the **g** tensor components reported here and those of the pure [CuMg] complex[8] is found to be good, particularly in view of the uncertainty of the measurement of $g_{\parallel}$ in the powder spectrum of the pure material.

[CuNi]. The [CuNi] spectra (Figure 3, full lines) are much more difficult to analyze than those of [CuMg], since the resonant fields of the three magnetically inequivalent binuclear sites are distinct. Again, hyperfine structure is present, splitting each resonance of the k_3k_1 and k_1k_2 planes into four equidistant lines. Because of the very low abundance (1.19%) of the ^{61}Ni isotope with $I = {}^3/_2$, this hyperfine structure arises exclusively from the coupling of the $S = {}^1/_2$ electronic ground state with the $I = {}^3/_2$ nuclear spin of copper. The contributions of the three magnetically inequivalent sites are clearly displayed in the k_2k_3 plane, whose normal was found to be only 17° from the trigonal axis. A total of twelve lines were expected in this plane, but only three broad envelopes are resolved, in agreement with the very weak value of $A_{\perp}$ (see below). The three envelopes are out of phase by 60° and two of them intersect every 30°. When H is parallel to k_3, the intensity of the high-field line is about twice that of the low-field line; two of the three magnetic sites, with their molecular x axes 30° from H, contribute to the high-field line, while only one magnetic site, with its molecular y axis parallel to H, corresponds to the low-field line. Inversely, when H is parallel to k_2, the low-field group of lines, which now represents the contributions of the two magnetic sites with their molecular y axes approximately 30° from H, becomes more intense than the high-field group. In the k_3k_1 and k_2k_1 planes, where H is rotated from the k_3 or the k_2 axis toward the c axis, eight hyperfine lines collapse into four equally intense lines, as expected.

The g and A parameters deduced from the analysis of the angular dependence of the $\mathbf{g}^2$ and $\mathbf{g}^2\mathbf{A}^2$ tensors for each of the three magnetic sites are given in Table I. The minimum principal g value is found along the c axis; its value is 2.22, in excellent agreement with that determined from the study of the pure compound.[8] In contrast, whereas the **g** tensor of the pure compound appears to be axial, in the diluted compound it exhibits a rhombic symmetry with $g_x = 2.25$ and $g_y = 2.36$, where the principal magnetic axes coincide with the molecular axes x and y. The maximum principal A value, equal to 69×10^{-4} cm^{-1} is found along the c axis. In the ab plane, the hyperfine parameter is found smaller than 10×10^{-4} cm^{-1} and cannot be determined with accuracy.

The appropriate spin Hamiltonian to describe the low-lying states in [CuNi] is

$$\mathcal{H} = \beta H\cdot(\mathbf{g}_{\mathrm{Cu}}\hat{S}_{\mathrm{Cu}} + \mathbf{g}_{\mathrm{Ni}}\hat{S}_{\mathrm{Ni}}) + \hat{S}_{\mathrm{Ni}}\cdot\mathbf{D}\cdot\hat{S}_{\mathrm{Ni}} - J\hat{S}_{\mathrm{Cu}}\cdot\hat{S}_{\mathrm{Ni}} + \hat{S}_{\mathrm{Cu}}\cdot\mathbf{D}_{\mathrm{CuNi}}\cdot\hat{S}_{\mathrm{Ni}} + \hat{I}_{\mathrm{Cu}}\cdot\mathbf{A}_{\mathrm{Cu}}\cdot\hat{S}_{\mathrm{Cu}} \quad (1)$$

where the meaning of the symbols, but the last one, has already been specified.[8] The last term is the copper(II) single-ion hyperfine structure term. The spin Hamiltonian associated with the $S = {}^1/_2$ ground pair state is

$$\mathcal{H}_{1/2} = \beta H\cdot\mathbf{g}_{1/2}\cdot\hat{S} + \hat{I}_{\mathrm{Cu}}\cdot(\mathbf{A}_{\mathrm{Cu}})_{1/2}\cdot\hat{S} \quad (2)$$

where the meaning of the symbols is obvious. The relations between $\mathbf{g}_{1/2}$, $\mathbf{g}_{\mathrm{Cu}}$, and $\mathbf{g}_{\mathrm{Ni}}$, on the one hand, $(\mathbf{A}_{\mathrm{Cu}})_{1/2}$ and $\mathbf{A}_{\mathrm{Cu}}$, on the other hand, are

$$\mathbf{g}_{1/2} = \frac{4\mathbf{g}_{\mathrm{Ni}} - \mathbf{g}_{\mathrm{Cu}}}{3} \quad (3)$$

$$(\mathbf{A}_{\mathrm{Cu}})_{1/2} = -{}^1/_3\mathbf{A}_{\mathrm{Cu}} \quad (4)$$

