Born–Haber cycle calculations for holmium it must be presumed that there is little difference between $HoCl_2$ and the observed $HoCl_{2.14}$ lattice in free energy per equivalent of reduction. Within this limitation the present findings are in excellent accord with predictions, especially when the latter are updated in light of more recent fundamental data. In particular the estimates hinge on experimental values of the enthalpies of formation of some of the known dichlorides[10] and a recent 2% change in the value for $EuCl_2$[24] is particularly significant. Taking this together with other small changes in fundamental data into account now yields calculated quantities which are in even better agreement with experimental observation; *viz.*, $\Delta H°_{298} \approx \Delta G°_{298} = +1 \pm 6$ kcal mol^{-1} for the disproportionation of $HoCl_2$, a value which is even more meaningful alongside the more firmly predicted relative stabilities of $DyCl_2$ and $ErCl_2$, 6 ± 6 and -6 ± 6 kcal mol^{-1}, respectively.[25]

Some evidence for the formation of reduced holmium on irradiation of Ho_2O_3 and its limited stability in aqueous solutions has recently been noted.[26]

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Registry No. $HoCl_3$, 10138-62-2; Ho, 7440-60-0.

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Polyiodine Cations as Chlorometalate Salts. Synthesis and Nuclear Quadrupole Resonance Characterization of Triiodinium, Pentaiodinium, and Chlorodiiodinium Tetrachloroaluminates, I_3AlCl_4, I_5AlCl_4, and $I_2ClAlCl_4$

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Reactions of I_2 with ICl–$AlCl_3$ mixtures have been investigated by thermal, microscopic, and X-ray analysis. The system contains only the phases I_3AlCl_4, I_5AlCl_4, and $2ICl\cdot AlCl_3$ ($=I_2ClAlCl_4$) which melt at 45, 50–50.5, and 53°, respectively. Comparable polyhalogen derivatives of the anions $FeCl_4^-$, $HfCl_6^{2-}$, and $TaCl_6^-$ do not exist and neither do any compounds with compositions corresponding to I_4Cl^+, $I_3Cl_2^+$, I_2^+, or Br_3^+ with $AlCl_4^-$ or $SbCl_6^-$ anions or the phase $ICl\cdot TaCl_5$. Unfavorable physical characteristics of the three new phases preclude many normal methods of characterization but the ^{35}Cl and ^{127}I nqr and ^{27}Al nmr spectra for these and the compound ICl_2AlCl_4 provide substantial information, indicating that the compounds contain normal "ionic" $AlCl_4^-$ groups and therefore the cations I_3^+, I_5^+, I_2Cl^+, and ICl_2^+. A bonding angle of 97° is obtained from the observed ^{127}I data in I_3^+; I_2Cl^+ and ICl_2^+ appear closely analogous. Bond populations and atom charges inferred from the nqr data for these cations are given. Properties of chlorometalate anions which appear important for the stabilization of these cations are considered. The published estimation of the chloride ion affinity of $FeCl_3(g)$ is corrected to a value of about 85 kcal/mol.

Introduction

The value of acidic conditions in the synthesis of salts which contain homopolyatomic cations has been demonstrated in several ways, for example with $AlCl_3$ through the general reactions

$$MCl_n + nAlCl_3 + mM \rightarrow M_{m+1}{}^{n+}(AlCl_4^-)_n \quad (1)$$

where the reduced cation stabilized by the large anion may be, among others, Cd_2^{2+}, Bi_5^{3+}, Te_4^{2+}, and Se_8^{2+}.[1-5] The extension of this approach to the halogens that is reported in the present paper allows a comparable test of the stability of polyatomic cations for elements which are more noted for polyanion formation. As might be expected, iodine provides the most stable cation examples as well *via* the general reaction

$$ICl + AlCl_3 + nI_2 \rightarrow I_{2n+1}AlCl_4 \quad (2)$$

Characterization of new phases by ^{35}Cl and ^{127}I nqr spectroscopy proves to be particularly helpful.

