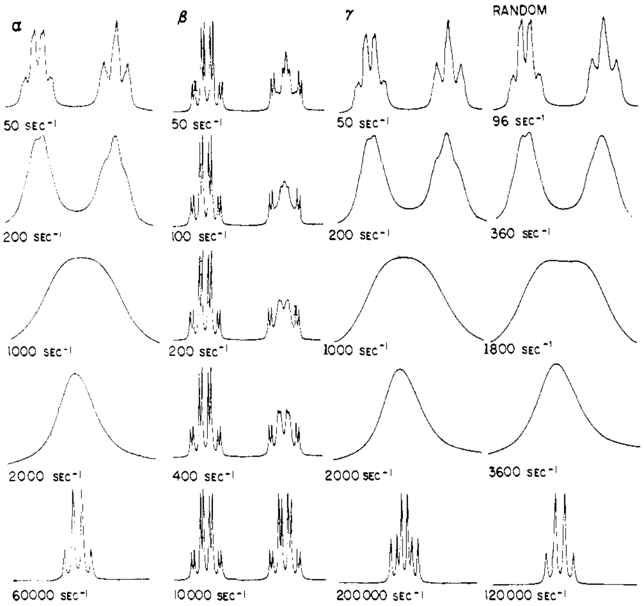

Figure 20. Calculated ^1H nmr line shapes for an H_2ML_3X system for the permutational mechanisms α, β, γ, and $(E + \alpha + \beta + \gamma)$ at several exchange rates. The calculated slow-exchange-limit spectra (identical in all cases) have been omitted from this figure and are the same as that shown at the bottom of Figure 16.

in terms of the five nuclei of spin $^1/_2$ which are involved in the nmr Hamiltonian (X is considered to have zero spin). The Hamiltonian is invariant to the permutations E and σ. Thus, there are $12/2 = 6$ unique high-resolution nmr Hamiltonians for the five-spin system. Decomposition of the group into double cosets with respect to the elements of C_s indicates that there are a total of four permutational subclasses[9] (Table IX). Only α of these permutational subclasses give the correct high-temperature-limiting quartet. Mechanism β averages the H–P coupling constants but does not average the hydride chemicals shifts so that the high-temperature limit consists of two, not quite first order, doublets of quartets. Mechanism γ averages the hydride chemical shifts but does not average the H–P coupling constants and the high-temperature limit is a doublet of triplets. Thus any mechanism corresponding to β alone or γ alone can be ruled out. Mechanism α gives the correct high-temperature limit since both the H–P coupling constants and hydride shifts are averaged; similarly, any linear combination of α, β, and γ will give the correct high-temperature limit. One such linear combination is the random exchange mechanism. By random exchange we mean all permutations in the E, α, β, and γ subclasses equally weighed. In Figure 20, the results of a complete density matrix simulation of the nmr line shapes expected from the permutational mechanisms α, β, γ and random exchange. The nmr parameters used in this calculation are quite similar to those given in Table VIII.

Germanium-73 Nuclear Magnetic Resonance Spectra of Germanium Tetrahalides

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Abstract: The ^{73}Ge chemical shifts for $GeCl_4$, $GeBr_4$, GeI_4, and all 12 of the mixed tetrahalogermanes have been measured. The chemical shifts of these species are not a linear function of halogen coordination, but show a second-order dependence which can be rationalized using the pairwise additivity model. The shielding effect of the halogens increases in the order Cl < Br < I. The rate at which halogens redistribute between germaniums in liquid mixtures of the neat tetrahalogermanes is slow.

Of the elements from group IV of the periodic table, germanium alone has heretofore escaped the attention of the nmr spectroscopist motivated toward the establishment of molecular structure. Although carbon-13, reflecting its position at the center of things chemical, has received the most study, silicon-29, tin-119, and lead-209 have all produced spectra suitable for establishing the chemical shift ranges experienced by these nuclei.

