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Nuclear Quadrupole Resonance Studies of Chelated Antimony Complexes. Part 5. Eight-Membered Rings Containing Phosphorus or Sulphur*

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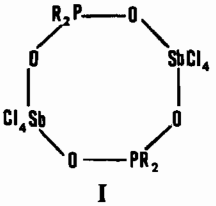
Abstract

The ^{35}Cl Nuclear Quadrupole Resonance spectra of two cyclic phosphorus-containing compounds, $((CH_3)_2PO_2SbCl_4)_2$ and $(Cl_2PO_2SbCl_4)_2$, and five sulphur-containing compounds, $(RSO_3SbCl_4)_2$, which have been supposed to have similar structures, are reported. The NQR spectra support the hypothesis that the sulphur compounds have similar structures to the phosphorus compounds while showing that for $(FSO_3SbCl_4)_2$ the symmetry of the eight-membered ring is different from that of the other six compounds.

Introduction

The preparation and crystal structures of several phosphorus-containing eight-membered rings of the general formula I have recently been reported [2–4]. The preparation of a number of sulphur-containing compounds of the general formula $(RSO_3SbCl_4)_2$ have likewise been reported and it has been postulated, on the basis of their molecular formula and on the evidence of their IR and Raman spectra, that they have the analogous structure **II** [5–7]. We report here the results of our studies of the ^{35}Cl NQR spectra of these compounds, which support this assignment.



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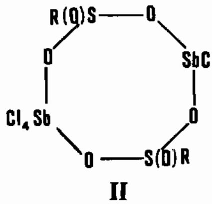

II

Experimental

Preparations

The compounds were prepared by the reported methods [2–7].

NQR Spectra

NQR spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared to harmonics from an internal crystal-controlled oscillator. Temperatures were measured with a Hewlett-Packard 2802 digital thermometer and varied between 77 K and room temperature with an Artronix 5301-E temperature controller.

Results and Discussion

The ^{35}Cl nulcear quadrupole resonance frequencies of two phosphorus-containing compounds of known structure and five sulphur-containing compounds, measured at 77 K, are shown in Talbe I. For most of the compounds the temperature dependence of the resonance frequencies has been measured in the range 77–300 K and the results fitted to a second-order polynomial:

$$F = F_o + AT + BT^2 \qquad (1)$$

The parameters of these equations are also given in Table I. None of the compounds showed a discontinuity in the temperature dependence; it may thus be confidently asserted that no change in the crystal structure occurs within the temperature range studied.

Although the ^{37}Cl resonances corresponding to the frequencies cited in Table I were observed in all cases, no signs of resonances ascribable to either of the two antimony isotopes were detected in the frequency range 15–50 MHz. It is our experience that antimony resonances are usually much broader and less intense than the chlorine resonances in compounds containing $SbCl_4$ or $SbCl_5$ fragments. The Mössbauer spectrum of $(Me_2PO_2SbCl_4)_2$ [8] indicates a ^{121}Sb coupling constant of 65 MHz, for such a coupling constant all the resonances for both antimony isotopes would fall in the range 10–20 MHz.

Two of the compounds in Table I have chlorine atoms attached to the phosphorus atom, **2**, or the sulphur atom, **6**. The frequencies which are due to these chlorine atoms are marked with a double asterisk. Their values are much as would be expected and will not be discussed further.

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*For Part 4, see ref. 1.

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TABLE I. ^{35}Cl NQR Frequencies (MHz), Measured at 77 K, and Their Quadratic Temperature Dependence (eqn. (1))[a]

