Inorg. Chem. **1993**, *32*, 3948–3951

Hexacoordinate Organobismuth Compounds

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Received December 23, 1992

The reaction of $Bi(C_6H_5)_5$ with LiC_6H_5 in diethyl ether or THF affords the unstable, yellow solid $Li(solvent)_n{}^+Bi(C_6H_5)_6{}^-$. In the monoclinic compound $Li^+(THF)_4Bi(C_6H_5)_6{}^-\cdot 2THF$ ($P2_1/c$, a = 1126.4(7) pm, b = 3500.8 (14) pm, c = 1400.1(7) pm, β = 100.93(4)°, Z = 4, T = −145 °C), the octahedral anion has approximately T_h symmetry. The compound $Bi(C_6H_5)_5$ forms a blue, crystalline 1:1 adduct in pyridine solution ($C2/c$, a = 1050.9(5) pm, b = 1777.6(7) pm, c = 1482.7(6) pm, β = 95.06(4)°, Z = 4, T = −145 °C) that has a structure comparable to that of $Bi(C_6H_5)_6{}^-$, except that the Bi···N contact is long (321(2) pm). In another blue adduct, $Bi(C_6H_5)_5\cdot 3$ pyridine ($P\bar{3}$, a = 1130.4(3) pm, c = 821.8(2) pm, Z = 1, T = −145 °C), the same bismuth environment is found, but the Bi···N contact is shorter (263.7(5) pm). Both the bismuth complex as well as the additional pyridine molecules are disordered in the 1:3 adduct.

Introduction

Recently, we have shown that the intense colors of pentaphenylbismuth and substituted derivatives thereof are due to charge transfers from the ligands to the bismuth atom.[1–4] A necessary condition for this charge transfer absorption is the square pyramidal structure that is typical for all known pentaarylbismuth compounds. The only known trigonal bipyramidal compound, $Bi(4\text{-}CH_3C_6H_4)_3(2\text{-}FC_6H_4)_2$, has a yellow color. Pentaarylantimony compounds, however, have a trigonal bipyramidal structure except for solvate free $Sb(C_6H_5)_5$.[5] Ab initio calculations on BiH_5, including relativistic effects, have shown that the HOMO is largely centered on the equatorial ligands, and the LUMO has largely Bi6s,6p character.[3] The stabilization of the LUMO by relativistic effects brings the absorption into the visible. The calculations also showed that trigonal bipyramidal BiH_5 should have a much wider HOMO–LUMO gap and therefore should not be deeply colored.

The same is predicted for octahedral $BiH_6{}^-$. Here the sixth coordination site is occupied by a ligand, whereas in square pyramidal BiH_5 the sixth site was occupied largely by the LUMO.[3] If these computational results are transferred to existing compounds, it means that the absorption of $Bi(C_6H_5)_5$ should shift to much shorter wavelengths if it is converted to $Bi(C_6H_5)_6{}^-$.

The $Bi(C_6H_5)_6{}^-$ anion has been reported in the literature.[6] It was formed when pentaphenylbismuth was treated with C_6H_5Li at low temperatures. However, the yellow crystalline compound decomposed reversibly into the starting materials upon warming to room temperature. The anion $Bi(C_6H_4)_4(2,2'\text{-}C_{12}H_8)^-$ was formed similarly and also decomposed upon warming to room temperature.[7]

Mononuclear main group compounds with six organic ligands are rare. Examples include $Li^+Sb(C_6H_5)_6{}^-$, which was prepared in a manner similar to that for $Li^+Bi(C_6H_5)_6{}^-$ and which is stable up to 185 °C,[8] $As(2,2'\text{-}C_{12}H_8)_3{}^-$,[6] and $Te(CH_3)_6$.[9]

One can assume that these main group compounds have an octahedral structure. However, the trigonal prismatic structures of $W(CH_3)_6$[10] and $Zr(CH_3)_6{}^{2-}$[11] demonstrate that the octahedron is not the most stable six-coordinate structure in all cases. So far there is no satisfying explanation for deviations from octahedral symmetry for d^0 compounds, but it seems that this phenomenon occurs if ligands are not π-donating and if the central atom-ligand bond is relatively nonpolar. The bond polarity in $Bi(C_6H_5)_5$, in terms of partial negative charge on the ligands, seems to be small. This is indicated by the charge transfer excitation from the ligand to the bismuth atom. Therefore, a trigonal prismatic structure for $Bi(C_6H_5)_6{}^-$ was not completely out of the question.

