as a similar observation has been reported for other ethanolate complexes (e.g., mono- and dialcoholate of BF_3).[11]

A undergoes oxidative addition reactions with organohalides. Similar reactions have been reported for tin(II) dihalides,[12] for dialkyl and diamido compounds,[13,14] and for some Ge(II) compounds.[15] Generally organometallic(IV) derivatives are obtained. In the case of the reaction of A with MeI, the expected initial product is $MeGe(OEt)_2I$ (eq 2). Since alkoxy

$$Ge(OEt)_2{\cdot}xEtOH + MeI \rightarrow MeGe(OEt)_2I + xEtOH \quad (2)$$

and iodo substituents on germanium readily redistribute at ambient temperatures, at least four methyl germanium compounds are anticipated at equilibrium (eq 3 and 4). The

$$2MeGe(OEt)_2I \overset{K_1}{\rightleftharpoons} MeGe(OEt)_3 + MeGe(OEt)I_2 \quad (3)$$

$$2MeGe(OEt)I_2 \overset{K_2}{\rightleftharpoons} MeGeI_3 + MeGe(OEt)_2I \quad (4)$$

proton NMR data (Table III) of the product mixture indicate four distinct Me–Ge singlets corresponding to each of the species in the equilibrium distribution. Assignments were made on the basis of unique methyl on germanium to methyl on ethoxy integrated areas and on comparable shifts for $MeGe(OMe)_nI_{3-n}$, which have been reported by Moedritzer et al.[16] Furthermore, equilibrium constants ($K_1 = 0.1$; $K_2 = 0.2$) can be estimated from area ratio data and are in reasonable agreement to those values reported for the methoxy equilibrium system (vis., $K'_1 = 0.152$, $K'_2 = 0.106$).

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Registry No. $Ge(OEt)_2$, 71872-05-4; $Ge(OEt)_2{\cdot}2EtOH$, 71872-04-3; GeI_2, 13573-08-5; NaOEt, 141-52-6; $CH_3Ge(OCH_2CH_3)_3$, 5865-91-8; $CH_3Ge(OCH_2CH_3)_2I$, 71872-06-5; $CH_3Ge(OCH_2CH_3)I_2$, 71872-07-6; CH_3GeI_3, 1111-91-7; MeI, 74-88-4.

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Synthesis and Characterization of a New Class of Bivalent Germanium Compounds

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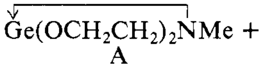
There has been considerable interest in the development of the chemistry of group 4 elements in the second oxidation state. Compounds of Sn(II) and Ge(II) have been viewed as electronic and structural analogues to singlet carbenes and silenes. These electron-deficient compounds have an extensive and varied chemistry owing to their capacity to act as acceptor species toward Lewis bases,[1-4] as donor ligands in transition metal complexes,[5,6] as precursors to new heterocyclic compounds,[7,8] and as intermediates in a variety of oxidative addition reactions.[9,10]

Two approaches have been used to elucidate Sn(II) and Ge(II) chemistry. One is the generation of bifunctional intermediates, generally by α-elimination in the presence of a trapping reagent.[11] The existence of the M(II) intermediate is deduced from the isolation and characterization of the M(IV) species. The second approach is to isolate and characterize an M(II) species which has been stabilized though steric or electronic effects. Although the latter approach has been successful for Sn(II) compounds,[12,13] it has been less fruitfully applied to Ge(II) compounds which appear to be more labile.[14]

We now wish to report the synthesis of a new class of Ge(II) compounds which are heterocyclic derivatives of the dialkoxides and are stabilized through an intramolecular, transannular dative bond between nitrogen and germanium. The compound, 5-methyl-5-aza-2,8-dioxa-1-germana(II)bicyclo[3.3.0]octane (A), is prepared by the transesterification of germanium(II) diethoxide–ethanol complex[14] with *N*-methyldiethanolamine (eq 1 and 2).

$$GeI_2 + 2NaOC_2H_5 + xC_2H_5OH \rightarrow Ge(OC_2H_5)_2{\cdot}xC_2H_5OH + 2NaI \quad (1)$$



$$Ge(OC_2H_5)_2{\cdot}xC_2H_5OH + MeN(CH_2CH_2OH)_2 \rightarrow \underset{\mathbf{A}}{Ge(OCH_2CH_2)_2NMe} + (x + 2)C_2H_5OH \quad (2)$$

Experimental Section

GeI_2 was prepared by methods described elsewhere.[15] Ethanol was dried by refluxing over magnesium metal and distilled under dry nitrogen immediately before use. *N*-Methyldiethanolamine was dried over sodium and distilled under vacuum. All solvents were dried and distilled by standard procedures. The infrared spectrum from 4000 to 400 cm^{-1} was recorded on a Perkin-Elmer 457 double beam spectrometer as Nujol and Fluorolube mulls on CsBr plates. Mass spectral data were obtained by using a Finnigan 3300 spectrometer. The proton NMR spectrum was recorded on dilute solutions with either a Varian A60 or HR220 spectrometer using Me_4Si as an internal reference.

