Vibrational and Chlorine-35 Nuclear Quadrupole Resonance Spectra of Some Complexes of ICl_4^- and $AuCl_4^-$. Part 1. Two Crystal Modifications of Trichlorosulphonium Tetrachloroiodate, $[SCl_3][ICl_4]$

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Two crystal modifications of $[SCl_3][ICl_4]$ have been characterised by elemental analysis, and Raman and n.q.r. spectroscopy. Analysis of the spectra indicates that both form I (stable) and form II (metastable) involve distortion from square planarity (D_{4h}) of the ICl_4^- ions, a conclusion independently confirmed recently by an *X*-ray diffraction study of form I. On the basis of the Raman and n.q.r. spectra, the distortion in form II is similar to that observed in $Na[ICl_4]\cdot 2H_2O$. The origins of these distortions are discussed in terms of secondary bonding interactions in the solid state.

IN a preliminary communication [1] Raman spectra of two crystalline modifications of a compound of empirical formula $SICl_7$ were presented. In the following text these two modifications are identified by the labels form I (stable species) and form II (metastable). Using simple site-group analysis (s.g.a.) an ionic formulation, $[SCl_3]$-$[ICl_4]$, was assigned for each modification. This interpretation is at variance with a previous analysis [2] of a Raman spectrum identical to that obtained from the form I isolated in the present work. In the previous study [2] the Raman spectrum was interpreted on the basis of a mixed crystal of $[SCl_3][ICl_2]$ and a novel species $SICl_3$. In the present paper, solid-state vibrational spectra are analysed in greater detail, aided by a recent *X*-ray diffraction study of the stable modification of $SICl_7$; [3] these, and ^{35}Cl n.q.r. spectra, are presented and discussed in relation to the distortion of the square-planar species.

EXPERIMENTAL

Preparations.—Form I of $[SCl_3][ICl_4]$ was prepared by chlorination of a finely ground mixture of iodine (1 g) and sulphur (1 g) in the absence of moisture. Chlorination was continued until all the excess of SCl_2 was displaced. Orange crystals were formed (Found: Cl, 60.7; I, 31.45. Calc. for $SICl_7$: Cl, 60.95; I, 31.15%). On a few occasions the product was contaminated with form II. Form II was obtained exclusively by dissolution of freshly prepared I_2Cl_6 in excess of SCl_2 followed by saturation with chlorine. Excess of SCl_2 was removed by decantation and the orange crystals dried in a current of dry chlorine (Found: Cl, 60.95; I, 31.0%).

Spectra.—Raman spectra were recorded on solid samples in sealed thin glass tubes using a Coderg PHO Raman spectrometer with 647.1-nm laser (krypton) excitation. Low-temperature spectra were measured in a cold cell controlled by a Beckmann RIIC proportional temperature system. Infrared spectra in the range 200—300 cm^{-1} were obtained from crushed crystals contained between Polythene plates using a Perkin-Elmer 325 spectrometer. N.q.r. spectra were recorded on a mid-range Decca spectrometer (5—55 MHz) using Zeeman modulation. Resonances were measured at 77 K and room temperature. Resonant frequencies were determined with an accuracy of ± 10 kHz by interpolation between the frequency markers which were calibrated by means of a frequency counter (Advance Instruments, TC16).

RESULTS AND DISCUSSION

Interconversion of the two crystal modifications of $[SCl_3][ICl_4]$ is of particular interest. Both exist as solids only under their own vapour pressures or in a chlorine atmosphere. Form II is exclusively precipitated when a homogeneous solution of either (*a*) form I or (*b*) I_2Cl_6 in SCl_2 is saturated with chlorine. Complete conversion into form I occurs on standing at room temperature for several weeks. This change is physically irreversible so that form I is regarded as the thermodynamically stable species and II the metastable modification. Heating form II in a sealed tube to *ca.* 60 °C results in decomposition to liquid SCl_2, chlorine gas, and iodine chlorides. A pure sample of form I separates again, but only on prolonged standing.

Raman shifts and ^{35}Cl n.q.r. frequencies for both modifications are summarised in Tables 1—3. Solid-state spectra have been reported for a variety of SCl_3^+ salts [4—6] but few detailed analyses for solid ICl_4^- compounds have been made. In particular, no analyses of ICl_4^- ions in low-symmetry environments are available. An isolated SCl_3^+ species belonging to the C_{3v} point group possesses four observable normal modes of vibration ($2A_1 + 2E$) all active in both i.r. and Raman. Characteristic Raman shifts for some SCl_3^+ compounds are listed in Table 1 including solid-state splittings for the doubly degenerate modes. Bands of comparable relative intensities are observed in the spectra of both forms I and II of $[SCl_3][ICl_4]$ with the symmetric stretching mode at *ca.* 280 cm^{-1} accidentally coincident with ICl stretching modes in each case. The SCl stretching modes occur at considerably lower frequencies than in other SCl_3^+ salts, however, approaching those in SCl_4 (Table 1). The structure of the latter is now believed [7] to resemble closely that of solid $SeCl_4$ and $TeCl_4$ [8] with discrete SCl_3^+ units linked by bridging chloride ions.

