0.2(5)
C(21)	2637(3)	3116(16)	1981(5)	1.5(6)	2.1(7)	1.8(6)	−0.7(5)	0.4(5)	−0.2(5)
C(22)	2797(3)	1700(17)	2021(5)	1.0(5)	3.3(7)	1.5(6)	0.0(5)	0.0(5)	0.4(5)

C(23)	2624(3)	335(16)	1898(5)	2.5(6)	2.6(7)	1.2(6)	2.0(6)	0.8(5)	0.7(5)
C(24)	2284(3)	384(15)	1718(5)	1.5(6)	2.0(6)	1.0(5)	−0.2(5)	0.5(4)	0.1(5)
C(25)	645(3)	1518(15)	875(5)	0.6(5)	1.8(6)	2.1(6)	0.8(5)	−0.4(4)	−0.2(5)
C(26)	463(3)	246(15)	607(5)	2.4(6)	1.6(5)	1.6(6)	0.9(5)	0.7(5)	0.0(5)
C(27)	243(3)	−576(15)	868(6)	1.9(6)	1.1(6)	4.2(8)	−0.6(5)	0.3(6)	−1.2(6)
C(28)	199(3)	−143(17)	1409(6)	1.5(6)	2.3(7)	3.6(7)	−0.1(6)	1.4(5)	0.9(6)
C(29)	373(3)	1081(17)	1690(5)	1.7(6)	3.5(7)	1.2(6)	−0.2(6)	0.5(5)	−0.2(6)
C(30)	591(3)	1883(15)	1430(5)	1.3(6)	1.5(6)	1.8(6)	−0.5(5)	−0.3(5)	−0.4(5)
C(31)	645(3)	3673(14)	−207(5)	1.1(5)	1.2(6)	1.9(6)	−0.1(5)	0.7(5)	−0.2(5)
C(32)	634(3)	3212(15)	−778(6)	0.6(5)	1.9(6)	2.5(7)	0.7(5)	0.8(5)	0.0(5)
C(33)	440(3)	3943(16)	−1248(5)	1.9(6)	2.0(6)	2.0(6)	0.0(5)	0.0(5)	−0.9(5)
C(34)	255(3)	5181(17)	−1158(5)	2.3(6)	2.6(7)	1.0(6)	−0.2(6)	−1.4(5)	−0.7(5)
C(35)	255(3)	5680(16)	−598(6)	1.3(6)	2.0(7)	3.7(7)	−1.2(5)	0.5(5)	0.9(5)
C(36)	451(3)	4924(15)	−132(5)	1.5(5)	2.0(7)	1.5(6)	−0.2(5)	0.2(5)	−0.5(5)

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
F(2)	2685(2)	−2557(8)	4546(3)	1.7(1)	F(20)	2150(2)	4559(8)	1778(3)	1.9(1)
F(3)	2076(2)	−1335(9)	4240(3)	2.4(2)	F(21)	2805(2)	4459(9)	2084(3)	2.4(2)
F(4)	1986(2)	1811(9)	4136(3)	2.5(2)	F(22)	1872(2)	6662(9)	2798(3)	2.8(2)
F(5)	2513(2)	3769(8)	4317(3)	2.0(1)	F(23)	2219(2)	3950(9)	3069(3)	2.6(2)
F(6)	1872(2)	7570(8)	402(3)	2.1(3)	F(24)	2880(2)	4032(8)	3401(3)	1.9(1)
F(8)	1103(2)	2916(8)	5066(3)	2.1(1)	F(26)	498(2)	−194(9)	73(3)	2.9(2)
F(9)	786(2)	1526(9)	4069(3)	3.0(2)	F(27)	69(2)	−1775(10)	580(4)	4.0(2)
F(10)	896(2)	2454(9)	3020(3)	2.9(2)	F(28)	−10(2)	−951(10)	1655(4)	3.9(2)
F(11)	1331(2)	4788(9)	2966(3)	2.9(2)	F(29)	336(2)	1517(10)	2231(3)	3.3(2)
F(12)	1649(2)	3777(9)	−1045(3)	2.6(2)	F(30)	754(2)	3119(9)	1722(3)	3.0(2)
F(14)	1163(2)	−1236(8)	1113(3)	1.8(1)	F(32)	819(2)	1990(9)	−895(3)	2.4(2)
F(15)	871(2)	−2882(9)	1838(3)	2.5(2)	F(33)	435(2)	3508(9)	−1806(3)	2.8(2)
F(16)	1014(2)	−2233(9)	3008(3)	2.9(2)	F(34)	−61(2)	4045(10)	1607(3)	3.4(2)
F(17)	1429(2)	128(9)	3440(3)	2.7(2)	F(35)	70(2)	6918(10)	−508(4)	3.5(2)
F(18)	1695(2)	1905(8)	2702(3)	2.0(1)	F(36)	457(2)	5424(9)	418(3)	2.9(2)

