1532 J. Am. Chem. Soc. 1986, 108, 1532-1536

New Tetrapyrrolic Macrocycle: α,β,γ-Triazatetrabenzcorrole[†]

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Abstract: A previously reported divalent germanium phthalocyanine (PcGe^{II}) exhibiting unusual electronic and mass spectra when compared with a corresponding high-valent germanium phthalocyanine has been identified as hydroxygermanium α,β,γ-triazatetrabenzcorrole (TBC^{3-} Ge^{IV}OH). This was determined from elemental analyses (C, H, N, Ge, and O), spectral measurements (EI- and FD-MS, vis, IR, and ^{1}H NMR), measurements of chemical reactivity, and oxidative titration results. This TBC ring is a new tetrapyrrolic macrocycle. TBCs containing Si, Al, and Ga have also been produced in a reaction mixture of $NaBH_4$. This type of metalloid Pcs ring contractive reaction is generally observed to occur with the introduction of a reductive reagent such as $NaBH_4$ and H_2Se. The molecular symmetry of a TBCGe moiety is exactly C_1 or an approximately 2-fold symmetry showing some distortion.

Phthalocyanine (Pc) and porphyrin compounds, which are typical planar macrocycles, are of particular interest in many basic and applied researches concerning catalysts, photoconductors, photosensitizers, heme and chlorophyll biosystem models, conductive materials,[1] and photochemical hole-burning memories and molecular electronic devices.[2,3] Pcs containing group IIIA (13) and IVA (14) metalloids, first-row transition metals, and rare-earth metals can provide one-dimensional conductors, whose stacking structures are linearly controlled by covalent linkage (O, F, S, and organic molecules)[4-7] and by the out-of-plane structure of the central metal.[8,9]

Recently, Gouterman et al.[10] have reviewed the preparation and electronic spectra of Pcs containing lower valent metalloids and have compared them with those of corresponding higher valent metalloid Pcs. In their review, they pointed out the fact that PcGe^{IV} and PcP^{III} exhibit unusual electronic absorption spectra in contrast to the normal spectra of PcGe^{IV} and PcP^{V}. The Q bands and B bands of PcGe^{II} and PcP^{III} are markedly blue-shifted and red-shifted, respectively. They have proposed that the origin of such unusual spectra on PcP^{III} can be attributed to porphyrin-like four-orbital electronic transition, resulting from a closing of the energy gap between a_{1u} (first HOMO) and a_{2u} (second HOMO).[11] In addition, from mass spectra data, they have suggested that PcP^{III} has the possibility of another structure, e.g., $PcPH_2$.[11] However, from our preliminary EI- and FD-MS data for PcGe^{II},[12,13] the intense parent mass peak was observed to be m/z 589 (PcGe^{II} + 3) and not m/z 586 (PcGe^{II}).

To clarify the cause of this unusual electronic absorption and mass spectra for PcGe^{II}, the structure of PcGe^{II} was reinvestigated by means of elemental analyses (C, H, N, Ge, and O), IR, vis, FD and EI-MS, ^{1}H NMR, and chemical substitution reactions. This study concludes that the previously reported PcGe^{II} is not a divalent germanium phthalocyanine but a hydroxygermanium(IV) α,β,γ-triazabenzcorrole (TBCGeOH) formed by the ring contractive reaction of dichlorogermanium phthalocyanine.

Experimental Section

Measurements. Visible (vis) and second differential visible (2D-vis) absorption spectra were recorded by using a Hitachi 330 double-beam automatic spectrophotometer. Infrared (IR) absorption spectra were recorded with a JASCO 220 double-beam automatic infrared spectrophotometer. Field desorption ionization mass (FD-MS) spectra were obtained with a Hitachi M-80A mass spectrometer, and electron ionization mass (EI-MS) spectra were obtained by using a JEOL JMS-SG-02 mass spectrometer. A proton nuclear magnetic resonance (^{1}H NMR) spectrum was recorded with a Hitachi R-600 NMR spectrometer (FT, 60 MHz). A thermal gravimetric diagram (TG) was obtained by using Rigaku TG units. Elemental analyses for C, H, and N were carried out by using a Heraeus CHN-Rapid automatic elemental analyses instrument and those for Ge and O were performed at the Toray Research Center (Shiga, Japan).

Synthesis. (a) Dichlorogermanium(IV) Phthalocyanine ($PcGeCl_2$). This was prepared by the literature procedure.[14] Anal. Calcd for $C_{32}H_{16}N_8GeCl_2$: C, 58.69; H, 2.46; N, 17.07; Cl, 10.81. Found: C, 58.22; H, 2.34; N, 16.90; Cl, 10.22.

