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Synthesis of the First Poly(pyrazolyl)borate Complex of Germanium(II): Solid State Structure of [HB(3,5-Me$_2$pz)$_3$Ge]I·$^1/_2$CH$_2$Cl$_2$

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Introduction

The recent reports of poly(pyrazolyl)borate complexes of Sn(II)[1] and Pb(II)[2] spurred our investigation of the synthesis of similar complexes containing germanium. While a variety of germanium(II) π-cyclopentadienyl[3] and amide[4] complexes have been reported, very little has appeared about poly(pyrazolyl)borate complexes of the lighter group 14 atoms germanium[5] and silicon.[6] A complex of germanium(II) and pyrazolyl rings has been reported.[7]

We report here the synthesis and solid state structure of the first stable germanium poly(pyrazolyl)borate complex, [HB(3,5-Me$_2$pz)$_3$Ge]I (pz = pyrazole ring), and the synthesis of several related complexes.

Experimental Section

General Considerations. All solvents were dried over the appropriate desiccants and degassed prior to use. The following materials were obtained from Aldrich and were used as received: 3,5-Me$_2$-pzH and KBH$_4$. Thallium hexafluorophosphate and GeCl$_4$ were obtained from Strem and used as received. The compounds K[HB(3,5-Me$_2$-pz)$_3$][8] and GeCl$_2$(dioxane)[9] were synthesized by literature methods.

[HB(3,5-Me$_2$pz)$_3$Ge]Cl. To a stirred solution of GeCl$_2$(dioxane) (0.693 g, 3.00 mmol) in THF (30 mL) was added K[HB(3,5-Me$_2$pz)$_3$] (1.01 g, 3.00 mmol) from a solid addition tube. A large amount of white solid precipitated soon after the beginning of the addition. After the addition was complete, the suspension was stirred for 3 h. The solvent was then removed under vacuum and the resulting white solid extracted with CH$_2$Cl$_2$ (30 mL). After the remaining solid was filtered away, the solvent was removed under vacuum to yield a free-flowing white solid. The solid was dried under vacuum, 1.04 g (86%); mp = 86 °C (dec). The analytical sample was recrystallized by carefully layering hexanes on a concentrated solution of the material in CH$_2$Cl$_2$. The mass spectrum showed M$^+$ (M = [HB(3,5-Me$_2$pz)$_3$Ge]Cl), M$^+$ − Cl, and M$^+$ − pz*H clusters at *m/e* 406, 371, and 311, respectively. ^{1}H NMR (CDCl$_3$): δ 5.82 (s; 4-pz; 3H); 2.56, 2.34 (s, s; 3, 5 pz-Me; 6H, 6H). Anal. Calcd for C$_{15}$H$_{22}$BClGeN$_6$: C, 44.46; H, 5.47; N, 20.74. Found: C, 44.44; H, 5.33; N, 20.91.

[HB(3,5-Me$_2$pz)$_3$Ge]I·$^1/_2$CH$_2$Cl$_2$. A Schlenk flask was charged with [HB(3,5-Me$_2$pz)$_3$Ge]Cl (0.40 g, 1.0 mmol) and NaI (1.49 g, 10.0 mmol). Acetone (30 mL) was added via cannula. The suspension was stirred overnight. The then pale yellow solution was concentrated under vacuum to yield a pale yellow solid. This solid was extracted with CH$_2$Cl$_2$ (1 × 20 mL). The solvent was then removed under vacuum from the yellow filtered extract. The resulting yellow solid was dried under vacuum. The sample was then recrystallized by carefully layering hexanes on a concentrated solution of the solid in CH$_2$Cl$_2$, yielding X-ray quality crystals, 0.16 g (32%). The crystalline solid loses solvent at ~150 °C and melts over 219−222 °C. The mass spectrum showed M$^+$ − H (M = [HB(3,5-Me$_2$pz)$_3$Ge]I) and M$^+$ − I clusters at *m/e* 497 and 371, respectively. Each cluster had an isotope pattern that was consistent with its proposed formula. ^{1}H NMR (CDCl$_3$): δ 5.92 (s; 4-pz; 3H); 5.29 (s; H$_2$CCl$_2$; 1H); 2.67, 2.39 (s, s; 3, 5 pz-Me; 6H, 6H). Anal. Calcd for C$_{15}$H$_{22}$BGeN$_6$I·$^1/_2$CH$_2$Cl$_2$: C, 34.53; H, 4.30; N, 15.59. Found: C, 34.53; H, 4.14; N, 15.68.

