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Syntheses and properties of a thiacrown ether and its acyclic model compound modified with germanium moieties

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A thiacrown ether (1) and its acyclic model compound (2), modified with germanium moieties, were synthesized and their structures confirmed by NMR spectrometry and elemental analysis. The germanium atom, located in one of the side chains of 2, is pentacoordinated by virtue of a weak hypervalent O → Ge interaction. The cation capture/transport ability is almost null for both compounds, probably owing to the proximity of the cation and anion binding sites. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: thiacrown; organogermanium compound; cation transport; NMR; X-ray crystallography; NMR titration; H-tube test

INTRODUCTION

In our previous investigations, we reported selective transportation of halides by macrocycles containing germanium.[1,2] Though we could not determine the mechanism of anion binding/transportation mediated by germanium, this observation prompted an attempt to synthesize a variety of heteroditopic hosts in which germanium-containing moieties could act as an anion-binding host. In this context, so far, calixarenes,[3–6] azacrown ethers[7] and cyclophanes[8] modified with germanium-containing moieties have been reported.

Of these compounds, azacrown ethers appeared to be the most promising, although the positive contribution of germanium has not yet been confirmed.[9]

In these compounds, the role of nitrogen atoms was to connect the side chain, which contains germanium (anion binding site), to the crown ring (cation binding site). Since the germanium atom occupied a terminal position in the side chain, the cation and anion binding sites are well separated. In this regard, it was thought of interest to design heteroditopic hosts where cation and anion binding sites are closely located to see whether this distance would be important in simultaneous binding of cations and anions. With this in mind, a cyclic germanium compound, 9,9-diphenyl-2,5,13,16-tetraoxa-8,10-dithia-9-germabicyclo[15.4.0]henicosa-1(17),18,20-triene (**1**), where two poly(oxyethylene) units are connected, via sulfur, to the germanium-containing moiety was synthesized. The acyclic analog, 1,2-bis[2′-(2″-triphenylgermylthioethoxy)ethoxy]benzene (**2**), was synthesized for reference.

RESULTS AND DISCUSSION

Synthesis and characterization

Synthesis of **1** and **2** was performed in the manner outlined in Scheme 1. Thus, catechol (**3**) was reacted with 2-(2-chloroethoxy)ethyl-*p*-toluenesulfonate (**4**) in the presence of pyridine to afford 1,2-bis[2′-(2″-chloroethoxy)ethoxy]benzene (**5**).[10] It was expected that 1,2-bis[2′-(2″-mercaptoethoxy)ethoxy]benzene (**7**) could be obtained directly from **5**. However, it was found that the reaction did not proceed smoothly, and a substantial amount of unreacted **5** was recovered. Hence, we prepared 1,2-bis[2′-(2″-iodoethoxy)ethoxy]benzene (**6**), which has a more efficient leaving group. The reaction of **6** with thiourea followed by tetraethylenepentamine gave **7**. The reaction of **7** with dibromodiphenylgermane (Ph_2GeBr_2) or bromotriphenylgermane (Ph_3GeBr) afforded the desired **1** or **2** respectively.

The structures of **1, 2, 6** and **7** was confirmed by elemental analysis, and by ^1H and ^{13}C NMR spectrometry. It is

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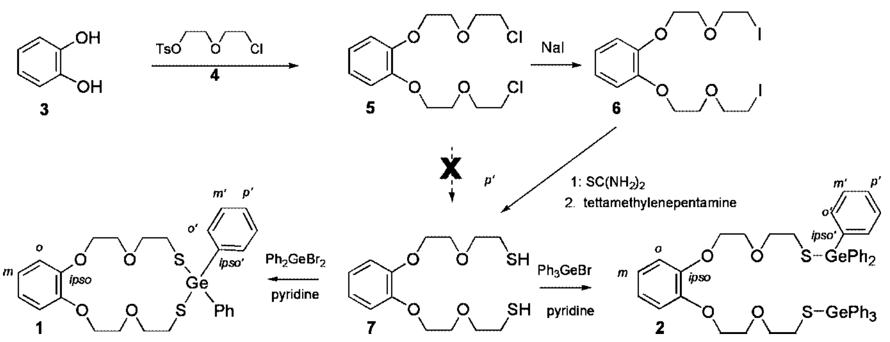

Scheme 1. Synthesis of **1** and **2**.