Results and Discussion

$Bi(C_6H_5)_6{}^-$. The reaction of $Bi(C_6H_5)_5$ and C_6H_5Li to form $Li^+Bi(C_6H_5)_6{}^-$ requires an excess of the lithium reagent as well as low temperatures to go to completion. Otherwise the blue-violet color of unreacted $Bi(C_6H_5)_5$ remains.

$$Li^+C_6H_5{}^- + Bi(C_6H_5)_5 \rightarrow Li^+B(C_6H_5)_6{}^- \qquad (1)$$

From concentrated solutions below 0 °C $Li(solvent)^+Bi(C_6H_5)_6{}^-$ can be obtained as yellow crystals that are thermally labile as well as very sensitive toward moisture. Because of this sensitivity, low temperature crystallography has been the sole analytical tool used so far. Crystals were obtained from both diethyl ether and tetrahydrofuran solutions. As expected, the lithium cations in the crystals are coordinated to solvent molecules. Two different types of crystal were obtained from diethyl ether solution. The first contained three formula units in the unit cell and disordered diethyl ether molecules surrounding the lithium ions;[12] in the second crystal type even the anions are disordered, or the crystals are systematically twinned.[13] The shape of the anion is apparently octahedral in both cases.

The compound $Li(THF)_4{}^+Bi(C_6H_5)_6{}^-\cdot 2THF$ crystallizes also as yellow crystals from THF solutions. The structure was established by collecting X-ray data at −145 °C and by using direct methods and difference Fourier analyses to solve the

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(12) a = 1013.6(6) pm, b = 1676.3(9) pm, c = 2101.3(9) pm, α = 71.08(3)°, β = 77.01(4)°, γ = 79.93(5)°, V = 3270(3) × 10^6 pm^3, $P\bar{1}$, Z = 3. Wallenhauer, S.; Seppelt, K. Unpublished results.

(13) a = 1766.1(8) pm, b = 1149.1(8) pm, c = 1176.4(8) pm, α = 89.90(8)°, β = 97.88(8)°, γ = 93.06(8)°, V = 2356(1) × 10^6 pm^3, $P\bar{1}$, Z = 2. Wallenhauer, S.; Seppelt, K. Unpublished results.

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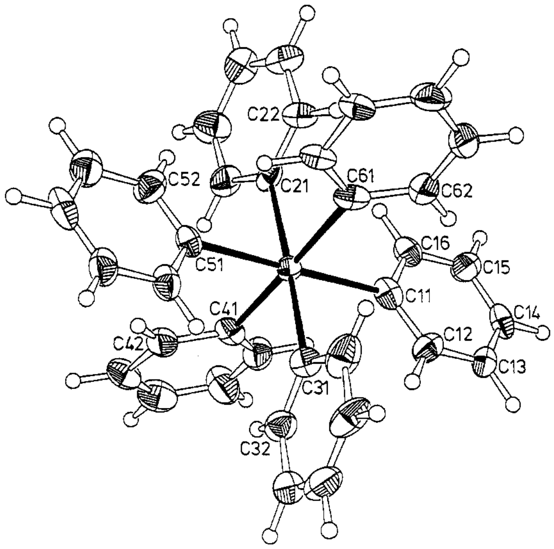

Figure 1. ORTEP drawing of the $Bi(C_6H_5)_6^-$ anion in $Li(THF)_4^+Bi(C_6H_5)_6^- \cdot 2THF$, with thermal ellipsoids shown at the 50% probability level.

structure. The Li^+ cations are coordinated by four oxygen atoms of THF molecules in a nearly perfect tetrahedral manner with Li···O distances of 190(2)–198(2) pm. Furthermore two uncoordinated THF molecules are found in the asymmetric unit of the lattice.

