Nuclear Quadrupole Resonance Studies of Chelated Antimony Complexes. Part III. The Carboxylates: RCO_2SbCl_4 *

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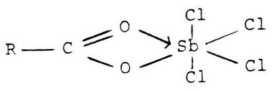
Z. Naturforsch. **41 a,** 179–185 (1986); received July 23, 1985

The ^{35}Cl, ^{121}Sb and ^{123}Sb resonance frequencies for seventeen tetrachloro(carboxylato)antimony V compounds, RCO_2SbCl_4, are reported. The results confirm the difference in the effects of the substituent on the equatorial chlorine atoms and the axial chlorine atoms of the $SbCl_4$ group, previously remarked in Parts I and II of this series, and this effect has been put on a more quantitative basis by correlating the observed frequencies with the pK's of the corresponding acids.

The compounds with R = isopropyl and R = cyclopropyl both show a phase change in the region of 140 K which may correspond to reorientation of the substituent about the $R-CO_2$ axis.

Introduction

Previous articles in this series [1, 2] have shown that the two *trans* chlorine atoms in the $SbCl_4$ fragment ("axial chlorine atoms") are distinguished from the *cis* pair of chlorine atoms, which lie in the plane of the ring system ("equatorial chlorine atoms"), both by their ^{35}Cl resonance frequencies and by the way in which these frequencies vary as a function of the nature of the substituents in the chelate ring. Parts I and II were concerned with five and six-membered rings, respectively, and, in addition to the effect of substituents, they indicated a substantial effect of ring size. We have therefore extended these studies to four-membered ring systems, the carboxylates (I), which have, in addition to the light thrown on the effect of ring size, the merit of providing a wide range of well-defined substituent effects through the possibility of varying the substituent R.



(I)

* Presented at the VIIIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Darmstadt, July 22–26, 1985.

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Experimental

Preparations

The carboxylates were all prepared according to the general method described by Laber and Schmidt [3–5]: the reaction between a suspension of the anhydrous sodium salt of the carboxylic acid in methylene chloride and antimony pentachloride. For the compounds cf. Table 1. Compounds **1–4** and **6–10** were described in these references. Satisfactory mass-spectra and analyses for carbon, hydrogen and chlorine for the previously-unreported compounds, **5** and **11–17** were obtained. The melting points/boiling points of these compounds are:

5 95 °C (b.p., 10^{-2} mm); **11** 125 °C;
12 131 °C; **13** 119 °C; **14** 110 °C;
15 90 °C; **16** 110 °C;
17 95 °C (b.p., 10^{-2} mm).

Nuclear Quadrupole Resonance Spectra

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

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Table 1. ^{35}Cl resonance frequencies (MHz at 77 K) and temperature dependences of the carboxylates. The last column shows the pK of the parent acid measured in water at 25 °C.

