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Nuclear Quadrupole Resonance Studies of Chelated Antimony Complexes. Part 6. Tricyclic Molecules

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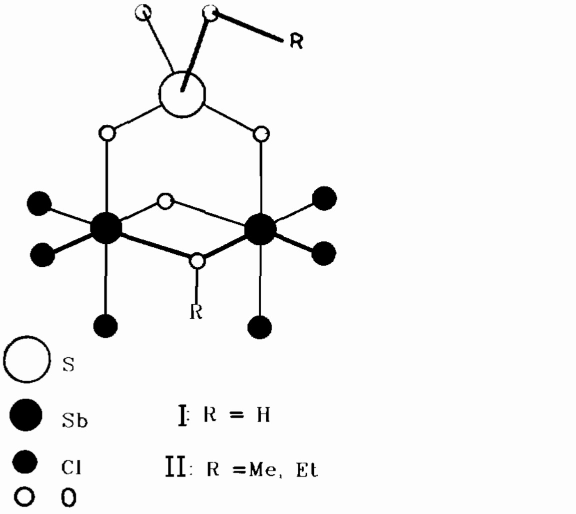
Abstract

The ^{35}Cl Nuclear Quadrupole Resonance spectra of three tricyclic molecules of known structure containing $SbCl_3$ fragments have been measured. Several other analogous compounds have been shown, by a combination of ^{35}Cl, ^{121}Sb and ^{123}Sb NQR spectroscopy, to have similar structures. The relationship between bond length and ^{35}Cl resonance frequency for these compounds containing $SbCl_3$ fragments was investigated; the resonance frequency is less sensitive to bond length than related complexes containing the $SbCl_4$ group.

Introduction

Sulphuric acid reacts with antimony pentachloride and water in solution in methylene chloride to yield the tricyclic molecule (**I**) [1]. Methylsulphonic acid has been shown to form both hydroxy- and alkoxy-bridged complexes (**II**) when an alcohol is substituted for water in the reaction mixture [2, 3]. Carboxylic acid analogues of **I** had previously been prepared [4, 5] and the crystal structures of three sulphur-containing compounds together with that of the hydroxy-bridged acetic and trichloracetic acid derivatives were reported in the original publications. We have extended these studies to the preparation of the alkoxy-bridged carboxylates using the method employed for the sulphur derivatives and have characterised them by measurement of their NQR spectra.



Experimental

Preparations

d,h-Î-Hydrogensulphato-e-Î-hydroxo-f-Î-oxo-bis-[trichloroantimony(V)] (**6**) was prepared according to the published method [1], in which one molar equivalent of a solution of sulphuric acid in dry methylene chloride is added to a mixture of two molar equivalents of antimony pentachloride and two molar equivalents of water in the same solvent. The hydroxy-bridged derivatives of the carboxylic acids were prepared by an analogous method in which the corresponding carboxylic acid replaces sulphuric acid, while for the alkoxy-bridged derivatives, methanol or ethanol replaces water in the reaction mixture. These last compounds were more stable than the hydroxy derivatives and, unlike them, yielded NMR spectra in deuterochloroform with no difficulty. Their proton chemical shifts, listed in Table 1, are in complete agreement with the assigned structure. The acetylacetonate (**10**) was prepared according to the published method [7] and the

Table 1. ^{1}H NMR Chemical Shifts for Alkoxy-bridged Complexes in Solution in Deuterochloroform

Compound number	Group	Shift (ppm)
7	CH_3O-	4.22
8	CH_3-	1.56
	$-CH_2O-$	4.78
9	$(CH_3)_3C-$	1.35
	CH_3-	1.53
	$-CH_2O-$	4.75

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benzoylacetophenone derivative (**11**) by the straightforward extension of this.

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 crystal structures of the hydroxy-bridged derivative of acetic acid (**1**) [4], of trichloracetic acid (**3**) [5], and of the similar derivative of sulphuric acid (**6**) [1], show that, in all cases, the molecule is unsymmetric and the two $SbCl_3$ fragments are inequivalent. In accordance with this there are six distinct ^{35}Cl resonances for each molecule (Table 2). The resonances are weak and no sign of resonances from the ^{121}Sb or ^{123}Sb nuclei could be detected.

