Table I. ^{73}Ge NMR Parameters for Tetrasubstituted Germanes of the Type RX_4 or RX_3X'

compd	X	δ(Ge)[a]	$\nu_{1/2}$/Hz	T_1[b]/ms (temp/K)
1	Me[c]	0.0	1.3	378 (343) 313 (315) 295 270 (277) 223 (255) 208 (240)
2	Et[c]	17.3	1.7	274 (323) 250 175 (279) 135 (255) 96 (240) 67 (214)
3	Ph[d,e]	−31.6	6	. . .
4	2-furyl[d]	−112.8	11	20
5	2-thienyl[d,e]	−95.5	8	44
6	Cl[b]	30.9	1.2	287
7	Me[f]	6.3	54	

[a] Relative to external tetramethylgermane. [b] At 303 K unless specified. [c] In $CDCl_3$. [d] In Me_2SO-d_6 (saturated solution). [e] At 329 K. [f] $X' = CH_2CH_2COOH$.

because of its electric quadrupole moment that tends to cause an excessive broadening of ^{73}Ge resonances,[1] and so far, only a limited number of ^{73}Ge resonances have been recorded for compounds of the type GeR_4 or GeR_3R', where R or R′ is an alkyl, a substituted alkyl, or a halogen.[2-4] Here, we will describe chemical shifts and spin–lattice relaxation times (T_1) of some tetrasubstituted germanes.

In Table I, ^{73}Ge NMR parameters of a variety of symmeterical molecules, tetrahmethyl- (**1**), tetraethyl- (**2**), tetraphenyl- (**3**), tetrakis(2-furyl)- (**4**), tetrakis(2-thienyl)- (**5**), and tetrachlorogermanes (**6**) are listed. As an example of an unsymmetrical germane, β-(trimethylgermyl)propionic acid (**7**) was included. The symmetrical species **1**–**6** gave reasonably sharp signals $\nu_{1/2}$ = 1.2–11 Hz) while **7** has $\nu_{1/2}$ of 54 Hz. It was reported that for unsymmetrical species of the type GeR_3R', $\nu_{1/2}$ ranges from 20 to 300 Hz.[4] This broadening is expected to reflect, as is the case with ^{14}N resonances, the electric field gradient.

For a variety of compounds, Zinmane et al.[4] reported a correlation given below between the ^{73}Ge chemical shifts, δ(Ge), and ^{29}Si chemical shifts, δ(Si), of compounds of the type Me_3MR' (M = Si, Ge), where R′ is either substituted alkyl or alkenyl residues.

$$\delta(\text{Ge}) = 1.85\ \delta(\text{Si}) + 1.52 \qquad \text{rms} = 0.970$$

We attempted a similar correlation between R_4Ge and R_4Si, where R = Me, Et, Ph, and 2-furyl to obtain

$$\delta(\text{Ge}) = 2.01\ \delta(\text{Si}) + 1.11 \qquad \text{rms} = 1.00$$

It is interesting to notice that the slope is not very far from that reported by Zinmane et al.,[4] although in the latter correlation Ge nuclei bonded to sp^3- rather than sp^2-hybridized carbons are involved. In view of much abundant shift data for ^{29}Si, this correlation will be of help in predicting ^{73}Ge chemical shifts.

To the best of our knowledge there seems no systematic report on ^{73}Ge spin-lattice relaxation times (T_1) of organogermanium compounds although those of ^{29}Si,[5] ^{117}Sn,[6] and ^{207}Pb[7] have been investigated to some extent. In Table I, the ^{73}Ge and T_1 values of **1**, **2**, and **4**–**6** determined by the inversion-recovery method are recorded. For **1** and **2**, T_1 values determined at various temperatures were also listed. A plot of ln T_1 as a function of $1/K$ gave a straight line (rms = 0.989 for **1**, 0.996 for [2]) with a negative slope. This kind of temperature dependency of T_1 values is often observed for cases where either the dipolar or quadrupolar relaxation is predominant. The former mechanism is not important for ^{73}Ge, a quadrupolar nucleus. Indeed, we found that the NOE enhancement factor for **1** and **2** is null within the range of experimental error. Thus, the main pathway of relaxation is quadrupolar. If the spin-rotation relaxation is operative at any significant extent, the plot of ln T_1 vs. $1/K$ cannot be a straight line for a wide range of temperature since this relaxation shows a reverse temperature dependency to that of dipolar or quadrupolar relaxations. All of our present observations indicate that ^{73}Ge relaxes exclusively via quadrupole mechanism[8] within the range of experimental error.