This is consistent with some significant anion–cation interaction in both modifications of $[SCl_3][ICl_4]$ (see below).

The remaining bands in both spectra may be ascribed to ICl_4^- ions. An isolated ICl_4^- species with D_{4h} symmetry will possess six observable modes of vibration: three (A_{1g}, B_{1g}, and B_{2g}) Raman-active only, three (A_{2u} and $2E_u$) i.r. active only, and one inactive (B_{2u}) mode. If ICl_4^- ions occupy lattice sites of low symmetry the degeneracies may be lifted and, in the limiting case, nine Raman-active fundamentals would be predicted. Vibrational data for most other ICl_4^- compounds [9,10] are consistent with retention of the centre of symmetry. In a detailed investigation of solid $Cs[ICl_4]$,[11] factor-group splittings were detected at high resolution but, because both the site symmetry (C_{2h}) and the unit-cell group (D_{3h}) of ICl_4^- are centrosymmetric, the Raman spectrum at low resolution might otherwise be interpreted simply in terms of D_{4h} point-group symmetry. The two Raman-active I–Cl stretching modes in $Cs[ICl_4]$ and other salts are observed at *ca.* 260 and 280 cm^{-1}. In form II of $[SCl_3][ICl_4]$ two strong I–Cl stretching modes are observed at similar frequencies, but in form I these modes are shifted to 282 and 296 cm^{-1} respectively. The strong similarity between the Raman frequencies due to ICl_4^- in form I of $[SCl_3][ICl_4]$ and those in $K[ICl_4]\cdot H_2O$ has already been noted.[1] Also, in both form I and $K[ICl_4]\cdot H_2O$ weak Raman bands, in addition to the two strong Raman stretching bands expected for a D_{4h} species, are observed at similar wavenumbers to those in the i.r. spectra of other ICl_4^- salts.[1] It was very difficult to obtain i.r. spectra for the $[SCl_3][ICl_4]$ species but a spectrum of form I in the range 220—350 cm^{-1} showed coincident absorptions for all the Raman shifts in the region, consistent with the absence of the centre of symmetry.

TABLE 1

Solid-state Raman shifts (cm^{-1}) of the SCl_3^+ ion in various complexes

Mode (based on C_{3v} point group)	$[SCl_3][AlCl_4]$ (ref. 4)	$[SCl_3][SbCl_6]$ (ref. 5)	$[SCl_3][SO_3Cl]$ (ref. 6)	SCl_4 (ref. 7)	Form I	Form II
$\nu_1(A_1)$	494	501	509	449	485	482
$\nu_2(A_1)$	271	280	282	281	279	282
$\nu_3(E)$	516	524	519	471	498	496
	530	535	526		512	510
$\nu_4(E)$	206	210	221	?	212	205
			228		220	218

Form I crystallises with the $P2_1/c$ (C^5_{2h}) space group with four molecules per unit cell.[3] Both sulphur and iodine are located on C_1 sites. At the moderate resolution employed the Raman spectrum can be adequately explained on the basis of site-group analysis. Considerable overlap among the external modes precluded complete identification of the 12 predicted (s.g.a.) bands. Assignments are listed in Table 2.

TABLE 2

Solid-state Raman shifts (cm^{-1}) of the ICl_4^- ion in forms I and II of $[SCl_3][ICl_4]$, $K[ICl_4]\cdot H_2O$, and $Na[ICl_4]\cdot 2H_2O$

Free ion D_{4h}	Site group (form I) C_1	Form I at 130 K	$K[ICl_4]\cdot H_2O$	Approximate description	Form II * at 130 K	$Na[ICl_4]\cdot 2H_2O$ at 130 K
A_{1g}	A	300vs	291s	ν(ICl)	284vs	289s
B_{1g}	A	146m	135 146 (sh)	δ(ClICl)	144mw	142mw
B_{2g}	A	282vs	271s	ν(ICl)	260s	268s
A_{2u}	A	152w (sh)	152w	δ(ClICl)	155w	153vw
B_{2u}	A	?	?		?	?
E_u	A	258mw	248m	ν(ICl)	250w	248vw
	A	247m	212w	ν(ICl)	228w	235vw
E_u	A	128w	122w	δ(ClICl)	130w	138vw
	A	113w	114vw	δ(ClICl)	114w	120vw

* Site group unknown.

