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CHEMICAL SPECIFIC CYCLOADDITION OF DIETHANOLAMINE TO GERMANIUM DIOXIDE

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Abstract—A specific cycloaddition of various diethanol amines to germanium dioxide is described. The N-alkyl and N—H diethanolamines give the trimeric cyclotrigermoxane, **1**, and monomeric spiro-germocane, **2**, respectively. An equilibrium between **1, 2** and their precursor, the geminal dihydroxygermocane, **3**, is observed. Complex **3** can be trapped by using α-hydroxydiphenylacetic acid to give a stable spiro-germocane, (α-hydroxydiphenylaceto-O,O′)(iminodiethanolato-N,O,O′)germanium(IV) (**4**) in high yield. These complexes have been characterized by elementary analysis, IR, ^{1}H and ^{13}C NMR and mass spectra.

Recently, an increasing number of papers have reported the preparation of germanium complexes from germanium dioxide[1–3] because it is easily handled and gives high yields, particularly in the preparation of spiro-germanium complexes.[4] Also a new route towards the synthesis of alkylgermanes from these germanium complexes has been reported.[5]

In previous reports, we described the structure of dihydroxo(iminodiethanolato-N,O,O′)germanium(IV) (**3c**)[6] and the preparation of its derivatives.[7] In general, the two hydroxy groups of complex **3** were easily replaced by bichelating ligands.[8] This result led to a method of synthesizing relevant spiro-germanium complexes.

On the other hand, none of the specific cycloaddition was known in germanium coordination chemistry. We now present here a specific cycloaddition of diethanolamines with germanium dioxide. The N-alkyl diethanolamine reacted with germanium dioxide to give the tris(N-alkyl iminodiethanolato-N,O,O′) cyclotrigermoxane(IV) (**1**), whereas the N—H diethanolamine led to the monomeric species: bis(iminodiethanolato-N,O,O′) germanium(IV)(**2**). An equilibrium between these final adducts, **1** and **2**, and the dihydroxygermocane **3** was observed. Also reported here is the use of α-hydroxydiphenylacetic acid as an trapping agent for **3**.

EXPERIMENTAL

All chemicals were commercially available and were used without further purification. ^{1}H and ^{13}C NMR were recorded on a JEOL EX 400(400 MHz) spectrometer. Mass spectra were recorded on a JEOL-D300 (30 or 70 eV) mass instrument. Infrared spectra were measured on a BIO-RAD FTS-40ft IR spectrometer with KBr in pellet form. Elementary analyses were determined on a Perkin–Elmer 2400 instrument.

Synthesis of tris(N-*methyliminodiethanolato*-N,O,O′)*cyclotrigermoxane* (**1a**) *and tris*(N-n-*butyliminodiethanolato*-N,O,O′)*cyclotrigermoxane* (**1b**)

(1) *From germanium dioxide*. N-Methyldiethanolamine (1.20 g, 10 mmol) was added to a mixture of germanium dioxide (1.05 g, 10 mmol) and water (2 cm^3) and refluxed for 2 h. After cooling, xylene (50 cm^3) and absolute alcohol (100 cm^3) were added and the water was removed by azeotropic distillation. Concentration of the solvent to *ca* 30 cm^3 then crystallization was followed by

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cooling at low temperature (0–5°C). Complex **1a** was obtained as a white crystalline solid, yield 1.20 g, 54%, m.p. 55–57°C. Found: C 28.6; H 5.4; N 6.7; Calc.: C 29.1; H 5.3; N 6.8%. Mass spectrum (EI, 70 eV, relative intensity) *M/z* 618 (M^+, 3).

The same method was used to prepare **1b** from germanium dioxide, yield 45%, m.p. 89–91°C. Found: C 38.4; H 6.7; N 5.4.; Calc.: C 38.7; H 6.8; N 5.6%. Mass spectrum (EI, 70 eV, relative intensity); *M/z* 744 (M^+, 3).