The $Bi(C_6H_5)_6^-$ anion in this salt has an approximately octahedral structure. Deviations from the ideal bond angles of 90 and 180° are less than or equal to 2.6° (see Figure 1 and Table I). Also all six Bi–C bond lengths are very similar (232.4–236.4(11) pm). The addition of one C_6H_5 group to the square pyramidal $Bi(C_6H_5)_5$ molecule leads to a lengthening of the axial Bi–C bond. This is 221 pm long in $Bi(C_6H_5)_5$.[1] The basal Bi–C bonds are only lengthened a little. In $Bi(C_6H_5)_5$ the four basal phenyl groups are equally twisted with respect to the basal plane in the manner of a propeller. This orientation also changes upon addition of the sixth phenyl group: in $Bi(C_6H_5)_6^-$ opposite phenyl groups are nearly coplanar and the planes of adjacent phenyl groups are nearly perpendicular.

The effective symmetry of the $Bi(C_6H_5)_6^-$ anion is T_h, which is rarely found in chemistry. Other examples of T_h symmetry species are $[Pt(P(C_2H_5)_3)_2]_6C_{60}$[14] and $Co(NO_2)_6^{3-}$.[15] It is probably the minimization of repulsive energy that leads to this peculiar structure.

The $Bi(C_6H_5)_5$–Pyridine System. We had earlier found that cold, dilute THF solutions of $Bi(C_6H_5)_5$ afford needle-shaped, blue crystals of a $Bi(C_6H_5)_5$/THF adduct.[1,16] The crystal structure of this compound could not be solved, possibly because of severe disorder problems. However, it was obvious that a THF molecule occupied the sixth coordination site around the Bi atom. In order to solve the problem of solvated $Bi(C_6H_5)_5$, pyridine was tested as solvate.

$Bi(C_6H_5)_5$ also dissolves in pyridine to give a blue-violet solution, which produces two different types of crystals, depending on temperature and concentration. From concentrated solutions of $Bi(C_6H_5)_5$ below −5 °C, rectangular, violet crystals of $Bi(C_6H_5)_5 \cdot C_5H_5N$ are obtained. The $Bi(C_6H_5)_5$ moiety has a square pyramidal structure as in the unsolvated molecule (see Figure 2 and Table II). But the angles C–Bi–C between basal phenyl groups are now closer to 180° (170.0, 154.8°).[1] The Bi···N contact is quite long (321(2) pm), which therefore may be considered a pure electrostatic interaction. The orientation of the six rings surrounding the bismuth atom is similar to the situation in $Bi(C_6H_5)_6^-$: Opposite rings are approximately parallel, though only to within 20°, and adjacent rings are approximately perpendicular.

Table I. Positional and Equivalent Isotropic Thermal Parameters of $Li(THF)_4^+Bi(C_6H_5)_6^- \cdot 2THF$