We can now report that the pattern and range of chemical shifts displayed by germanium-73 are consistent with those exhibited by other group IV elements. The range in the case of the germanium tetrahalides spans 1117 ppm between $GeCl_4$ and GeI_4, which falls between the 1550 ppm range for the corresponding tin compounds and the 395 ppm range for the corresponding carbon compounds. In addition, the halogen-dependence pattern for the germanium shifts, with the tetraiodide signal occurring to high field of the tetrachloride signal, is the same as that observed for the tetrahalo compounds of the other main-group elements, such as ^{11}B,[1] ^{13}C,[2] ^{27}Al,[3] ^{29}Si,[4] ^{71}Ga,[5] ^{115}In,[6] and ^{119}Sn.[7]

The germanium tetrahalides constitute the best

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series of model compounds for ^{73}Ge study in view of their direct comparability with the analogous compounds of the other group IV elements which have received nmr study. At the same time it can be seen that the ^{73}Ge method provides the neatest means of characterizing the mixed tetrahalides of germanium. Previous Raman studies report the existence of all 15 of the tetrahalides involving chlorine, bromine, and iodine, and assign the different stoichiometries on the basis of the a_1 vibrational modes.[8] The relatively simple nmr spectra obtained for these systems confirm the earlier conclusions drawn from the more complex Raman spectra.

Experimental Section

Chemical Shift Measurements. Germanium-73 nmr spectra were observed at 2.08 MHz using a Varian 4200B wide-line spectrometer with a V-4210A variable-frequency oscillator and a V-3400 9-in. electromagnet with Fieldial stabilization and sweep capability. Resonance signals were recorded as derivatives of either dispersion or absorption modes and the calibration of spectra was effected by the generation of audiofrequency side bands (*ca.* 250 Hz). All spectra were obtained at room temperature under slow passage conditions, and chemical shifts in ppm are quoted relative to neat $GeCl_4$. The quoted precision of the chemical shifts (±3 ppm) takes account of the calibration uncertainty. Positive shifts denote increased shielding of the germanium nucleus with resonances shifted to high field.

Line Widths. The ^{73}Ge isotope is unique among the main group elements of group IV in that, with nuclear spin $I = {}^9/_2$, it is the only nmr-active isotope with a spin greater than $^1/_2$, and hence the only one with a nuclear electric quadrupole moment. As a result of this quadrupole moment, any electric field gradient at the germanium nucleus generated by the bonded atoms will give rise to an inherently broad germanium resonance. The 7.8% natural abundance and low detection sensitivity (1.4×10^{-3} relative to protons at the same field strength) of ^{73}Ge, coupled with the inherent breadth of the lines, restrict the detection of resonance signals to relatively concentrated solutions (≥ 1 *M*). Line widths of approximately 25 Hz were observed for samples of the neat tetrahalides, a value which represents the homogeneity limit of the magnet used in the study. By analogy with ^{27}Al resonances in AlX_4^- species,[3] the natural line width for ^{73}Ge in a halogen environment having T_d symmetry is probably considerably less than 25 Hz. In the study of halogen redistribution products, the lowered concentration of each species necessitated the use of increased power levels and higher modulation frequencies to produce a signal-to-noise ratio adequate for obtaining chemical shift information. Under these circumstances, accurate line width measurements for the mixed tetrahalides were precluded.

Sample Preparation. The germanium tetrahalides were obtained as "ultra-pure" grade from Alfa Inorganics. Further purification of these samples did not alter the resonance lines or redistribution rates. Carbon disulfide was distilled and stored over Linde 3A molecular sieve. Samples were prepared in 15-mm o.d. nmr tubes under anhydrous conditions by employing standard vacuum line and drybox techniques. $GeCl_4$ and $GeBr_4$ were studied as neat liquids and in carbon disulfide solution, while GeI_4 was studied as a saturated solution in carbon disulfide. The three 1:1 mole ratio samples involving two different halogens and the 1:1:1 mole ratio sample involving all three halogens were prepared from the parent tetrahalides. In each case, 5 mmol samples of each tetrahalide were mixed, and carbon disulfide was added where necessary to bring GeI_4 into solution. Carbon disulfide did not alter the resonance positions of either $GeCl_4$ or $GeBr_4$.

