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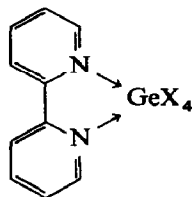
⁷³Ge NMR of hexacoordinate organogermanium compounds

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Abstract

In contrast to earlier claims, the formation of hexacoordinated Ge species in solution and its associated decrease in the rate of intermolecular exchange can now be observed by way of a dramatic upfield shift of $\Delta \delta \approx -350$ ppm, relative to the tetracoordinate parent compounds, in ⁷³Ge NMR spectra;



X = Cl, NCS

The current outlook for the practical application of ⁷³Ge NMR spectroscopy [1], particularly in the case of penta and hexacoordinate germanium compounds [2], is rather gloomy owing to the unfavourable NMR properties (spin $I = 9/2$ and extremely low $\gamma = -0.9331 \cdot 10^7$ rad T⁻¹ s⁻¹) of the only natural occurring, magnetically active germanium isotope—⁷³Ge [3,4].

Nevertheless, we recently reported the first observation of ⁷³Ge NMR resonance for hexacoordinated germanium in the anion [Ge(NCS)₆]²⁻ [5,6]. Here we report the ⁷³Ge chemical shifts for a series of hexacoordinated organogermanium derivatives, namely the GeX₄L₂ complexes (X = Cl, NCS, L₂ = 2,2'-bipyridine [Bpy], 1,10-phenanthroline [Phen]).

The data obtained (see Table 1) enabled us for the first time to determine directly the ⁷³Ge NMR shift associated with a change in coordination of the Ge atom from the tetracoordinated (compound 8) to the hexacoordinated state. The shift ($\Delta \delta$) of -334.6 ppm for L₂ = Bpy (compound 1) and -351.3 ppm for L₂ = Phen (compound 6) suggests the formation of a stronger complex in 6. The transition from neutral complex 5 to anion 7 is accompanied by an additional upfield shift of the

Table 1

^{73}Ge and ^{14}N NMR parameters of hexacoordinated organogermanium derivatives and related compounds in acetone- d_6 ^a

| No. | Compound | δ ^{73}Ge | $\Delta\nu_{1/2}$ (^{73}Ge) | δ ^{14}N ^b |
|-----|-----------------------------------------|---------------------------|----------------------------------------|---------------------------------------|
| 1 | GeCl_4Bpy ^c | -313.7 | 35 | - |
| 2 | $\text{GeCl}_3(\text{NCS})\text{Bpy}$ | -319.5 | 22 | -226.1 |
| 3 | $\text{GeCl}_2(\text{NCS})_2\text{Bpy}$ | -327.1 | 35 | -232.9 |
| 4 | $\text{GeCl}(\text{NCS})_3\text{Bpy}$ | -340.2 | 32 | -237.5 |
| 5 | $\text{Ge}(\text{NCS})_4\text{Bpy}$ | -351.8 | 48 | -242.2 |
| 6 | GeCl_4Phen | -319.4 | 150 | - |
| 7 | $[\text{Ge}(\text{NCS})_6]^{2-}$ | -442.5 | 50 | -225.0 |
| 8 | GeCl_4 ^d | +30.9 | 2 | - |

^a ^{73}Ge and ^{14}N NMR spectra were recorded on a Bruker WM-360 spectrometer at 12.56 and 26.0 MHz, respectively, in 5-mm sample tubes. Chemical shifts (δ) are in ppm, line widths at half-height ($\Delta\nu_{1/2}$) in Hz. ^b For NCS groups. The broad signal ($\Delta\nu_{1/2} \approx 800$ Hz) observed at ca. -130 ppm was attributed to Bpy. For compound 1 δ $^{15}\text{N} = -123.0$ ppm. ^c In dimethylsulphoxide- d_6 . ^d Ref. 7.

