

THE PREPARATION, ISOMERIZATION, AND CHARACTERIZATION OF SOME PHOSPHAGERMA- AND ARSAGERMACARBORANES

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SUMMARY

Treatment of the disodium salts of 7,8- and 7,9- $B_9H_9CHE^{2-}$ with germanium diiodide in refluxing benzene results in the formation of 1,2,3- and 1,2,7- GeB_9H_9CHE ($E = P$ or As), icosahedral boranes containing three different heteroatoms in the cage. Heating 1,2,7- GeB_9H_9CHP at 512° for 8 hours in an evacuated sealed tube yields a mixture of three new isomers one of which has been isolated and characterized.

INTRODUCTION

The discovery of carboranes containing atoms other than boron and carbon in the cage originally involved only transition metals¹, but has recently been extended to include several non-transition elements including $BeC_2B_9H_{11} \cdot N(CH_3)_3$ ², $CH_3-MC_2B_4H_6$ ^{3a} ($M = Ga, In$), $B_9C_2H_{11}M(C_2H_5)^{3b}$ ($M = Ga, Al$), $B_{10}H_{10}CHP$ ⁴, $B_{10}H_{10}CHAs$ ⁵, $B_{10}H_{10}CHSb$ ⁵, $B_{10}H_{10}CHGeCH_3$ ⁵ and $MC_2B_9H_{11}$ ($M = Ge, Sn, Pb$)⁶.

This paper describes the preparation, isomerization, and characterization of a new member in the series of heteroatom-containing carboranes, GeB_9H_9CHE ($E = P$ or As). This represents the first example of a polyhedral borane with three different main-group heteroatoms in the cage.

EXPERIMENTAL

General comments

Boron (^{11}B) NMR spectra at 70.6 MHz were obtained with a Varian HR-220 spectrometer. Spectral integrals were obtained with a Lasico optical planimeter. All ^{11}B spectra were externally referenced to $BF_3 \cdot O(C_2H_5)_2$. Proton NMR spectra were obtained with a Varian HA-100 or HR-220 spectrometer.

Carbon, hydrogen, boron, and phosphorus analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. The analytical data for the new compounds described in this article are given in Table 1. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 621 instrument. The intensities are reported as vs, very strong; s, strong; m, medium; or w, weak.

Low resolution mass spectra were obtained with an Atlas CH-7 instrument. High resolution mass spectra were run on an AEI MS-9 instrument.

TABLE I

ANALYTICAL DATA OF PHOSPHAGERMA- AND ARSAGERMACARBORANES

Compound	Analysis, found (calcd.) (%)			
	C	H	B	P
1,2,3-GeB ₉ H ₉ CHP	5.65 (5.39)	4.53 (4.52)	43.34 (43.64)	
1,2,7-GeB ₉ H ₉ CHP	5.75 (5.39)	4.53 (4.52)	43.89 (43.64)	13.60 (13.89)
1,2,3-GeB ₉ H ₉ CHAs	4.05 (4.50)	4.16 (3.78)		
1,2,7-GeB ₉ H ₉ CHAs	4.69 (4.50)	3.90 (3.78)	36.66 (36.45)	

Reported melting points were done in sealed capillaries and are uncorrected. All reactions were carried out under an atmosphere of prepurified nitrogen.

Starting materials

Benzene was freshly distilled from sodium metal and stored over Linde Type 4A molecular sieves before use. Sodium hydride, as a 57% oil dispersion, was purchased from Ventron, Inc. Germanium tetraiodide was obtained from Alfa Inorganics and germanium diiodide was prepared by the method of Foster⁷.

Trimethylammonium salts of 7,8- and 7,9-B₉H₁₀CHP⁻ and 7,8- and 7,9-B₉H₁₀CHAs⁻

The crude tetramethylammonium salt of the B₉H₁₀CHP⁻ or the B₉H₁₀-CHAs⁻ ion was dissolved in a 80/20 mixture of acetonitrile/water and slowly passed through a five-fold excess exchange capacity of sodium ion exchange resin. After removal of solvent the resulting white hygroscopic material was dissolved in a minimum of water and a saturated aqueous solution of trimethylamine hydrochloride added until precipitation was complete. Recrystallization was readily accomplished from acetone/water to give yields of product ranging from 70–90%.