TABLE 2. The ^{35}Cl NQR Frequencies of Hydroxy- and Alkoxy-bridged Complexes (I and II) and Dimeric Propanedioneonates (III) (MHz at 77 K)

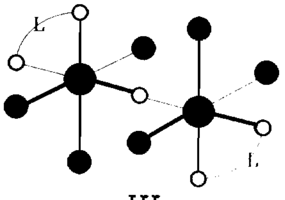
R	R′	Frequency (MHz)	*A* (MHz)	*B* (kHz K^{-1})	*C* (Hz K^{-2})
I					
1 CH_3CO_2	H	25.778			
		26.121			
		26.384			
		26.652			
		27.036			
		27.277			
2 $C(CH_3)_3CO_2$	H	26.122	26.279	−1.9548	−2.3790
		26.122	26.292	−1.9172	−2.7753
		26.334	26.451	−1.2766	−2.2856
		26.576	26.643	−0.7532	−1.5095
		26.718	26.867	−1.6958	−2.2180
		27.051	27.149	−1.1351	−0.4438
3 CCl_3CO_2	H	26.591	26.720	−1.5407	−0.6932
		26.892	27.049	−1.8725	−1.1773
		27.123	27.299	−2.1707	−0.2759
		27.340	27.406	−0.6756	−1.4191
		27.416	27.617	−2.5245	−0.6940
		27.921	28.026	−1.2276	−0.9177
		40.389*	40.828	−5.4964	0.0219
		40.733*	41.131	−4.5668	−5.9125
		40.874*	41.291	−5.2718	−4.3294
4 CBr_3CO_2	H	26.328	26.450	−1.6066	−0.7146
		26.862	27.007	−1.6792	−1.2805
		27.133	27.278	−1.6637	−1.3991
		27.133	27.257	−1.6363	0.5311
		27.469	27.658	−2.2200	−1.4364
		28.092	28.244	−1.7736	−0.0432
5 $CHCl_2CO_2$	H	26.32			
		26.32			
		26.42			
		26.49			
		26.53			
		26.62			
		26.66			
		26.82			
		26.87			
		27.03			
		27.47			
		27.52			
		27.61			

(continued)

TABLE 2. *(continued)*

R	R′	Frequency (MHz)	*A* (MHz)	*B* (kHz K^{-1})	*C* (Hz K^{-2})
		27.68			
		27.80			
		28.04			
		28.24			
		28.40			
		38.51*			
		38.98*			
		38.98*			
		39.54*			
		39.67*			
		39.88*			
6 HSO_4	H	27.523			
		27.657			
		27.867			
		28.053			
		28.138			
		28.527			
II					
7 CCl_3	CH_3	24.980	25.068	−1.0587	−0.7689
		25.371	25.514	−1.7785	−0.3918
		26.966	27.079	−1.3003	−1.4723
		27.142	27.202	−0.6545	−1.2295
		27.380	27.499	−1.3614	−1.0088
		28.117	28.210	−1.0457	−1.5491
		*40.425	40.676	−2.5392	−7.8422
		*40.608	40.803	−1.9741	−6.0004
		*41.392	41.558	−1.5177	−7.1933
8 CCl_3	C_2H_5	25.192	25.175	0.2876	−2.1296
		25.633	25.730	−1.8446	0.1861
		26.770	26.968	−2.3380	−1.0508
		26.820	27.130	−3.9747	1.2314
		27.697	27.880	−2.4013	1.2827
		27.697	27.904	−2.6613	1.0373
9 $C(CH_3)_3$	C_2H_5	25.126	25.192	−0.7788	−1.1190
		25.292	25.357	−0.6168	−2.4377
		25.846	26.044	−2.5566	0.3632
		26.210	26.410	−2.4239	−1.0555
		26.535	26.665	−1.5733	−1.1491
		27.211	27.363	−1.8407	−1.0258
III					
10 L: acetylacetone		23.43			
		23.58			
		24.73			
		24.87			
		25.17			
		26.61			
11 L: benzoylacetophenone		24.400			
		24.916			

There is no grouping of the ^{35}Cl resonances which might allow an attribution to one or the other of the antimony sites; this same lack of grouping is apparent in the Sb–Cl bond lengths. For all three molecules the spread in ^{35}Cl resonance frequency is rather small, approximately 1.5 MHz; the spread in bond lengths is of the order of 3.0 pm. Our previous studies of systems containing the $SbCl_4$ fragment showed that a decrease in Sb–Cl bond length of 1 pm corresponds to an increase of approximately 1.0 MHz in resonance frequency [6], moreover the resonance frequency for a given bond length is higher for the $SbCl_4$ fragment than for the $SbCl_3$ fragment. To obtain further data on this point we have studied another molecule of known structure [7] having an $SbCl_3$ fragment attached to three oxygen atoms (III). The NQR resonance frequencies for this acetylacetonate and the related benoylacetophenone derivative are likewise shown in Table 2. If it is assumed that the RQN frequencies may be attributed to the individual Sb–Cl bonds in the inverse order of their bond lengths, the relationship between resonance frequency (MHz) and bond length (pm), for this set of eighteen pairs of data for **1**, **3** and **10**, becomes



III

$$\text{Frequency} = 152.36 - 0.5455 \times \text{bond length}$$

The R^2 value for this correlation is the very satisfactory 0.9668.