Table 1. ^{1}H chemical shifts for **1**, **2**, **5**, **6** and **7**[a]

	2	3	5	6	7	*o*	*m*	*o′*	*m′*	*p′*
1	4.13	3.88	3.83	2.89		6.85–6.91	6.85–6.91	7.38–7.42	7.64–7.67	7.38–7.42
2	3.97	3.57	3.45	2.62		6.83–6.88	6.83–6.88	7.37–7.41	7.61–7.63	7.37–7.41
5	4.18	3.90	3.85	3.66		6.92	6.92			
6	4.18	3.89	3.86	3.29		6.93	6.93			
7	4.17	3.85	3.71	2.72	1.65	6.92	6.92			

[a] ^{1}H chemical shifts (in $CDCl_3$) are in δ (ppm) relative to the internal standard, tetramethylsilane (TMS).

Table 2. ^{13}C chemical shifts for **1**, **2**, **5**, **6** and **7**[a]

	2	3	5	6	*ipso*	*o*	*m*	*ipso′*	*o′*	*m′*	*p′*
1	69.15	69.59	72.25	27.36	148.80	113.47	121.18	135.37	128.61	133.57	130.27
2	69.21	68.65	72.38	26.87	148.89	115.13	121.59	135.08	128.42	134.60	129.70
5	69.85	68.90	71.54	42.85	148.76	114.77	121.67				
6	69.47	68.90	72.17	3.18	148.75	114.75	121.66				
7	69.46	68.74	72.97	24.45	148.82	114.71	121.61				

[a] ^{13}C chemical shifts (in $CDCl_3$) are in δ (ppm) relative to the internal standard (TMS).

interesting to note that **2** crystallizes from acetonitrile with one molecule of solvent of crystallization, which was proved by elemental analysis, the ^{1}H NMR spectrum and by X-ray crystallography.

When the reaction between **7** and Ph_3GeBr was carried out in acetonitrile, the product was, as expected, i.e. **2** · CH_3CN. It must be added that the crystals of the product of the reaction between **7** and Ph_2GeBr_2 in acetonitrile did not contain a solvent molecule.

NMR spectra

There are virtually no published data on the NMR spectra of **5**–**7**, except for one report for **5**, which described only two ^{1}H chemical shift values.[11] Hence, we attempted the full assignment of the ^{1}H and ^{13}C NMR spectra of **5**–**7**, as well as of **1** and **2**.

The assignment was based of the combination of ^{1}H and ^{13}C NMR signals, H–H COSY, HMQC and HMBC. The results are summarized in Tables 1 and 2.

Solid-state structure of 2

It was expected that the solid-state structures of **1** and **2** would be of help in understanding the role of the germanium in cation binding by the ring or by the side chain. Unfortunately, **1** failed to afford crystals good enough for X-ray crystallographic analysis.

The reaction to prepare **2** in benzene gave a pale-yellow oil. Recrystallization of this oil from acetonitrile afforded colorless crystals. From elemental analysis and an X-ray crystallographic study, it turned out that the crystal contains one molecule of solvent, CH_3CN.

When the reaction was carried out in CH_3CN, the product was **2** · CH_3CN. It must be added that the crystals of the product of the reaction between 7 and Ph_2GeBr_2 in acetonitrile did not contain a solvent molecule. Figure 1 shows the ORTEP drawing of **2** · CH_3CN, and Table 3 lists its representative geometric parameters.

It is interesting to note that in one side chain, the Ge2···O4 interatomic distance is 3.40 Å, which is slightly

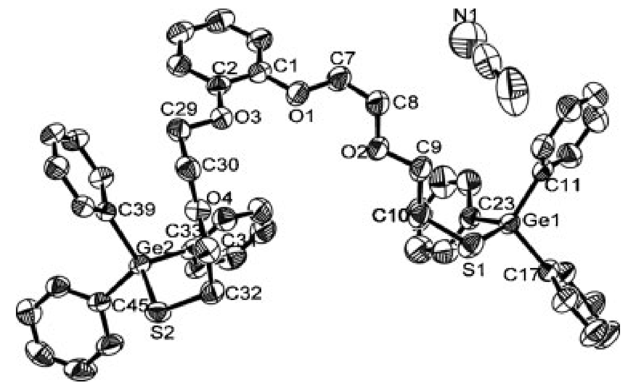

Figure 1. ORTEP drawing of **2** · CH_3CN; hydrogen atoms have been omitted for clarity.

