Vibrational and Nuclear Quadrupole Resonance Spectra of Some Complexes of ICl_4^- and $AuCl_4^-$. Part 2.[1] Trichlorochalcogen Tetrachloroaurates $[ACl_3][AuCl_4]$ (A = S, Se, or Te)

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Analysis of solid-state vibrational and ^{35}Cl n.q.r. spectra of the isomorphous compounds $[SCl_3][AuCl_4]$ and $[SeCl_3][AuCl_4]$ indicates that the $AuCl_4^-$ ion is considerably distorted from D_{4h} symmetry. *X*-Ray powder patterns show that $[TeCl_3][AuCl_4]$ adopts a different crystal structure, and n.q.r. and vibrational spectra are consistent with a less severe distortion of the $AuCl_4^-$ ion. The origin of the distortions is discussed in terms of possible secondary bonding interactions in the crystals.

Recent work has revealed some unusual effects in the vibrational and n.q.r. spectra of trichlorosulphonium tetrachloroiodate, $[SCl_3][ICl_4]$ which can exist in two distinct crystal modifications at room temperature.[1] Subsequent attempts to prepare $SeCl_3^+$ and $TeCl_3^+$ tetrachloroiodates all proved unsuccessful, but we now report an investigation of the tetrachloroaurate analogues $[ACl_3][AuCl_4]$ (A = S, Se, or Te). Some n.q.r. data for these complexes have been reported presiously [2,3] but our conclusions, based on more extensive results including vibrational spectra, differ in several important respects. The $AuCl_4^-$ ion appears to be highly distorted from D_{4h} symmetry in $[SCl_3][AuCl_4]$ and $[SeCl_3][AuCl_4]$, similar to the ICl_4^- ion in $[SCl_3][ICl_4]$ (form I),[1,4] and consistent with *X*-ray powder photographs which have shown that these three compounds are isomorphous. The $AuCl_4^-$ ion in $[TeCl_3][AuCl_4]$, although asymmetric as indicated by the spread of n.q.r. frequencies, is less severely distorted, and this compound adopts a different crystal structure.

Experimental

Materials.—All the compounds were moisture sensitive and manipulations were carried out in a nitrogen-filled dry-box. $[SCl_3][AuCl_4]$ was prepared by reaction of Au_2Cl_6 with excess SCl_2 in a current of dry Cl_2 at 60 °C until the initial yellow precipitate was free from particles of gold. Excess SCl_2 was decanted and the yellow solid dried in a current of dry Cl_2 (Found: Cl, 52.0; Au, 40.9. Calc. for $AuCl_7S$: Cl, 52.0; Au, 41.3%). $[SeCl_3][AuCl_4]$ was prepared using a method modified from a previous report,[5] namely heating under reflux a homogeneous solution of Au_2Cl_6 and $SeCl_4$ in $AsCl_3$–$POCl_3$ with passage of dry chlorine. The resulting orange crystals were separated by decantation, washed with SO_2Cl_2 and dried in a current of dry chlorine (Found: Cl, 47.0. Calc. for $AuCl_7Se$: Cl, 47.4%). $[TeCl_3][AuCl_4]$ was prepared by heating a solution of $TeCl_4$ and Au_2Cl_6 in $AsCl_3$ under reflux. Isolation and drying of the orange crystals were as in the above preparation (Found: Cl, 43.1. Calc. for $AuCl_7Te$: Cl, 43.3%).

Spectra.—Raman spectra were recorded on solid samples sealed in thin glass tubes using a Coderg PHO Raman spectrometer with 647.1 nm laser (krypton) excitation. I.r. spectra were obtained from crushed crystals between polyethylene plates, using a Perkin-Elmer 325 spectrometer (200—400 cm^{-1}) and a Grubb-Parsons NPL ' Cube ' interferometer (50—400 cm^{-1}).

N.q.r. spectra were recorded on a mid-range Decca spectrometer (5—55 MHz) using Zeeman modulation. Resonant frequencies (± 10 kHz) were determined by interpolation between frequency markers calibrated using a frequency counter (Advance Instruments, TC16).