(b) (Benzyloxy)germanium(IV) α,β,γ-Triazatetrabenzcorrole (TBCGeOBz). A mixture of $PcGeCl_2$ (2.0 g, 3.0 mmol) and $NaBH_4$ (0.37 g, 0.98 mmol) was stirred at 160 °C in a mixture of benzyl alcohol (50 mL) and anisole (25 mL) for 2 h in an Ar gas atmosphere. The hot mixture was filtered under reduced pressure, and anisole in the filtrate was evaporated under reduced pressure at 100 °C. The residual mixture was successively washed with ether, and the resulting solid was repeatedly extracted with hot xylene. The dark-green extract was evaporated under reduced pressure at 70 °C. The residue was again washed with ether and dried in a vacuum for 1 day at 100 °C. The product was a blue fine needle, and the yield was 0.85 g (42%): FD-MS, m/z (rel intensity) 679

[†] In this paper the periodic group notation in parentheses is in accord with recent with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III → 3 and 13.)

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Table I. Results of Elemental Analysis on TBC Derivatives

	found (%)					calcd (%)				
compound	C	H	N	Ge	O	C	H	N	Ge	O
TBCGeOH	65.50	2.85	16.15	13.05	3.70	65.36	2.91	16.66	12.34	2.72
$PcGe^{II}$[a]	65.86	2.91		12.63		65.39	2.76	19.14	12.41	0.00
TBCGeOBz	69.33	3.30	14.77		3.15	69.07	3.42	14.45		2.36
TBCGeF + $0.5H_2O$	63.90	2.85	16.04			64.15	2.86	16.35		
$(TBCGe)_2O$	66.85	2.65	16.63		1.64	66.38	2.79	16.92		1.38
$TBCNa_3$ + $2(diglyme)_2$	62.29	4.98	11.60		12.82	63.23	5.31	11.73		11.49

[a] Note data from ref 14.

(M^+, 100), 589 ($(M - C_7H_7 + H)^+$, 100); EI-MS, *m/z* (rel intensity) 679 (M^+, 40), 572 ($(M - OCH_2Ph)^+$, 31), 589 ($(M - C_7H_7 + H)^+$,7), 1158 ($[(M - C_7H_7) + (M - OCH_2C_6H_5) - H_2O]^+$, 100); IR (KBr) ν (CH_2) 2920 w, 2860 w, ν (Ge–O–C) 1040 w; vis ($CHCl_3$) λ (ϵ M^{-1} cm^{-1}) 415 (3.6×10^4), 442 (8.0×10^4), 668 (br, 4.5×10^4); 2D-vis ($CHCl_3$, $\Delta\lambda = 3$ nm) λ (nm) (rel absorbance) 414 (0.13), 424 (0.07), 437 (0.31, 443 (1.00), 607 (0.02), 650 (0.12), 664 (0.08), 676 (0.13).

(c) Hydroxygermanium(IV) α,β,γ-Triazatetrabenzcorrole (TBCGeOH). This compound was identical with previously reported $PcGe^{II}$,[10,15] as will be discussed later. TBCGeOBz (0.50 g, 0.4 mmol) was refluxed in a mixture of concentrated (10 mL) and ethanol (50 mL) for 10 min. The hot mixture was filtered under reduced pressure and washed with ethanol and then dried in vacuum for 1 day at 100 °C. The product was a dark-green fine needle, and the yield was 0.41 g (94%). FD-MS, *m/z* (rel intensity) 589 (M^+, 100), 1158 ($(2M - H_2O)^+$, 10); EI-MS, *m/z* (rel intensity) 589 (M^+, 100), 572 ($(M - OH)^+$, 33), 1158 ($(2M - H_2O)^+$, 15); ^1H NMR (D_2SO_4, internal $(CH_3)_4Si$) 9.1 (8 H, m, TBC ring internal H), 10.2 (8 H, m, ring external H); IR (KBr) ν (GeO–H) 3250 w, ν (Ge–OH) 718 m; vis ($CHCl_3$) λ (nm) (ϵ M^{-1} cm^{-1}) 415 (4.2×10^4), 444 (8.7×10^4), 663 (br, 4.5×10^4); 2D-vis ($CHCl_3$, $\Delta\lambda = 3$ nm) λ (nm) (rel absorbance) 414 (0.15), 424 (0.01), 436 (0.36), 443 (1.00), 649 (0.12), 664 (0.15).

(d) Fluorogermanium(IV) α,β,γ-Triazatetrabenzcorrole (TBCGeF). TBCGeOH (0.40 g, 0.68 mmol) was reacted with 50% HF (50 mL) in a Teflon flask for 2 h at 60 °C. The product was filtered under reduced pressure and dried in vacuum for 1 day at 150 °C. The product was a dark-blue fine needle, and the yield was 0.38 g (100%): EI-MS, *m/z* (rel intensity) 591 (M^+, 100), 572 ($(M - F)^+$, 3); IR (KBr) ν(Ge–F) 480 w, ν(Ge–OH) disappearance 718 m; vis ($CHCl_3$) λ (ϵ M^{-1} cm^{-1}) 415 (4.1×10^4), 424 (8.5×10^4), 662) (br, 4.5×10^4); 2D-vis ($CHCl_3$, $\Delta\lambda = 3$ nm) λ (nm) (rel absorbance) 414 (0.16), 423 (0.05), 436 (0.34), 442 (1.00), 650 (0.12), 663 (0.11).