Table 3. Selective bond lengths (Å) and angles (°) of **2** · CH_3CN

Bond length	
Ge1–S1	2.222
Ge1–C11	1.949
Ge1–C17	1.941
Ge1–C23	1.938
Ge1–O2	5.000
Ge2–O4	3.399
Ge2–S2	2.223
Ge2–C33	1.945
Ge2–C39	1.936
Ge2–C45	1.957
Bond angle	
S1–Ge1–C11	112.20
S1–Ge1–C17	106.35
S1–Ge1–C23	108.18
S2–Ge2–C33	111.71
S2–Ge2–C39	114.01
S2–Ge2–C45	100.54
Torsion angle	
O1–C7–C8–O2	72.53
O2–C9–C10–S1	−176.72
O1–C1–C2–O3	0.31
O3–C29–C30–O4	−72.29
O4–C31–C32–S2	−72.06

shorter than the sum of van der Waals radii of the germanium and oxygen atoms (3.64 Å).[12] This fact indicates there is hypercoordination between Ge2 and O4. Since formation of a five-membered ring seems to be a driving force for hypercoordination, and since a five-membered ring is formed by Ge2···O4 interaction, this observation is understandable.

Judging from the torsion angles (Table 3), the O1–C7–C8–O2, O3–C29–C30–O4 and O4–C31–C32–S2 atoms adopt a gauche conformation while the O2–C9–C10–S1 atoms have a trans conformation.

Table 4. Cation transport experiments[a]

	1
$NaNO_3$	−0.06
KNO_3	−0.2
$AgNO_3$	0.0

[a] The figures are the change of concentration of cations in the receiver phase (in ppm).

The trans conformation of the O1–C7–C8–O2 atoms may be the reason why the corresponding interatomic distance Ge1–O2 is much longer (>5 Å). This difference in the structure of two side chains may also be due to the presence of the solvent molecule (CH_3CN) near one of the side chain.

Since the all bond angle S–Ge–C(*ipso*) are close to the ideal tetrahedral value, sulfur and three ipso carbon atoms form a tetrahedron with the germanium atom in the center. Thus, the hypercoordinated structure of Ge1 is a monocapped tetrahedron with a small distortion towards a trigonal bipyramid geometry.

Cation transport ability

The cation transport ability of **1** was determined using the H-tube method.[13] The results are summarized in Table 4. It seems that **1** does not have ability to transport cations. One possible explanation is repulsion between the electropositive germanium and the cation.

Titration experiment

It has been established that the host–guest binding can be monitored by the chemical shift change caused by incremental addition of the guest salt to the solution of the host in an appropriate solvent.[14,15]

Titration experiments were carried out for both **1** and **2**. Their spectra did not change upon addition of $NaNO_3$, $Mg(NO_3)_2$ or $Ca(CO_3)_2$, indicating that neither was a good host for cations.

There may be several reasons for this failure. First, it is well known that replacement of an oxygen atom in the crown ring by a sulfur atom causes a decease in its cation capturing ability, as indicated by the lower complex formation constant for the thiacrown.[16] Second, the presence of electropositive germanium in the crown might repel the approach of cations. In other words, the cation binding site and anion binding site are preferably well separated, as was shown by a crown ether modified with a tin-containing side chain.[17]

It is also known that thiacrown ethers have much greater affinity for Ag^+.[16] So, we attempted titration experiment with $AgNO_3$. However, both **1** and **2** gave identical products upon addition of $AgNO_3$, as indicated by their ^1H NMR spectra. Furthermore, no signals due to the $-CH_2CH_2O-$ moiety were detected. Thus, it is likely that cleavage of the Ge–S bonds occurred.

CONCLUSIONS

In order to see whether the presence of a germanium-containing moiety located near to the crown ring will enhance simultaneous cation and anion capture/transport, a thiacrown ether (**1**) and its acyclic model compound (**2**) modified with germanium moieties were prepared and characterized. Cation transport and NMR titration experiments indicated that neither compound exhibited ion capture/transport ability. These observations seem to suggest that cation binding and anion binding sites need to be well separated for effective capture/transport properties.