(2) *From dihydroxo*(N-*methyliminodiethanolato*-N,O,O′)*germanium*(IV)(**3a**). To a solution of **3a** (2.24 g, 10 mmol) in ethanol (50 cm^3), xylene was added and the solution was distilled to removed the water being formed. Concentration of the solvent to *ca* 30 cm^3 then crystallization was followed by cooling at low temperature (0–5°C); complex **1a** was obtained as needle crystals, yield 2.14 g, 95%. The same method was used to prepare **1b** from **3b**, yield 90%.

Synthesis of bis(*iminodiethanolato*-N,O,O′)*germanium*(IV)(**2a**) *and bis*(*iminodiisopropanolato*-N,O,O′)*germanium*(IV)(**2b**)

(1) *From germanium dioxide.* Diethanolamine (2.12 g, 20 mmol) and germanium dioxide (1.05 g, 10 mmol) were used; the synthetic procedure was as same as that for complex **1**. Complex **2a**, yield 2.55 g, 90%. m.p. 245–247°C. Found: C 33.8; H 6.4; N 9.9.; Calc.: C 34.4; H 6.4; N 10.3% Mass spectrum (EI, 70 eV, relative intensity): *M/z* 279 (M^+, 9).

The same method was used to prepare **2b** from germanium dioxide, yield 3.19 g, 92%, m.p. 267–269°C. Found: C 42.6; H 7.9; N 7.9.; Calc.: C 43.4; H 7.8; N 8.4%. Mass spectrum (EI, 30 eV, relative intensity): *M/z* 355 (M^+, 2).

(2) *From dihydroxo*(*iminodiethanolato*-N,O,O′)*germanium*(IV)(**3c**). To a solution of **3c** (2.09 g, 10 mmol) in methanol (50 cm^3), diethanolamine (1.09 g, 10 mmol) was added and the solution was refluxed for 30 min. Then followed the procedures as those prepared from germanium dioxide, yield 1.99 g, 95%.

Synthesis of (*α-hydroxydiphenylaceto*-O,O′)(*iminodiethanolato*-N,O,O′)*germanium*(IV)(**4b**) *and α-hydroxydiphenyl* - O,O′) (*iminodiisopropanolato* - N, O,O′)*germanium*(IV)(**4d**)

Germanium dioxide(1.05 g, 10 mmol) was added to a solution of N-*n*-butyldiethanolamine (1.60 g, 10 mmol) in water (50 cm^3) and the reaction mixture was refluxed for 1 h. The solution was concentrated under reduced pressure to a sticky liquid then a solution of α-hydroxydiphenylacetic acid (2.28 g, 10 mmol) in ethanol (100 cm^3) and xylene (50 cm^3) was added and the resulting mixture was refluxed for 1 h. The solvent was removed by azeotropic distillation to *ca* 40 cm^3, then crystallization was followed by cooling. The crystalline solid was filtered and dried *in vacuo* to afford complex **4b**, 4.37 g, 95%, m.p. 248°C. Found: C 67.2; H 5.6; N 3.1; Calc.: C 67.4; H 5.6; N 3.1%. Mass spectrum (EI, 70 eV, relative intensity): *M/z* 413 ($M^+ - CO_2$, 12).