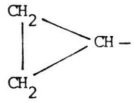
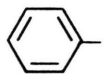
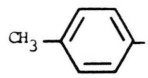
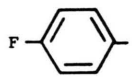
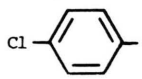
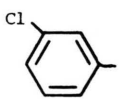
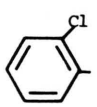
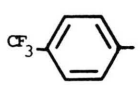
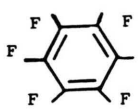
Number	R	Frequency (MHz at 77 K)	Relative intensity	Temperature dependence			pK
				ν_0 (MHz)	A (kHz K^{-1})	B (Hz K^{-2})	
1	CH_3-	25.582	1	25.66	− 0.659	− 4.6	4.75
		25.604	1	25.79	− 0.750	− 4.6	
		26.898	1	27.14	− 2.91	− 2.3	
		27.072	1	27.16	− 0.679	− 4.9	
2	C_2H_5-	25.119	1	25.18	− 0.455	− 4.0	4.87
		25.540	1	25.69	− 1.57	− 2.4	
		26.015	1	26.15	− 1.38	− 3.6	
		26.319	1	26.43	− 0.958	− 5.6	
		26.475	1	26.55	− 0.630	− 4.0	
		26.532	1	26.64	− 0.857	− 5.7	
		27.314	1	27.50	− 2.02	− 3.5	
		27.501	1	27.64	− 1.31	− 4.6	
3	$(CH_3)_2CH-$	25.209	1	25.35	− 1.91	1.4	4.84
		25.448	1	25.34	4.37	−40.0	(17 °C)
		27.075	1	27.33	− 3.17	− 0.2	
		27.434	1	27.65	− 2.43	− 2.2	
4	$(CH_3)_3C-$	25.346	1	25.42	− 0.454	− 7.8	5.03
		25.736	1	25.78	− 0.110	− 9.2	(18 °C)
		27.308	1	27.37	− 0.245	− 8.0	
		27.650	1	27.74	− 0.590	− 8.6	
5		25.075	1				4.83
		25.314	1				
		25.577	1				
		25.889	1				
		25.947	1				
		25.981	1				
		26.020	1				
		26.091	1				
		26.475	1				
		26.585	1				
		26.737	1				
		26.932	1				
		27.131	1				
		27.242	1				
		27.440	1				
6	CH_2Cl-	26.087	2				2.85
		26.275	2				
		26.284	2				
		26.750	1				
		27.377	2				
		27.560	2				
		27.744	1				
		38.498	2				
		39.185	1				
7	$CHCl_2-$	26.161	2				1.48
		27.660	1				
		28.280	1				
		39.470					
8	CCl_3-	27.075	1	27.16	− 0.735	− 3.8	0.70
		27.309	1	27.44	− 1.29	− 4.7	
		27.781	1	27.86	− 1.06	− 4.1	
		27.781	1	27.95	− 2.02	− 2.6	
		41.078	1	41.08	− 1.72	−11	
		41.111	1	41.26	− 1.10	−11	
		41.519	1	41.72	− 1.66	− 9.3	

Table 1 (continued)

Number	R	Frequency (MHz at 77 K)	Relative intensity	Temperature dependence			pK
				ν_0 (MHz)	A (kHz K^{-1})	B (Hz K^{-2})	
9	CF_3-	27.408	1				0.23
		27.858	1				
		27.950	1				
		28.011	1				
10		25.494	1	25.59	− 1.04	− 1.8	4.19
		27.250	1	27.42	− 2.01	− 2.0	
11		25.292	1	25.39	− 1.07	− 2.5	4.36
		25.938	1	26.02	− 0.798	− 2.9	
		27.052	1	27.15	− 0.999	− 3.4	
		27.692	1	27.84	− 1.62	− 2.6	
12		25.484	1	25.54	− 0.461	− 2.4	4.18
		25.680	1	25.77	− 0.901	− 2.1	
		27.084	1	27.19	− 1.26	− 1.8	
		27.221	1	27.34	− 1.40	− 2.2	
13		25.541	1	25.66	− 1.39	− 1.1	
		26.108	1	26.24	− 1.58	− 0.5	3.98
		27.143	1	27.33	− 2.22	− 0.0	
		27.748	1	27.94	− 2.27	− 0.4	
		35.243		35.45	− 2.43	− 0.3	
14′		25.190		24.83	− 0.183	− 1.4	3.82
		25.860		26.28	− 1.05	− 2.3	
		27.504		27.20	− 1.59	− 2.0	
		27.703		27.98	− 1.83	− 2.4	
		35.977		35.95	− 1.15	− 4.6	
14″		24.810	1				
		26.200	1				
		27.058	1				
		27.810	1				
		35.826					
15		24.759	1				2.92
		25.597	1				
		27.698	1				
		27.826	1				
		37.015					
16		25.136		25.17	− 0.166	− 4.5	3.5*
		25.822	1	25.93	− 1.04	− 3.2	
		27.143	1	27.28	− 1.39	− 4.6	
		27.830	1	27.97	− 1.37	− 4.3	
17		25.799	1				
		26.168	1				1.75
		27.934	1				
		28.295	1				

* Estimated from the pK of 4.94 measured in 50% ethanol. In this solvent the pK of benzoic acid is 5.71.