The ICl_4^- ion in $K[ICl_4]\cdot H_2O$ is shown to be very distorted; a crystal-structure determination has shown that the I–Cl bond lengths are all different, ranging from 242 to 260 pm.[12] The room-temperature ^{35}Cl n.q.r. spectrum is consistent with this pattern, showing four lines at widely separated frequencies from 28.17 to 16.84 MHz.[13] The distortion from D_{4h} symmetry was attributed to electrostatic cation–anion interactions, since there are more potassium ions close to the chlorine at the longest distance from the iodine than to any of the others, and hydrogen bonding appeared to be unimportant in determining the stereochemistry of the ICl_4^- ion.[12] It follows, therefore, that the shift of I–Cl stretching modes to higher frequency may arise from strong anion–cation association in a non-covalent lattice, *i.e.* from a secondary bonding interaction of the type described by Alcock.[14] On the basis of this theory, it would appear that the secondary bonding interaction in form II of

$[SCl_3][ICl_4]$ is appreciably weaker than in form I, since the Raman-active I–Cl stretching vibrations of form II occur at normal frequencies.

In order to test this hypothesis, the ^{35}Cl n.q.r. spectra of forms I and II were measured at 77 K and room temperature. Ions ICl_4^- with D_{4h} symmetry are expected to exhibit either a single ^{35}Cl resonance frequency if all anions within the unit cell are equivalent (as found for anhydrous $K[ICl_4]$),[15] or a group of closely spaced lines if there are crystallographically distinct types of ICl_4^- ions present. The average frequency at ambient temperatures is *ca.* 22.35 MHz.[16] Unequal distortion of the ICl_4^- ion as a result of cation–anion interactions would result in each different type of chlorine nucleus experiencing a different electric field gradient, and hence up to four ^{35}Cl n.q.r. lines (or groups of lines due to crystallographic effects) would be observed, possibly at widely differing frequencies depending on the extent of the distortion. As mentioned above, $K[ICl_4]\cdot H_2O$ shows particularly marked splitting, with four ^{35}Cl n.q.r. lines spread over *ca.* 13 MHz.[13] Nevertheless the mean frequency is very close to that found in the symmetrical ions, suggesting that the positive and negative deviations of the electric field gradients are also averaged out to a considerable degree.[16] Similar behaviour has been observed in tetrachloroaurates,[16] which are often structurally related to tetrachloroiodates.

TABLE 3

Chlorine-35 n.q.r. frequencies (MHz) for forms I and II of $[SCl_3][ICl_4]$, $K[ICl_4]\cdot H_2O$, and $Na[ICl_4]\cdot 2H_2O$

	$[SCl_3][ICl_4]$ (Form I)		$K[ICl_4]\cdot H_2O$ (ref. 13)		$[SCl_3][ICl_4]$ (Form II)		$Na[ICl_4]\cdot 2H_2O$ (ref. 19)	
	296 K	77 K	296 K	77 K	296 K	77 K	296 K	77 K
ICl_4^-	15.30	14.85	16.85	16.95	19.80	20.07	20.574	20.010
	20.54	20.95	20.15	20.25	21.65	21.58	22.184	22.656
	25.57	25.90	24.85	24.90	22.90	23.53	22.896	23.251
	27.47	28.12	28.18	28.28	24.95	25.25	23.281	23.827
mean	22.22	22.46	22.51	22.60	22.33	22.61	22.234	22.436
SCl_3^+	41.818	42.637			41.80	42.90		
	41.367	42.091			41.35	42.45		
	40.753	41.726			40.75	41.80		
mean	41.313	42.151			41.30	42.38		

Form I of $[SCl_3][ICl_4]$ shows four ^{35}Cl n.q.r. signals from the anion, at similar frequencies to those from $K[ICl_4]\cdot H_2O$; this result strongly supports the supposition that the anions are distorted, and that the structures may be similar. There is one distinct difference, however; the lowest-frequency resonance from form I at *ca.* 15 MHz has an anomalous positive temperature coefficient, whereas the lines from $K[ICl_4]\cdot H_2O$ all show a normal temperature dependence. The lowest-frequency ^{35}Cl n.q.r. signals from both $Na[ICl_4]\cdot 2H_2O$ and $Na[AuCl_4]\cdot 2H_2O$ also exhibit a positive temperature coefficient, which was attributed to strong hydrogen bonding between this chlorine and a water molecule.[17–19] In $K[ICl_4]\cdot H_2O$, on the other hand, it is believed that the contribution of water molecules to the strong low-symmetry electric field created at ICl_4^- sites is slight,[12,13] and this effect was not observed. Hydrogen bonding is not possible in $[SCl_3][ICl_4]$, and the anomalous temperature coefficient of the lowest ^{35}Cl n.q.r. frequency is almost certainly due to a strong secondary covalent-bonding interaction between sulphur and one of the chlorines in ICl_4^-, which is present at both 77 K and room temperature, in agreement with the conclusions from the Raman spectroscopic data. The ^{37}Cl resonances corresponding to the three highest-frequency signals from the anion were also observed, although of low intensity.