Discussion

The parent compounds $SeCl_4$ and $TeCl_4$ differ from SCl_4 in that anionic derivatives of the types ACl_5^- and ACl_6^{2-} are known, as well as the cationic species ACl_3^+. In addition, both anionic (ICl_4^-) and cationic (ICl_2^+) species derived from iodine trichloride (I_2Cl_6) are well characterised spectroscopically.[1,6,7] All attempts either by solid phase or solution reactions to isolate a product from I_2Cl_6 and ACl_4 (A = Se or Te) were unsuccessful, however. Reaction of the chalcogen tetrahalides with Au_2Cl_6 produced species of the type $[ACl_3]^+$-$[AuCl_4]^-$ with no spectroscopic evidence for anionic chalcogen–halide, cationic gold–halogen or the known Au^I species $AuCl_2^-$.[8] Under chlorine-deficient conditions the product contained $AuCl_4^-$ contaminated with metallic gold. Unlike the compound $[SCl_3][ICl_4]$[1] there was no spectroscopic indication that any of the three compounds could be prepared in more than one crystalline form. In contrast with $[SCl_3][ICl_4]$ they were all obtained as crystalline solids, easily manipulable under dry nitrogen and with no tendency to dissociate at ambient temperature.

Vibrational assignments for the ACl_3^+ species are well established from a variety of complexes, solid-state effects having been considered in some detail for the SCl_3^+ ion.[1] Raman shifts for the $SeCl_3^+$ and $TeCl_3^+$ ions indicate that, for formally ionic salts, Se–Cl stretching modes (ν_1 and ν_3) occur at *ca.* 416 and 394 cm^{-1} with corresponding values for the Te–Cl modes at 390 and 370 cm^{-1}.[9-11] Assignments for the square planar $AuCl_4^-$ ion have been established from solution studies [12] but, as with ICl_4^- compounds, detailed solid-state analyses are limited.

Average ^{35}Cl n.q.r. frequencies for the $AuCl_4^-$ ion lie between 27.5 and 28.0 MHz at 77 K.[13] It is clear, however, that not all the compounds contain $AuCl_4^-$ with D_{4h} symmetry. For example, $Na[AuCl_4]\cdot 2H_2O$ and its deuteriated analogue, which are isomorphous with $Na[ICl_4]\cdot 2H_2O$, exhibit four lines spread over *ca.* 3.5 MHz, the lowest frequency showing an anomalous positive temperature coefficient attributed to hydrogen bonding.[14,15] Chlorine-35 n.q.r. spectra for a variety of SCl_3^+-containing compounds [1-3,16,17] show either two lines in a 2 : 1 intensity ratio or three equal intensity lines at 77 K within a narrow frequency range. Three lines have been reported for the

Table 1. Solid-state vibrational wavenumbers (cm^{-1}) for the complexes $[ACl_3][AuCl_4]$ (A = S, Se, or Te)

$[SCl_3][AuCl_4]$			$[SeCl_3][AuCl_4]$			$[TeCl_3][AuCl_4]$			
I.r. 77 K	Raman 130 K	Assignment	I.r. 77 K	Raman 130 K	Assignment	I.r. 77 K	Raman 130 K	Assignment	$K[AuCl_4]$ (Ref. 12)
	512m	$\nu_3(E)$, SCl_3^+							
	497ms			400vs	$\nu_1(A)$ and $\nu_3(E)$, $SeCl_3^+$				
				390ms			386m	$\nu_1(A_1)$, $TeCl_3^+$	
				384w (sh)			368mw	$\nu_3(E)$, $TeCl_3^+$	
	483vs	$\nu_1(A_1)$, SCl_3^+							
	360m	$AuCl_4^-$ stretches	365m (sh)	367ms	$AuCl_4^-$ stretches				
352s,br	354w (sh)			360w			357vs	$\nu_1(A_1)_g$, $AuCl_4^-$	347 $\nu_1(A_{1g})$
				352mw		353s		$\nu_6(E_u)$, $AuCl_4^-$	356 $\nu_6(E_u)$
			350s,br						
340w (sh)	343vs			341 s					
320mw	322s			338			332m	$\nu_4(B_{2g})$, $AuCl_4^-$	324 $\nu_4(B_{2g})$
269s	270m	$\nu_2(A_1)$, SCl_3^+	316m (sh)	318 mw					
				314					
				205w	$\nu_2(A_1)$ and $\nu_4(E)$, $SeCl_3^+$				
219w	218w	$\nu_4(E)$, SCl_3^+	197 m	194s		204w			
206m	206w		186	186w (sh)		188m			173 $\nu_7(E_u)$
188m	186ms	$AuCl_4^-$ deformations	176m (sh)	172m	$AuCl_4^-$ deformations		189mw	$\nu_2(B_{1g})$, $AuCl_4^-$	171 $\nu_2(B_{1g})$
173w	174w		165m	164w (sh)		180m	176mw	$\nu_2(A_1)$, $TeCl_3^+$	151 $\nu_3(A_{2u})$
144ms	146vw		146m	147w		160ms	158 w	$\nu_4(E)$, $TeCl_3^+$	
124w	120w		126m	128w		144ms	152		
97w	95vw		105 w	110 w		138w (sh)			
			92	96		120w			