In a typical reaction in the synthesis of $Ge(OCH_2CH_2)_2NMe$ (A), 1.5 g of freshly cut sodium was reacted with 50 mL of ethanol. A 31-mL sample of the resulting alcoholic sodium ethoxide solution was then added to 200 mL of toluene in a 500 mL round-bottom flask. The solution was degassed under vacuum and 2.5 g of GeI_2 was added

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Table I. ^{74}Ge Peaks of the Principal Ions in the Mass Spectrum of $Ge(OCH_2CH_2)_2NMe$

m/e	ion	% peak
191	$Ge(OC_2H_4)_2NCH_3^{+\cdot}$	22
161	$Ge(OC_2H_4)N(CH_2)CH_3^{+\cdot}$	100
147	$Ge(OC_2H_4)N\ CH_3^{+\cdot}$	4
146	$Ge(OC_2H_4)N\ CH_2^{+}$	27
131	$Ge\ N(CH_2)_2(CH_3)^{+\cdot}$	27
118	$Ge\ OC_2H_4^{+\cdot}$; $GeONCH_2^{+}$	13
117	$Ge\ N(CH_2)(CH_3)^{+\cdot}$	46

with stirring under dry nitrogen to form a colorless solution containing $Ge(OEt)_2\cdot x EtOH$.[14] The solution was filtered and the volume was reduced to 100 mL. The precipitate (NaI) was removed by filtration and 2.0 mL (80% based on GeI_2) of *N*-methyldiethanolamine was added with stirring. Solvents were removed under vacuum at ambient temperature. In order to complete the removal of ethanol, we added 50 mL of toluene, the solution was stirred for 10 min, and the solvents were removed under vacuum. The latter step was repeated until an aqueous extract of the condensate gave a negative iodoform test for ethanol.[16] The residue is a white solid which can be purified by sublimation at 70 °C (10^{-4} torr): yield based on amine, 55%; mp 71 °C. Anal. Calcd for $C_5H_{11}O_2NGe$: C, 31.64; H, 5.80; N, 7.38 Ge, 38.3. Found: C, 31.42; H, 6.16; N, 7.11; Ge, 38.5. Compound A is soluble in benzene, chlorobenzene, and toluene, and insoluble in pentane and cyclohexane. The molecular weight of A, determined by vapor pressure equilibration in toluene (Signer tube method[17]), is 185 (189). IR (cm^{-1}): 2929 (m), 2900 (m), 2875 (s), 2845 (s), 2795 (s), 2670 (m), 1452 (s), 1440 (s), 1420 (w), 1363 (m), 1354 (m), 1345 (m), 1335 (w), 1300 (m), 1270 (s), 1253 (s), 1201 (m), 1165 (m), 1143 (w), 1030 (s, br), 990 (s), 913 (w), 883 (s), 877 (s), 758 (m), 620 (s), 570 (s), 545 (s), 490 (s), 433 (m).

The principal fragmentation peaks for ^{74}Ge containing ions in the mass spectrum of A are given in Table I. Proton NMR data of A at −18, 30, and 54 °C in chlorobenzene are given in Table II.

A 60-mg sample of A was placed in a weighing bottle and stored in a desiccator under dry oxygen for 2 days with a weight gain of 1 mg and no change in the melting point or in the infrared spectrum. A dissolves in aqueous acid and gives a positive calomel precipitation test indicating that germanium is in the second oxidation state.

Results and Discussion

A new class of heterocyclic Ge(II) compounds has been synthesized by the transesterification of germanium(II) diethoxide–ethanol complex with *N*-methyldiethanolamine (B) (eq 1 and 2). The product, $Ge(OCH_2CH_2)_2NMe$ (A), is a white crystalline solid which is stable to dry oxygen but hydrolyzes readily. Compound A precipitates calomel in aqueous medium to confirm the low oxidation state of germanium. Unlike germanium(II) dialkoxides, which are associated in solution, soluble only in the presence of donor ligands such as alcohols or DMF and cannot be isolated analytically pure,[14,18] A is a monomer in toluene and can be purified by sublimation.