EXPERIMENTAL

General

All manipulations were performed under an inert atmosphere of nitrogen or argon. Dry, oxygen-free solvents were employed throughout. Diethyl ether was distilled from sodium before use. Benzene was distilled from lithium aluminum hydride before use.

^{1}H NMR spectra were determined on JEOL EX-400 and ECP-500 spectrometers, operating at 400 MHz or 500 MHz respectively, ^{13}C NMR spectra were determined on JEOL EX-400 and ECP-500 spectrometers, operating at 100 MHz or 125 MHz respectively; the chemical shifts are reported in δ (ppm) with respect to TMS. Atomic absorption spectra were determined with the aid of an Hitachi 12–8100 polarized Zeeman atomic absorption instrument.

Synthesis and characterization

*1,2-Bis[2′-(2″-iodoethoxy)ethoxy]benzene (**6**)*

To an acetone (150 ml) solution of NaI (15.02 g; 100 mmol) was added dropwise an acetone solution (25 ml) of 1,2-bis[2′-(2″-chloroethoxy)ethoxy]benzene (**5**; 12.95 g; 40.1 mmol), which was prepared by the method described in the literature,[10] and the mixture was refluxed for 24 h. After cooling, the solvent was removed, and the residue was dissolved in diethyl ether, and the ether layer was washed twice with $NaHSO_3$ (5%) and water. The organic layer was dried over anhydrous $MgSO_4$. By filtration and evaporation of the solvent, a yellow viscous oil of **6** (1.17 g; 2.29 mmol) was isolated in 32.8% yield. Anal. Found: C, 33.35; H, 4.04. Calc. for $C_{14}H_{20}I_2O_4$: C, 33.22; H, 3.98%.

*2,2′-[1,2-Phenylenebis(oxy-2,1-ethanediyloxy)]bis (ethanethiol) (**7**)*

A solution of thiourea (3.81 g; 50.0 mmol) in ethanol (30 ml) was refluxed under nitrogen, to which a solution of **6** (10.12 g; 20.0 mmol) in ethanol (20 ml) was added dropwise, and the mixture was refluxed for 2 h. Tetraethylenepentamine (9.47 g; 20.0 mmol) was added dropwise under reflux. The reflux was continued for another 2 h. After cooling, 5% H_2SO_4 (50 ml) was added, and the mixture was extracted with diethyl ether. The organic layer was washed twice with water, and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under nitrogen to afford **7** in 83.0% yield (5.28 g; 16.6 mmol). Anal. Found: C, 53.02; H, 6.99. Calc. for $C_{14}H_{22}O_4S_2$: C, 52.80; H, 6.96%.

*2,2′-[1,2-Phenylenebis(oxy-2,1-ethanediyloxy)]bis (ethylthiotriphenylgermane) (**2**)*

(a) *In benzene*. Under a nitrogen stream, to a solution of **7** (3.55 g; 11.1 mmol) and pyridine (2.66 g; 33.6 mmol) in benzene (200 ml) there was added dropwise a solution of Ph_3GeBr (8.55 g, 22.3 mmol) in benzene (100 ml). The solution was stirred for 30 h at room temperature. 5% H_2SO_4 (100 ml) was added, and the solution was extracted with diethyl ether (300 ml). The organic layer was washed twice with water and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the residue was treated by gel permeation chromatography (GPC), but **2** could not be isolated.

The same reaction was carried out with refluxing. Thus, under a nitrogen stream, to a solution of **7** (0.59 g; 1.9 mmol) and pyridine (0.60 g; 7.6 mmol) in benzene (50 ml) was added dropwise a solution of Ph_3GeBr (1.17 g; 3.0 mmol) in benzene (25 ml). The solution was refluxed for 24 h at room temperature. After cooling, 5% HCl (50 ml) was added, and the solution was extracted with diethyl ether (100 ml). The organic layer was washed twice with water and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the residue was treated using GPC to give a colorless viscous oil, which was recrystallized from acetonitrile to afford colorless crystals which were analyzed for $C_{52}H_{53}Ge_2NO_4S_2$, i.e. **2** · CH_3CN, in 22% yield (0.38 g; 0.41 mmol); m.p. 64.7–67.0 °C. Anal. Found: C, 64.47; H, 5.58; N, 1.23. Calc. for $C_{52}H_{53}Ge_2NO_4S_2$: C, 64.70; H, 5.53; N, 1.45%. In the ^{1}H NMR spectra, a signal of CH_3CN with the intensity of three protons, appears at δ 2.00.