(e) μ-Oxobis(germanium(IV) α,β,γ-triazatetrabenzcorrole) ($(TBCGe)_2O$). TBCGeOH (10 mg) was heated to 500 °C and then cooled to room temperature in a stram of N_2. This process was monitored with a TG system. A 1.7% weight loss (theoretical 1.53%) was observed in the 370–410 °C range. The product was a blue-black fine needle, and the yield was 9.8 mg (100%). EI-MS, *m/z* (rel intensity) 1158 (M^+, 100), 588 ($(M - TBCGe)^+$, 7), 572 ($(M - TBCGeO)^+$, 3); IR (KBr) ν_{as} (Ge–O–Ge) 892 s, ν_s (Ge–O–Ge) 867 s, ν (GeO–H) disappearance 3250 w, and ν(Ge–OH) disappearance 718 m; vis (pyridine) λ (nm) (ϵ M^{-1} cm^{-1}) 416 (3.0×10^4), 446 (8.2×10^4), 661 (br, 4.2×10^4); 2D-vis (pyridine, $\Delta\lambda = 3$ nm) λ (nm) (rel absorbance) 416 (0.20), 437 (0.44), 445 (1.00), 649 (0.12), 664 (0.13).

(f) Trisodium α,β,γ-Tetrabenzcorrolebis(diglyme) ($TBCNa_3(diglyme)_2$). A mixture of $PcGeCl_2$ (0.50 g, 0.76 mmol) and $NaBH_4$ 0.10 g (2.6 mmol) was stirred at 150 °C in diglyme (30 mL) for 2 h in an Ar gas atmosphere. The solvent was evaporated under reduced pressure at 60 °C. The resultant was repeatedly extracted with hot toluene, and the extract was evaporated under reduced pressure at 60 °C. The solid was dried in a vacuum for 2 days at 60 °C. The product was a blue needle, and the yield was 53 mg. EI-MS was not obtained, due to decomposition: IR (KBr) ν (C–H, diglyme) 2920 m, 2875 m, ν (C–O–C, diglyme) 1100 br s; vis ($CHCl_3$) λ (nm) (ϵM^{-1} cm^{-1}) 416 (4.6×10^4), 443 (7.5×10^4), 610 (br, 2.3×10^4), 676 (8.4×0^4) 2D-vis ($CHCl_3$, $\Delta\lambda = 3$ nm) λ (nm) (rel absorbance) 413 (0.27), 422 (0.14), 435 (0.18), 441 (0.60), 451 (0.19), 606 (0.07), 636 (0.06), 650 (0.14), 674 (1.00).

(g) Dihydroxygermanium(IV) Phthalocyanine ($PcGe(OH)_2$). This was prepared by the literature procedure.[14] Anal. Calcd for $C_{32}H_{18}N_8O_2Ge$: C, 62.08; H, 2.93; N, 21.02. Found: C, 61.88; H, 3.15; N, 20.84. IR (KBr) ν (GeO–H) 3500 s, ν (Ge–OH) 640 s.

(h) TBCGeOH from $PcGe(OH)_2$ with H_2Se. $PcGe(OH)_2$ (0.32 g, 0.52 mmol) was reacted in quinoline (40 mL) for 10 min at room temperature, for 20 min at 100 °C, for 20 min at 120 °C, and 4 h at 160 °C, in bubbling H_2Se/Ar (50/50 wt%) gas. The hot reaction mixture was filtered, and the filtrate was allowed to cool for 2 days. The precipitate was filtered under reduced pressure and washed with ethanol and acetone and then dried in a vacuum for 1 day at 100 °C. The product was a dark-green powder, and the yield was 0.24 g (82%). This product was identified as TBCGeOH from elemental analyses (C, H, and N), IR, and vis spectra.

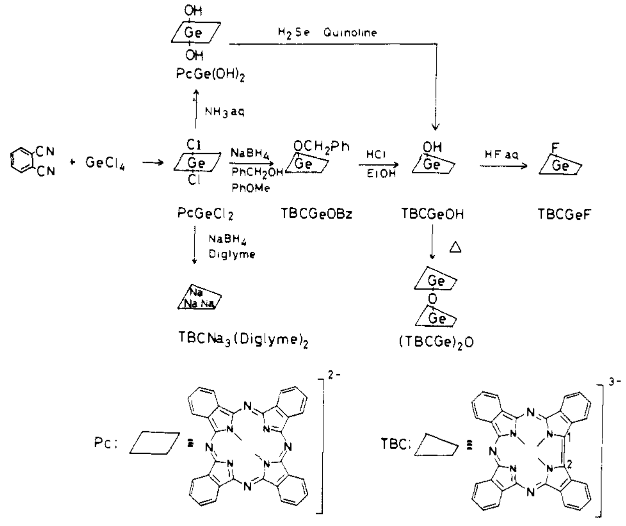

Figure 1. Synthetic scheme of TBC derivatives.