atom	x	y	z	B, Å^2
Bi	0.0965(0)	0.3782(0)	0.7595(0)	2.11
C11	0.2707(10)	0.3459(3)	0.8331(9)	2.79
C12	0.3335(11)	0.3546(3)	0.9254(9)	3.19
C13	0.4376(10)	0.3362(4)	0.9689(9)	3.27
C14	0.4821(10)	0.3060(3)	0.9197(10)	3.11
C15	0.4225(11)	0.2961(3)	0.8257(9)	3.40
C16	0.3153(10)	0.3155(3)	0.7801(9)	2.76
C21	0.0732(10)	0.3394(3)	0.6191(8)	2.65
C22	0.1383(11)	0.3472(3)	0.5549(9)	3.31
C23	0.1171(12)	0.3251(3)	0.4573(9)	3.72
C24	0.0334(12)	0.2949(3)	0.4448(10)	3.89
C25	−0.0294(12)	0.2874(4)	0.5216(10)	4.24
C26	−0.0103(11)	0.3084(3)	0.6076(9)	3.32
C31	0.1135(10)	0.4177(3)	0.8949(8)	2.60
C32	0.0607(11)	0.4074(3)	0.9736(9)	3.27
C33	0.0672(12)	0.4327(4)	1.0564(9)	4.34
C34	0.1263(12)	0.4681(4)	1.0570(9)	4.09
C35	0.1799(12)	0.4786(3)	0.9790(10)	4.03
C36	0.1772(12)	0.4537(3)	0.8975(10)	4.16
C41	−0.0221(10)	0.3357(3)	0.8280(8)	2.64
C42	−0.1460(11)	0.3416(4)	0.8182(9)	3.49
C43	−0.2233(11)	0.3143(3)	0.8505(9)	3.58
C44	−0.1706(13)	0.2797(4)	0.8967(10)	4.31
C45	−0.0464(12)	0.2736(4)	0.9069(10)	4.77
C46	0.0251(11)	0.3016(4)	0.8723(9)	3.57
C51	−0.0775(10)	0.4126(3)	0.6858(9)	2.41
C52	−0.1385(11)	0.4032(3)	0.5955(9)	3.52
C53	−0.2440(11)	0.4243(4)	0.5491(10)	3.99
C54	−0.2828(11)	0.4542(4)	0.5988(11)	3.91
C55	−0.2200(11)	0.4644(3)	0.6927(10)	3.77
C56	−0.1187(10)	0.4432(3)	0.7357(9)	3.28
C61	0.2144(11)	0.4196(3)	0.6837(8)	2.54
C62	0.3407(11)	0.4137(3)	0.6978(0)	3.25
C63	0.4126(11)	0.4357(4)	0.6470(9)	3.77
C64	0.3573(13)	0.4644(4)	0.5796(9)	4.02
C65	0.2314(12)	0.4703(4)	0.5673(9)	3.78
C66	0.1609(11)	0.4480(3)	0.6183(8)	3.03
O1	0.1654(7)	0.0776(2)	0.5439(6)	4.04
C111	0.0568(12)	0.0557(4)	0.5087(10)	4.23
C112	0.0557(13)	0.0492(4)	0.3997(10)	5.03
C113	0.1234(12)	0.0846(4)	0.3739(10)	4.17
C114	0.2235(11)	0.0886(3)	0.4648(9)	3.85
O2	0.0693(9)	0.0831(3)	0.7341(7)	5.99
C121	−0.0458(16)	0.1014(5)	0.7235(12)	6.95
C122	−0.1297(18)	0.0746(6)	0.7633(15)	8.88
C123	−0.0406(16)	0.0505(5)	0.8327(13)	7.24
C124	0.0777(13)	0.0458(4)	0.7889(10)	5.23
O3	0.3521(8)	0.0793(2)	0.7473(6)	4.96
C131	0.4367(13)	0.1037(4)	0.8178(11)	5.60
C132	0.5438(15)	0.0770(5)	0.8522(12)	6.94
C133	0.4838(14)	0.0391(4)	0.8493(11)	6.06
C134	0.3872(12)	0.0392(4)	0.7582(10)	4.55
O4	0.2132(8)	0.1542(3)	0.6799(7)	5.66
C141	0.2674(12)	0.1788(4)	0.6175(10)	4.95
C142	0.2574(15)	0.2190(4)	0.6537(12)	6.74
C143	0.1880(15)	0.2160(5)	0.7371(14)	7.56
C144	0.1929(19)	0.1756(6)	0.7674(15)	9.41
O5	0.0461(12)	0.1578(3)	0.9380(9)	8.82
C151	0.1377(15)	0.1774(5)	1.0062(12)	6.68
C152	−0.0354(18)	0.1743(5)	1.0730(15)	9.10
C153	0.1001(17)	0.1705(5)	1.1049(14)	8.09
C154	−0.0646(20)	0.1538(6)	0.9756(16)	10.12
O6	−0.3840(19)	0.1811(6)	0.6897(15)	15.46
C161	−0.2545(18)	0.2243(5)	0.6427(15)	8.81
C162	−0.3790(23)	0.2228(7)	0.6784(18)	12.18
C163	−0.1884(23)	0.1977(7)	0.7046(19)	12.05
C164	−0.2729(25)	0.1640(7)	0.6989(17)	11.98
Li1	0.2033(20)	0.0991(6)	0.6755(16)	4.29

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(16) $a = b = 1105.3(6)$ pm, $c = 851.9(5)$ pm, $\gamma = 120°$, $V = 902(1) \times 10^6$ pm^3, $Z = 1$, $T =$ °C. Wallenhauer, S.; Seppelt, K. Unpublished results.