In general the identity and stability of the particular polyatomic cations achieved in such acidic systems must depend on not only the basicity or pCl of the anion formed but also to some extent on the size and charge on this group, but the relative importance of these factors appears complex and is not well understood.[4] Notwithstanding, chloride ions dissociated from chloro anions of low stability can in the present study be viewed as destabilizing polyiodine cations by stabilization of ICl. Some exploration of the anion factors has therefore been included through use of the metal chloride acids which could generate the anions $FeCl_4^-$, $HfCl_6^{2-}$, $TaCl_6^-$, and $SbCl_6^-$.

Previous knowledge of polyiodine cations has been largely limited to solution species I_3^+, I_5^+, and the equilibrium pair I_2^+ and I_4^{2+}, all of which have been inferred by spectroscopic, conductometric, and cryoscopic studies of solutions in sulfuric[6,7] and fluorosulfuric[8,9] acids. Prior to preliminary communication of the present work[10] the only solid derivatives reported for any of the polyiodine cations were the phases $I_2M_2F_{11}$ (M = Sb, Ta)[11] and I_3SO_3F,[12] while the synthesis of I_7SO_3F has been reported subsequently.[13] All four of these compounds have remained structurally uncharacterized except that the ir data for I_3SO_3F indicate an appreciable perturbation of the spectrum of the isolated SO_3F group is produced by the I_3 group or ion.[14]

Experimental Section

Materials. Iodine (Fisher Certified reagent grade) was vacuum sublimed once to separate less volatile impurities. The specifications for the iodine monochloride (99% purity, Research Organic/Inorganic Chemical Corp.) indicated ICl_3 was the main impurity (≤1%) while the material contained only 0.001% Br_2. The material was sublimed once at 0° in the course of the synthesis procedure. Commercial anhydrous aluminum chloride was sublimed twice prior to use, once through a frit under high vacuum and then under 30 Torr Ar to remove $FeCl_3$. Commercial $FeCl_3{\cdot}6H_2O$ was dehydrated with refluxing $SOCl_2$ and then twice vacuum sublimed at 200° through a frit under *ca.* 50 Torr of Cl_2. $SbCl_5$ was purified and handled as before[15] as was also $HfCl_4$.[4] The $TaCl_5$ was prepared by Dr. R. M. Friedman by reaction of Cl_2 with the metal (Fansteel, the largest impurities being 45 ppm of N, <25 ppm of W, 15 ppm of O) at 375–425° followed by vacuum sublimation. All materials were manipulated and reacted under either rigorous drybox or vacuum conditions except that the transfer and weighing of I_2 and the initial transfers of ICl and $SbCl_5$ to storage containers were performed in a polyethylene glove bag filled with dry N_2.

Synthesis Reactions. The polyiodine tetrachloroaluminate samples were prepared by combining stoichiometric amounts of I_2, ICl, and $AlCl_3$ in evacuated, sealed Pyrex or Vycor tubes. For vacuum manipulations all containers were fitted with Teflon needle valves (Fischer-Porter) and Halocarbon grease was used on the glass joints. For a typical preparation a known amount of ICl was first obtained by vacuum sublimation from a stock container at 0° into a preweighed container at −196°. The stock container was kept at 0° to minimize disproportionation of ICl to ICl_3 and I_2; under these conditions, the amount of the bright yellow ICl_3 present was visually estimated to be <2% of the weight of ICl. After determination of the ICl weight by difference, a 1 mol % excess of each of the calculated amounts of I_2 and $AlCl_3$ for the desired composition was weighed and transferred in the drybox under argon, the extra amounts being taken to allow for loss by volatilization and hydrolysis. The weighed amount of ICl was then sublimed to the reaction tube at −196°, the tube was sealed under vacuum, and the contents were allowed to react at 100 to 125°. At this stage the samples remained as black viscous liquids at room temperature and these could usually be solidified only if repeatedly quenched in liquid N_2 and partially remelted with warm water. Once initiated, complete crystallization of ~5 g required ~15 min. Samples involving potential anion formers other than $AlCl_3$ were handled analogously. A few experiments involving Br_2 used handling techniques similar to those for ICl, while Cl_2 when needed was measured volumetrically from the liquid at −80°.