[HB(3,5-Me$_2$pz)$_3$Ge]PF$_6$. A Schlenk flask was charged with [HB(3,5-Me$_2$pz)$_3$Ge]Cl (0.10 g, 0.25 mmol). Acetone (30 mL) was added to dissolve most of the solid. Via a solid addition tube, TlPF$_6$ (0.9 g, 0.25 mmol) was slowly added to the stirred suspension. The flask was shielded from the light and allowed to stir for 1 h. The remaining solid was filtered away to yield a colorless solution. Removal of the solvent under vacuum yielded a white solid, 0.09 g (70%); mp = 230 °C (dec). The positive ion FAB mass spectrum showed M$^+$ (M = [HB(3,5-Me$_2$pz)$_3$Ge]) and M$^+$ − pz*H at *m/e* 371 and 275, respectively. ^{1}H NMR (CDCl$_3$): δ 6.00 (s; 4-pz; 3H); 2.53, 2.41 (s, s; 3, 5 pz-Me; 6H, 6H). Anal. Calcd for C$_{15}$H$_{22}$BF$_6$GeN$_6$P: C, 35.00; H, 4.31; N, 16.33. Found: C, 34.56; H, 4.33; N, 16.05.

X-ray Structure Determination of [HB(3,5-Me$_2$pz)$_3$Ge]I·$^1/_2$CH$_2$Cl$_2$. A crystal of suitable size was mounted in a glass capillary. Preliminary examination and data collection were performed with Mo Kα radiation. Cell constants and an orientation matrix for data collection were determined from the least-squares fit of 25 reflections (10° < 2θ < 12°). From the systematic absences and from subsequent least-squares refinement, the space group was determined to be *C*2/*c* (#15). Data were collected to a maximum 2θ of 50°. A total of 7353 reflections were collected, of which 2584 were unique and not systematically absent. As a check on crystal and electronic stability, three representative reflections were measured every 120 min. These data showed no significant trends. Lorentz and polarization corrections were applied to the data. No absorption correction was made. Intensities of equivalent reflections were averaged. The structure was solved using a combination of the Patterson heavy-atom method (SHELXS-86)[10] and Fourier techniques. The Patterson method revealed the positions of the germanium and iodine atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. These included a group of peaks assigned as half of a disordered molecule of methylene chloride which had been used as solvent. It was modeled as two chlorine atoms each at half-occupancy and two carbon atoms each at one-quarter-occupancy. Hydrogen atoms were placed in calculated positions on all appropriate atoms except those in the disorder solvent and included in the refinement but were restrained to ride on the atoms to which they are bonded. In the final cycles of least-squares refinement, the disordered solvent atoms were refined with isotropic thermal parameters and all other non-hydrogen atoms were refined with anisotropic thermal parameters. The largest peak in the final difference Fourier was an iodine residual of 1.4 e/Å^3. The results of the structure determination are shown in Tables 1 and 2 and in Figure 1.