1-Phospha-2-carba-3-germa-closo-dodecaborane(10)

A solution of 0.700 g (3.28 mmol) of the trimethylammonium salt of 7,8-B₉H₁₀CHP⁻ in 25 ml of benzene was added to 0.158 g (6.59 mmol) of NaH (0.277 g of 57% oil dispersion which had been washed twice with hexane and once with benzene). The mixture was maintained at reflux for an additional 3 h while a stream of argon swept over the system to remove the gaseous by-products formed (trimethylamine and hydrogen). Anhydrous GeI₂ was then added as a benzene slurry over a period of one hour and the resulting reaction mixture was heated at 70–75° for 15 h under an argon atmosphere. The yellow-orange residue obtained after removal of solvent *in vacuo*, was sublimed at 80° and 10⁻³ mmHg for 24 h to give 0.500 g (68% yield) of product. An analytically pure sample was obtained by TLC. A benzene solution of the white sublimate was applied to a 20 cm × 20 cm silica gel TLC plate and eluted with benzene. Sublimation of the extracted material yielded a pure crystalline product. The compound melted at 340–343° with decomposition.

The infrared spectrum exhibits absorption maxima at 3007 m, 2511 vs, 1390 w, 1119 m, 1010 m, 980 m(sh), 968 s, 910 w, 855 m, 750 w, 725 s(sh), 715 s, 670 w, 629 m, 437 m, and 367 w cm^{-1} . The proton NMR spectrum (acetone- d_6) shows a broad doublet centered at τ 7.23 ppm, $J(^{31}\text{P}-^1\text{H})$ 16 Hz.

The low voltage mass spectrum cuts off at m/e 228 corresponding to the ($^{76}\text{Ge}^{11}\text{B}_9^1\text{H}_{10}^{12}\text{C}^{31}\text{P}$) $^+$ parent ion.

1-Phospha-2-germa-7-carba-closo-dodecaborane(10)

This compound was prepared from the 7,9- $\text{B}_9\text{H}_{10}\text{CHP}^-$ ion by the method used for the 1,2,3-isomer, except that after the addition of anhydrous GeI_2 , the resulting reaction mixture is maintained at reflux for 24 h. The compound was observed to melt with decomposition at 410–415 $^\circ$.

The infrared spectrum contains absorption maxima at 3010 w, 2539 vs, 1390 w, 1133 m, 1093 w, 1028 w, 972 s, 873 w, 858 w, 757 w, 725 s, 621 w, 435 w and 366 w cm^{-1} . The proton NMR spectrum (acetone- d_6) shows a broad singlet at τ 6.54 ppm.

The low voltage mass spectrum cuts off at m/e 228 corresponding to the ($^{76}\text{Ge}^{11}\text{B}_9^1\text{H}_{10}^{12}\text{C}^{31}\text{P}$) $^+$ parent ion.

Pyrolysis of 1-phospha-2-germa-7-carba-closo-dodecaborane(10)

1,2,7- $\text{GeB}_9\text{H}_9\text{CHP}$ (0.500 g, 2.22 mmol) was sealed into a evacuated Carius tube and pyrolyzed for 8 h at 512 $^\circ$. The product mixture was sublimed at 80 $^\circ$ *in vacuo* (10^{-3} mmHg) to obtain 0.198 g (37% yield) of sublimate. The GLC/mass spectrum indicated the presence of three isomers of $\text{GeB}_9\text{H}_9\text{CHP}$ with retention times of 0.53* (60%), 0.62 (10%) and 0.76 (30%). The sublimate was applied to a column (193 cm \times 2 cm) containing Activity Grade I silica gel and eluted with pentane to obtain the pure isomer with retention time of 0.53.

The infrared spectrum shows absorption maxima at 2553 vs, 2438 w(sh) 1379 w, 1119 s, 1028 m, 964 w, 905 w, 724 s, 715 w(sh) and 434 w cm^{-1} . The proton NMR spectrum (acetone- d_6) shows a broad singlet at τ 5.50 ppm. The low voltage mass spectrum cuts off at m/e 228 corresponding to the ($^{76}\text{Ge}^{11}\text{B}_9^1\text{H}_{10}^{12}\text{C}^{31}\text{P}$) $^+$ parent ion.