Thermal Analysis. The thermal analysis containers described before[2] were filled as above to give 4–6 g of sample and sealed; the mixture was allowed to react and placed in a deep, double-walled jacket which was in turn contained in an ice bath or a furnace depending on the temperature region to be studied. Microscopic examination of samples in sealed containers provided a useful adjunct to the thermal analysis and X-ray characterization of compounds and mixtures.

X-Ray Data. Debye–Scherrer powder diffraction data were obtained with samples sealed in 0.3-mm Lindemann glass capillaries using a 11.46-cm radius camera and Ni-filtered Cu Kα radiation. Because of the pastelike consistency of many samples they were usually ground together with an equal volume of powdered Pyrex glass before loading into the capillaries. For identification purposes the stronger 30% of the distances (Å) observed with intensities in parentheses (10 high) are as follows: α-I_3AlCl_4, 5.73 (5), 3.39 (10), 2.70 (3), 2.54 (3), 2.208 (3), 1.523 (3); I_5AlCl_4, 7.59 (10), 6.12 (7), 5.38 (5), 5.20 (8), 4.27 (5), 4.06 (6), 3.85 (10), 3.60 (7), 3.40 (10), 3.26 (5), 3.08 (5), 2.95 (9), 2.86 (5), 2.73 (10), 1.996 (5), 1.920 (7), 1.892 (5); $I_2ClAlCl_4$, 5.50 (5), 5.01 (5), 4.52 (5), 4.34 (10), 3.26 (9), 3.00 (5), 2.90 (9), 2.84 (9), 2.77 (7), 2.54 (5), 2.218 (8), 2.079 (5), 1.521 (7). I_3AlCl_4 and $I_2ClAlCl_4$ do not appear to be isomorphous.

Spectra. Electronic spectra were run on a Cary 14 spectrophotometer with samples mulled with Halocarbon grease or oil. Far-infrared spectra were searched on a Beckman Model IR-11. Because the samples of interest attack polyethylene and Nujol rapidly, they were examined between thin sheets of Teflon directly or they were mulled with Fluorolube. The ^{35}Cl and ^{127}I nqr spectra were obtained using a Wilks NQR-1A superregenerative spectrometer and a wide-line induction spectrometer as described previously.[16] Samples were crystallized and annealed directly in the 15- or 22-mm diameter container. The ^{37}Cl data were checked whenever an assignment ambiguity was conceivable. The broad-line nmr spectrum of ^{27}Al was measured on the same samples using a spectrometer described by Torgeson.[17] Data from repetitive scans were stored in a 400-channel analyzer for a 6–8 hr period.

Analyses. Weighed samples were dissolved in 0.5 *N* H_2SO_4 at 0° in a closed container after which a solution of KI was added to dissolve the I_2 and reduce the IO_3^- formed in the initial reaction

$$5I_xAlCl_4 + 3H_2O \rightarrow IO_3^- + [(5x-1)/2]I_2 + 5Al^{3+} + 20Cl^- + 6H^+ \qquad (3)$$

Total iodine was then determined by titrating aliquots with standard thiosulfate. Chlorine was determined gravimetrically from a 50:50 water–acetone mixture. Interference from I^- was eliminated by oxidizing the iodide in an aliquot with nitrite followed by heating to expel the I_2 produced.

Results and Discussion

The investigations of the potential synthesis of I_xAlCl_4 phases were carried out "neat" in the I_2–(ICl + $AlCl_3$ (1:1)) pseudobinary system, the indicated proportions of ICl and $AlCl_3$ being chosen so that all of the chlorine from ICl could be bound as $AlCl_4^-$ on reduction (eq 2).

Thermal analysis provided the best information. Although nearly all compositions studied exhibited such large supercooling that cooling data were meaningless, adequate data could be obtained from careful heating curve analysis of shock-crystallized materials. In extremely difficult cases this technique had to be replaced with visual observations at hourly intervals as the crystalline sample was equilibrated at a series of increasing temperatures, this procedure allowing the liquidus point to be bracketed to ±1–2°.