Results and Discussion

^{35}Cl Resonance Frequencies

The ^{35}Cl resonance frequencies, measured at 77 K, of the various carboxylates are shown in Table 1. For the 3-chlorobenzoate (**14**) two distinct phases were observed, **14′** transforming slowly to **14″** in the course of a few days. Most of the compounds showed four resonance frequencies corresponding to each of the four distinct chlorine atoms on the $SbCl_4$ fragment. The benzoate (**10**) shows just two frequencies indicating that the molecule retains its maximum intramolecular symmetry within the crystal lattice, while the propionate (**2**), the monochloracetate (**6**) and the cyclopropane carboxylate (**5**) have more than four resonances indicating that, for these compounds, the unit cell contains more than one distinct molecule. For the monochloroacetate this multiplicity of crystal sites is also reflected in the two resonance frequencies of the organochlorine nucleus. Furthermore, one of the sites seems, on the basis of intensity measurements, to be twice as abundant as the other, and in addition the least abundant species has an element of symmetry such that the two high-frequency resonances (equatorial chlorines) are equivalent. This implies that, for this species, the carbon chlorine bond lies in the plane bisecting the $Cl_{eq}SbCl_{eq}$ angle.

The temperature dependence of these frequencies was determined in the range 77 K to room temperature. All were, as usual, negative and, with the exception of **3** and **5** which revealed a phase change (Fig. 1), were continuous. Differential thermal analysis confirmed that for the propionate the phase change is second order. The temperature dependences were fitted to a second order polynomial

$$\nu = \nu_0 + AT + BT^2 \qquad (1)$$

and the parameters of this polynomial for each frequency are also shown in Table 1.

One of the major difficulties in interpreting NQR frequencies is the unpredictable effect of the neighbouring molecules, clearly exemplified by the multiple resonances for **2**, **5**, **6** and **14**. The only way of overcoming this is to study a series of compounds which are sufficiently similar for the scatter in the resonance frequencies to be due mainly to solid state effects and thus permit their proper statistical

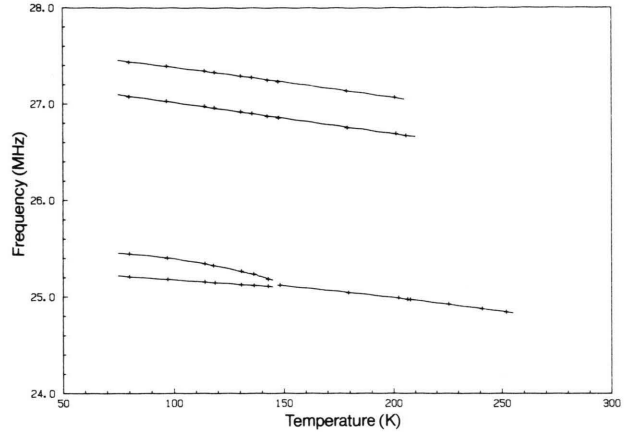


Fig. 1. The temperature dependence of the ^{35}Cl resonance frequencies of **3**.

evaluation. It is thus necessary to select from the 17 carboxylates shown here those for which the effects of the substituent on the properties of the carboxylate group are sufficiently similar for them to be neglected.

The electronic effect of the carboxylate groups can be characterized in a variety of ways, the most straightforward of which is without doubt the dissociation constant of the parent acid. Also shown in Table 1 is, therefore, the pK of the acid, measured in aqueous solution at 25 °C. The pK's shown in Table 1 range from 0.23 to 5.03. The pK's of acetic acid and benzoic acid are very similar, as indeed are those of all the aliphatic acids which do not contain a heteroatomic substituent, together with most of the *para*-substituted benzoic acids. We have therefore grouped together the results for compounds **1** to **5** and **10** to **13**, covering a pK range of 3.98 to 5.03, and present them in the form of a histogram in Figure 2. The double peak, separated by 1.7 MHz, in the distribution is clearly visible, and, as in Parts I and II, we attribute this to the difference between axial chlorine atoms and equatorial chlorine atoms.