Results and Discussion

Recharacterization of $PcGe^{II}$. Figure 1 illustrates the synthetic scheme of TBC derivatives. Joyner et al.[15] concluded that the reduction product of $PcGeCl_2$ with $NaBH_4$ was $PcGe^{II}$ from elemental analyses (C, H, and Ge), IR and UV–vis spectra, and oxidative titration of the central metal by the Elvidge method.[16]

Figure 2 illustrates the observed and calculated EI-MS spectra for the four TBCGe derivatives prepared in this study. The calculated mass peak patterns are in good agreement with the observed results, taking into account the isotopic natural abundance of ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge. From either the EI- or FD-MS spectra for TBCGe derivatives, the expected elimination patterns for these compounds are found. Especially, either the hydroxy or benzyl group attached to Ge is found to be easily eliminated and dehydrated. (See Experimental Section.)

Table I gives the results of elemental analyses for the five TBC derivatives. The observed values are in good agreement with the calculated values of the corresponding TBC derivatives. The observed values of C, H, and Ge for TBCGeOH are consistent with the calculated values for both TBCGeOH and $PcGe^{II}$. However, only 7 atoms of N are observed, whereas there are 1.4 atoms of O. The extra 0.4 atoms of O may be due to an inaccuracy in the CO reduction method.

With respect to the formal charge of both the Pc ring and Ge atom in $PcGe^{II}$, Joyner et al.[14] concluded that Ge and Pc are 2+ and 2–, respectively, since the observed value of the oxidation agent/mole was in close agreement with the calculated value of it obtained by using the Elvidge method: obsd 3.1 equiv and calcd for $PcGe^{II}$ 4 equiv. However, the observed value for $PcGe^{II}$ fully

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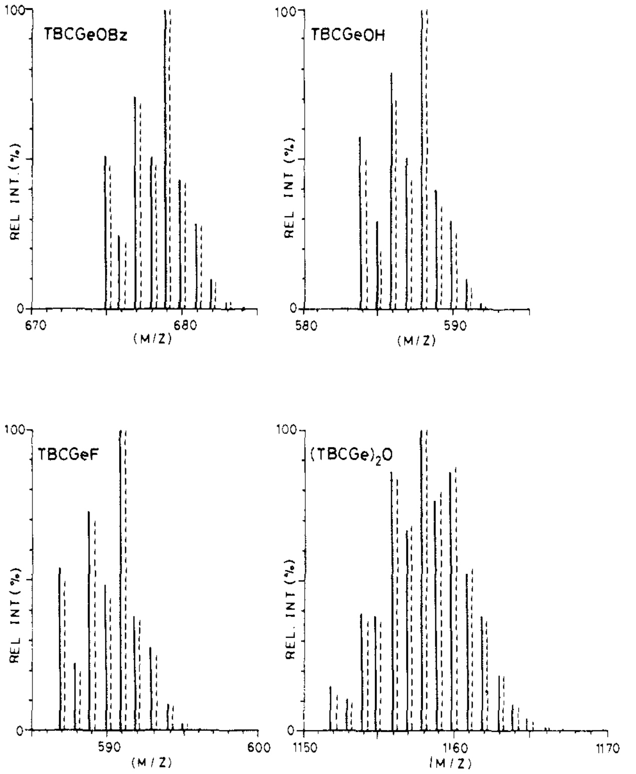

Figure 2. Observed (solid line) and calculated (dotted line) EI-MS spectra for TBCGe derivatives.

supports the calculated one for TBCGeOH since if PcGe^{II} is TBCGeOH with a formal charge of TBC^{3-} Ge^{4+} OH^{1-}, TBCGeOH should have 3 equiv/mol.

The TBCGeOBz compound was isolated as the precursor of TBCGeOH, by carefully treating the reaction product toward water and acid. TBCGeOBz resulted in TBCGeOH even when it was refluxed in ethanol. Since Joyner et al.[15] treated the crude TBCGeOBz with water and dilute HCl, it is considered that TBCGeOBz is converted to TBCGeOH (= PcGe^{II}), supporting that the hydroxy group of TBCGeOH has an expected chemical reactivity. (See Figure 1).

Joyner et al.[15] also reported that the purified PcGe^{II}, sublimed in a vacuum at 357 °C, was identified as a β-polymorphism, showing the additional IR bands at 887 and 860 cm^{-1}. However, at slightly above this temperature, a small weight loss was observed due to the dehydration of TBCGeOH. Moreover, the additional intense IR bands were seen due to the stretching modes of the Ge–O–Ge bonds at 892 and 867 cm^{-1}. This is considered to be caused by the disappearance of the corresponding IR bands resulting from the GeOH bonds. Similarly, PcGe(OH)$_2$ dehydrated in the 340–380 °C range can lead to an O-linked PcGe polymer ((PcGeO)$_n$) with an intense IR band at 860 cm^{-1} which is assigned as the stretching mode of the Ge–O–Ge bonds.[17,18] From these results, it is thought that the IR bands at 887 and 860 cm^{-1} should be assigned as the Ge–O–Ge bonds and not the β-polymorphism. It is thought that the sublimed PcGe^{II} partially included (TBCGe)$_2$O.