TABLE 2

COORDINATES OF ATOMS (Bi,Pt,Ge × 10^5; P,F,C × 10^4) AND ANISOTROPIC (Bi,Pt,Ge) AND ISOTROPIC (P,F,C) THERMAL FACTORS (Å^2) $T = \exp[-1/4(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + \ldots + 2B_{23}b^*c^*kl)]$ IN THE STRUCTURE OF II

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Bi(1)	6930(12)	57 077(7)	18 108(9)	1,50(9)	0,89(7)	2,27(7)	0,00(7)	1,69(8)	−0,21(7)
Bi(2)	6419(12)	67 074(7)	34 981(10)	2,3(1)	0,74(7)	2,47(9)	−0,09(8)	2,05(8)	−0,22(8)
Pt	24 020(11)	58 497(7)	24 340(9)	1,29(9)	0,59(7)	1,91(8)	0,05(7)	1,54(8)	−0,02(7)
Ge(1)	21 835(32)	63 394(19)	34 499(25)	2,1(3)	1,2(2)	1,7(2)	−0,5(2)	1,6(2)	0,0(2)
Ge(2)	1238(31)	67 763(19)	20 793(25)	2,2(3)	0,5(2)	2,5(2)	0,0(2)	1,9(2)	0,0(2)
Ge(3)	2140(30)	56 209(19)	29 781(25)	1,7(3)	0,6(2)	2,6(2)	−0,4(2)	1,8(2)	−0,2(2)

Atom	x	y	z	B_{iso}	Atom	x	y	z	B_{iso}
P(1)	2356(8)	5455(5)	1335(6)	0,9(2)	C(54)	3773(26)	5593(17)	977(20)	1,0(8)
P(2)	3853(8)	5886(5)	2883(6)	1,5(2)	C(55)	4292(27)	5158(17)	2848(21)	1,1(9)
C(1)	2862(29)	7113(18)	3664(22)	1,8(9)	C(56)	3814(27)	4707(18)	2934(21)	1,3(9)
C(2)	3372(30)	7294(19)	4261(23)	2(1)	C(57)	4091(31)	4115(21)	2963(24)	3(1)
C(3)	3881(38)	7911(24)	4353(29)	5(1)	C(58)	4842(30)	4027(20)	2823(24)	3(1)
C(4)	3688(35)	8193(24)	3739(27)	5(1)	C(59)	5333(30)	4483(19)	2738(24)	3(1)
C(5)	3192(32)	8045(21)	3159(25)	3(1)	C(60)	5048(31)	5048(20)	2716(23)	2(1)
C(6)	2721(25)	7470(17)	3063(20)	0,7(8)	C(61)	4330(26)	6412(17)	2462(20)	1,0(9)
C(7)	2488(27)	5935(17)	4369(21)	1,3(9)	C(62)	3767(29)	6773(20)	1981(23)	2(1)
C(8)	2424(29)	8876(18)	−19(22)	1,9(9)	C(63)	4018(28)	7224(18)	1595(22)	1,6(9)
C(9)	2600(30)	9113(20)	613(23)	3(1)	C(64)	4914(35)	7222(22)	1697(27)	4(1)
C(10)	2883(30)	9686(19)	674(23)	2(1)	C(65)	5552(38)	6845(25)	2135(29)	6(2)
C(11)	2913(30)	9955(20)	100(24)	3(1)	C(66)	5184(33)	6464(21)	2479(21)	4(1)
C(12)	2756(29)	9685(19)	−501(23)	2,1(9)	C(67)	4433(30)	6087(19)	3799(23)	2(1)
C(13)	285(26)	7541(18)	1678(21)	1,5(9)	C(68)	4523(28)	5704(19)	4361(22)	2,0(9)
C(14)	704(29)	8037(19)	2112(22)	2,1(9)	C(69)	4947(32)	5850(22)	5030(25)	3(1)
C(15)	932(27)	8543(17)	1876(21)	1,4(9)	C(70)	5425(37)	6377(24)	5217(29)	5(1)
C(16)	702(29)	8577(18)	1157(22)	1,8(9)	C(71)	5417(44)	6788(31)	4681(34)	8(2)
C(17)	249(29)	8178(19)	693(23)	2(1)	C(72)	4921(38)	6633(22)	3961(25)	4(1)
C(18)	80(28)	7633(19)	962(22)	1,9(9)	C(73)	−3171(50)	7794(32)	3234(39)	9(2)
C(19)	−1156(27)	6815(18)	1696(21)	1,6(9)	C(74)	−3546(42)	7925(32)	3690(32)	7(2)