SCl_3^+ ion in $[SCl_3][AuCl_4]$.[2] Studies of $SeCl_3^+$ and $TeCl_3^+$ salts are very limited; n.q.r. frequencies have been reported for $[SeCl_3][SbCl_6]$[11] and $SeCl_4$[11,18,19] but the latter, consisting of distinct tetramers of $SeCl_3^+$ units, cannot be correlated readily with a simple ionic compound. Five lines at 77 K, one of double intensity in each case, were reported for $[SeCl_3][AlCl_4]$ and $[SeCl_3][GaCl_4]$, and attributed to the presence of two crystallographically non-equivalent molecules in the unit cell,[3] whereas only three equally intense lines due to Se–Cl were observed at both 77 K and 296 K in the previous study of $[SeCl_3][AuCl_4]$.[3] For $[TeCl_3][AuCl_4]$, on the basis of signal intensities three resonances at both 77 and 296 K were assigned to chlorine atoms bonded to tellurium, although the Te–Cl frequency range overlaps the Au–Cl region.[3] Apart from this, n.q.r. frequencies at 298 K have been measured for $TeCl_4$[20,21] and $[TeCl_3][AlCl_4]$ [21] only, with resonances at 29.420, 29.574, and 30.570 MHz in the latter compound. The crystal structure of this compound [22] indicates strong secondary bonding interactions [23] between $AlCl_4^-$ and Te but unfortunately no ^{35}Cl n.q.r. frequencies for $AlCl_4^-$, which might be affected by these interactions, were reported.

$[SCl_3][AuCl_4]$ *and* $[SeCl_3][AuCl_4]$.—Vibrational assignments for the complexes are summarised in Table 1. On the basis of simple point group symmetry, four vibrational modes ($2A_1$ and $2E$) are expected for a pyramidal (C_{3v}) ACl_3^+ ion. Since the *X*-ray powder photographs indicate that both complexes are isomorphous with form I of $[SCl_3][ICl_4]$, SCl_3^+, $SeCl_3^+$, and $AuCl_4^-$ can all be considered to occupy C_1 sites in the lattice and hence six Raman shifts can be assigned to the ACl_3^+ ions as a result of splitting of degenerate (E) vibrations. For $[SCl_3][AuCl_4]$, the pattern of the stretching modes at 482, 492, and 512 cm^{-1} is similar to that in $[SCl_3][ICl_4]$ but the frequencies are significantly lower than those observed in 'simple' ionic salts such as $[SCl_3][SbCl_6]$,[9] suggesting significant anion–cation interaction. A similar pattern of lower-frequency shifted stretching vibrations is observed for the $SeCl_3^+$ modes.

Eight Raman shifts can be assigned to the $AuCl_4^-$ ion by analogy with the solid-state i.r. and Raman spectra of $K[AuCl_4]$.[12] Since only three Raman-active vibrations are predicted for an isolated D_{4h} $AuCl_4^-$ species and since some of the observed bands correspond to modes formally active in the i.r. only, this provides confirmation of the lower site symmetry in a distorted $AuCl_4^-$ ion. Unlike ICl_4^- there are no large frequency shifts in the $AuCl_4^-$ stretching modes compared to free ion values, but this may be accounted for, to some extent, by the greater mass and electropositive nature of the Au atom. During the course of this investigation, n.q.r. frequencies in excellent agreement with those reported here were published from independent work in Russia.[2,3] The interpretation, however, overlooked various points arising from the present comparative study. In contrast with $[SCl_3][ICl_4]$, ^{35}Cl n.q.r. frequencies were not observed for the cation at ambient temperature and this was plausibly ascribed to free rotation of SCl_3^+. The large frequency range for the anion (>5 MHz at 77 K) was considered indicative of a chlorine-bridged structure, $Cl_3S \cdots Cl \cdots AuCl_3$,[2] and, by analogy with the subsequent work on the selenium and tellurium compounds,[3] the highest frequency line from the anion was presumably assigned to the bridging chlorine, although this was not clear from the report.[2]