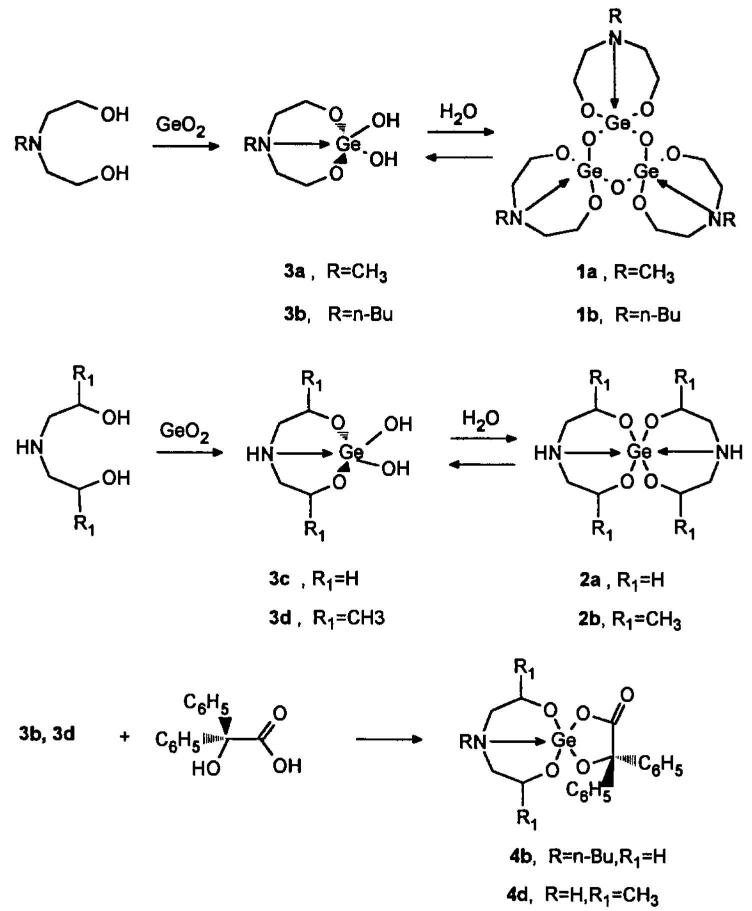
The same method was used to prepare **4d** from germanium dioxide(1.05 g, 10 mmol) and di-isopropanolamine(1.33 g, 10 mmol) in 92% (3.96 g) yield. Complex **4d**, m.p. > 300°C. Found: C 55.7; H 5.3; N 3.2; Calc.: C 55.3; H 5.4; N 3.2%. Mass spectrum (EI, 70 eV, relative intensity): *M/z* 387 ($M^+ - CO_2$, 10).

RESULTS AND DISCUSSION

The overall reaction is summarized in Scheme 1. Complex **1** was prepared from GeO_2 and N-alkyl(methyl or *n*-butyl) diethanolamine in 1 : 1 or 1 : 2 (GeO_2 : diethanolamine) molar ratio in water. After the water was removed completely by azeotropic distillation, followed by crystallization *in situ*, **1a** and **1b** were obtained as white crystalline solids. These novel cyclotrigermoxanes were rare, though their analogues (dialkylcyclogermoxanes) are well known.[10] Reactions of **1a** and **1b** with traces of water yield their stable precursors **3a** and **3b**, respectively. Alternatively, the self-condensation of **3a** and **3b** also afforded the cyclotrigermoxanes **1a** and **1b**, respectively.[11] This indicated that complexes **1a, 1b** and **3a, 3b** are in an equilibrium due to the presence of water.

Complex **2a** had been prepared from tetraethoxygermanium by Mehrota *et al.*,[11] but the same method from germanium dioxide can also afford **2**, except the molar ratio is 1 : 2 (GeO_2 : N—H diethanolamine). Recrystallization of **2a** in aqueous solution afforded complex **3c**. Complex **2a** can also be prepared from **3c**, but complex **2b** cannot because **3d** cannot be isolated.

In a previous investigation, it was found that complexes **1a** and **2a** readily reacted with benzilic acid and gave the mixed-ligand spiro-germocanes in high yields.[7] Besides, Holmes[12] reported that it was more stable for a penta-coordinated germanium complex when an electron-withdrawing group is located at the axial site and a sterically congested group at the equatorial site. Thus α-hydroxydiphenylacetic acid satisfied this demand and was used successfully to trap **3d**, forming the spiro-germocane **4d**.