No crystal structures of the carboxylates are available, so that the correlation with bond-length of Parts I and II is not possible here. We have, however, succeeded in performing a Zeeman study of a large single crystal of the pivalic acid derivative, **4** [6], which has shown that the two lower frequencies are to be attributed to the axial chlorine atoms. It is therefore assumed that, as in the previous series, the

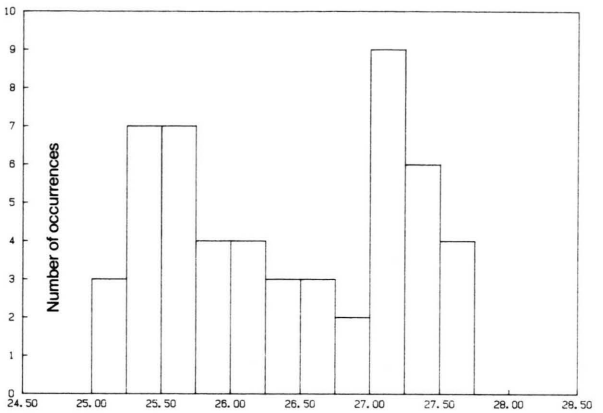


Fig. 2. The distribution of the ^{35}Cl resonance frequencies, measured at 77 K, for the compounds **1** to **5** inclusive and **10–13** inclusive, where the substituent has an electronic effect not markedly different from the methyl group (see text).

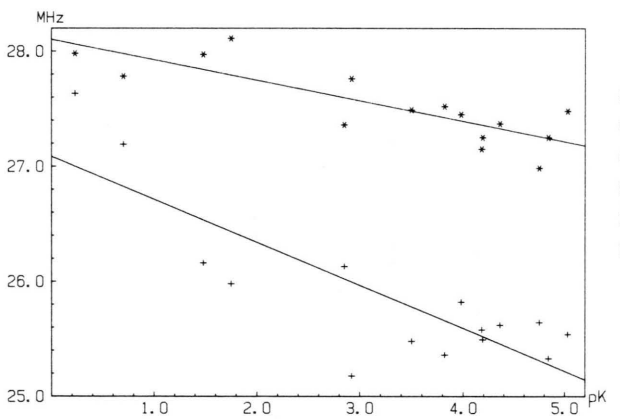
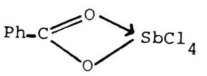
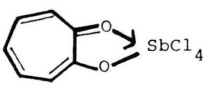
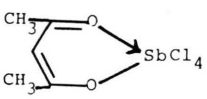


Fig. 3. The relationship between the pK of the parent acid, measured in aqueous solution at 25 °C, and the average value of the high frequency and low frequency resonances.

axial chlorine atoms have the lower and the equatorial atoms the higher frequencies.

For the compounds studied in Parts I and II the addition of electronegative substituents to the ring fragment increased all the ^{35}Cl resonance frequencies, but those of the axial chlorine atoms much more than those of the equatorial chlorine atoms, with the result that the axial/equatorial spread was considerably reduced. Inspection of the results in Table 1 shows that qualitatively this same phenomenon occurs for the carboxylates. In Fig. 3 the average frequencies of the axial chlorine atoms

Table 2. The effect of ring size on the ^{35}Cl resonance frequencies (MHz at 77 K).

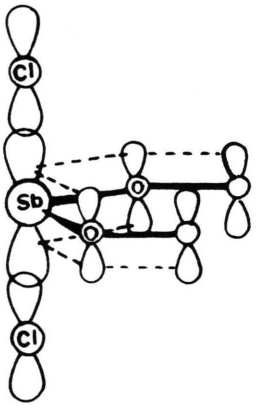
Molecule	*n*	^{35}Cl resonance frequencies (MHz at 77 K)	
		axial	equatorial
	4	25.494	27.250
	5	23.350	26.259
	6	24.272	25.776

and the average frequencies of the equatorial chlorine atoms are plotted as functions of the pK's of the parent acids. The different effect of the substituent on the axial and equatorial frequencies is clearly revealed. The two regression lines are respectively

$$\nu_{ax} = 27.085 - 0.373 \cdot pK$$
(correlation coefficient = 0.83);

$$\nu_{eq} = 28.101 - 0.177 \cdot pK$$
(correlation coefficient = 0.83). (2)