1-Arsa-2-carba-3-germa-closo-dodecaborane(10)

The method of preparation of this compound is similar to that of 1,2,3- $\text{GeB}_9\text{H}_9\text{CHP}$, except that after addition of GeI_2 to the disodium salt of 7,8- $\text{B}_9\text{H}_9\text{CHAs}^{2-}$ in benzene, the reaction was complete in 6 h when heated to 50 $^\circ$. Since the product proved to be solution unstable, removal of solvent and sublimation of the resulting residues at 70 $^\circ$ and 10^{-3} mmHg was effected without delay to give 0.053 g (10% yield) of white crystalline product. The compound melts at 385–390 $^\circ$ with decomposition. The infrared spectrum contains absorption maxima at 2900 w, 2521 vs, 1393 w, 1083 w, 1013 m, 970 s, 910 w, 858 w, 719 m, 600 m, and 346 m cm^{-1} . The proton NMR spectrum (acetone- d_6) shows a broad singlet at τ 6.81 ppm. The low voltage mass spectrum cuts off at m/e 272 corresponding to the ($^{76}\text{Ge}^{11}\text{B}_9^1\text{H}_{10}^{12}\text{C}^{75}\text{As}$) $^+$ parent ion.

* Relative to 1,2,3- $\text{GeB}_9\text{H}_9\text{CHP}$ = 1.00.

1-Arsa-2-germa-7-carba-closo-dodecaborane(10)

The method of preparation of this compound is similar to that of 1,2,4- $\text{GeB}_9\text{H}_9\text{CHP}$. The compound was observed to melt at $413\text{--}416^\circ$ with decomposition.

The infrared spectrum exhibits absorption maxima at 2516 vs, 1386 w, 1128 m, 1092 w, 1022 m, 970 s, 905 w, 864 w, 852 w, 757 w, 723 s, and 592 s cm^{-1} . The proton NMR spectrum (acetone- d_6) contains a broad singlet at τ 6.54 ppm.

The low voltage mass spectrum cuts off at m/e 272 corresponding to the $(^{76}\text{Ge}^{11}\text{B}_9^1\text{H}_{10}^{12}\text{C}^{75}\text{As})^+$ parent ion.

RESULTS AND DISCUSSION

The addition of GeI_2 to the $7,9\text{-B}_9\text{H}_9\text{CHP}^{2-}$ ion, generated in refluxing benzene as the disodium salt, resulted in the insertion of the metal into the vacant icosahedral position forming 1,2,7- $\text{GeB}_9\text{H}_9\text{CHP}$. The numbering system used in these icosahedral molecules is given in Fig. 1. The elemental analysis is consistent with the formulation $\text{GeB}_9\text{H}_9\text{CHP}$ for this new compound. The molecular formula was further confirmed by its low resolution mass spectrum and more definitely identified as such by its high resolution mass spectrum: calcd. for $(^{76}\text{Ge}^{11}\text{B}_9^1\text{H}_{10}^{12}\text{C}^{31}\text{P})^+$ 228.0572; found 228.0557.

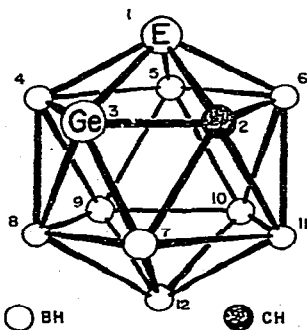


Fig. 1. Proposed structure for 1,2,3- $\text{GeB}_9\text{H}_9\text{CHE}$ ($\text{E} = \text{P}$ or As). The germanium atom in this compound may be "slipped" toward boron atoms 4, 7 and 8.