Results

The slow addition of K[HB(3,5-Me$_2$pz)$_3$] to a slight excess of GeCl$_2$(dioxane) in THF solution yields the ionic complex

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Table 1. Crystallographic Data for the Structural Analyses for $[HB(3,5\text{-}Me_2pz)_3Ge]I\cdot{}^1/_2CH_2Cl_2$

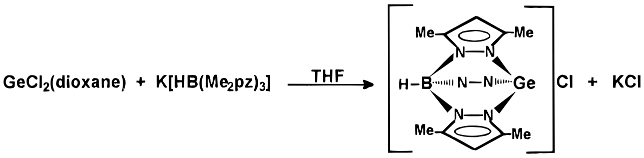
formula	$C_{15}H_{22}GeBIN_6\cdot{}^1/_2CH_2Cl_2$	*Z*	8
		crystal size, mm	0.30 × 0.30 × 0.20
crystal system	monoclinic	radiation (Å)	Mo Kα (0.71073)
space group	*C*2/*c*	temperature, deg	23
a, Å	22.342(3)	2θ range, deg	4.0 to 50.0
b, Å	12.531(3)	no. of rflns measd	7353
c, Å	17.003(2)	no. of rflns obsd	2584
β, deg	115.26(1)	R_F, %	0.068
V, Å^3	4305.3	R_{wF}, %	0.092

Table 2. Positional Parameters and Their Estimated Standard Deviations for $[HB(3,5\text{-}Me_2pz)_3Ge]I\cdot{}^1/_2CH_2Cl_2$

atom	*x*	*y*	*z*	*B* (Å^2)
I	0.41246(6)	0.3051(1)	0.00470(7)	4.64(2)
Ge	0.39786(7)	0.3586(1)	0.46291(9)	2.69(3)
N11	0.3807(5)	0.3588(9)	0.3373(7)	3.0(3)
N12	0.3361(5)	0.2879(9)	0.2807(6)	2.7(3)
N21	0.3945(6)	0.196(1)	0.4603(7)	3.4(3)
N22	0.3473(5)	0.1455(9)	0.3869(6)	2.4(2)
N31	0.2977(5)	0.351(1)	0.4195(7)	3.0(3)
N32	0.2611(5)	0.280(1)	0.3540(7)	2.7(3)
C13	0.3369(6)	0.300(1)	0.2017(8)	2.5(3)
C14	0.3830(7)	0.380(1)	0.2118(9)	3.2(3)
C15	0.4094(6)	0.414(1)	0.2960(8)	2.5(3)
C16	0.4613(7)	0.497(1)	0.3393(9)	3.5(3)
C17	0.2947(8)	0.239(1)	0.1245(9)	3.9(4)
C23	0.3571(6)	0.040(1)	0.4012(9)	2.9(3)
C24	0.4113(8)	0.027(1)	0.484(1)	4.7(4)
C25	0.4306(6)	0.126(1)	0.5145(9)	3.3(3)
C26	0.4837(7)	0.157(1)	0.6020(9)	3.9(4)
C27	0.3158(8)	−0.041(1)	0.334(1)	4.1(4)
C33	0.1975(6)	0.286(1)	0.3424(9)	2.9(3)
C34	0.1926(7)	0.360(1)	0.3988(9)	3.5(3)
C35	0.2567(7)	0.399(1)	0.4463(8)	3.0(3)
C36	0.2813(8)	0.479(1)	0.516(1)	4.6(4)
C37	0.1445(8)	0.221(2)	0.279(1)	5.6(5)
B1	0.2960(7)	0.211(1)	0.312(1)	2.7(4)
Cl1	0.4303(5)	0.0666(8)	0.2316(6)	5.3(2)* [a]
Cl2	0.4478(5)	0.0928(9)	0.2799(7)	6.0(2)*
C1a	0.490(3)	0.155(4)	0.244(6)	2.9(9)*
C1b	0.493(3)	0.172(5)	0.221(4)	4(2)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

$[HB(3,5\text{-}Me_2pz)_3Ge]Cl$. Similar reactions employing other potassium poly(pyrazolyl)borates did not produce stable products.



