Polyiodine Cations. Preparation and Nuclear Quadrupole Resonance Characterization of Tri-iodine and Penta-iodine Tetrachloroaluminates, $I_3^+AlCl_4^-$ and $I_5^+AlCl_4^-$

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Summary Compounds formulated as $I_3^+AlCl_4^-$, $I_5^+AlCl_4^-$, and $I_2Cl^+AlCl_4^-$ have been prepared and so characterized according to phase equilibria studies and nuclear quadrupole resonance spectroscopy data.

Polyatomic cations of such elements as bismuth, selenium, and tellurium[1,2] may be readily prepared as their tetrachloroaluminate salts by "neat" reactions in the pseudobinary systems $MCl_n{\cdot}nAlCl_3 + M$. Extension of these studies to iodine have now been found to give the first examples of solid compounds containing the polyiodine cations I_3^+ and I_5^+.

Phase identifications were accomplished with the aid of thermal analyses and *X*-ray powder patterns. The shiny black phase of composition $I_{3\cdot0\pm0\cdot15}AlCl_4$ melts congruently at 45 ± 1° and the green, metallic-appearing I_5AlCl_4 ($4{\cdot}8 < I/AlCl_4 < 5{\cdot}3$), slightly incongruently at 50·0 – 50·5°. The only other phase occurring in the general ICl–I_2–$AlCl_3$ ternary system is the known[3] phase $2ICl{\cdot}AlCl_3$ which will be formulated $I_2Cl^+AlCl_4^-$.

Table. *Pure quadrupole resonance data for* ^{127}I *and* ^{35}Cl *in some polyhalogen tetrachloroaluminates and related compounds at room temperature*

Compound	ν_Q(MHz)	Assignment
$I_2ClAlCl_4$	10·297	^{35}Cl in $AlCl_4^-$
	10·474	
	11·265	
	11·283	
	37·912	^{35}Cl in I_2Cl^+
	38·127	
	417·0	^{127}I, ν_1-central
I_3AlCl_4	10·129	^{35}Cl in $AlCl_4^-$
	10·590	
	11·093	
	11·452	
	415·0	^{127}I ν_1-terminal
	428·0	ν_1-terminal
	308·6	ν_1-central
	527·0	ν_2-central
I_5AlCl_4	10·988	^{35}Cl in $AlCl_4^-$
	11·086	
	11·124	
	11·449	
$NaAlCl_4$[a]	11·009	^{35}Cl in $AlCl_4^-$
	11·272	
	11·385	
	11·583	
ICl[b]	37·202	^{35}Cl
	440·9	^{127}I, ν_1
	451·46	
	902·46	^{127}I, ν_2
ICl_2AlCl_4[a]	11·31	^{35}Cl in $AlCl_4^-$-arbitrary resolution
	11·40	
	11·42	
	39·086	^{35}Cl in ICl_2^+
	38·690	
	458·0	^{127}I, ν_1-central

[a] Chlorine data from ref. 6. [b] Chlorine datum at −196°, ref. 7; iodine data from ref. 8.

The identification of these compounds as $AlCl_4^-$ compounds, as opposed to possibilities involving molecular such as with chlorine bridging between aluminum and iodine groups or with aluminium having an expanded octet, has been accomplished primarily by means of n.q.r. spectroscopy. Measurement[4] of ^{35}Cl resonances in salts of Na^+, Co_2^+, Te_4^{2+}, Hg_3^{2+}, and ICl_2^+ of known structure have demonstrated the feasibility of identifying the $AlCl_4^-$ anion (and distinguishing it from $Al_2Cl_7^-$) by n.q.r. spectroscopy, thereby avoiding the ambiguity in i.r. data often produced by solid state perturbations.[5]

Data for ^{35}Cl and ^{127}I resonances in the compounds considered here as well as for some related phases are given in the Table. The evident presence of relatively unperturbed $AlCl_4^-$ groups is indicated by both the number and the range of resonance frequencies.[5] The ^{35}Cl resonances in ICl_2^+ and the postulated I_2Cl^+ (chlorine terminal) ion appear consistent with the expected effect of the hypothetical addition of Cl^+ or I^+ to the ICl molecule, the ^{35}Cl resonance in ICl (37·2 MHz) increasing to 37·9 and 38·1 in I_2Cl^+ and then to 38·7 and 39·1 in ICl_2^+.

It is possible to predict the resonance frequency of the central iodine in the ICl_2^+ cation and the geometry of the I_3^+ cation using established equations relating observed ^{127}I frequencies to bonding and structural parameters. For a simple bonding picture, two equivalent bonding orbitals are considered to form by overlap of hybrid orbitals formed from s, p_x, and p_y atomic orbitals on the central iodine atom with pure p orbitals on terminal halogens, the remaining hybrid orbital on iodine and all other atomic orbitals being filled and substantially non-bonding. The hybrid orbitals and the equations used to relate the molecular quadrupole coupling constant (e^2Qq_{mol}) and asymmetry parameter (η) to the population of the bonding orbital(s) are as recently published.[9] Values of $e^2Qq_{\text{mol}} = 2515{\cdot}9$ MHz, $\eta = 0{\cdot}35$, and $\nu_1 = 433{\cdot}2$ MHz are thus calculated for the ^{127}I resonance of the central iodine atom in the ICl_2^+ cation with the aid of the 96·7° bond angle for ICl_2^+,[10] the ^{35}Cl (cation) data,[6] and a value of $e^2Qq_{\text{atm}} = 2298{\cdot}8$ MHz for ^{127}I.[11] The 433·2 MHz value compares well with the observed frequency of 458 MHz (Table). A similar interpretation of the results for I_3^+, assuming $\eta = 0$ for the terminal iodine atoms, yields a charge distribution of $+0{\cdot}21$ and $+0{\cdot}24$ for the terminal iodine atoms and $+0{\cdot}76$ for the central atom, and a bond angle of 97° between two bonding orbitals on the latter. The model thus accounts for 19·79 of the 20 valence electrons in I_3^+. In view of the limitations of the model this evaluation of the charge distribution is very reasonable.

The resonance data for the central iodine atom in the series I_3^+, I_2Cl^+ (angle unknown), and ICl_2^+ show an entirely reasonable progression (308·6, 420, and 457 MHz) on increasing substitution of chlorine for iodine.

Cations with the three stoicheiometries reported here have been noted before in sulphuric and fluorosulphuric acid solutions[12,13] but not in solid compounds. A solid tetrachloroaluminate of the other polyiodine cation found in HSO_3F solution, I_2^+ (or its dimer) does not form.

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