The PcGe(OH)$_2$ compounds were also converted to TBCGeOH by means of a H$_2$Se gas treatment. The purpose of this reaction was to obtain a Se-linked PcGe polymer ((PcGeSe)$_n$) such as (PcGeS)$_n$[6] for application to one-dimensional conductors. Although no (PcGeSe)$_n$ was obtained, PcGe(OH)$_2$ was also found to undergo a contractive reaction of the Pc ring due to the elimination of the bridged N in the Pc ring under reductive reaction conditions.

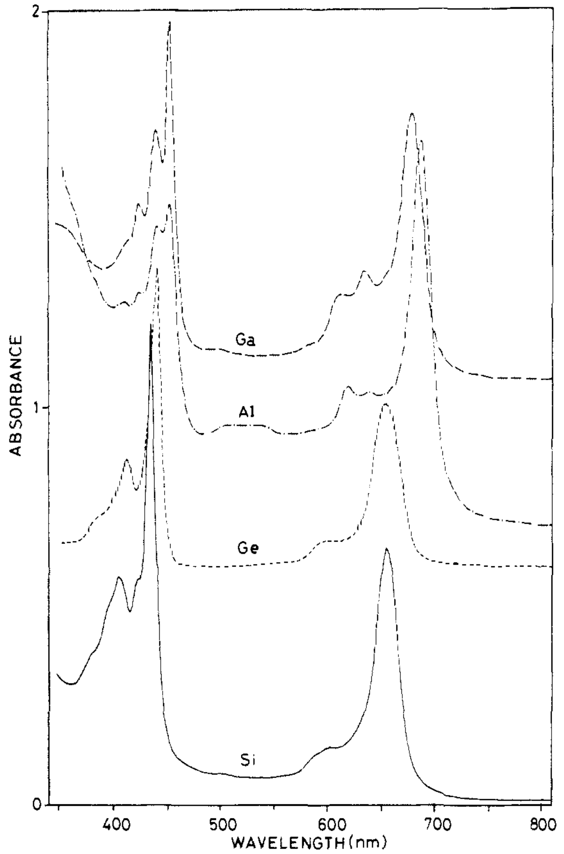

Figure 3. Vis absorption spectra of metalloid TBC derivatives (measuring solvent: isopropyl alcohol, room temperature).

Characterization of Other Metalloid TBCs. To examine the generality of this contractive reaction in the Pc ring, other metalloid Pcs containing SiCl$_2$, SnCl$_2$, AlCl, GaCl, and metal-free Pc(PcH$_2$) were reduced with NaBH$_4$ in a mixture of benzyl alcohol and anisole in the same manner as that for preparing TBCGeOBz.

Figure 3 shows the vis absorption spectra of the reaction mixture for these metalloid Pcs and PcGeCl$_2$ systems, pipetted off from their reaction mixtures. Except for the PcSnCl$_2$ and PcH$_2$, the characteristic species show the vis absorption spectra at 440–450 and 650–680 nm.

Such species might be attributed to the corresponding metalloid TBC derivatives and show the following contractive reactions: PcSiCl$_2$ → TBCSiOBz, or TBCSiOH, PcAlCl → TBCAl, PcGaCl → TBCGa. This is because these vis spectra closely resemble those for TBCGe derivatives and have some dependence on the cental metalloid. This indicates that this type of the ring contractive reaction in Pc compounds containing the reductive reagent generally occurs when both Cl, which is attached to the metalloid, and bridge N in the Pc ring are eliminated.

The PcP^{III} compound, which exhibits unusual electronic absorption and mass spectra,[10,11] may have a TBCP^{V}=O. The O is due to water and/or oxygen. This is because the UV-vis absorption spectra of PcP^{III} closely resemble that of TBCGeOH (= PcGe^{II}) and the observed MS parent peak for (PcP^{III} + 2)$^+$ (m/z 545.5) is consistent with the calculated results for (TBCP^{V} = 0)$^+$ (m/z 545).

Unfortunately, except for TBCGe derivatives, the metalloid TBC derivatives could not be isolated. This is because the TBCAl and TBCGa were rapidly decomposed in contact with water and/or air. The TBCSiOBz was initially quite stable but gradually decomposed. The EI-MS spectra for impure TBCSiOBz or TBCSiOH compounds were obtained as follows: m/z (rel intensity) 543 (M$^+$, 59), 526 ((M − OH)$^+$, 6), 1068 ((2M − H$_2$O)$^+$, 100) and other coupling peaks between TBCSiOH and PcSi(OBz)$_2$. PcSnCl$_2$ and PcH$_2$ did not show corresponding TBC derivatives from vis spectra. When the decrease rate of the characteristic absorption bands for the TBC ring in wet ethanol