Our results suggest strongly, however, that the Au–Cl signal at lowest frequency arises from a chlorine involved in secondary bonding. The crystal structure [4] of form I of $[SCl_3][ICl_4]$ indicates that two chlorine atoms from ICl_4^- in this compound, corresponding to the longest I–Cl distances, are involved in secondary bonding to sulphur, and to these the lowest frequency n.q.r. lines are assigned. Indeed there appears to be a very good correlation between I–Cl bond length and ^{35}Cl n.q.r. frequency in tetrachloroiodates.[13] The lowest frequency ^{35}Cl line from $Na[AuCl_4]\cdot 2H_2O$ (or $Na[AuCl_4]\cdot 2D_2O$) was similarly assigned to the chlorine affected by hydrogen bonding,[14,15] which is expected to give the longest Au–Cl distance. The n.q.r. results for form I of $[SCl_3][ICl_4]$[1] are compatible with two bridging chlorines and a rather asymmetric bridge, with similarly asymmetric terminal chlorines. As mentioned above, the *X*-ray powder photographs indicate that form I of $[SCl_3][ICl_4]$ is isomorphous with both $[SCl_3][AuCl_4]$ and $[SeCl_3][AuCl_4]$. These *X*-ray results are not in-

Table 2. Chlorine-35 n.q.r. frequencies (MHz) for $[ACl_3]^+[AuCl_4]^-$ at various temperatures

	ACl_3^+			$AuCl_4^-$		
A	295 K	193 K	77 K	295 K	193 K	77 K
S	n.o.*	n.o.	42.760	29.870	30.225	30.600
	n.o.	n.o.	42.335	27.577	27.775	27.955
	n.o.	n.o.	41.305	27.360	27.640	27.912
				25.217	25.217	25.214
Se	37.230	37.500	37.700	31.825	32.250	32.655
	36.775	37.180	37.475	26.770	26.860	26.975
	36.220	36.675	37.020	26.480	26.750	26.910
				23.825	23.938	24.030
Te	30.987	31.360	31.675	28.902	29.226	29.508
	29.255	29.545	29.800	27.473	27.660	27.808
	28.790	29.073	29.322	26.650	26.873	27.040
				25.445	25.675	25.878

* n.o. = Not observed.

consistent with the ^{35}Cl n.q.r. frequencies for $[SCl_3][AuCl_4]$, which support a structure with a greater asymmetry in the bridge than in form I of $[SCl_3][ICl_4]$. Further support for the assignment of the lowest frequency line from $[SCl_3][AuCl_4]$ as taking part in secondary bonding is provided by the temperature dependence of the n.q.r. frequencies (Table 2). In form I of $[SCl_3][ICl_4]$ the lowest frequency n.q.r. line showed an anomalous positive temperature coefficient, attributed to a strong secondary covalent interaction.[1] In the work of Fokina *et al.*[2,3] a very small negative temperature dependence for the lowest frequency ^{35}Cl signal for $[SCl_3][AuCl_4]$ was observed, in contrast to the very small anomalous (positive) temperature dependence in the present work. In either case the change in frequency from 77 K to ambient temperature is much smaller for this line than for any of the other Au–Cl signals. It has been suggested recently that a characteristic of secondary bridging halogen n.q.r. signals is that their temperature coefficients are less negative than for symmetrically bridging halogens, and may even be positive in some cases.[24] The n.q.r. results also indicate that secondary bonding is weaker in $[SCl_3][AuCl_4]$ than in form I of $[SCl_3][ICl_4]$, as shown by the smaller range of ^{35}Cl n.q.r. frequencies and the smaller temperature coefficient for the lowest frequency line. In addition, the failure to observe signals from SCl_3^+ in $[SCl_3][AuCl_4]$ at room temperature, previously attributed to rotation of the cation,[2] would also imply rupture of the secondary bonds.