Results and Discussion

Single-line ^{73}Ge spectra have been obtained for $GeCl_4$ and $GeBr_4$ in carbon disulfide solution, from which chemical shifts for each of these three compounds have been obtained. The three separate 1:1 binary mixtures of the parent tetrahalides each give rise after equilibration to a 5-line ^{73}Ge spectrum assignable to the five possible GeX_nY_{4-n} ($0 \leq n \leq 4$) binary tetrahalogermanes arising from redistribution of halogen atoms. These three spectra are illustrated diagramatically in Figure 1. The relative signal intensities in each of these spectra appeared to be in the ratio 1:4:6:4:1 expected for random distribution of halogens. In order to observe the weakest signals, however, the irradiation power level had to be increased to a degree such that a valid comparison of signal intensities was not possible.

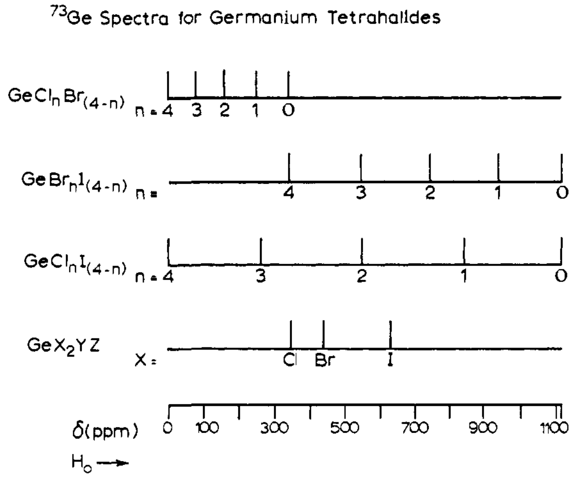

Figure 1. Diagramatic representation of the ^{73}Ge nmr spectral line positions for the germanium tetrahalides.

The 1:1:1 mixture of $GeCl_4$, $GeBr_4$, GeI_4–CS_2 gave rise, after a redistribution time of 10 hr at room temperature, to a spectrum containing nine resonance lines. Six of these were assigned to $GeCl_3I$, $GeCl_2I_2$, $GeBr_2I_2$, $GeClI_3$, $GeBrI_3$, and GeI_4 on the basis of the spectral data obtained from the binary mixtures. The remaining three resonances at δ 347, 438, and 632 ppm were assigned to $GeCl_2BrI$, $GeClBr_2I$, and $GeClBrI_2$, respectively. The intense resonance at 347 ppm was assigned to $GeCl_2BrI$ since the equilibrium concentration of $GeBr_4$ (δ 343 ppm) in the mixture will be very small. The relationship of the line positions for these three ternary mixed halides to those for the binary mixed halides is illustrated in Figure 1.

The nuclear shielding of the germanium caused by the attached halogen atoms is consistent with the pattern of nuclear shielding already established for halogens bonded to other main group elements; namely, metal nucleus shielding increases in the order Cl < Br < I. If one assumes that each halogen makes a constant shielding contribution to the germanium nucleus, independent of that from the other three halogens present, as has been done for the tetrahalostannanes,[7] the chemical shift for each of the mixed tetrahalogermanes can be calculated using the three single halogen shielding parameters δ_X' (X = Cl, Br, I) given in Table II and obtained from the expression $\delta_X' = {}^1/_4\delta_{GeX_4}$. The shifts calculated using this first-order theoretical approach are given in Table I under the heading "δ first order" and are seen to involve deviations from the observed values as large as 18 ppm, with an average deviation for all 12 calculated shifts of 10 ppm. These deviations, which lie well outside the ±3 ppm uncertainty limits of the observed shifts, indicate the presence of a second-order effect upon the germanium shielding resulting from halogen–halogen interaction.

[8] C. Cerf and M. B. Delhaye, *Bull. Soc. Chim. Fr.*, 2818 (1964).