The chloride anion in $[HB(3,5\text{-}Me_2pz)_3Ge]Cl$ can be easily replaced with other weakly coordinating anions (I^- and PF_6^-) in metathetical reactions to yield the corresponding ionic complexes $[HB(3,5\text{-}Me_2pz)_3Ge]X$. Attempts to substitute a wide variety of more strongly coordinating anionic ligands, with reagents such as $Na[S_2CNEt_2]$, K[OBu^t], LiMe, $K[N(SiMe_3)_2]$, K(SPh), and $Na(C_5H_5)$, lead to decomposition of the starting material. This decomposition includes the reaction of $[HB(3,5\text{-}Me_2pz)_3Ge]Cl$ with another equivalent of $K[HB(3,5\text{-}Me_2pz)_3]$ in an effort to synthesize $[HB(3,5\text{-}Me_2pz)_3]_2Ge$. Reaction with NaCN leads to reisolation of starting material.

We were able to obtain X-ray quality crystals of $[HB(3,5\text{-}Me_2pz)_3Ge]I\cdot{}^1/_2CH_2Cl_2$. Successful solution of the single crystal X-ray structure revealed well-separated germanium-based cations and iodide anions. An ORTEP diagram of the cation is shown in Figure 1. The coordination geometry about germanium is derived from a distorted tetrahedron with three of the sites occupied by nitrogen from the η^3-$[HB(3,5\text{-}Me_2pz)_3]$ ligand and the lone pair on germanium presumably occupying the fourth site. The shortest Ge···I distance is over 4 Å, clearly indicating the lack of any covalent interaction between these atoms. Selected bond distances and angles are listed in Table 3.

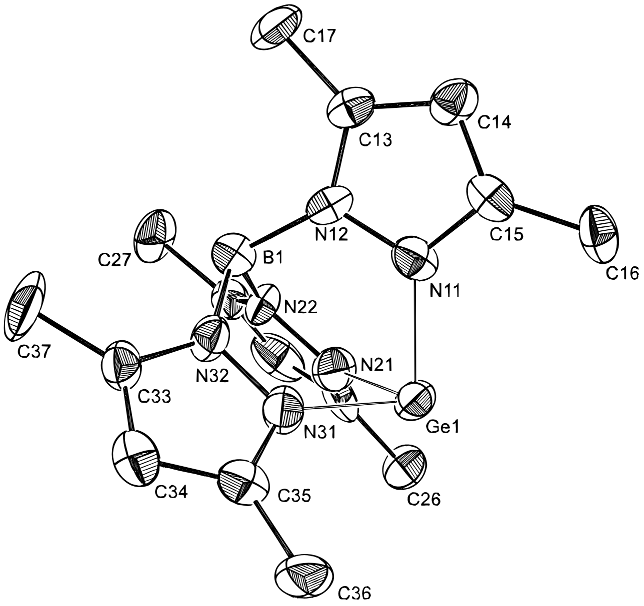


Figure 1. ORTEP diagram for $[HB(3,5\text{-}Me_2pz)_3Ge]^+$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[HB(3,5\text{-}Me_2pz)_3Ge]I\cdot{}^1/_2CH_2Cl_2$ with Estimated Standard Deviations in Parentheses

Bond Distances			
Ge−N11	2.00(1)	Ge−N31	2.04(1)
Ge−N21	2.05(1)		
Bond Angles			
N11−Ge−N21	89.4(5)	Ge−N31−N32	120.3(9)
N11−Ge−N31	86.2(5)	N12−B−N22	106(1)
N21−Ge−N31	85.2(5)	N12−B−N32	107(1)
Ge−N11−N12	119.8(9)	N22−B−N32	105(1)
Ge−N21−N22	119(1)		