The ICl–AlCl₃ System. The phase relationships in this binary system are considered first since they have a bearing on the reduction observations in the ternary. The equimolar starting composition of $AlCl_3$ and ICl reacts to form equal amounts of the adduct $2ICl{\cdot}AlCl_3$ and $AlCl_3$, consistent with the first report of the binary system and that intermediate phase by Fialkov and Shor.[18] However preliminary measurements of the melting properties of the equimolar mixture in part of the ternary system study were found to be in such substantial disagreement with the phase diagram reported earlier that a partial reinvestigation of the ICl–$AlCl_3$ binary system was necessary.

The phase data reported by Fialkov and Shor, substantially only the liquidus results, are summarized in Figure 1 as the dashed curve, with the dotted portion representing a region of severe supercooling where data could not be secured. The maximum in the liquidus at 110° and 36–37% $AlCl_3$ was the sole identification they provided for the phase $2ICl{\cdot}AlCl_3$ (33.3% $AlCl_3$), and that melting point turns out to be seriously

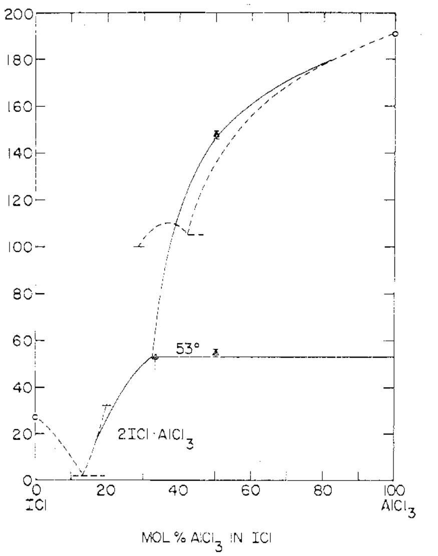


Figure 1. The proposed phase relationships in the system $ICl–AlCl_3$ (solid line) *vs.* the liquidus data reported by Fialkov and Shor[18] (dashed–dotted line).

in error. The source and purity of the starting materials and the method of containing these were not stated, but they did note extreme difficulties with the thermal analysis.

A heating curve of the previously reacted equimolar $ICl–AlCl_3$ mixture (50 mol %, Figure 1) clearly reveals a thermal effect (eutectic or peritectic) at 53–56° below a liquidus point at 146–149°, the latter comparing with a ~136° reported before. The composition $2ICl \cdot AlCl_3$ was then found to exhibit only a thermal halt at 53 ± 1°, which visually corresponded to a sharp melting which left traces of $AlCl_3$ floating on the black liquid. Microscopic examination of crystallized and annealed samples with $ICl:AlCl_3$ ratios <2.0 revealed free $AlCl_3$ while samples containing 29, 25, and 17 mol % $AlCl_3$ ($ICl:AlCl_3 > 2.0$) could be fractionated into the new phase and an increasing amount of excess ICl. Only the first of those three compositions could be crystallized. The 33.3% mixture appeared to be the single phase $2ICl \cdot AlCl_3$, which is purplish black with a metallic sheen, is brown-yellow in thin sections, and resembles solid I_2 to some extent. The earlier and erroneous phase data may have resulted from too rapid heating curve analysis; in any case the correct identification of the composition of the intermediate phase would seem to have been nearly fortuitous from the evidence published.

This $2ICl \cdot AlCl_3$ phase will later be shown to be constituted $I_2Cl^+AlCl_4^-$ (rather than $I_3^+ICl_2^+(AlCl_4^-)_2$ or some molecular formulation) on the basis of nqr spectra.

The System $I_2–ICl–AlCl_3$. The phase results obtained in the pseudobinary system $I_2–(ICl + AlCl_3\ (1:1))$ are shown in Figure 2. All samples required alternate and repeated cycling between liquid nitrogen and warm water temperatures to gain crystals. Liquidus data for samples containing more than 60% I_2 could be obtained only by the repeated equilibration coupled with visual observations described earlier. No samples exhibited free ICl, consistent with Figure 1.