Employing a similar procedure 1,2,3- $\text{GeB}_9\text{H}_9\text{CHAs}$, 1,2,3- $\text{GeB}_9\text{H}_9\text{CHP}$ and 1,2,7- $\text{GeB}_9\text{H}_9\text{CHAs}$ have been prepared and characterized. In the case of both phosphagerma- and arsagermacarboranes, the 1,2,7-isomer is more stable thermally than the 1,2,3-isomer. This observation can be understood in terms of greater charge separation expected in the 1,2,7-isomer relative to the 1,2,3-isomer (where the three heteroatoms are located at the vertices of one of the triangular faces of the icosahedron). All the new compounds can be stored in air at room temperature for several weeks with negligible decomposition and, except for 1,2,3- $\text{GeB}_9\text{H}_9\text{CHAs}$, can be readily recrystallized from benzene/hexane. Since 1,2,3- $\text{GeB}_9\text{H}_9\text{CHAs}$ proved to be quite solution unstable, it is best purified by sublimation at 70° *in vacuo*. Attempts to prepare the analogous phosphastanna- and phosphaplumbacarborane compounds using the described procedure were unsuccessful.

The infrared spectra of the new compounds are quite similar. They all exhibit

absorptions near 3000–3020, 2500–2550, and 1390 cm^{-1} characteristic of C–H stretching, and B–H stretching and C–H deformation frequencies respectively. The absence of absorptions in the region 2150–1800 cm^{-1} characteristic of Ge–H stretching motions⁸ suggests that the germanium atom exists as a “bare center” in these molecules.

The proton NMR spectrum of 1,2,3- $\text{GeB}_9\text{H}_9\text{CHP}$ consists of a broad doublet (J 16 Hz) at τ 7.23 ppm assigned to the proton attached to the carbon atom and the splitting attributable to ^{31}P – ^1H spin–spin coupling. The other compounds exhibit only a broad singlet ranging from τ 6.54 to 6.81 ppm in their proton NMR spectra assigned to the proton attached to carbon. The ^{11}B NMR spectra of the new heteroatom carboranes are presented in Figs. 2–5. In the case of 1,2,3- $\text{GeB}_9\text{H}_9\text{CHP}$ and 1,2,3- $\text{GeB}_9\text{H}_9\text{CHAs}$ seven of the nine possible boron resonance doublets of area one are observed while two doublets of area one remain coincident. Complete interpretation of the spectra of the two 1,2,7-isomers was not possible because of extensive overlap of the individual doublets although both are consistent with a pattern of nine non-equivalent boron atoms.

Selective base degradation of 1,2- and 1,7- $\text{B}_{10}\text{H}_{10}\text{CHP}$ using piperidine results in removal of a boron atom producing the 7,8- $\text{B}_9\text{H}_{10}\text{CHP}^-$ and 7,9- $\text{B}_9\text{H}_{10}\text{CHP}^-$ ions, respectively⁴. An attempt to remove a boron atom from 1,2,7- $\text{GeB}_9\text{H}_9\text{CHP}$ using this amine led to selective removal of the metal atom and regeneration of the 7,9- $\text{B}_9\text{H}_{10}\text{CHP}^-$ ion.