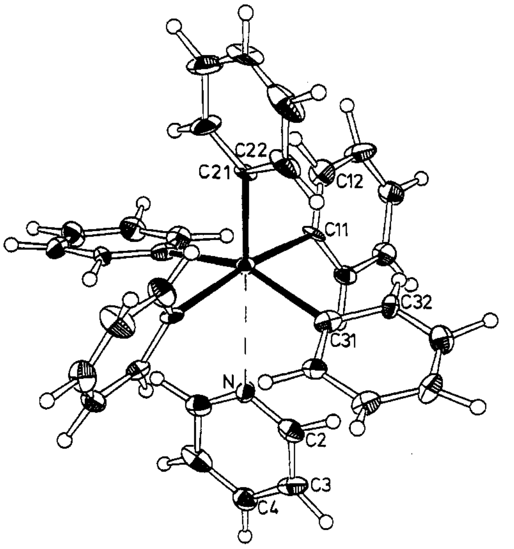

Figure 2. ORTEP drawing of the $Bi(C_6H_5)_5{\cdot}NC_5H_5$ complex, with thermal ellipsoids shown at the 50% probability level.

Table II. Positional and Equivalent Isotropic Thermal Parameters of $Bi(C_6H_5)_5{\cdot}C_5H_5N$

atom	*x*	*y*	*z*	*B*, Å^2
Bi	0.0000(0)	0.0923(0)	0.2500(0)	1.37
C11	0.1579(9)	0.1038(6)	0.3699(6)	1.36
C12	0.1812(12)	0.0452(8)	0.4259(9)	2.05
C13	0.2725(13)	0.0477(8)	0.4994(8)	3.06
C14	0.3415(11)	0.1131(7)	0.5161(7)	2.50
C15	0.3200(11)	0.1752(7)	0.4605(7)	2.05
C16	0.2269(10)	0.1710(6)	0.3864(7)	1.77
C21	0.0000(0)	−0.0356(9)	0.2500(0)	1.94
C22	−0.0705(13)	−0.0728(8)	0.3072(10)	3.19
C23	−0.0714(15)	−0.1510(9)	0.3075(11)	4.30
C24	0.0000(0)	−0.1889(13)	0.25800(0)	4.60
C31	0.1530(10)	0.1210(6)	0.1499(7)	1.90
C32	0.2801(9)	0.1137(6)	0.1788(7)	1.61
C33	0.3707(10)	0.1300(7)	0.1194(7)	2.30
C34	0.3323(11)	0.1518(8)	0.0319(7)	2.46
C35	0.2050(11)	0.1577(7)	0.0033(8)	2.42
C36	0.1140(11)	0.1422(7)	0.0625(7)	2.01
N1	0.0000(0)	0.2724(8)	0.2500(0)	1.89
C2	0.0913(11)	0.3108(7)	0.2164(7)	2.08
C3	0.0959(12)	0.3897(7)	0.2145(8)	2.55
C4	0.0000(0)	0.4287(10)	0.2500(0)	2.75

Since $Bi(C_6H_5)_5$ dissolves only in solvents that have donor qualities like ethers or amines, it can be assumed that in solution such 1:1 complexes are always formed.

The $Bi(C_6H_5)_5$/pyridine solution also forms, at lower temperatures, needle shaped crystals that turned out to be a 1:3 phase. The trigonal unit cell contains two pyridine molecules that lie perpendicular to the 3-fold axes of the lattice (see Figure 3 and Table III). This implies a disorder of the nitrogen atom and the five carbon atoms of these solvate molecules, giving perfect regular hexagons.

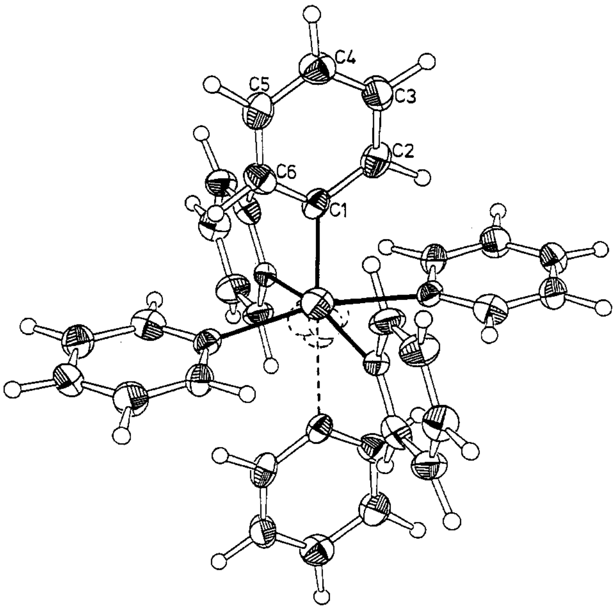

Figure 3. ORTEP drawing of the $Bi(C_6H_5)_5{\cdot}C_5H_5N$ complex in $Bi(C_6H_5)_5{\cdot}3C_5H_5N$, with thermal ellipsoids shown at the 50% probability level. The noncoordinating pyridine molecules have been omitted for clarity. The Bi atom appears at six close lying positions due to disorder of the pyridine molecule. In the figure one Bi position and one nitrogen position were arbitrarily chosen.