Free $AlCl_3$ was visible at room temperature in reacted samples containing less than 50 mol % I_2 but was no longer found at that or more reduced compositions. This observation together with the liquidus data shown indicates the composition of the first reduced phase has an $I:AlCl_4$ ratio of 3.0 ± 0.15 (50 ± 2 mol % I_2), hereafter identified as I_3AlCl_4, and melts congruently at 45 ± 1°. The phase is the most difficult to crystallize and occurs as shiny black platelets, dark brown-red in thin sections. The 15° arrest for less reduced compositions is presumably the eutectic for the ternary system $I_3AlCl_4–ICl_2AlCl_4–AlCl_3$. The presence of the (depressed) $I_2ClAlCl_4$ melting point plus the 15° eutectic indicates derivatives of I_2^+ or I_4^{2+} (33 mol % I_2) do not occur in this system.

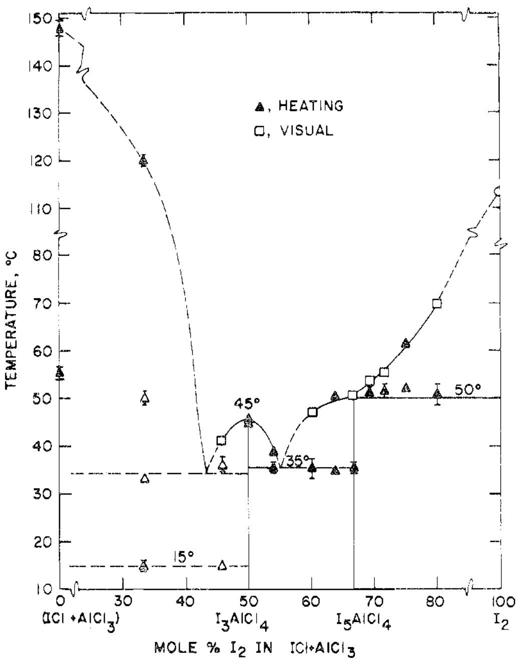


Figure 2. The phase relationships of I_3AlCl_4 and I_5AlCl_4 in the section $(ICl + AlCl_3)–I_2$: ▲, heating curve analysis; □, visual observation after equilibration.

The second reduced phase was found to have the composition $4.80 < I:AlCl_4 < 5.27$ (64.5–68.1 mol % I_2) and to melt slightly incongruently at 50.0–50.5°. The compound forms greenish black needles with a metallic reflectance; thin sections are again dark brown-red, very similar to anhydrous $FeCl_3$. The lower limit of composition possible for this phase was determined with reasonable accuracy from the phase relationships; however the upper limit was less well defined. The powder patterns of samples containing 66.7 and 71.4 mol % I_2 appeared identical, but free iodine could be found in patterns of samples containing ≥75 mol % I_2. Extraction of excess I_2 from the new phase with CCl_4 or $CHCl_3$ was not successful because of partial dissociation of the product under these conditions (see below), but careful sublimation of I_2 did yield the phase. The stated upper limit of composition for this phase was best established from a 69% sample by successive fractional crystallization followed by separation when only about 20% liquid remained and, ultimately, analysis. In this case the thermal shocking initiated crystallization of only I_5AlCl_4, and the I_2 remained in the supercooled liquid which was separated. The empirical composition so obtained was $I:AlCl_4 = 5.13$ with a 98% recovery; if it is assumed that the low recovery was entirely because of I_2 loss in the drybox (the most unfavorable circumstance), the upper limit is the stated $I_{5.27}AlCl_4$. The two reduced phases are easily distinguished microscopically, and both of these together with ICl_2AlCl_4 were found to be qualitatively diamagnetic.

The powder pattern results were unique for the indicated phases and of reasonably good quality considering the pastelike nature of the polyiodine phases. However these data could be obtained only for a limited number of compositions across the phase region shown in Figure 2; in particular the low-melting eutectics at 15, 34, and 35° frustrated attempts to obtain data on samples containing less than 50 and ~52–64% I_2.

