The ^{19}F and ^{1}H Nuclear Magnetic Resonance Spectra of Some Germanium Tetrafluoride Complexes

By A. D. ADLEY, D. F. R. GILSON, and M. ONYSZCHUK*

(*Department of Chemistry, McGill University, Montreal* 2, *Canada*)

MUETTERTIES[1] has discussed the ^{19}F n.m.r. spectra of a series of octahedral complexes of germanium tetrafluoride, $GeF_4 2L$ in which the ligands (L) were Me_2SO, Me_2NCHO, $Me_2C{=}NOH$, C_5H_5N, and Me_2NPh. The spectra consisted of a single resonance over the temperature range "from well above room temperature to the freezing point of the solution," but neither the exact temperature range nor the solvent were given. All the complexes were reported to decompose rapidly in water.

We have prepared adducts of GeF_4 with 6-hexanolactam (I), δ-valerolactam (II), and 2,6-dimethyl-γ-pyrone (III). Analyses corresponded to the formula $GeF_4,2L$. However, in contrast to the compounds reported by Muetterties, these complexes could be recovered unchanged from aqueous solutions at room temperature. Tetramethylurea (IV) formed an air and moisture sensitive 1:2 adduct, and the bidentate donors tetramethylenediamine (V) and αα′-bipyridyl (VI) gave 1:1 complexes. The behaviour of (V) and (VI) in water has not been examined. For all complexes except those with (V) and (VI), which bond *via* the nitrogen atom, the i.r. spectra indicated that co-ordination occurred through the carbonyl group in agreement with previous studies on these ligands.[1,2]

The ^{19}F and ^{1}H n.m.r. data summarized in Tables 1 and 2 were obtained using saturated solutions in chloroacetonitrile. Germanium tetrafluoride appears to form an unstable complex with this solvent. The ^{19}F spectrum of a solution of GeF_4 in chloroacetonitrile showed only a singlet at $-11°$, 41·7 p.p.m. from external trifluoroacetic acid, which shifted downfield to 40·0 p.p.m. at $-30°$. The complexes of the monodentate ligands (I), (II), and (III) all showed broad resonances at room temperature with widths at half-peak height of approximately 200 Hz. On cooling, the two triplets of an A_2X_2 spectrum appeared, indicating that exchange was occurring at room temperature and that the *cis*-isomer was present at lower temperatures. A single line was also present in the spectra of the complexes of the monodentate ligands, which is tentatively assigned to the *trans*-isomer, since the intensity and shift remained essentially constant over the temperature range studied. The spectra of complexes with (V) and (VI) at room temperature showed the A_2X_2 pattern expected for the *cis*-complexes with bidentate ligands.

For those adducts in which co-ordination occurred through the carbonyl group, the chemical shifts of the A and X fluorine nuclei did not vary significantly. For the adduct of (V), a saturated bidentate nitrogen donor, both triplets shifted to higher field by about the same amount, but for the complexes with (VI) a considerable upfield shift occurred for the high-field triplet. The coupling constant, J_{FF}, showed no dependence on the ligand.

TABLE 1

^{19}F *n.m.r. measurements in chloroacetonitrile*

Compound	Temperature (°C)	Chemical shifts in p.p.m. relative to external CF_3CO_2H (Coupling constant J in Hz)			
GeF_4·2 (I)	22	33·2;	35·8;	43·0;	47·2
	−10 to −35	33·2, t	35·8;[a]	39·7;[b]	47·1, t
		J_{FF} 62·3 ± 3·9			J_{FF} 61·5 ± 2·7
GeF_4·2 (II)	22	32·5	34·4;	42·2;	45·2
	−4·5 to −15·5	32·2, t	34·5;[a]	41·8;[b]	45·6, t
		J_{FF} 60·2 ± 3·2			J_{FF} 61·9 ± 2·3
GeF_4·2 (III)	22	37·7; 42·3			
	−44	35·7,[c] t	36·9;[a]	40·1;[b]	54·4, t
		J_{FF} 66·5 ± 3·5			J_{FF} 60·5 ± 7·0
GeF_4·2 (IV)	22	37·1			
	−59	29·4, t	35·4[a]		48·9, t
		J_{FF} 63·8 ± 1·5			J_{FF} 60·9 ± 2·9
GeF_4· (V)	22	53·6, t			68·0, t
		J_{FF} 59·3 ± 3·6			J_{FF} 55·9 ± 1·9
GeF_4· (VI)[d]	22	36, t			69, t
		J_{FF} 50 Hz			J_{FF} 58

[a] Tentatively assigned to the *trans*-isomer.

[b] A weak resonance not yet identified.

[c] Only the first two parts of the low-field triplet were observed with the third part believed to be hidden under the more intense singlet at 36·9 p.p.m.

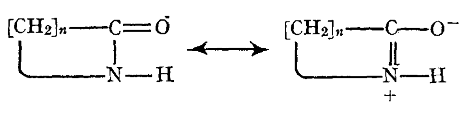
[d] Results are only estimates because of low solubility in chloroacetonitrile.

TABLE 2

^1H *n.m.r. chemical shifts in p.p.m. relative to internal tetramethylsilane*

Compound	N–H	α–CH_2	β,γ,δ–CH_2	ω-CH_2
(I)	6·7	3·2	1·7	2·4
GeF_4·2 (I)	8·8	3·4	1·8	2·6
	N–H	α-CH_2	β,γ-CH_2	δ-CH_2
(II)	7·1	3·3	1·7	2·3
GeF_4·2 (II)	8·5	3·5	1·8	2·5
	α-H	β-Me		
(III)	6·0	2·2		
GeF_4·2 (III)	7·1	2·5		
	Me			
(IV)	2·8			
GeF_4·2 (IV)	3·0			

The lactams may be described as a resonance hybrid of two structures:



Co-ordination through the carbonyl group should enhance the contribution of the second form and thereby account for the large downfield shift for the nitrogen-proton in adducts of (I) and (II). Alternatively, the shift might be due to an anisotropic effect arising from the proximity of the N–H group to the GeF_4 moiety. The protons on the carbon atoms adjacent to the C=O and N–H groups which are respectively four and five bonds from the germanium atom show a much smaller shift. As expected, the ethylenic protons in the adduct of (III) showed the largest downfield shift. The protons in the complex of (IV) which are all equivalent, and five bonds removed from the germanium atom, showed a small shift.

Preliminary ^{19}F n.m.r. measurements on an aqueous solution of the valerolactam complex showed an AX_4 spectrum indicating the possible presence of a $[GeF_5(OH)]^{2-}$ species. The apparent molecular weight of the original complex in aqueous solution was about one-quarter the calculated value, as observed by Muetterties.[1]

The ^{19}F n.m.r. spectrum of SiF_4. (α,α′-bipyridyl), the only SiF_4 complex we have examined so far, consisted of the two triplets of equal intensity at room temperature in chloracetonitrile (δ 45·0 p.p.m., J_{FF} 12·9 ± 0·7 Hz and δ 67·4 p.p.m., J_{FF} 12·0 ± 1·5 Hz), confirming its *cis*-structure.

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