Compound	Frequency	F_0 (MHz)	A (kHz/K)	B (Hz/K^2)
$[(CH_3)_2PO_2SbCl_4]_2$ (1)	24.189			
	24.490			
	25.497			
	26.212			
$[(Cl_2PO_2SbCl_4]_2$ (2)	26.160			
	26.573			
	26.774			
	28.387			
	29.568**			
	29.812**			
$[CH_3SO_3SbCl_4]_2$ (3)	26.14			
	26.91			
	27.61			
	28.45			
$[CH_3OSO_3SbCl_4]_2$ (4)	26.635	26.67	−0.185	−3.37
	27.034	27.16	−1.628	−0.43
	28.557	28.57	−0.040	−2.07
	28.880	28.92	−0.356	−2.99
$[FSO_3SbCl_4]_2$ (5)	27.980*	28.14	−1.867	−0.97
	28.019*	28.14	−1.510	−0.93
	28.972	29.01	−0.481	−0.22
	28.972	28.97	0.047	−0.67
	29.832	29.9	−0.854	−0.79
	30.118	30.16	−0.445	−0.92
$[ClSO_3SbCl_4]_2$ (6)	27.650	27.75	−1.136	−1.55
	28.100	28.24	−1.565	−1.86
	29.250	29.26	−0.058	−1.57
	30.421	30.52	−1.136	−2.02
	38.362**	38.73	−3.866	−9.11
$[CF_3SO_3SbCl_4]_2$ (7)	27.852	27.91	−0.566	−2.70
	27.969	27.91	−1.500	−2.79
	30.403	30.50	−1.046	−2.58
	30.497	30.58	−0.794	−2.96

[a] Resonances marked with a single asterisk have a relative intensity twice that of the other resonances for that compound, those marked with a double asterisk are ascribed to the chlorine atom attached to the phosphorus or the sulphur atoms.

Both the phosphorus compounds have been shown [2, 4], to have a centrosymmetric configuration for the eight-membered ring. Thus both $SbCl_4$ fragments are identical and, in agreement with the results shown in Table I, only four distinct resonances are expected. The Sb–Cl bond lengths vary quite widely, however. We have previously reported [9, 10] an excellent correlation between the Sb–Cl bond length in compounds containing the $SbCl_4$ fragment and this correlation would appear to exist in these two complexes. Thus we have shown that, on average, a decrease in bond length of 1.0 nm produces an increase in the ^{35}Cl frequency of approximately 1.0 MHz. For the present two compounds the total frequency spread is 4.2 MHz compared to a bond length spread of 7.5 nm.

Our previous studies of chelated molecules containing the $SbCl_4$ fragment [9, 10] showed that the two chlorine atoms in the plane of the chelate ring, 'equatorial' chlorine atoms, had shorter Sb–Cl bond lengths and higher ^{35}Cl resonance frequencies than the two other chlorine atoms in the $SbCl_4$ fragment, the 'axial' chlorine atoms. Such a distinction does not appear to apply to these two compounds, there being no clear grouping either of bond lengths or NQR frequencies. In the previously-studied compounds the chelate fragment was essentially planar, a situation very different from the present puckered rings. Thus long-range effects are significant to the electronic structure of these compounds.

Of the five sulphur-containing compounds whose NQR spectra are reported here, four present the same pattern of four distinct resonance frequencies. These four frequencies are spread over a range of approximately 2.5 MHz within each compound, similar to that (2.1 MHz) observed for the two phosphorus-containing compounds, and, again like the phosphorus compounds, without any systematic grouping of the resonance frequencies. As is to be expected, in both sets of compounds an increase in the electron-withdrawing power of the substituents increases the average resonance frequency. Thus the replacement of two methyl groups by two chlorine atoms in the phosphorus compounds increases the average frequency by 1.9 MHz while the replacement of one methyl group by a chlorine atom in the sulphur compounds **3** and **4** increases the frequency by 1.6 MHz. This similarity in the pattern of resonance frequencies between the two series strongly supports the previous hypothesis that the four sulphur-containing compounds **3**–**6** all have the structure **II**.

The remaining sulphur compound, **7**, shows six resonances. Two of these, however, are approximately twice as intense as the other four, probably implying that the molecule has two distinct $SbCl_4$ fragments, each of which possesses a plane of symmetry which renders two of the chlorine atoms equivalent. It is, of course, impossible to tell whether the factor which renders the two $SbCl_4$ fragments inequivalent is to be found within the molecule or only at the level of the crystalline environment.

The resonance frequencies of the sulphur compounds $(CH_3SO_3SbCl_4)_2$ and $(ClSO_3SbCl_4)_2$ are higher by some 2.0 MHz than their phosphorus analogues $((CH_3)_2PO_2SbCl_4)_2$ and $(Cl_2PO_2SbCl_4)_2$. This is a direct consequence of the higher electron-withdrawing power of the sulphonate groups as manifested by the lower pK_a of the sulphonic acids (≈ 0.5) compared to the phosphonic acids (≈ 4.5). The change in average resonance frequency produced by this change of 4 pK_a units is similar to that observed in the carboxylates [9].

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