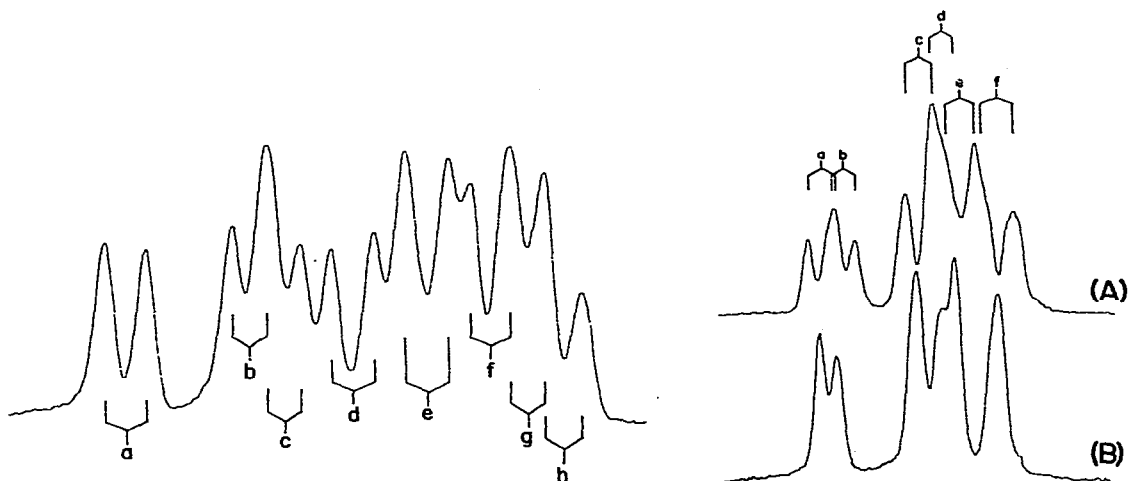


Fig. 2. The 70.6 MHz ^{11}B NMR spectrum of 1,2,3- $\text{GeB}_9\text{H}_9\text{CHP}$ in benzene. Chemical shifts [ppm relative to external $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$], number of borons and coupling constants (Hz) are: (a) -14.2 (1B), 150; (b) -7.9 (1B), ≈ 127 ; (c) -5.8 (1B), ≈ 117 ; (d) -2.5 (1B), 155; (e) $+1.3$ (2B), 155; (f) $+4.3$ (1B), ≈ 140 ; (g) $+6.4$ (1B), ≈ 123 ; and (h) $+8.4$ (1B), ≈ 137 .

Fig. 3. (A). The 70.6 MHz ^{11}B NMR spectrum of 1,2,7- $\text{GeB}_9\text{H}_9\text{CHP}$ in benzene. Chemical shifts [ppm relative to external $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$], number of borons and coupling constants (Hz) are: (a) -7.5 (1B), ≈ 145 ; (b) -6.0 (1B), ≈ 130 ; (c) $+0.04$ (2B), ≈ 150 ; (d) $+1.9$ (1B), ≈ 130 ; (e) $+3.02$ (2B), ≈ 150 ; and (f) $+6.3$ (2B), ≈ 165 .
(B). Proton decoupled spectrum of 1,2,7- $\text{GeB}_9\text{H}_9\text{CHP}$ in benzene.

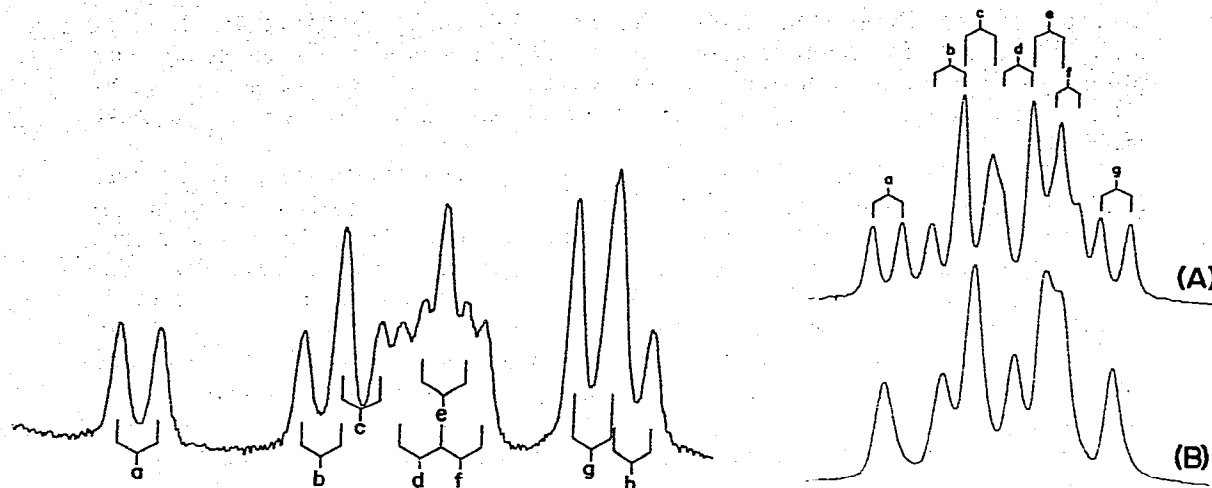


Fig. 4. The 70.6 MHz ^{11}B NMR spectrum of 1,2,3- $\text{GeB}_9\text{H}_9\text{CHAs}$ in benzene. Chemical shifts [ppm relative to external $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$], number of borons and coupling constants (Hz) are: (a) -16.7 (1B), 140; (b) -7.3 (1B), ≈ 150 ; (c) -5.2 (1B), ≈ 140 ; (d) -2.2 (1B), ≈ 150 ; (e) -1.1 (1B), ≈ 140 ; (f) -0.14 (1B), ≈ 145 ; (g) $+6.7$ (2B), ≈ 145 ; and (h) $+8.6$ (1B), ≈ 135 .