Experimental Section

^{73}Ge NMR spectra were recorded on JEOL FX-90Q spectrometer equipped with a low-frequency insert operating at 3.10 MHz in a 10-mm tube at 30 °C. The typical conditions of measurement are as follows: pulse width, 150 μs (90°); spectral width, 100–1000 Hz; number of scans, 100–1000; pulse delay, 50 ms; data points, 2048–8192. T_1 values were determined by the inversion-recovery method with a minimum delay of $10T_1$: all the samples in $CDCl_3$ were degassed by the freeze–thaw method.

The compounds used in this investigation are all known compounds except for **7**[9] and were prepared according to the standard method.

Note Added in Proof. After the submission of our paper, we found a paper treating ^{73}Ge relaxation in some alkyl- and alkoxygermanes: Sekatsis, I. P.; Liepins, E.; Zicmane, I. A.; Lukevits, E. *Zh. Obshch. Khim.* **1983**, *53*, 2064.

Registry No. **1**, 865-52-1; **2**, 597-63-7; **3**, 1048-05-1; **4**, 55811-78-4; **5**, 62473-54-5; **6**, 10038-98-9; **7**, 33076-65-2; ^{73}Ge, 15034-58-9.

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Piezochromism of Nickel(II) Complexes with Tetraaza Macrocyclic Ligands in Water

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It is well-known that Ni(II) complexes with macrocyclic ligands (L) exist in water in an equilibrium between yellow,

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low-spin, square-planar NiL^{2+} and violet or blue, high-spin, pseudooctahedral $NiL(H_2O)_2^{2+}$ as described by[2]

$$NiL^{2+} + 2H_2O \rightleftharpoons NiL(H_2O)_2^{2+} \quad (1)$$

The effects of inert additives and of temperature on this equilibrium have been investigated for several ligands.[3-9] However, study of the effect of pressure, another important variable, has been done only for one ligand hitherto.[9] The pressure effect on an equilibrium constant gives a magnitude of the reaction volume (ΔV) through

$$\Delta V = -RT \, d \ln K/dP \quad (2)$$

The magnitude of ΔV of equilibrium 1 should be important in relation to the interpretation of the activation volume of complex ion reactions.[10-12] In equilibrium 1 the electrical charge on the complex is identical on both sides. Hence, the electrostrictive contribution should be negligible in the ΔV of equilibrium 1.[13] Two competing intrinsic volume changes can be expected: a negative one (ΔV_{coord}) due to the transfer of two water molecules from the bulk into the coordination sphere and a positive one (ΔV_{expan}) due to the expansion of the macrocyclic molecular aperture associated with the spin state change from singlet to triplet. Thus, the experimental value of ΔV for equilibrium 1 gives information as to which contribution is dominant.

In the present work, the visible absorption spectra of aqueous mixtures of NiL^{2+} and $NiL(H_2O)_2^{2+}$ have been measured under high pressure up to 3.6 kbar, where L is 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1-(17),2,11,13,15-pentaene (L^1), 1,4,8,11-tetraazacyclotetradecane (L^2), 1,4,7,10-tetraazacyclotetradecane (L^3), -cyclopentadecane (L^4), and -cyclohexadecane (L^5) (Figure 1). The K values of equilibrium 1 have been calculated at each pressure, and the ΔV's have been obtained therefrom.

Experimental Section

The nickel(II) complexes $[NiL^1](ClO_4)_2$,[7] $[NiL^2](ClO_4)_2$,[14] $[NiL^3](ClO_4)_2$,[8] $[NiL^4](ClO_4)_2$,[8] and $[NiL^5](ClO_4)_2$[8] were obtained according to the literature. The purity was confirmed by elemental analysis. Chemicals of analytical reagent grade were used. Deionized water was distilled.