We already discussed the validity of relation 3.[8] As far as the hyperfine interaction is concerned, the validity of relation 4 is nicely checked for the well-determined principal value of the **A** tensor, since $(A_{\parallel\mathrm{Cu}})_{1/2} = 69 \times 10^{-4}$ cm^{-1} and the corresponding value in the same direction for [CuMg] is $A_{\mathrm{Cu}} = 222 \times 10^{-4}$ cm^{-1}. We find the agreement to be quite good[12] and definitely better than that found in two similar single-crystal studies.[2,11] The fact that the smallest value of the hyperfine coupling could not be established is also a check of relation 4 since the perpendicular value for the pair estimated from the corresponding one in [CuMg] should be less than 10×10^{-4} cm^{-1}.

The agreement found between the observed hyperfine parameters in [CuNi] and [CuMg] and those deduced from the spin Hamiltonian (1) suggests that the approximations on which it is based are valid.[8] These approximations are as follows: (i) the wave functions of the real electrostatic Hamiltonian (including spin–orbit coupling and Zeeman terms) appropriate to describe the low-lying pair states are Heitler–London functions constructed from eigenfunctions of local Hamiltonians; (ii) the coupling between ground configuration (Cu$^{\mathrm{II}}$Ni$^{\mathrm{II}}$) and metal–metal change-transfer configuration (Cu$^{\mathrm{III}}$Ni$^{\mathrm{I}}$ or Cu$^{\mathrm{I}}$Ni$^{\mathrm{III}}$) is not taken into account. Furthermore, we can specify the range of validity of the relations (3) and (4). In [CuNi], the isotropic exchange is found to be of medium magnitude. But if $|J|$ were very small, the total spin S would not be a good quantum number any longer and the meaning of the Hamiltonian (2) would vanish. At the other extremity, if J were very negative, the Heitler–London description of the low-lying states, which is implicity required by the spin Hamiltonian (1), would not be appropriate any longer.

Since we did not observe any EPR transition within the upper quartet state of [CuNi], we were not able to check relations relative to zero-field splitting effects, similar to (3) and (4), as has been done with other heterobinuclear systems.[4,5,7] In order to specify the range of validity of the approximations required by the spin-Hamiltonian formalisms (1) and (2), we shall study other Cu(II)–Ni(II) pairs with smaller doublet–quartet energy gaps. To conclude, we want to emphasize that the [CuNi] complex considered in this note is apparently the first heteropair for which we have both the energy gap between low-lying spin states owing to accurate magnetic measurements on the pure material and the details of the electronic structure of the ground state owing to this EPR study on a doped diamagnetic host lattice. We also wish to point out that [CuCo] could be used as EPR-silent host lattice for investigating the properties of low-lying states in other pairs.[13]

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Registry No. CuCo(fsa)$_2$en(H$_2$O)$_2$, 62109-46-0; Mg, 7439-95-4; Ni, 7440-02-0.

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(12) One of the reviewers suggested that an additional term in the Hamiltonian (1) of the form $\hat{I}_{\mathrm{Cu}}\cdot A'_{\mathrm{Cu}}\cdot\hat{S}_{\mathrm{Ni}}$ could account for the weak deviation with regard to relation 4.

(13) In fact, making use of this conclusion, we also prepared [CuCo] doped with Mn with an initial Mn:Co ratio of 1:20. Unfortunately, the EPR spectrum of the resulting well-shaped crystals proved to be of prohibiting complexity.

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Germanium-73 Chemical Shifts and Spin–Lattice Relaxation Times of Some Tetrasubstituted Germanes

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As compared with NMR spectroscopy of other group 4B elements, that of ^{73}Ge has attracted less attention chiefly

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.

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

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

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

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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