The foregoing phases appear to be the only ones formed in a general ternary system $I_2–ICl–AlCl_3$. Specifically, compositions with 50 and 66.7% I_2 in $ICl + 2AlCl_3$ as the other component were prepared in order to test for the formation of possible $Al_2Cl_7^-$ salts of I_3^+ and I_5^+, analogous to the situation with Te_4^{2+},[19] but free $AlCl_3$ and the stated phases were found both by visual means and by X-rays. Likewise the possible formation of the postulated[7] I_4Cl^+ and $I_3Cl_2^+$ was tested by allowing the compositions $I_2 + 2ICl + AlCl_3$ and $3ICl + AlCl_3$, respectively, to react but without success as both products contained free ICl and other known phases. The remaining possibilities $I_2Cl_3^+$ and ICl_4^+ were not considered as they lie outside of the system studied and would require ICl_3, ICl_2^+, or Cl_2 for synthesis. The compound ICl_2AlCl_4 is already known.[20]

Other synthetic reactions were briefly explored which avoided the use of ICl but which instead admixed relatively inert products with the desired ones. The reactions

$$KIO_3 + 7I_2 + 8AlCl_3 \rightarrow 5I_3AlCl_4 + KAlCl_4 + Al_2O_3 \qquad (4)$$

$$3I_2O_5 + 72I_2 + 40AlCl_3 \rightarrow 30I_5AlCl_4 + 5Al_2O_3 \qquad (5)$$

do evidently proceed to completion and yield the indicated polyiodine products after 2–3 days at 180–200°, and other stoichiometries would presumably also succeed. On the other hand attempted syntheses of the new phases by refluxing appropriate quantities of I_2, ICl, and $AlCl_3$ in CCl_4, $CHCl_3$, or CH_3CN were uniformly unsuccessful, unreacted iodine precipitating in all cases on cooling or concentration.

Other Anions. The synthesis of phases of stoichiometries appropriate to the formation of I_3^+, I_5^+, or I_2Cl^+ groups was also attempted utilizing other acidic metal chlorides to form the counteranion, namely, with $FeCl_3$, $TaCl_5$, and $HfCl_4$ in amounts which would lead to the quantitative formation of $FeCl_4^-$, $TaCl_6^-$, and $HfCl_6^{2-}$. Reactions were tried for all of the nine possible cation–anion combinations except for $(I_3)_2HfCl_6$ and I_5TaCl_6. The metathetical reaction between $NaFeCl_4$ and I_3AlCl_4 was also run to ensure that a kinetic barrier was not a factor. In addition the syntheses of Br_3^+ salts with $AlCl_4^-$ and $SbCl_6^-$ anions as well as of $Br_2ClSbCl_6$ were also tried, utilizing the reaction of the acidic chloride with the appropriate mixture of Br_2 and Cl_2. Mercury lamp irradiation was also tried as an aid to the $SbCl_5$ reactions. But in none of these 10 attempts was the synthesis of a new phase achieved when success was measured in terms of either the disappearance of appreciable amounts in one of the reactants or the formation of a solid product which melts at room temperature or above. In all cases the presence of the original components, especially I_2, ICl, or Br_2, was very evident. Vigorous conditions were again used to induce crystallization, but all of the low-temperature solids appeared to be either unreacted components or glasses rather than crystals, although this conclusion was of course based only on observations of melting *in situ*.

In the course of this we have been unable to confirm the formation of an adduct with the composition $ICl \cdot TaCl_5$, mp 102°, reported by Safonov, *et al.*[21] The reactions of both 1:1 and 2:1 mixtures of these components at 135° for 3 hr followed by slow cooling give heterogeneous products which at room temperature show ICl at high activity and clear crystals of $TaCl_5$. The 1:1 composition exhibits a large fraction of free ICl after 1 day at 95°, 7° below the melting point claimed for the compound with that composition.