In Table 2 is shown the effect of ring size on the resonance frequencies, using the value of the benzoate reported here as being typical of a fairly neutral substituent together with that of the tropolonate (1) as a representative of a five-membered ring and the acetylacetonate (2) for the six-membered ring. The effect of ring size on the axial and equatorial frequencies is completely different. The equatorial resonance frequencies decrease regularly with increasing ring size whereas the axial resonances exhibit an alternating behaviour in the series shown here. This alternation in the axial resonance frequencies tends to support the suggestion made in Part II that there is a conjugation between the pi-system of the ring and the 5p orbitals of the antimony atom, which contribute to the bonding of the axial chlorine atoms (II).



(II)

$^{121,123}Sb$ *Resonance Frequencies*

Resonances ascribable to the antimony nuclei are, in our experience, much less intense than those arising from the ^{35}Cl nuclei, and these compounds are no exception inasmuch as only half the compounds reported in Table 1 show any signs of them. For each distinct molecular site, five resonances, three from ^{123}Sb with $I = 7/2$ and two from ^{121}Sb with $I = 5/2$, may be expected. Owing to the higher natural abundance of the ^{121}Sb nucleus (57.25%), its higher magnetic moment (3.34 nuclear magnetons compared to 2.53 for ^{123}Sb) and its lower spin, the two resonances for ^{121}Sb are always notably more intense than any of the three arising from ^{123}Sb, and, of these, that corresponding to the transition $5/2 \leftrightarrow 7/2$ is always the weakest. These facts have the consequence that, even when antimony resonances are observed, it is often not possible to observe all five of them. The observation of three resonances, however, yields an unambiguous assignment of the coupling constant, and even when only two weak resonances can be seen there can usually be but little hesitation in ascribing them to the ^{121}Sb nucleus.

The antimony resonances collected in Table 3 have been assigned in this way. As for the results reported in Parts I and II, they cover both a wide range of coupling constants (78.8 MHz to 145.8 MHz for the ^{121}Sb nucleus) and of asymmetry parameters (0.192 to 0.537). Perhaps most striking is the difference between the asymmetry parameters of the two sites in the propionate (0.293 and 0.455). However as shown in Part I, the antimony coupling tensor of such hexacoordinated species is particularly sensi-

Table 3. $^{121,123}Sb$ resonance frequencies (MHz at 77 K) and the corresponding coupling constants and asymmetry parameters.

