^{93}Nb Nuclear Magnetic Resonance in Solutions of the Halides of Niobium(v)

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Summary The ^{93}Nb n.m.r. spectra of mixtures of $NbCl_5$ and $NbBr_5$ were examined, and all of the seven possible species of niobium(v) halides were found to be present in the concentrations expected for random halogen distribution.

It has been shown in studies of halogen derivatives of carbon,[1,2] silicon,[3] and tin[4] that the chemical shift of the central atom in the tetrahedral molecule is a smooth function of composition in series of the type MCl_nBr_{4-n} (n = 0—4) M = ^{13}C, ^{29}Si, or ^{119}Sn.

The object of our study of ^{93}Nb n.m.r. spectra is to obtain similar data for niobium compounds. The niobium resonances were measured using a broad-line spectrometer (6 MHz) with audio-phase-sensitive detection. The resonances were accordingly recorded as the derivative of the dispersion or absorption mode. The areas of the n.m.r. peaks were obtained by planimetry of the recorded signals and are accurate to within $\pm 10\%$. Chemical shifts were measured from NbF_5 dissolved in 48% HF as an external reference.

Upon mixing two niobium pentahalides such as $NbCl_5$ and $NbBr_5$ dissolved in acetonitrile, and allowing them to stand for some time, a random redistribution of the halogen substituents takes place and results in the formation of expected quantities of mixed halides of the type $NbCl_nBr_{6-n}$ ($n = 0$—6). The ^{93}Nb resonance spectrum of a 1 : 1 molar mixture of these compounds shows an individual band for each mixed halide (Figure 1). By carrying out intensity measurements of the roughly equally spaced bands, it is possible to estimate approximately the amount of species present. The observed intensities are in good agreement with those expected for a random redistribution of the halogen substituents.

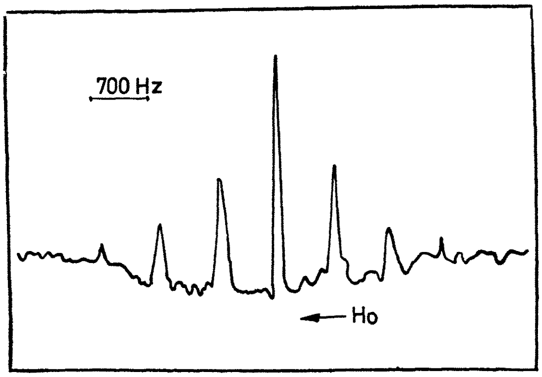

FIGURE 1. ^{93}Nb *spectrum of an equimolar mixture of* $NbCl_5$ *and* $NbBr_5$ *dissolved in acetonitrile.*

Following the method of Calingaert,[5] the intensity of each species was calculated by applying the laws of random distribution.

In the case where there is only one kind of central atom M, with co-ordination number 6, and two different kinds of ligand, the number of different species is equal to 7, and the concentration of each species is given by the corresponding term of the binomial expansion $(r_1 + r_2)$.[6] The quantities r_1 and r_2 are the mole fractions of the chlorine and bromine atoms, respectively. Denoting r_1 by r, and r_2 by $(1 - r)$, we obtain corresponding values of the concentrations of each mixed niobium halide component. The r-values were determined and the expected concentration in the final mixture was calculated taking into account the composition of the original mixture. As an illustration, the calculated and observed concentrations of all seven species in the system $NbCl_nBr_{6-n}$ are shown in Table 1.

TABLE 1

Calculated and observed concentrations of species in a 1 : 1 *molar mixture of* $NbCl_5$ *and* $NbBr_5$

Anion	Concentration (arbitrary units) Calc.[a]	Obs.
$NbCl_6^-$	0·05	0·08
$NbCl_5Br^-$	0·3	0·28
$NbCl_4Br_2^-$	0·78	0·74
$NbCl_3Br_3^-$	1·00	1·00
$NbCl_2Br_4^-$	0·78	0·73
$NbClBr_5^-$	0·3	0·3
$NbBr_6^-$	0·05	0·09

[a] Normalized to 1·00.

Thus, according to the model used for random distribution, we conclude that the maximum number of halide atoms in the first co-ordination sphere of the niobium is six in the solution in question.

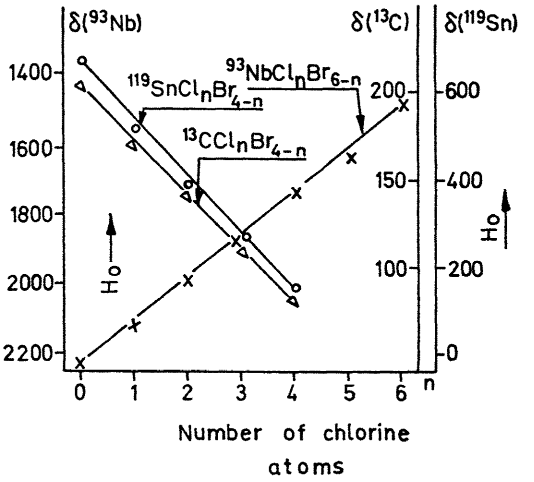

FIGURE 2. *Plot of the* ^{13}C,[1,2] ^{119}Sn,[4] *and* ^{93}Nb *chemical shifts against the number of chlorine atoms.*

The ^{93}Nb chemical shifts of the mixed halides with the variable mole ratios $NbCl_5$: $NbBr_5$ are summarised in Table 2. The widths of ^{93}Nb resonances are slightly vari-

TABLE 2

^{93}Nb *chemical shifts of species present in mixtures of niobium*(V) *halides* (*p.p.m. from* NbF_6^-; ± 5 p.p.m.)

Mole fraction		Nb halide						
$NbCl_5$	$NbBr_5$	$NbCl_6^-$	$NbCl_5Br^-$	$NbCl_4Br_2^-$	$NbCl_3Br_3^-$	$NbCl_2Br_4^-$	$NbClBr_5^-$	$NbBr_6^-$
1	0	1490	—	—	—	—	—	—
0	1	—	—	—	—	—	—	2220
0·8	0·2	1485	1617	1742	1869	—	—	—
0·5	0·5	1492	1621	1744	1868	1989	2112	2225
0·2	0·8	—	—	—	1874	1998	2114	2235

able. The width of each individual line measured as peak to peak was in the range 30—100 Hz. The broadest resonances were observed for $NbCl_nBr_{6-n}^-$ ($n = 1,2,4,5$) ions at the power levels normally used. (The widths are accurate to about ±10%).

It is of interest to note the correlation of ^{93}Nb chemical shifts with the composition in the series of $NbCl_nBr_{6-n}^-$ and also with electronegativities of halogen attached to niobium atoms. As was found for ^{13}C, ^{69}Ga (ref. 6), ^{27}Al (ref. 7), ^{29}Si, and ^{119}Sn nuclei in tetrahalides, the shielding decreases as the electronegativity of the attached halogen increases.

The effects of substitution on the shielding of ^{93}Nb nuclei are opposite in sign to the effects of substitution on the shielding of ^{13}C and ^{119}Sn nuclei in compounds with tetrahedral symmetry. Figure 2 illustrates these features of the chemical shifts in compounds of tetrahedral and octahedral symmetry around the central atom.

Such behaviour on the part of ^{93}Nb chemical shifts may be characteristic of systems with *d*-orbitals participating in chemical bonding.

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