With form II of $[SCl_3][ICl_4]$, four ^{35}Cl resonances from the anion are again observed, but spread over a narrower frequency range (Table 3). The pattern resembles to some extent the splitting observed in $Na[ICl_4]\cdot 2H_2O$.[17] The lowest ^{35}Cl resonance frequency does not show an anomalous temperature coefficient in this case, consistent with the hypothesis that the secondary bonding interaction is much weaker than in form I, as is the much smaller spread of frequencies. Nevertheless, the n.q.r. results show clearly that the ICl_4 ion does not have full D_{4h} symmetry in this modification either. It has been noted previously that, from the limited crystallographic data available, there appears to be a close correlation between bond length and ^{35}Cl n.q.r. frequency in tetrachloroiodates.[16] On this basis, it is predicted that form II should have four unequal I–Cl bond lengths in the anion, ranging from *ca.* 247 to *ca.* 255 pm. The ^{37}Cl resonance corresponding to the highest-frequency line only was detected in this instance since the run was terminated at 18.7 MHz.

Three ^{35}Cl resonances were observed from the SCl_3^+ cation in both modifications of the compound (Table 3). The frequencies closely resemble those reported from the SCl_3^+ cation in $[SCl_3][SbCl_6]$ [20] and other SCl_3^+ salts.[21]

The good agreement between the spectroscopic predictions and the subsequent *X*-ray diffraction results [3] leads to confidence in the conclusions from further work (in preparation) on secondary bonding interactions in some related compounds of the types $[ACl_3][MCl_4]$ (A = S, Se, or Te; M = I or Au).

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REFERENCES

[1] A. Finch, P. N. Gates, and T. H. Page, *Inorg. Chim. Acta*, 1977, **25**, L49.

[2] Y. Tavares Forneris and R. Forneris, *J. Mol. Structure*, 1975, **24**, 205.

[3] A. J. Edwards, *J.C.S. Dalton*, 1978, 1723.

[4] H. E. Doorenbos, J. C. Evans, and R. O. Kagel, *J. Phys. Chem.*, 1970, **74**, 3385.

[5] H. Gerding and D. J. Stufkens, *Rev. Chim. Minérale*, 1969, **6**, 795.

[6] H. Gerding, D. J. Stufkens, and H. Gijben, *Rec. Trav. Chim.*, 1970, **89**, 619.

[7] M. Feuerhahn and R. Minkwitz, *Z. anorg. Chem.*, 1976, **426**, 247.

[8] B. Buss and B. Krebs, *Angew. Chem. Internat. Edn.*, 1970, **9**, 463.

[9] H. Stammreich and R. Forneris, *Spectrochim. Acta*, 1960, **16**, 363.

[10] J. P. Huvenne and P. Legrand, *Canad. J. Spectroscopy*, 1972, **17**, 105.

[11] J. P. Huvenne, B. Boniface, F. Wallart, and P. Legrand, *Spectrochim. Acta*, 1975, **A31**, 1937.

[12] R. J. Elema, J. L. de Boer, and A. Vos, *Acta Cryst.*, 1963, **16**, 243.

[13] B. P. Cozzini, *Diss. Abs.*, 1966, **B27**, 1850.

[14] N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.

[15] Y. Kurita, D. Nakamura, and N. Nayakawa, *J. Chem. Soc. Japan, Pure Chem. Sec.*, 1958, **79**, 1093.

[16] K. B. Dillon and T. C. Waddington, *Inorg. Nuclear Chem. Letters*, 1978, **14**, 415.

[17] C. W. Fryer and J. A. S. Smith, *J. Chem. Soc. (A)*, 1970, 1029.

[18] A. Sesane, T. Matuo, D. Nakamura, and M. Kubo, *J. Magn. Reson.*, 1971, **4**, 257.

[19] A. Sasane, T. Matuo, D. Nakamura, and M. Kubo, *Bull. Chem. Soc. Japan*, 1970, **43**, 1908.

[20] R. M. Hart, M. A. Whitehead, and L. Krause, *J. Chem. Phys.*, 1972, **56**, 3038.

[21] P. Gilmore, R. J. Lynch, and T. C. Waddington, unpublished work.