Scheme 1. Cycloaddition of diethanolamine to germanium dioxide.

Infrared spectra

Distinctive features in the infrared spectra of these germanium complexes **1–4** are listed in Table 1. Two characteristic broad bands of precursors **3a** appear in the range of 819–835 and 644–765 cm^{-1} and are attributed to the Ge—O asymmetric and Ge—O symmetric stretching bands respectively. Once the two hydroxy groups are replaced by N-methyl diethanolamine (**1a**), the Ge—O asymmetric stretching band becomes sharp and appears at 848 cm^{-1} and the Ge—O symmetric stretching band shifts to a lower wave number which suggests increasing rigidity of the diethanolamine moiety.[8] A similar trend can be found in complexes **1b** and **2a** when compared to their precursors **3b** and **3c**, respectively. As expected, the stretching band of the carbonyl groups of **4** shows a much lower wave number[7] compared to α-hydroxydiphenylacetic acid (1732 cm^{-1}). The shift in wave number suggests that the Ge—O bond in **4** is slightly weaker than in **3**.

Table 1. The Ge—O stretching band (cm^{-1}) of complexes 1–3 and the C=O stretching band (cm^{-1}) of 4

Complex	ν_{as}(Ge—O)	ν_s(Ge—O)	ν_s(C=O)
1a	848	br 617–648[a]	
3a	br 819–834	br 644–765	
1b	829	621	
3b	br 815–832	646	
2a	1010	635	
3c	934	669	
2b	979	626	
4b	839		1705
4d	837		1685

[a] br = broad.

Mass spectra

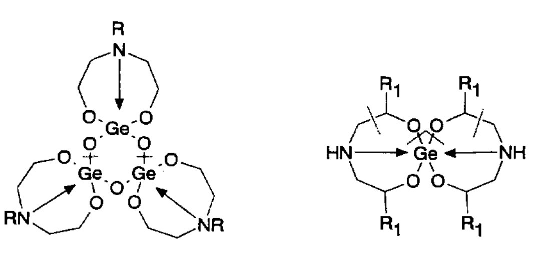
Table 2 lists the molecular ion peaks and the base peaks of complexes **1**, **2** and **4**. Interestingly, the mass spectra of **1a** and **1b** are almost identical to those of their precursors **3a** and **3b**, respectively, though the elementary analyses and the infrared

Table 2. The molecular ion peaks and base peaks of the electron impact mass spectra of complexes **1**, **2** and **4**

Complex	M^+(relative intensity)	Base peak(fragment)
1a	618(3)	222($M^+ - O[(RN(CH_2CH_2O)_2)_2Ge]_2$) ($R = CH_3$)
1b	744(3)	262($M^+ - O[(RN(CH_2CH_2O)_2)_2Ge]_2$) ($R$ = *n*-Bu)
2a	279(9)	249($M^+ - CH_2O$)
2b	355(2)	311($M^+ - CH_3CHO$)
4b		413($M^+ - CO_2$)
4d		387($M^+ - CO_2$)

spectra are different. Moreover, the base peak of **1** is the loss of $O[(RN(CH_2CH_2O)_2)_2Ge]_2$ ($R = CH_3$ or *n*-Bu) giving a fragment derived from a dihydroxygermocane, as illustrated in Fig. 1. This observation indicates that the gas-phase self-condensation of **3a** and **3b** leads to the cyclotrigermocanes **1a** and **1b**, respectively. Forming a spirocyclic germocane such as complex **2** is not possible because of the lack of such a fragment.