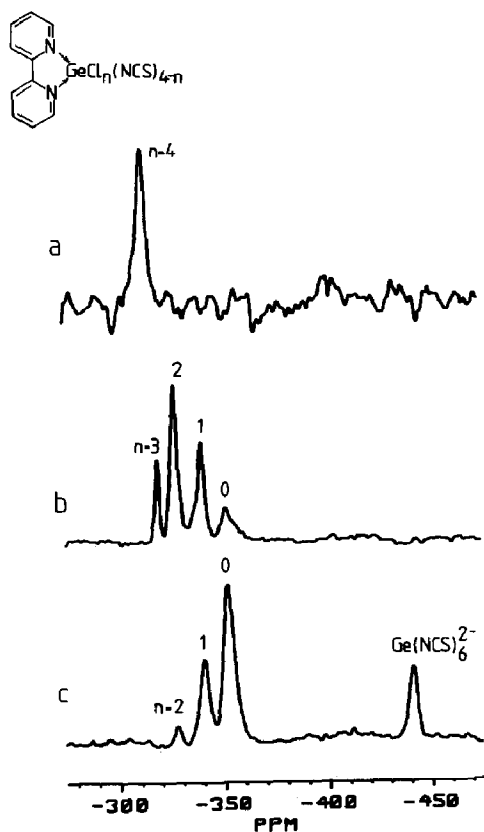


Fig. 1. 12.56 MHz ^{73}Ge NMR spectra of hexacoordinate Ge complexes. (a) $\text{GeCl}_4 \cdot \text{Bpy}$ in $(\text{CD}_3)_2\text{SO}$; (b) $\text{GeCl}_4 \cdot \text{Bpy} + \text{KSCN}$ (1 : 1) in acetone- d_6 (the ^{73}Ge signal of $\text{GeCl}_4 \cdot \text{Bpy}$ does not appear because of the low solubility of the compound in acetone); (c) the same starting compounds at the ratio 1 : 4.

^{73}Ge resonance. This agrees well with the results of CNDO/2 calculations which indicate an increase in ^{73}Ge shielding with increasing negative charge on the germanium atom in tetracoordinated derivatives [7].

The spectra depicted in Fig. 1 reflect the possible applications of ^{73}Ge NMR to the study of chemical reactions involving hexacoordinated Ge derivatives. Thus, it is possible to estimate from ^{73}Ge NMR the degree of substitution of the Cl atoms by NCS groups when KSCN is added to a suspension of compound **1** in acetone- d_6 and to observe the formation of anion **7** in an excess of KSCN. These spectra also indicate that intermolecular exchange between Ge substituents in hexacoordinated derivatives **1–5** proceeds slowly (on the NMR time scale), in contrast to their tetracoordinated derivatives $\text{GeCl}_n(\text{NCS})_{4-n}$ [6], i.e. complex formation stabilizes the $\text{GeCl}_4(\text{NCS})_{4-n}$ molecules.

Additional information on the structure of compounds **1–5** is provided by $^{14/15}\text{N}$ NMR spectra. A large (50–57 ppm) upfield shift of the ^{14}N and ^{15}N resonances of Bpy in compounds **1–5** (see footnote to Table 1) with respect to free ligand ($\delta^{15}\text{N} = -73.1$ ppm in DMSO- d_6) is consistent with the involvement of the nitrogen lone pair in the $\text{N} \rightarrow \text{Ge}$ bond formation [8]. The values of ^{14}N chemical shifts for NCS groups suggest that these groups are bonded to Ge via the N atom but not via S [5,6].

We did not observe ^{73}Ge resonances for $\text{GeBr}_4 \cdot \text{Bpy}$ or $\text{GeI}_4 \cdot \text{Bpy}$ complexes [9*], but the results obtained here allow us regard the practical applicability of ^{73}Ge NMR spectroscopy in studies on hexacoordinate Ge complexes with a little more optimism.

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- 9 Complexes of GeX_4 with Bpy or Phen were synthesized by the addition of GeX_4 to equimolar amounts of Bpy or Phen in absolute benzene cooled to 0°C . After 1 hr, the sample was heated to room temperature and the precipitate was filtered and washed with absolute benzene. The formation of complex was established by ^1H NMR (360 MHz). For compound **1** in DMSO- d_6 : $\delta^1\text{H}$ (ppm) = 8.05 (4, 4'), 8.50 (5, 5'), 8.99 (6, 6'), and 9.68 (3, 3'). For X = Br, I and NCS similar values of $\delta^1\text{H}$ were found. For compound **6** in DMSO- d_6 : $\delta^1\text{H}$ (ppm) = 8.65 (3, 8), 8.78 (5, 6), 9.50 (4, 7), 9.78 (2, 9).

* Reference number with asterisk indicates a note in the list of references.