C(20)	−1570(29)	7275(18)	1868(23)	2,0(9)	C(75)	−3282(53)	7815(34)	4336(41)	11(2)
C(21)	−2475(32)	7307(20)	1562(25)	3(1)	C(76)	−2412(43)	7650(28)	4608(34)	7(2)
C(22)	−2875(36)	6923(23)	1145(28)	5(1)	C(77)	−2029(46)	7513(33)	4157(37)	8(2)
C(23)	−2471(31)	6456(20)	1000(24)	3(1)	C(78)	−2430(48)	7564(33)	3497(39)	9(2)
C(24)	−1614(30)	6418(20)	1260(23)	3(1)	F(2)	3644(18)	8010(11)	−105(14)	3,9(7)
C(25)	−1027(25)	5520(16)	2720(20)	0,9(8)	F(3)	4361(21)	8026(13)	4958(16)	5,5(8)
C(26)	−1553(25)	5868(15)	2935(19)	0,3(7)	F(4)	4098(21)	8708(13)	3803(16)	5,8(8)
C(27)	−2344(29)	5777(20)	2731(22)	3(1)	F(5)	3007(16)	8327(11)	2549(13)	3,1(6)
C(28)	−2761(30)	5389(19)	2192(23)	2(1)	F(6)	2167(14)	7301(9)	2421(11)	1,7(5)
C(29)	−2292(30)	5098(20)	1879(23)	3(1)	F(8)	2166(16)	2894(11)	−24(13)	3,1(6)
C(30)	−1458(27)	5154(18)	2138(21)	1,5(9)	F(9)	2589(18)	8848(12)	1209(14)	4,0(7)
C(31)	658(28)	4988(18)	3654(22)	1,7(9)	F(10)	3043(19)	9978(12)	1298(14)	4,3(7)
C(32)	730(29)	5041(18)	4377(22)	1,9(9)	F(11)	3159(18)	10523(12)	121(14)	4,5(7)
C(33)	−1073(29)	9663(19)	104(23)	2,1(9)	F(12)	2755(15)	5043(10)	3904(12)	2,0(5)
C(34)	−1333(30)	9110(20)	276(23)	3(1)	F(14)	991(15)	7967(10)	2835(12)	2,2(5)
C(35)	−1237(29)	9032(19)	970(23)	2(1)	F(15)	1334(17)	8961(11)	2314(13)	3,1(6)
C(36)	904(27)	4443(17)	3517(21)	1,4(9)	F(16)	854(16)	9128(11)	911(13)	3,2(6)
C(37)	1964(24)	5954(15)	633(19)	0,3(8)	F(17)	17(17)	8229(11)	−16(13)	3,1(6)
C(38)	1696(25)	6508(16)	748(19)	0,5(8)	F(18)	−276(15)	7204(10)	523(12)	2,2(5)
C(39)	1468(29)	6923(18)	217(22)	1,9(9)	F(20)	−1133(16)	7680(11)	2314(13)	3,0(6)
C(40)	1492(28)	6800(19)	−436(22)	1,8(9)	F(21)	−2779(19)	7803(12)	1765(15)	4,7(7)
C(41)	1745(28)	6222(18)	−589(22)	1,7(9)	F(22)	−3698(20)	6991(13)	889(16)	5,6(8)
C(42)	1973(28)	5838(20)	−61(22)	2,1(9)	F(23)	−2969(18)	6062(12)	573(14)	4,3(7)
C(43)	1688(25)	4795(16)	1120(19)	0,6(8)	F(24)	−1326(15)	5952(10)	1036(12)	2,3(5)
C(44)	1149(30)	4664(20)	450(24)	3(1)	F(26)	−1212(16)	6229(11)	3446(13)	2,8(6)
C(45)	603(30)	4181(20)	304(23)	3(1)	F(27)	−2872(18)	6101(12)	2973(14)	3,7(6)
C(46)	698(34)	3818(22)	878(26)	4(1)	F(28)	−3584(19)	5360(13)	1929(15)	5,0(7)
C(47)	1239(29)	3890(23)	1559(23)	2(1)	F(29)	−2631(18)	4699(11)	1386(14)	3,8(6)
C(48)	1749(28)	4396(19)	1680(22)	1,8(9)	F(30)	−999(16)	4802(11)	1838(13)	2,8(6)
C(49)	3328(25)	5238(16)	1170(19)	0,5(8)	F(32)	445(16)	9431(10)	−438(12)	2,5(5)
C(50)	3514(27)	4601(18)	1148(21)	1,5(9)	F(33)	1149(17)	10253(11)	559(13)	3,1(6)
C(51)	4181(29)	4466(18)	937(22)	2,1(9)	F(34)	−1690(18)	8730(11)	−204(14)	3,7(6)
C(52)	4711(32)	4855(20)	820(24)	3(1)	F(35)	−1543(17)	8520(11)	1163(13)	3,7(6)
C(53)	4552(30)	5445(19)	828(23)	2(1)	F(36)	−834(17)	9336(11)	2168(13)	3,4(6)