Table III. Positional and Equivalent Isotropic Thermal Parameters of $Bi(C_6H_5)_5{\cdot}3C_5H_5N$

atom	*x*	*y*	*z*	*B*, Å^2
Bi	0.0104(4)	−0.0104(4)	0.5195(6)	3.67
C1[a]	0.1994(5)	0.0996(5)	0.3345(5)	1.97
C2	0.2087(5)	0.1736(5)	0.2017(7)	3.06
C3	0.3249(6)	0.2399(5)	0.1065(6)	2.89
C4	0.4384(5)	0.2317(5)	0.1520(7)	2.89
C5	0.4323(5)	0.1578(5)	0.2866(7)	3.01
C6	0.3138(6)	0.0940(5)	0.3762(6)	2.80
C11[a]	0.4155(6)	0.8038(5)	0.2852(7)	3.43
C12[a]	0.4687(5)	0.7207(7)	0.2816(7)	4.04

[a] One sixth of these atoms is statistically a nitrogen atom.

Table IV. Selected Bond Lengths (pm) and Bond Angles (deg)

	$Li^+(THF)_4Bi(C_6H_5)_6^-{\cdot}2THF$	
Bi–C	232.8, 236.2, 232.6, 232.4, 236.4, 235.1(11)	
C–Bi–C	87.8–92.4(4); 177.5–177.9(4)	
	$Bi(C_6H_5)_5{\cdot}C_5H_5N$	$Bi(C_6H_5)_5{\cdot}3NC_5H_5$
$Bi–C_{apical}$	227.3(16)	211.9(5)
$Bi–C_{basal}$	233.1(9), 233.9(10)	240.0. 238.4(5)
Bi···N	320.2(16)	263.7(5)
$C_{apical}–Bi–C_{basal}$	95.0(3), 102.6(3)	98.4(3)
$C_{basal}–Bi–C_{basal}$	170.0(3), 154.8(3)	163.2(3)
$N{\cdots}Bi–C_{axial}$	180(0)	180.0(0)

The organobismuth–pyridine adduct is also disordered. The $Bi(C_6H_5)_5{\cdot}C_5H_5N$ molecule has six different orientations with respect to the Bi···N contact. Therefore, it appears to be a regular octahedron with T_h symmetry, very much like the $Bi(C_6H_5)_6^-$ anion, if the Bi atom is fixed at 0, 0, 0.5. However, the fixed Bi atom in this model has very large thermal parameters. If instead the bismuth coordinates were not fixed, the resulting model had six close lying Bi positions. Of course only one of these positions can be occupied in a given adduct, which results in one short Bi–ligand bond, assigned to the $Bi–C_{ax}$ bond, four intermediate length Bi–ligand bonds, assigned to the $Bi–C_{eq}$ bonds, and one long Bi–ligand bond, assigned to the Bi···N contact. This model requires that the pyridine molecule has six different positions in a disordered manner. Due to the similarities of the C_6H_5 and C_5H_5N groups, these cannot be differentiated.

The disorder described above seems unusual, since it is the heavy atom that is disordered over six close lying positions, whilethe positions of the ligands are very accurate in spite of their disorder. Furthermore it is the low temperature modification that shows this disorder, whereas the high temperature form is not disordered. Even if one allows that in such a severely disordered structuce the bond lengths and bond angles may have larger errors than the one given by the computational program, it is obvious that the Bi···N contact in the 1:3 adduct is much shorter (263.7(5) pm) than in the nondisordered 1:1 adduct.