In the ^{35}Cl n.q.r. spectrum of $[SeCl_3][AuCl_4]$ the four Au–Cl resonances (Table 2) are spread over a wider frequency range ($\geqslant 8$ MHz) than in $[SCl_3][AuCl_4]$ and indeed this is the largest frequency splitting yet observed for a tetrachloroaurate. The range of values suggests that there is more distortion of the $AuCl_4^-$ ion in this instance, with the lowest frequency line corresponding to an appreciably longer Au–Cl bond and the highest frequency line to a much shorter Au–Cl bond than average, probably due to stronger secondary bonding than in the sulphur compound. In support of this hypothesis, ^{35}Cl resonances were observed at ambient temperatures and at 193 K from $SeCl_3^+$, as well as at 77 K, suggesting that the cation does not rotate freely in the lattice over this temperature range. While the larger size of $SeCl_3^+$ would tend to make motion more difficult, the results are entirely compatible with strong secondary bonding interactions in the solid state. In the work of Fokina *et al.*[2,3] n.q.r. frequencies at 77 K and room temperature are in good agreement with the present values, but the highest frequency Au–Cl line is assigned to bridging chlorine in a suggested structure $Cl_3Se \cdots Cl \cdots AuCl_3$,[3] which is not consistent with the results for form I of $[SCl_3][ICl_4]$[1] or $[SCl_3][AuCl_4]$. The line at 32.655 MHz (77 K) must be assigned to a chlorine bonded to gold, and logically would appear to arise from the Cl closest to Au,[13] probably *trans* to that involved in the strongest secondary bond to Se, and not the one furthest from Au. The temperature coefficient of the lowest frequency line from $[SeCl_3][AuCl_4]$, although negative, is much smaller than that of the highest frequency signal, again supporting its involvement in a secondary bonding interaction. The pattern of the Au–Cl n.q.r. frequencies is comparable to that for $[SCl_3][AuCl_4]$, suggesting that both compounds may have similar asymmetric bridged structures.

$[TeCl_3][AuCl_4]$.—*X*-Ray powder photographs indicate that this compound adopts a crystal structure different from that of the SCl_3^+ and $SeCl_3^+$ analogues. Both vibrational and n.q.r. spectra of $[TeCl_3][AuCl_4]$ are consistent with, at most, a very weak secondary bonding interaction. Three Raman shifts only are observed for the $AuCl_4^-$ ion (Table 1). This does not necessarily mean that the $AuCl_4^-$ ion can be considered in terms of D_{4h} symmetry as lower centrosymmetric point groups would still predict only three Raman-active modes. Such point groups would allow a splitting of the $AuCl_4^-$ degenerate deformation modes, consistent with the observed low-frequency i.r. spectrum. The $TeCl_3^+$ stretching modes at 368 and 386 cm^{-1} are close to analogous modes in other compounds (*cf.* 373 and 389 cm^{-1} in $TeCl_4{\cdot}GaCl_3$),[9] with no comparable lowering of frequency as seen in the SCl_3^+ and $SeCl_3^+$ salts, again consistent with minimal secondary interaction.

The n.q.r. spectrum is quite remarkable in that strong ^{35}Cl and ^{37}Cl frequencies from both $AuCl_4^-$ and $TeCl_3^+$ are observed at both ambient temperature and at 77 K (Table 2). The considerable overlap, however, between the Au–Cl and Te–Cl frequency ranges precludes unambiguous assignment on the basis of frequency alone. In the previous report, the three lowest frequency lines were assigned to Cl atoms bound to Au; the highest two, together with that at *ca.* 29.32 MHz (77 K), which gave higher signal intensities, to Cl atoms bound to Te, and the remaining signal (29.505 MHz at 77 K) to the bridging Cl atom in the structure $Cl_3Te \cdots Cl \cdots AuCl_3$.[3] Although the *X*-ray powder data indicate that this compound has a different structure from the sulphur and selenium analogues, it seems more probable that Cl atoms involved in secondary bonding or bridging would give Au–Cl signals at a frequency lower than average, corresponding to a longer Au–Cl bond. The range of frequencies for the $AuCl_4^-$ ion is smaller in this instance (<4 MHz), suggesting that any distortions from D_{4h} symmetry are smaller than in the previous structures. This separation is larger than crystallographic splittings, however, and indicates some variation in bond length, presumably due to weak secondary bonding interactions. Their weakness is confirmed by the normal temperature dependence observed for all four Au–Cl signals. The average frequency (27.558 MHz at 77 K) is within the normal range for tetrachloroaurates,[13] on the assumption that the Te–Cl signals have been correctly assigned. No rotation of the cation appears to occur but this is probably due to the larger size of $TeCl_3^+$ rather than to the strength of any secondary bonding.

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