In contrast, the mass spectra of **2a** and **3c** are totally different whether an electron impact or a FAB (fast atom bombardment) ionization method[13] is used. In the case of **3c**, we are unable to explain the spectrum because of its complicated nature. The mass spectrum of **2a** is similar to that of **2b**; both of the molecular ion peaks are clearly identified and fragment ions of $M^+ - R_1CHO$($R_1 = H$ or CH_3) are the base peaks.[14] Their spectra can be regarded as due to subsequent loss of R_1CHO (Fig. 1). The mass spectrum of **4** is similar to those previously described in spiro-germocane complexes, losing carbonyl groups as the predominant process.[7]



1 1a, R = CH_3
1b, R = n-Bu

2 2a, R_1 = H
2b, $R_1 = CH_3$

Fig. 1. Mass fragment of 1 and 2 under electron impact.

NMR spectra

The ^1H NMR spectral data of **1** and **2** are presented in Table 3. As these complexes all have the diethanolamine moiety, it is essential to inspect the chemical shifts of NH_2 and OCH_2 protons. The chemical shift of the OCH_2 protons of **3a** in CD_3OD show two broad multiplets at 3.8 and 3.9 ppm; the NCH_2 protons show a broad singlet at 2.7 ppm. This is attributed to the conformational exchange of the eight-membered ring which arises from the dissociation of the N → Ge bond. Such conformational exchange, the so-called Berry pseudorotation, also occurred in the silicon analogues.[15] In complex **1a**, however, the exchange is slow because of the formation of a spiro-germanium complex, the NCH_2 protons split into an ABX_2 absorption pattern[8] and the OCH_2 protons display a multiplet set. The same absorption pattern can be observed in the ^1H NMR spectrum of **1b**.

The ^1H NMR spectra of complexes **2** and **3c** were somewhat limited by their solubility. In both cases, deuterium oxide was used as solvent. The ^1H NMR spectrum of **2a** resembles its precursor **3c**, the only difference being a slightly upfield shift (0.2 ppm) of the NCH_2 protons of **2a**. This can be attributed to the shielding effect of the ring-current caused by the oxygen atoms. The ^1H NMR spectrum of **2b** is more complicated. All three sets of protons of OCH, NCH_2 and CH_3 yield multiplets. Because the carbon atoms of OCH and the nitrogen atom are both chiral in this molecule, stereoisomers display a more complicated pattern.

The ^{13}C NMR spectra seem to provide less information than the ^1H NMR spectra, because large differences are not observed between **1**, **2** and **3**. The main different feature is the chemical shift of the NCH_2 carbon of **1**, which displays an average of 3 ppm shift upfield from **3**, again, this agrees well with the shielding effect in the ^1H NMR spectrum.

Table 3. ^1H NMR spectral data (ppm, J in Hz) of the NCH_2 and OCH_2 protons of complex 1 and 2

Complex	NCH_2	OCH_2
1a	2.7, 2.9(ABX_2) J_{AB} = 18.1 Hz, J_{AX} = 5.8 Hz, J_{BX} = 6.4 Hz	3.8(m)
1b	2.8, 2.9(ABX_2) J_{AB} = 18.1 Hz, J_{AX} = 5.4 Hz, J_{BX} = 6.8 Hz	3.8(m)
2a	2.7(t, J = 5.4 Hz)	3.7(t, J = 5.4 Hz)
2b	2.6–2.8(m)	3.9–4.0(m)

The reason why the reaction of diethanolamine with germanium dioxide is specific is not clear, but a plausible explanation can be made in terms of the intramolecular N → Ge bond strength. Complex **3** can be appropriately referred to as a reactive intermediate in this reaction and the main difference among **3a**–**3d** is the different functional group on the nitrogen atom. When the hydroxy groups of **3a**(**3b**) are substituted by N-methyl(*n*-butyl) diethanolamine to form a pseudo-hexacoordinated spirogermocane such as **2**, the germanium centre will be too electron-rich because of the inductive effect of the methyl(*n*-butyl) group, and becomes unstable.

In conclusion, from the high yields, the spectrochemical studies of these complexes and the trapping reaction of dihydroxygermocanes, the products resulting from reaction of diethanolamines and germanium dioxide are unique and depend on the substituent at the nitrogen atom.

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