(b) *In acetonitrile*. Under nitrogen, to a solution of **7** (4.35 g; 13.7 mmol) and pyridine (3.95 g; 50 mmol) in acetonitrile (100 ml) was added a solution of Ph_2GeBr_2 (10.51 g; 27.4 mmol) in benzene (50 ml). The mixture was refluxed for 24 h. After cooling, the solvent was removed and the residue was extracted with diethyl ether. The organic layer was washed with 5% HCl (200 ml) and then three times with water, then dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated, and the residue was recrystallized from acetonitrile to afford **2** · CH_3CN in 35.3% yield (4.48 g; 4.84 mmol).

When **2** · CH_3CN was dried *in vacuo*, the CH_3CN molecule of crystallization was lost and white powder of **2** was obtained; m.p. 60.4–63.9 °C, as confirmed by ^{1}H NMR.

*9,9-Diphenyl-2,5,13,16-tetraoxa-8,10-dithia-9-germabicyclo[15.4.0]henicosa-1(17),18,20-triene (**1**)*

(a) *In benzene*. Under nitrogen, to a solution of **7** (0.49 g; 1.54 mmol) and pyridine 0.41 g (5.2 mmol) in benzene (200 ml), Ph_2GeBr_2 (0.60 g; 1.55 mmol) in benzene (50 ml) was slowly added (>24 h) with stirring. Stirring was continued for another 24 h at room temperature. A 2% HCl (30 ml) solution was added, and the organic layer was separated. The organic layer was added dropwise with water, and dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was purified by GPC to afford a yellow viscous liquid. Recrystallization from diethyl ether gave colorless crystals of **1** in 33.4% yield (0.28 g; 0.52 mmol); m.p. 84.3–86.2 °C. Anal. Found: C, 57.41; H, 5.74. Calc. for $C_{26}H_{30}GeO_4S_2$: C, 57.48; H, 5.57%.

(b) *In acetonitrile.* With the expectation to obtain **1** with solvent of crystallization, the reaction between **7** (0.955 g; 3.00 mmol) and Ph_2GeBr_2 (1.16 g; 3.00 mmol) under the same reaction conditions described above, except that the solvent used was acetonitrile. A similar workup afforded **1**, without the solvent of crystallization, in 56.7% yield (0.94 g; 1.7 mmol).

Cation transport experiment

The apparatus used and the experiment conditions are much the same as described previously.[18] Thus, an aqueous solution of an appropriate salt MX (0.1 mol dm^{-3}) was placed in the source phase, and in the organic phase a $CHCl_3$ solution of the host (1.0 mmol l^{-1}; 7 ml) was placed. After stirring gently for 24 h, the concentration of the cation in the receiving phase (pure water; 3 ml) was determined by atomic absorption spectroscopy.

X-ray crystallography

Intensity data, $\theta_{max} = 27.5°$, were collected on a Rigaku RAXIS-RAPID imaging plate four-circle diffractometer using the θ–2θ scan technique. The structure was solved by direct methods (SIR 92[19]) and refined by a full-matrix least-squares procedure (teXsan[20]). $C_{52}H_{53}Ge_2NO_4S_2$, $M = 965.30$, triclinic, $P\bar{1}$, $a = 9.666(2)$, $b = 15.423(2)$, $c = 17.377(2)$ Å, $\alpha = 74.011(7)$, $\beta = 86.835(9)$, $\gamma = 75.945(6)°$, $V = 2415.6(6)$ Å^3, $Z = 2$, $D_{calc} = 1.327$ g cm^{-3}; unique reflections: 10 875; number of reflections with $I > 2\sigma(I)$: 7129; $R = 0.041$, $Rw = 0.083$. CCDC deposition no. = 262 039.

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