Characterization. The physical properties of I_3AlCl_4, I_5AlCl_4, and $I_2ClAlCl_4$ are such that the possible means of characterization are severely limited. The polyiodides decompose with loss of ICl and I_2 sufficiently easily that their lifetimes as small crystals in the drybox are no more than 20 min, the low-melting eutectics (Figure 2) causing them to melt while decomposing. The adduct $2ICl \cdot AlCl_3$ appears to boil and decompose in 1–2 min. All three compounds appear to form good-quality crystals under microscopic examination but the decomposition properties effectively prevented the mounting of single crystals in capillaries. Likewise, their shoe polish consistency and reactivity precluded observation of any ir data. Thin Teflon sheets were the only materials sufficiently inert to hold the products but the materials tended to clump together rather than to remain mulled, and they frequently melted in the beam of the spectrometer and coalesced. On the other hand, features of the electronic spectra of mulls with Fluorolube oil held between silica plates were discernible and reproducible though broad. These are listed in Table I where they are compared with data reported for the presumably similar cations in liquid HSO_3F. The correspondence between the solid and solution spectra for each of the I_5^+ and I_2Cl^+ species appears good, especially when it is noted that the 270-nm peak missing in solid I_5AlCl_4 is the weakest of the lot in solution and that the 230-nm absorbance for I_2Cl^+ is in an inaccessible region in the solid. Since the spectra of I_2Cl^+ and I_3^+ in solution are somewhat similar, they do not provide any clarification of the actual components present in the compound $I_2ClAlCl_4$.

Table I. Electronic Spectra (nm) of Some Tetrachloroaluminate Phases and HSO_3F Solutions[a]

Cation	$AlCl_4$ salt	HSO_3F soln[b]
I_3	490 m, 410 w, sh, 345 s	470 m, 305 s
I_5	485 m, 350 m, 245 s	450 m, 345 s, 270 m, 240 s
I_2Cl	475 m, 450 m, 310 s	461 m, 300 s, ~230

[a] Key: s, strong; m, medium; w, weak; sh, shoulder. [b] References 8 and 14.

Nqr Measurements. The availability of an nqr spectrometer capable of measurements up to 600 MHz, well into the cationic iodine region, and the detection of moderate to strong resonances in the compounds of interest allowed a substantial characterization of these new salts, as to both the occurrence of relatively unperturbed $AlCl_4^-$ anions and the nature and configuration of the cations therein.

The nqr data obtained for the three compounds of interest plus that for ICl_2AlCl_4[16,22] are listed in Table II; in all cases the $AlCl_4^-$ data would appear to be complete if there is one independent anion per unit cell. On the other hand the iodide data are substantially incomplete for the I_5 phase and are partially so for $I_2ClAlCl_4$. The presence of two chlorine resonances in the cation region for the latter compound indicates two independent atoms per unit cell.

A clear indication of the dimorphism of I_3AlCl_4 was encountered when a new ^{35}Cl spectrum was found for a sealed sample left standing at room temperature for about 1 year. The new and apparently harder β phase melted close to the temperature observed earlier for α form and readily re-formed on cooling (as judged by the nqr spectrum) as long as the melting process was incomplete so that a few crystals remained. However, when the fusion was complete, the sample again required vigorous thermal shocking in order to produce crystals and these showed the former resonance set of what is taken to be the low temperature (α) form which is metastable at room temperature. Iodine data for the β form could not be observed with the smaller diameter container necessary for chlorine measurements.

The ^{35}Cl data for $AlCl_4^-$ in these compounds give direct support for their formulation in terms of relatively ionic groups. Parallel work[16] with compounds of known or probable structure has shown that ^{35}Cl resonances in nominally "ionic" $AlCl_4^-$ compounds (*e.g.*, with Na^+, Ga^+, Te_4^{2+}, ICl_2^+, and Bi_5^{3+} cations) average 10.6–11.3 MHz, with a range of ≤1 MHz for the individual compounds, whereas structurally demonstrated coordination of $AlCl_4^-$ groups to the cation (Co^{2+}, Hg_3^{2+}) or the formation of $Al_2Cl_7^-$ anions not only appreciably elongates the Al–Cl bonds to bridging atoms but also causes the ^{35}Cl resonances both to increase in range and to move to higher frequencies. Individual frequencies in the last group

Table II. Nqr Data for ^{35}Cl and ^{127}I in Tetrachloroaluminates at Room Temperature