Table I. ^{73}Ge Chemical Shift Values[a]

		Calculated shifts			
Species	δ_{obsd},[b] ppm	δ first order	Devn	δ $\Sigma c_{ij}\eta_{ij}$	Devn
$GeCl_4$	0	(0)		−1	1
$GeCl_3Br$	78	86	6	75	3
$GeCl_2Br_2$	161	172	11	158	3
$GeClBr_3$	250	257	7	248	2
$GeBr_4$	343	(343)		345	2
$GeCl_4$	0	(0)		0	
$GeCl_3I$	262	279	17	268	6
$GeCl_2I_2$	549	559	10	545	4
$GeClI_3$	839	838	1	830	9
GeI_4	1117	(1117)		1123	6
$GeBr_4$	343	343		345	2
$GeBr_3I$	544	537	7	541	3
$GeBr_2I_2$	739	730	9	736	3
$GeBrI_3$	932	924	8	930	2
GeI_4	1117	(1117)		1123	6
$GeCl_2BrI$	347	365	18	352	5
$GeClBr_2I$	438	451	13	443	5
$GeClBrI_2$	632	644	12	637	5

[a] Relative to $GeCl_4$; positive values represent increased shielding and upfield shifts. [b] Error limits which include calibration uncertainty are ±3 ppm.

This second-order effect can be accommodated from the theoretical point of view by using the "pairwise additivity" model outlined by Vladimiroff and Malinowski.[9] By recognizing the change caused by one substituent in the wave functions for all neighboring substituents, this model allows one to calculate the chemical shift for a central atom by the summing of pairwise interaction parameters for all substituents taken as adjacent pairs. For the pseudo-tetrahedral molecules which we have in the present case, this involves the summing of six pairwise additivity parameters corresponding to the six edges of a solid tetrahedron. Table II gives the six halogen pairwise additivity parameters which were obtained from the 15 observed chemical shift values using a multiple linear regression analysis in which the six η parameters were treated as independent variables. Table I gives the 15 chemical shift values calculated using this model. The values obtained compare sufficiently well with the observed values that the model can be used both to predict chemical shift values for unobserved species within an observable system and to verify spectral assignments of observed lines within a many-line spectrum.

Table II. Derived ^{73}Ge Shielding Parameters (ppm)

First-order approximation	Pairwise additivity parameters
$\delta'_{\mathrm{Cl}} = 0$	$\eta_{\mathrm{Cl-Cl}} \simeq 0$
$\delta'_{\mathrm{Br}} = 85.8$	$\eta_{\mathrm{Br-Br}} = 57.8$
$\delta'_{\mathrm{I}} = 279.3$	$\eta_{\mathrm{I-I}} = 187.3$
	$\eta_{\mathrm{Cl-Br}} = 25.4$
	$\eta_{\mathrm{Cl-I}} = 89.7$
	$\eta_{\mathrm{Br-I}} = 123.1$
	Intercept = −1.2

Previous Raman studies[8] have identified the 15 redistribution products of this germanium(IV) halide system. The redistribution products are reported to be inseparable,[10] and the redistribution times for these species in solution are quoted to be "very fast."[8] In the present study, where precautions to prevent hydrolysis were taken, very slow redistribution rates have been observed both with neat mixtures and with concentrated carbon disulfide solutions of germanium tetrahalides.[11] Where the intensity changes of the ^{73}Ge resonance lines for a neat equimolar mixture of $GeCl_4$–$GeBr_4$ were followed at 28°, the time taken for the $GeCl_4$ signal to decrease to half its initial intensity was 250 min. In addition, the peak intensities in the five-line spectrum resulting at equilibrium are approximately those one calculates for a random Calingaert[12] distribution of halogens. A similar study of the tetrahalostannanes[1] shows a random redistribution among the various possible tetrahalides but shows a *rapid* redistribution rate, although acknowledging that some hydrolysis might have occurred.

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[10] M. L. Delwaulle, F. Francois, M. Delhaye, and D. Buisset, *J. Phys. Radium*, **15**, 206 (1954).

[11] Standard vacuum line and drybox techniques were employed in sample preparation to exclude moisture.

[12] G. Calingaert and H. A. Beatty, *J. Amer. Chem. Soc.*, **61**, 2748 (1939).