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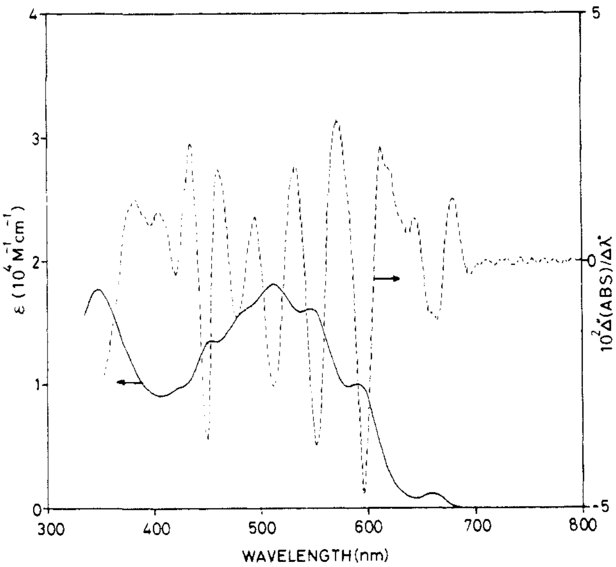

Figure 4. Vis and 2D-vis absorption spectra of the red compound formed by decomposition of TBCGeOH under light illumination ($[TBCGeOH]_0 = 2.5 \times 10^{-5}$ M in 1-chloronaphthalene).

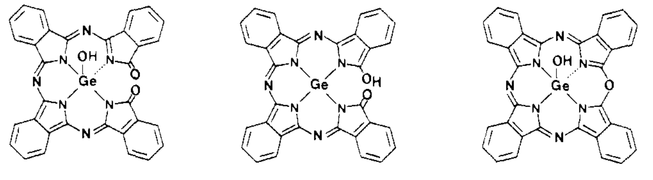

Figure 5. Proposed chemical structures of the red compound.

at 400–500 nm are estimated from, a qualitative stability of TBC derivatives is in the following order: TBCGe ≫ TBCSi > TBCAl > TBCGa. The reason why only TBCGe derivatives could be stably isolated may be due to the relation between the covalent or cationic radius of the cental metalloids and internal hole radius of the TBC ring. Thereore, only Ge would satisfy the precise condition which is just fit into the internal hole of the TBC ring, while the sp^3 covalent radii for metalloids the cationic radii are as follows:[19] Si (1.17 Å), Ge (1.22 Å), Sn (1.40 Å), and P (1.10 Å); are Si^{IV} (0.38 Å), Ge^{IV} (0.,54 Å), Sn^{IV} (0.71 Å), Al^{III} (0.45 Å), Ga^{III} (0.60 Å), and P^{III} (0.34 Å).

TBCGe derivatives in solution are very light sensitive compounds, as previously reported by Joyner et al.[15] In examples, the color of TBCGeOH in dilute solution changes from green to red when placed under room light overnight. Figure 4 shows the vis spectra of the red solution. Apparently the characteristic Q and B bands of TBCGeOH are disappeared, and the new and broad bands are appeared. From the 2D-vis spectrum, the red compound has at least eight bands in the visible region. Unfortunately, this compound could not be isolated because of strong adhesion in the silica gel column. Although the exact chemical structure of the red compound is not clear, this compound may be a ring-cleavage or ring-expansion compound of the TBCGeOH, as would be expected from the chemical or photochemical reactivity of the 1–2 position of TBC ring. (See Figure 1.) Predicted structures of the red compound are shown in Figure 5.

The fact that the extremely stable Pc ring easily loses a bridge N is quite unusual. To explain this novelity, we wish to propose a possible scheme of the Pc ring contraction reaction even with no experimental evidence. This mechanism may help the new syntheses of TBC analogues, e.g., TBCCo, TBCFe, and TBCCr. Figure 6 illustrates the reductive ring contraction scheme of $PcGeCl_2$ with $NaBH_4$. The first step shows the two Cl elimination process from Ge. This is based on the fact that only metalloid Pcs containing Cl lead to the ring contraction reaction. Next,

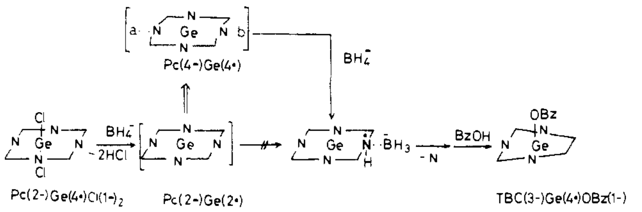

Figure 6. Proposed scheme of the Pc ring contraction reaction for the $PcGeCl_2$–$NaBH_4$ system. N means the bridged N of the Pc or TBC ring.

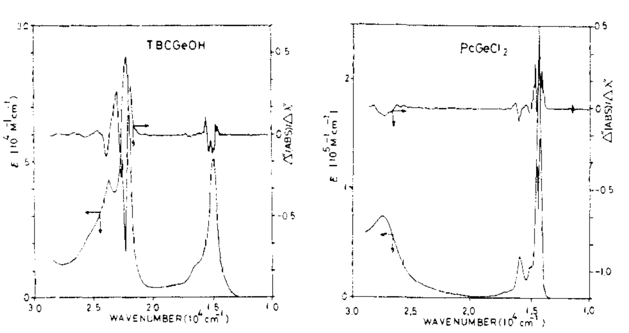

Figure 7. vis and 2D-vis absorption spectra for TBCGeOH and $PcGeCl_2$, (measuring solvent; 1-chloronaphthalene, room temperature).