The absorption spectra were measured on a thermostated (20.0 ± 0.1 °C) Hawley and Chase type high-pressure optical cell.[15,16] This cell was fitted to a Nihon Bunko, Model UVIDEC 505, double-beam spectrophotometer. The path length of the sample solution was 1.38 cm at 1 bar. The reference was air. The contraction of the solution volume[17] and the slight variation of the path length under high pressure were taken into account. The latter was calculated from the pressure dependence of the absorption intensity at 523 nm of 0.2 mM $KMnO_4$ aqueous solution and at 372 nm of 0.07 mM $K_2Cr_2O_7$ in 0.05 M KOH aqueous solution (1 mM = 10^{-3} mol dm^{-3}). Essentially the same results were obtained from both solutions. The path length contracts by 1.18% at 400 bar and by 2.12 ± 0.05% at pressure higher than 800 bar.

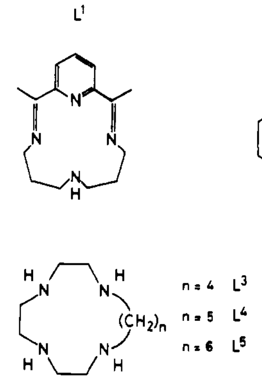

Figure 1. Ligands used in this study.

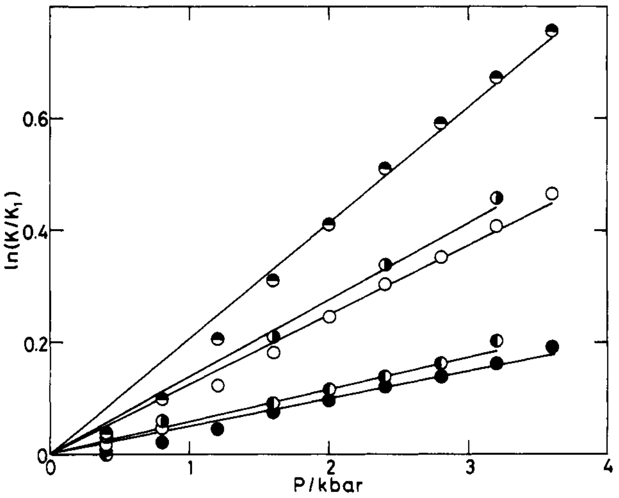

Figure 2. Pressure dependence of ln (K/K_1) at 20 °C in 0.1 M $NaClO_4$ (c = total concentration of the complex at 1 bar): ◐, L = L^1, c = 3.15 mM; ●, L = L^2, c = 12.5 mM; ⊖, L = L^3, c = 6.05 mM; ○, L = L^4, c = 8.52 mM; ◑, L = L^5, c = 8.09 mM.

Results and Discussion

In the piezochromic spectra of $[NiL^1](ClO_4)_2$, the absorption intensity around 400 nm due to the low-spin species decreased and that around 720 nm due to the high-spin species slightly increased at high pressures. Isosbestic point was maintained at ca. 600 nm, corresponding to that at 590 nm in its thermochromic spectral change.[7] Thus, it is clear that in the case of L = L^1 equilibrium 1 is displaced to the right with an increase in pressure. The piezochromic spectral changes in the case of L = L^2–L^5 were essentially analogous to each other. For example, in the case of $[NiL^3](ClO_4)_2$ the absorption around 450 nm due to the low-spin species decreased and those around 357, 565, and 900 nm due to the high-spin species increased at high pressures. The isosbestic points were maintained at 370 and 540 nm, corresponding to those at 374 and 550 nm observed in its thermochromic spectral change.[8] Thus, for L = L^2–L^5, the high-spin species is also favored at high pressures.

Values of $K = [NiL(H_2O)_2^{2+}]/[NiL^{2+}]$ were calculated at each pressure from the optical density at 395 nm (ϵ_l = 1011, ϵ_h = 1.5) for L = L^1,[7] at 445 nm (ϵ_l = 64.5, ϵ_h = 0) for L = L^2,[3] at 450 nm (ϵ_l = 160, ϵ_h = 0) for L = L^3,[8] at 450 nm (ϵ_l = 131, ϵ_h = 0) for L = L^4,[8] and at 455 nm (ϵ_l = 120, ϵ_h = 1.0) for L = L^5,[8] where ϵ_l and ϵ_h represent the extinction coefficient of the low- and the high-spin species, respectively. The results were treated by the linear approximation: ln (K/K_1) = aP, where K_1 is the K value at 1 bar (Figure 2). The ΔV's are