benzene (in air) the product melts with decomposition at 200—205°C, but its colour begins to change a little at 135°C.

Synthesis of $[(C_6F_5)_2Ge]_3Bi_2Pt(PPh_3)_2 \cdot C_6H_6$ *(II)*

A solution of 0.76 g (1.66 mmol) of $Pt(PPh_3)_3$ in 10 ml of benzene was added to a solution of 1 g (0.61 mmol) of compound I in 10 ml of benzene at 20°C. The mixture was concentrated by evaporation of solvent in vacuo. The dark cherry crystals which precipitated were separated by decanting and washed once with cold benzene and three times with hexane to give 1.25 g (98%) of II. After recrystallization from benzene the product melts with decomposition at 158—160°C.

References

1 M.N. Bochkarev, N.I. Gur'ev and G.A. Razuvaev, J. Organometal. Chem., 162 (1978) 289.
2 L. Pauling, The Nature of the Chemical Bond., 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.
3 V.I. Sokolov, V.V. Bashilov, O.A. Reutov, M.N. Bochkarev, L.P. Maiorova and G.A. Razuvaev, J. Organometal. Chem., 112 (1976) C47.
4 M.N. Bochkarev, L.P. Maiorova, G.A. Razuvaev, V.I. Sokolov, V.V. Bashilov and O.A. Reutov, J. Organometal. Chem., 131 (1977) 399.
5 V.T. Bychkov, S.N. Titova and I.V. Lomakova, Zh. Obshch. Khim., 46 (1976) 2629.
6 L.G. Kuzmina, T.V. Timofeeva, Yu.T. Struchkov and M.N. Bochkarev, Zh. Structurn. Khim., (1980) in press.
7 A. Karipides, C. Forman, R.H.P. Thomas and A.T. Reed, Inorg. Chem., 13 (1974) 811.
8 L.G. Kuzmina, Yu.T. Struchkov, V.V. Bashilov, V.I. Sokolov and O.A. Reutov, Izv. Acad. Nauk SSSR, Ser. Khim., 3 (1978) 621.
9 M.N. Bochkarev, L.P. Maiorova and G.A. Razuvaev, Zh. Obshch. Khim., (1980) in press.
10 R.G. Gerr, M.Yu. Antipin, N.G. Furmanova and Yu.T. Struchkov, Kristallographia, 24 (1979) 951.