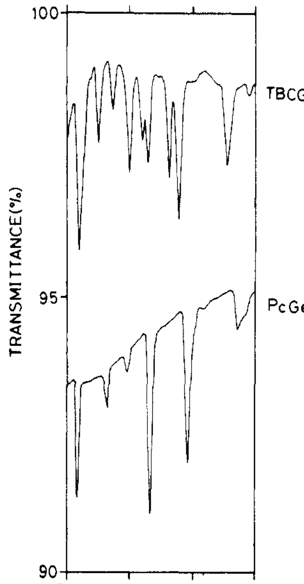

Figure 8. IR absorption spectra in the ring deformation region for TBCGeOH and $PcGeCl_2$ (KBr).

$Pc^{2-}Ge^{4+}Cl_2{}^{1-}$ is converted to be $Pc^{2-}Ge^{2+}$. Immediately, $Pc^{2-}Ge^{2+}$ turns out to be $Pc^{4-}Ge^{4+}$ through a intramolecular charge-transfer reaction from the $4P_z$ level of Ge to the e_g level of the Pc ring. This is because $Pc^{2-}Ge^{2+}$ is thermodynamically unstable. $Pc^{4-}Ge^{4+}$ cannot hold a planar structure and lead to bending of the Pc ring along the a–b axis, which includes two bridged N of the Pc ring, arising from the spin pairing of two electrons in the e_g level. These intramolecular charge-transfer reaction, spin pairing, and bending of the Pc^{4-} ring are supported from our preliminary results by using the extended Hückel molecular orbital calculation.[24] Then, the bridged N of the bended $Pc^{4-}Ge^{4+}$ reacts with BH_4^- (or BH_3) and is eliminated. Finally, TBCGeOBz is formed.

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Table II. Electronic Absorption Parameters and Partial Assignments in TBCGeOH and $PcGeCl_2$

compound	E,[a] cm^{-1}	A[b]	ϵ,[c] M^{-1} cm^{-1}	f,[d] erg·cm
TBCGeOH (C_1)	14 820	$Q_1(0'-0'')$		
	14 950	$Q_2(0'-0'')$	5.1×10^4	0.09
	15 250	$Q_3(0'-0'')$		
	22 270	$B_1(0'-0'')$	8.9×10^4	
	22 620	$B_1(0'-0'')$		0.31
	23 830	$B_3(0'-0'')$	4.4×10^4	
$PcGeCl_2$ (D_{4h})	14 310	$Q(0'-0'')$ ($e_g \leftarrow a_{1u}$)	2.6×10^5	0.23
	27 300	$B(e_g \leftarrow a_{2u})$	7.3×10^4	0.59

[a] Note E is the electronic transition energy. [b] A is the assignments for electronic transition. [c] ϵ the molar absorption coefficient per liter. [d] f the oscillator strength. All measurements were carried out in 1-chloronaphthalene at room temperature.

The chemistry of TBC^{3-} will be opened concerning biological models, such as vitamin B_{12} coenzyme models,[20] or conductive materials. To date, there have been no synthetic reports on TBC macrocycles which are homologues of corrole ring compounds. As is well-known, Pcs without side groups have poor solubility in organic solvents (10^{-4} M) and exhibit polymorphism. In contrast to Pcs, TBCs have good solubility (TBCGeOH, ca. 10^{-2} M in hot 1-chloronaphthalene).

Molecular Symmetry of the TBCGe Moiety. The differences in the vis and IR spectra between TBC and Pc rings have been studied. Figure 7 shows the vis and 2D-vis spectra for both TBCGeOH and $PcGeCl_2$ in 1-chloronaphthalene. Figure 8 shows the IR absorption spectra in the ring deformation (ϕ_{C-C}) region (400–700 cm^{-1}) for both TBCGeOH and $PcGeCl_2$. Table II summarizes the electronic absorption parameters and partial assignments in TBCGeOH and $PcGeCl_2$.

From Figure 7 and Table II, it can be seen that $PcGeCl_2$ possesses a degenerated and sharp $Q(0'-0'')$ band at 14 310 cm^{-1}, which is assigned to the allowed ($e_g \leftarrow a_{1u}$), and additional weak vibrational bands (0'-1' and 0'-2''). It also has the broad and intense B bands (Soret band), which are assigned to the allowed transition ($e_g \leftarrow a_{2u}$). These electronic absorption spectra of $PcGeCl_2$ are expected from molecular symmetry with D_{4h}.[1a,b]

On the other hand, although TBCGeOH has two characteristic Q and B bands at ca. 450 and 660 nm, it is found from a study of the 2D-vis spectrum that both $Q(0'-0'')$ and $B(0'-0'')$ bands are more complex than in $PcGeCl_2$ as would be expected since the symmetry is necessarily reduced from D_{4h} to C_{2v}. Such splitting of the electronic spectra arises from the splitting of the degenerated first LUMO (e_g) of Pc having D_{4h} symmetry, in analogy with PcH_2 with D_{2h} symmetry.[1a,b]

With respect to the oscillator strength (f), shown in Table II, Q and B bands for TBCGeOH are found to be only 40–50% of the corresponding bands for $PcGeCl_2$. The decrease in f may indicate that there is a lack of planarity in TBCGeOH, which is suggestive of the good solubility of TBCGeOH in organic solvents.