Comp. Nr.	Frequency (MHz)	Assignment	η (±0.002)	$\lvert eQV_{zz}\rvert$ (±0.3 MHz)
1	10.03	^{123}Sb (1/2 → 3/2)		
	14.88	^{121}Sb (1/2 → 3/2)		^{121}Sb: 94.0
	16.70	^{123}Sb (3/2 → 5/2)	0.228	
	25.58	^{123}Sb (5/2 → 7/2)		^{123}Sb: 119.9
	27.92	^{121}Sb (3/2 → 5/2)		
	Site I			
2	12.37	^{123}Sb (1/2 → 3/2)		
	17.45	^{121}Sb (1/2 → 3/2)		^{121}Sb: 106.8
	18.69	^{123}Sb (3/2 → 5/2)	0.293	
	28.97	^{123}Sb (5/2 → 7/2)		^{123}Sb: 136.2
	31.49	^{121}Sb (3/2 → 5/2)		
	Site II			
	13.81	^{123}Sb (1/2 → 3/2)		
	16.58	^{123}Sb (3/2 → 5/2)		^{121}Sb: 97.7
	17.59	^{121}Sb (1/2 → 3/2)	0.455	
	26.21	^{123}Sb (5/2 → 7/2)		^{123}Sb: 124.7
	28.24	^{121}Sb (3/2 → 5/2)		
4	8.09	^{123}Sb (1/2 → 3/2)		
	12.30	^{121}Sb (1/2 → 3/2)		^{121}Sb: 78.8
	14.11	^{123}Sb (3/2 → 5/2)	0.192	
	21.49	^{123}Sb (5/2 → 7/2)		^{123}Sb: 100.7
	23.49	^{121}Sb (3/2 → 5/2)		
	Site I			
6	19.11	^{123}Sb (1/2 → 3/2)		
	20.32	^{123}Sb (3/2 → 5/2)		^{121}Sb: 121.3
	23.19	^{121}Sb (1/2 → 3/2)	0.537	
	32.16	^{123}Sb (5/2 → 7/2)		^{123}Sb: 154.7
	34.65	^{121}Sb (3/2 → 5/2)		
	Site II			
	18.24	^{123}Sb (1/2 3/2)		
	19.88	^{123}Sb (3/2 → 5/2)		^{121}Sb: 118.4
	22.33	^{121}Sb (1/2 → 3/2)	0.518	
	31.45	^{123}Sb (5/2 → 7/2)		^{121}Sb: 151
	33.92	^{121}Sb (3/2 → 5/2)		
8	21.67	^{123}Sb (1/2 → 3/2)		
	24.59	^{123}Sb (3/2 → 5/2)		^{121}Sb: 145.8
	26.95	^{121}Sb (1/2 → 3/2)	0.489	
	38.85	^{123}Sb (5/2 → 7/2)		^{123}Sb: 185.9
	41.95	^{121}Sb (3/2 → 5/2)		
10	12.9			
11	13.89	^{121}Sb (1/2 → 3/2)	0.394	^{121}Sb: 80.0
	23.34	^{121}Sb (3/2 → 5/2)		
12	9.77	^{123}Sb (1/2 → 3/2)		
	14.27	^{121}Sb (1/2 → 3/2)		^{121}Sb: 89.1
	15.74	^{123}Sb (3/2 → 5/2)	0.251	
	24.18	^{123}Sb (5/2 → 7/2)		^{123}Sb: 113.5
	26.40	^{121}Sb (3/2 → 5/2)		

Table 4. Temperature dependence of the principal values of the quadrupole coupling tensors of the ^{121}Sb nucleus (the absolute signs of the principal values of the coupling tensor are indetermined).

Compound number	Component	$e^2 Qq_i$ (MHz)	A_i (kHz K^{-1})	B_i (Hz K^{-2})
2 Site I	eQV_{XX}	− 37.7	0.032	5.2
	eQV_{YY}	− 69.7	7.76	− 20
	eQV_{ZZ}	107.4	− 7.77	− 14
Site II	eQV_{XX}	− 25.6	− 17.0	29
	eQV_{YY}	− 72.4	19.2	− 6.7
	eQV_{ZZ}	98.0	− 2.20	− 22
4	eQV_{XX}	− 30.8	− 14.6	16
	eQV_{YY}	− 47.6	9.56	− 15
	eQV_{ZZ}	78.5	5.20	− 2.1
12	eQV_{XX}	− 32.4	− 10.4	− 2.3
	eQV_{YY}	− 55.7	− 2.4	+ 7.4
	eQV_{ZZ}	88.1	13.2	− 6.1

tive to small molecular deformations, and this is certainly the explanation of the wide variations in these parameters. In these circumstances any prolonged discussion of the antimony coupling constants is inappropriate, particularly since the signs of the coupling constants are unknown.

The temperature dependence of the antimony resonances has been determined for some of the compounds shown in Table 3. The resultant values of the principal values of the coupling tensors were fitted to a second order polynomial

$$e^2 Qq_i = e^2 Qq_{0i} + A_i T + B_i T^2; \quad i = xx, yy, zz. \quad (3)$$

The results are shown in Table 4. Both positive and negative values for the temperature dependence of $e^2 Qq_{zz}$ can be seen in Table 4, and this implies that intramolecular vibrations of one sort or another contribute strongly to the temperature dependence.

Conclusion

The distinction between the ^{35}Cl NQR frequencies of axial and equatorial chlorine atoms in these chelated complexes is confirmed, as is their different susceptibility to the nature of the chelate ring. As before, the antimony NQR parameters scatter widely, as expected for hexacoordinated antimony nuclei.

We thank C.-F. Matthey and P. Richert for their help with the chemical syntheses. – We thank the Swiss National Research Fund for their support.

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