It is interesting that the blue color of $Bi(C_6H_5)_5$ persists, whether it is solvent free, weakly solvated (THF), or strongly solvated (pyridine). This is an indication that the MO scheme remains

Table V. Crystal Data and Experimental Details

	$Li^+(C_4H_8O)_4$- $Bi(C_6H_5)_6^-$· $2C_4H_8O$	$Bi(C_6H_5)_5$· C_5H_5N	$Bi(C_6H_5)_5$· $3C_5H_5N$
fw	798.93	673.61	831.81
a, pm	1126.4(7)	1050.9(5)	1130.4(3)
b, pm	3500.8(14)	1777.6(7)	1130.4(3)
c, pm	1400.1(7)	1482.7(6)	821.8(2)
α, deg	90	90	90
β, deg	100.93(4)	95.06(4)	90
γ, deg	90	90	120
V, $10^6 \times pm^3$	5420(5)	2759(2)	909.5(5)
T, °C	–145	–140	–140
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P\bar{3}$ (No. 147)
Z	4	4	1
scan area	2–20	2–20	2–20
octands	$\pm h,+k,\pm l$	$+h,+k,\pm l$	$\pm h,+k,\pm l$
scan method	ω	ω–2δ	ω–2δ
no. of reflcns			
measd	5459	2257	2858
indep	5094	2037	944
$I \geq 3\sigma(I)$	4185	1787	869
no. of params	458	213	97
R	0.049	0.064	0.044
R_w	0.053	0.063	0.029

qualitatively the same in all three cases. It changes only in the very strongly bound $Bi(C_6H_5)_6^-$ anion.

Experimental Section

General Procedures. All manipulations and reactions were carried out under argon in carefully dried solvents. For some experiments a glovebox with continuously purified argon was used. Diethyl ether, pyridine, and THF were dried by sodium and molecular sieves. $Bi(C_6H_5)_5$ was prepared as previously described.[8]

Lithium Hexaphenylbismuthate–THF Complex, $Li(THF)_4^+Bi(C_6H_5)_6^-$·2THF. A 0.67-mmol sample of $Bi(C_6H_5)_5$ was dissolved in 12 mL of THF. Then 1.4 mmol LiC_6H_5 in a 7:3 diethyl ether/cyclohexane solution was added at –78 °C. A yellow suspension was obtained. When this was warmed to room temperature, the color turned blue-violet (the color change was reversible). This solution was pressed with argon through a thin Teflon tube into a glass ampule that was then sealed off. Crystallization of the yellow compound occurred in the ampule upon cooling to 0 and –18 °C. Similar results were obtained in diethyl ether solution.[12,13]

$Bi(C_6H_5)_5$–Pyridine Adducts. $Bi(C_6H_5)_5$ was dissolved in pyridine, and the solution was sealed into glass ampules. When these ampules were cooled to –5 °C, $Bi(C_6H_5)_5$·C_5H_5N crystallized. The violet crystals had a plate-like, rectangular shape. When the ampules were cooled further to –20 °C, hexagonal needles of $Bi(C_6H_5)_5$·$3C_5H_5N$ were formed. Both adducts melted at room temperature.

Suitable crystals were mounted at –100 °C on an Enraf Nonius CAD 4 diffractometer (Mo Kα radiation, graphite monochromator), using a special low temperature crystal mounting device as described previously.[17,18] Lattice constants were established by fine orientation of 25 reflections with $10° < \theta < 20°$. X-ray reflection intensities were measured in a conventional way by scanning across the reflection allowing 10–100 s for each reflection (one-fourth of this time was used for background measurement). After the usual Lorentz and polarization corrections, the structure was solved with the heavy atom method. Light atoms were found in difference Fourier maps.[19]

After the absorption correction[20] all atoms except the atoms of the solvate molecules in $Li(THF)_4^+Bi(C_6H_3)_6^-$·2THF were refined anisotropically. Hydrogen atoms on the phenyl rings were calculated. In the pyridine adducts of $Bi(C_6H_5)_5$ the positions of the hydrogen atoms were calculated at first, then refined with fixed vibrational parameters. In case of $Bi(C_6H_5)_5$·$3C_5H_5N$ the bismuth atom was refined isotropically in six equivalent positions that are so close that they overlapped.

Further experimental details of the crystal structures are listed in Tables IV and V.

Acknowledgment. We are indebted to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this work.

Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters, complete listings of bond lengths and angles, and a drawing of one molecular unit for $Li(THF)_4^+$-$Bi(C_6H_5)_6^-$·2THF (10 pages). Ordering information is given on any current masthead page.

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