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Table I. Thermodynamic Parameters at 20 °C in 0.1 M $NaClO_4$ for the Reaction $NiL^{2+} + 2H_2O \rightleftharpoons NiL(H_2O)_2{}^{2+}$

L	ΔV^a/ cm^3 mol^{-1}	ΔS/J K^{-1} mol^{-1}	ΔH/ kJ mol^{-1}	K_1
L^1	−1.4 ± 0.1	−59[b]	−21[b]	4.72[b]
L^2	−1.2 ± 0.1	−84[c]	−23[c]	0.45[c]
L^3	−5.0 ± 0.2	−71[d]	−20[d]	0.72[d]
L^4	−3.0 ± 0.2	−88[d]	−23[d]	0.32[d]
L^5	−3.4 ± 0.2	−84[d]	−26[d]	1.76[d]

[a] Obtained in this work. [b] Reference 7. [c] Reference 3. [d] Reference 8.

calculated by eq 2: $\Delta V = -RTa$. All the ΔV's in Table I are negative, and the equilibria shift to the right under high pressure, consistent with the pressure–coordination rule.[18] The small absolute value of ΔV can be understood by the cancellation between the negative ΔV_{coord} and the positive ΔV_{expan}.

Fabbrizzi has pointed out that the two water molecules in the high-spin species occupy cis positions when L is 12-membered 1,4,7,10-tetraazacyclodecane (L^6) or 13-membered 1,4,7,10-tetraazacyclotridecane (L^7).[19] On the other hand, the high-spin species should have the trans configuration when L is 14-membered L^2 or 15-membered 1,5,9,12-tetraazacyclopentadecane (L^8). The small cavity size of the L^6 or L^7 ligand should be the critical factor for the cis configuration.[19] The magnitude of the reaction entropy of equilibrium 1 may further characterize this configurational difference in the high-spin species: $\Delta S = -126$ J K^{-1} mol^{-1} for L = L^7 and $\Delta S = -84$ J K^{-1} mol^{-1} for L = L^2.[19] Cavity sizes of the ligands L^1–L^5 are large enough to accommodate Ni^{2+} in a planar fashion. The ΔS's in Table I also suggest the trans configuration for these ligands. Thus, the high-spin complexes with ligands L^1–L^5 should probably have the trans configuration. On this assumption, ΔV_{expan} can be estimated as $\Delta V_{\text{expan}} = 2\pi r(\Delta r)hN$.

For the $[NiL^2]^{2+}$ complex, the outer radius (r) and the thickness (h) of the macrocyclic molecular plane can be estimated as 4.5 and 4.0 Å respectively, by using the X-ray analytical results and the CPK molecular model.[20] The average Ni–N bond distance (2.067 Å)[21] in the six-coordinated $[NiCl_2L^2]$ is longer by 0.122 Å than that (1.945 Å)[20] in the four-coordinated $[NiL^2](PF_6)_2$. Similarly, the average Ni–N bond distance in $[NiCl_2L^9]\cdot 2CHCl_3$ is longer by 0.122 Å than that (1.959 Å) in the $[NiL^9]Cl_2\cdot 2H_2O$, where L^9 is [7*R*-(*S*),14*S*(*R*)]-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.[22] Thus, an expansion of $\Delta r = 0.12$ Å should be caused by the coordination of the two water molecules. Then, for L = L^2 system, $\Delta V_{\text{expan}} = 8.1$ cm^3 mol^{-1} can be estimated. Thus, the magnitude of ΔV_{coord} may be obtained by equating $\Delta V_{\text{coord}} + \Delta V_{\text{expan}}$ to the ΔV for L = L^2: $\Delta V_{\text{coord}} + 8.1 = -1.2$. Then, $\Delta V_{\text{coord}} = -9.3$ cm^3 mol^{-1} can be obtained, from which the molar volume of coordinated water in the high-spin species for L = L^2 may be deduced as 13.4 cm^3 mol^{-1}, since the molar volume of bulk water is 18.0 cm^3 mol^{-1} at 20 °C.

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