The mass spectrum of A (Table I) consists of a polyisotopic germanium cluster of the monomer unit $Ge(OC_2H_4)_2NMe^{+\cdot}$ (*m/e* (A) 191) and principal fragments corresponding to elimination of either C_2H_4O (*m/e* 147) or CH_2O (*m/e* 161, 131). A salient feature of the mass spectrum is the persistence of nitrogen in the fragment ions even after loss of two OCH_2 units which suggests the existence of a germanium–nitrogen bond in the parent molecule. A similar fragmentation pattern has been observed for analogous tin(II) compounds,[13] organostannatranes,[19] and organosilatranes.[20] The ^{1}H NMR spectrum of A (Table II) consists of two triplets and a singlet corresponding to OCH_2, NCH_2, and NMe protons, respectively. The triplets are centrosymmetric, representative of AA′BB′ spin–spin coupling comparable to that found in B, metallatranes,[19] and *N*-organostannoatranes.[13] The deshielding of the OCH_2 protons (−0.4 ppm) relative to analogous protons in B is evidence for the Ge–O bond. Similar deshielding of $M-O-CH_2$ protons relative to the parent alcohol occurs in germanium(II) dialkoxides,[14] tin(II) dialkoxides,[21] and organometallatranes.[19] The deshielding of the NMe proton (−0.2 ppm) relative to B is consistent with the direction expected for inductive effects owing to the presence of the transannular dative bond.[13] Similar shift changes of this magnitude have been noted for all molecules containing the metallatrane structure.[19] As observed in the analogous tin(II) compound,[13] the NCH_2 protons are unaffected by the dative interaction ($\Delta\delta$ (Ge(II)), 0.02 ppm). This may well be a result of a compensation of effects, namely, deshielding due to the dative bond and shielding due to the inductive effect of the methyl group.

Table II. Proton NMR Spectra of $Ge(OCH_2CH_2)_2NMe$ and $(HOCH_2CH_2)_2NMe$ in Chlorobenzene

		δ (*J*, Hz)		
	T, °C	OCH_2	NCH_2	NMe
$Ge(OCH_2CH_2)_2NMe$	−18	3.90 br[a]	2.33 br	2.24 s
	30	3.96 t (6)	2.38 t (6)	2.33 s
	54	3.97 t (6)	2.42 t (6)	2.37 s
$(HOCH_2CH_2)_2NMe$[b]	30	3.58 t (6)	2.40 t (6)	2.10 s
	54	3.56 t (6)	2.43 t (6)	2.16 s

[a] $w_{1/2}$ = 20–25 Hz. [b] Negligible change in δ as a function of concentration below 10% by volume in chlorobenzene.

There is no significant effect of temperature on the NMe absorption from −18 to 54 °C. Thus, it appears that Ge(II)←N like Sn(II)←N[13] and Si(IV)←N[19] is stable to dissociation in this temperature range. This is in sharp contrast to observations with Sn(IV)←N compounds whose spectra have been interpreted in terms of a dissociation–association mechanism.[19,22] The ring methylene proton absorptions are sharp triplets above room temperature indicating rapid ring conformational changes on the NMR time scale. As the temperature is lowered the triplets become broad singlets ($w_{1/2}$, 20–25 Hz) consistent with a decrease in the rate of conformational exchange.

The infrared spectra of A and B are similar above 700 cm^{-1}. Strong absorptions in A at 620 and 570 cm^{-1} have been associated with Ge–O modes as reported for the parent diethoxide (i.e., 635, 585 cm^{-1}).[14] A prominent absorption at 545 cm^{-1} in A, which occurs where no bands exist in the respective diethoxide, has been tentatively assigned to the Ge(II)←N bond. The assignment is reasonable on the basis of the report by Hsu and Geanangel of a lower frequency band (500–600 cm^{-1}) believed to be associated with the Sn(II)←N bond in trimethylamine adducts with tin(II) halides.[4]

The preparation of other derivatives is currently under way and the scope of the chemistry of this unusual adduct is being explored.

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Registry No. A, 71872-15-6; GeI_2, 13573-08-5; $Ge(OEt)_2\cdot 2EtOH$, 71872-04-3; *N*-methyldiethanolamine, 105-59-9.

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