Discussion

The complexes $[HB(3,5\text{-}Me_2pz)_3Ge]X$ represent the first stable germanium poly(pyrazolyl)borate complexes and the first poly(pyrazolyl)borate complex of germanium(II).[5] The ionic character of these complexes is indicated by their poor solubility in even polar solvents (CH_2Cl_2, $CHCl_3$, and THF). For comparison, the analogous tin compound, $[HB(3,5\text{-}Me_2pz)_3]SnCl$, shown to be molecular in the solid state by X-ray crystallography, is soluble in toluene.[1a] In addition, the ^1H NMR spectrum of $[HB(3,5\text{-}Me_2pz)_3Ge]Cl$ in $CDCl_3$ maintains only one pyrazole ring environment down to −59 °C, and the chemical shift is essentially invariant with changes in temperature, indicating that the anion does not coordinate to the germanium or that the resulting neutral species is highly fluxional. However, both the chloride and iodide complexes give mass spectra under conventional electron impact conditions (not FAB) that contain low-intensity peaks that are consistent with $\{[HB(3,5\text{-}Me_2pz)_3Ge]X\}^+$ or $\{[HB(3,5\text{-}Me_2pz)_3Ge]X\}^+ -$ H fragments, indicating some degree of ion pairing in the gas phase. In contrast to the ionic character of these poly-

(pyrazolyl)borate complexes, monocyclopentadienyl germanium(II) complexes[3] of the formula Cp*GeX (Cp* = pentamethylcyclopentadienyl, X = Cl, $CH(SiMe_3)_2$, cyclopentadienyl derivative) are neutral complexes with the ligand X coordinated to the germanium center. In fact, the cationic species $[\eta^5\text{-Cp*Ge}]^+$ forms only with very noncoordinating anions.[3a]

The structure of the cation in $[HB(3,5\text{-}Me_2pz)_3Ge]I$ does not contain any unusual bond distances or angles. The cation most resembles an octahedral $M^{II}[HB(3,5\text{-}R_2pz)_3]_2$ complex with one of the poly(pyrazolyl)borate ligands removed. The only similar compound to $[HB(3,5\text{-}Me_2pz)_3Ge]^+$ that has been reported is $(THF)_3Na(pz_3)Ge$.[7] This complex also possesses a distorted tetrahedral geometry about germanium with three of the positions occupied by nitrogen atoms from pyrazolyl rings that bridge the sodium atom and the lone pair on germanium in the fourth position. However, the larger size of the sodium atom in this complex relative to the boron atom in $[HB(3,5\text{-}Me_2pz)_3Ge]^+$ causes the germanium−nitrogen bond distances to be 0.065 Å shorter and the N−Ge−N angles to be 9.3° larger. The average N−N nonbonded distance about the germanium is also greater in $(THF)_3Na(pz_3)Ge$ (2.92 Å) than that in $[HB(3,5\text{-}Me_2pz)_3Ge]^+$ (2.79 Å).

Another complex that is similar to the cation $[HB(3,5\text{-}Me_2pz)_3Ge]^+$ is $[HB(3,5\text{-}Me_2pz)_3]MgCH_2SiMe_3$.[11] This is an interesting comparison since Ge(II) and Mg(II) have similar radii.[12] Both complexes have a distorted tetrahedral geometry about the metal center with three sites occupied by the three nitrogen donor atoms of a $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand. In the magnesium complex a bulky alkyl group occupies the fourth site whereas in the germanium complex a lone pair is assumed to occupy this site. The average metal−nitrogen distances in the two complexes are very similar (Ge−N = 2.03 Å; Mg−N = 2.077 Å), but the average N−N nonbonded distance within the poly(pyrazolyl)borate ligand in $[HB(3,5\text{-}Me_2pz)_3Ge]^+$ is 0.15 Å shorter than that in $[HB(3,5\text{-}Me_2pz)_3]MgCH_2SiMe_3$. The average N−M−N angles are also smaller in the germanium cation (86.9°) than in the magnesium complex (90.0°).

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Supporting Information Available: Tables of complete data collection information, bond distances, angles, anisotropic thermal parameters, and positional parameters of H atoms (8 pages). Ordering information is given on any current masthead page.

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