The ^{35}Cl resonance frequencies for three other hydroxy-bridged derivatives of carboxylic acids, pivalic (**2**), trichloracetic (**3**) and tribromacetic acid (**4**), respectively, are also shown in Table 2. All conform to the previous pattern with six narrowly-spaced ^{35}Cl resonances.

For **3** and **4** all ten resonances expected for two antimony sites were also observed and the results are reported in Table 3, together with the corresponding coupling constants and asymmetry parameters. The difference in coupling constant between each site is very marked, particularly as far as the asymmetry parameter is concerned, but such differences for a six-coordinated nucleus are not easily interpreted when the local symmetry is so low.

The last of the hydroxy-bridged compounds reported in Table 2 is the derivative of dichloracetic acid (**5**). Sixteen resonances for the $SbCl_3$ fragments can be seen, two of these are more intense than the others and are thought to consist of two overlapping lines so that eighteen resonances are present in all. This hypothesis is born out by the results for the organochlorine atoms where there are five resonances, one of which is more intense than the others, corresponding again to two overlapping lines. Thus for this compound there are apparently three inequivalent molecules, each containing two distinct $SbCl_3$ groups.

TABLE 3. ^{121}Sb and ^{123}Sb NQR Frequencies and Coupling Constants (MHz at 77 K) of Tricyclic Antimony Chloride Complexes[a]

Compound number	^{121}Sb resonance frequency	^{123}Sb resonance frequency	^{121}Sb coupling constant	Asymmetry parameter
3				
Site I	31.89 43.12	27.48 25.51 40.17	153.9	0.650
Site II	21.92 38.08	16.17 22.48 35.04	129.8	0.350
4				
Site I	32.16 45.40	27.20* 26.72 42.23	160.7	0.601
Site II	20.69 38.95	13.89 23.35 35.70	131.1	0.221
7				
Site I	43.36 58.11	37.60 34.40 54.14	207.6	0.661
Site II	37.38 54.60	31.15 32.04 50.75	192.0	0.563
8				
Site I	40.75 56.56	34.75 33.34 52.63	200.8	0.621
Site II	38.18 59.83	30.57 35.09 55.44	207.7	0.480
9				
Site I	29.57 52.78	21.15 31.32 48.47	179.2	0.310
Site II	31.32 58.65	21.15 35.09 53.70	197.6	0.231

[a] The resonance frequencies are given in the order 1/2–3/2, 3/2–5/2 and, for the ^{123}Sb isotope, 5/2–7/2.

The above pattern of six ^{35}Cl resonance frequencies centered around 27 MHz also obtains for the alkoxy derivatives, and thus completely supports the attribution of the tricyclic structure to these compounds. All three compounds **7**, **8** and **9** show ^{121}Sb and ^{123}Sb resonances which are again very similar to the corresponding resonances for the hydroxy derivatives thus strongly supporting the tricyclic structure with two inequivalent $SbCl_3$ fragments.

The temperature-dependence of the ^{35}Cl resonance frequencies for several of these compounds – as usual, always negative – has been determined in the range 77 K to room temperature and the results fitted to eqn. (1), a second-order polynomial.

$$F = F_0 + AT + BT^2 \qquad (1)$$

The parameters of this equation are also given in Table 2; they are in the range which we have previously observed for a variety of compounds containing Sb—Cl bonds [5].

The ^{35}Cl NQR spectrum of compounds containing the CCl_3 group often fades out as the temperature is increased owing to the onset of internal rotation of the CCl_3 fragment. For the hydroxy-bridged trichloracetic acid derivative these resonances were visible up to 260 K while for the methoxy-bridged compound they disappeared at 200 K. For the ethoxy-bridged molecule ^{35}Cl resonances from the organic fragment could not be observed even at 77 K. Presumably the increasing volume of the substituent on the oxygen bridge decreases the steric hindrance of the CCl_3 group, which is therefore likely to be mainly intermolecular in origin.

Finally Table 2 shows the ^{35}Cl data for two related complexes containing an $SbCl_3$ group in a hexacoordinated environment in which the three other ligands are oxygen atoms (**III**). The frequencies are similar to those of the previous complexes and, in accordance with its crystal structure [7], the acetylacetonate (**10**) shows six distinct resonances whereas in distinction to this the benzoylacetophenone derivative apparently has two equivalent $SbCl_3$ groups.

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