Fig. 5. (A). The 70.6 MHz ^{11}B NMR spectrum of 1,2,7- $\text{GeB}_9\text{H}_9\text{CHAs}$ in benzene. Chemical shifts [ppm relative to external $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$], number of borons and coupling constants (Hz) are: (a) -9.4 (1B), 160; (b) -4.8 (1B), ≈ 160 ; (c) -2.5 (2B), ≈ 165 ; (d) $+0.68$ (1B), ≈ 150 ; (e) $+2.9$ (2B), ≈ 153 ; (f) $+4.4$ (1B), ≈ 130 ; and (g) $+8.4$ (1B), ≈ 165 .

(B). Proton decoupled spectrum of 1,2,7- $\text{B}_9\text{H}_9\text{CHAs}$ in benzene.

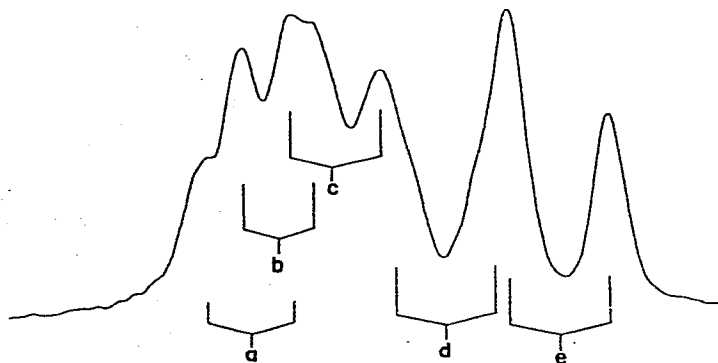


Fig. 6. The 70.6 MHz ^{11}B NMR spectrum in benzene of the isolated isomer from pyrolysis of 1,2,4- $\text{GeB}_9\text{H}_9\text{CHP}$. Chemical Shifts [ppm relative to external $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$], number of borons and coupling constants (Hz) are: (a) -1.8 (1B), ≈ 155 ; (b) -1.2 (2B), ≈ 130 ; (c) $+0.35$ (2B), ≈ 150 ; (d) $+3.05$ (2B), ≈ 170 ; and (e) $+5.9$ (2B), ≈ 170 .

Thermal isomerization of 1,2,7- $\text{GeB}_9\text{H}_9\text{CHP}$ in a sealed Carius tube for 8 h produced a mixture of three new compounds in moderate yield. GLC/mass spectrum analysis of the mixture revealed that each compound contained a parent peak cut off at m/e 228; corresponding to the $^{76}\text{Ge}^{11}\text{B}_9^{1}\text{H}_{10}^{12}\text{C}^{31}\text{P}^+$ ion. The most abundant isomer (retention time 0.53) was separated by column chromatography. The ^{11}B

NMR spectrum of the new isomer is given in Fig. 6. The range of chemical shifts of the various boron resonances in this spectrum is much smaller than the range in the spectra of the 1,2,3- and 1,2,7-isomers. This decrease in chemical shift range is the usual trend observed when the heteroatoms are more widely separated in an icosahedral framework. The relatively short GLC retention time of the new isomer suggests that it is less polar than 1,2,3- and 1,2,7- $\text{GeB}_9\text{H}_9\text{CHP}$. This is also consistent with greater heteroatom separation in the isomerized product. The proton NMR chemical shift of the hydrogen attached to carbon in the new isomer is at lower field than that found for 1,2,3- and 1,2,7- $\text{GeB}_9\text{H}_9\text{CHP}$. The trend to lower field CH proton shifts with increased heteroatom separation was also observed in the phospho- and arsa-carboranes⁹. Three lines of evidence suggest that the heteroatoms in the isomerized product are more widely separated than is present in 1,2,7- $\text{GeB}_9\text{H}_9\text{CHP}$. Determination of the exact positions of the heteroatoms will require an X-ray crystallographic study.

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