From Figure 8, we can see that in the ϕ_{C-C} region, $PcGeCl_2$ has the four characteristic peaks, resulting from the Pc ring structure with D_{4h} molecular symmetry,[21] while TBCGeOH has eight peaks. The splitting of the ϕ_{C-C} peaks of the macrocycles are as follows: $PcGeCl_2 \rightarrow$ TBCGeOH ϕ_{C-C} (cm^{-1}); 430 → 410 + 445, 509 → 522 + 538, 570 → 572 + 580, 640 → 628 + 650. This splitting of ϕ_{C-C} peaks can also be explained as the result of the decrease in the molecular symmetry of the TBC ring.

In this way, both the vis and IR spectra as well as the solubility of TBCGeOH indicate that the molecular symmetry of the TBC ring has dropped from 4-fold to 2-fold. There may be also additional distortion from C_{2v} to C_2, C_s, or C_1. Indeed, a CPK molecular model for TBCGeOH, which can be partially expressed as a actual structure, cannot have a planar structure of a TBCGe moiety. Figure 9 shows the proposed structural models for a TBCGe moiety, where + indicates displacement above the page plane and −below the page plane.

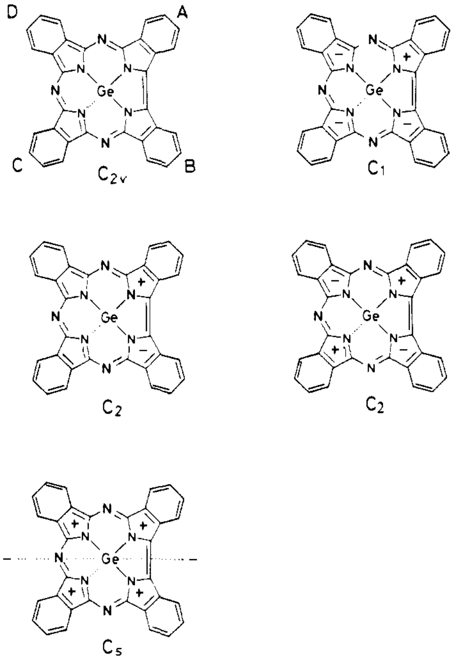

Figure 9. Proposed molecular structural models for the TBCGe moiety.

In four adjacent isoindoline planes (A, B, C, and D), the steric hindrance of a pair between A and B is rather large compared with that of other pairs such as A and C, B and D, and C and D, if the TBCGe moiety lies in the plane. Therefore, the TBCGe moiety should be displaced above or below the GeN_4 plane, as shown in Figure 6. Such distortion has also been reported even for such Pc compounds as $(PcSnO)_n$,[17] PcPb,[22] and PcK_2 $(diglyme)_2$.[23]

Conclusion

A previously reported divalent germanium phthalocyanine ($PcGe^{IV}$), which showed unusual vis and MS spectra when compared with a corresponding high-valent germanium phthalocyanine, has been identified as hydroxygermanium α,β,γ-triazatetrabenzcorrole ($TBC^{3-}Ge^{IV}OH$) from elemental analyses (C, H, N, Ge, and O), EI- and FD-MS, vis (normal and second differencial), IR, ^1H NMR, measurements of its chemical reactivity, and previously reported results. From the vis absorption spectra, TBCs containing Si, Al, and Ga were produced in a mixture of corresponding chlorinated metalloid Pcs and sodium borohydride and were observed to be less stable to water and/or oxygen. $PcGe(OH)_2$ resulted in TBCGeOH following H_2Se gas treatment, although no $(PcGeSe)_n$ polymers were obtained. In addition, the previously reported trivalent phosphorous phthalocyanine (PcP^{III}) which was also reported to have unusual vis and MS spectra has the possibility of being $TBCP^{V}{=}O$, in analogy with TBCGeOH. Such a ring contractive reaction of metalloid Pcs is found to generally occur by introducing reductive reagents such as $NaBH_4$ and H_2Se. The molecular symmetry of the TBCGe moiety was exactly C_1 or an aproximately 2-fold symmetry (C_{2v}, C_2, or C_s) with some distortion. This is supported by its solubilty, a CPK molecular model, and a comparison of vis and IR spectra between TBCGeOH and dichlorogermanium phthalocyanine with the D_{4h} molecular symmetry.

Acknowledgment. We thank Yuhei Mori for his useful discussions on the electronic structure of Pc and TBC rings. We also thank Yuzo Katatama and Kei Murase for their encouragement throughout this work.

Registry No. $PcGe^{II}$, 34228-03-0; $PcGeCl_2$, 19566-97-3; TBCGeOBz, 100228-58-8; TBCGeOH, 100205-78-5; TBCGeF, 100205-79-6; $(TBCGe)_2O$, 100228-59-9; $TBCNa_3$, 100205-80-9; $PcGe(OH)_2$, 16971-95-2; Pc, 574-93-6.