			$AlCl_4^-$ data, MHz	
Compd	ν_Q,[a] MHz	Assignment	Av	Range
α-I_3AlCl_4	10.129	^{35}Cl in $AlCl_4^-$	10.82	1.32
	10.590			
	11.090			
	11.452			
	308.6	^{127}I central (ν_1)		
	415	^{127}I terminal (ν_1)		
	428			
	527	^{127}I central (ν_2)		
β-I_3AlCl_4	9.960	^{35}Cl in $AlCl_4^-$	10.74	1.13
	10.874			
	11.046			
	11.091			
I_5AlCl_4	10.988	^{35}Cl in $AlCl_4^-$	11.16	0.46
	11.086			
	11.124			
	11.449			
	400 ± 5	^{127}I		
$I_2ClAlCl_4$	10.297	^{35}Cl in $AlCl_4^-$	10.83	0.99
	10.474			
	11.265			
	11.283			
	37.912	^{35}Cl in I_2Cl^+		
	38.127			
	417	^{127}I central (ν_1)		
ICl_2AlCl_4[b]	10.802	^{35}Cl in $AlCl_4^-$	11.09	0.61
	10.843			
	11.297			
	11.413			
	38.690	^{35}Cl in ICl_2^+		
	39.086			
	458	^{127}I central (ν_1)		

[a] The uncertainty is ±1 in the last figure given unless otherwise noted. [b] ^{35}Cl data in $AlCl_4^-$ are from ref 16 and in ICl_2^+ are from ref 22. The latter were confirmed in the present study.

thus appear as high as 12.6–13.0 MHz, whereas transitions in the "ionic" calibration groups are all in the range 10.2–11.6 MHz.[16] Among the data for the new compounds only the slightly larger range for α-I_3AlCl_4, indicating a greater range of chlorine environments in the anion, would appear unusual though the individual values and the data for the β form are not especially noteworthy. In general the compounds in Table II qualitatively appear to contain $AlCl_4^-$ groups which exhibit chlorine environments much as occur in "ionic" salts and will therefore be considered as such hereafter.

Some ^{27}Al nmr measurements gave further confirmation of the relatively high-symmetry environment about aluminum in the three new compounds which is implied by the above nqr data. The quadrupole coupling constant for ^{27}Al in these is sufficiently small that in all cases only a single transition was observed less than 10 Oe wide ($\nu_Q \geq 6$ MHz). The upper limit of the coupling constant calculated therefrom is 1.9, 1.1, and 0.7 MHz for α-I_3AlCl_4, I_5AlCl_5, and I_2AlCl_4, respectively. These are in the same range as the 1.6-MHz coupling constant similarly deduced for $Te_4^{2+}(AlCl_7^-)_2$ where the anion distortion[19] appears to be quite effective in reducing the field gradient about the aluminum atom.[16]

Trends observed in the resonances in the triatomic cation groups in these compounds, Table II, are consistent with the indicated assignments to V-shaped ions, a geometry both indicated by bonding considerations and known for $ICl_2^+AlCl_4^-$.[20] Thus ^{35}Cl transition frequencies plausibly change from 37.20 MHz in ICl (77°K)[23] to average values of 38.02 and 38.90 MHz in the $AlCl_4^-$ salts of I_2Cl^+ and ICl_2^+, respectively, the trend arising through the inductive effect of the addition of a hypothetical I^+ or Cl^+, respectively, to the iodine in ICl. Likewise ν_1 for the central iodine changes from 309 MHz in I_3^+ to 417 MHz in I_2Cl^+ and to 458 MHz in ICl_2^+. Terminal iodine comparisons are limited to 421 MHz in $I_3^+AlCl_4^-$ and 517 MHz in $I_2Cl^+(SbCl_6^-)$.[15] The single ^{127}I resonance observed in I_5^+ is more characteristic of terminal iodine in a chain structure but very little else can be ascertained regarding this cation with the present incomplete data set. The identification of $2ICl \cdot AlCl_3$ as $I_2Cl^+AlCl_4^-$ rather than $I_3^+ICl_2^+(AlCl_4^-)_2$ on the basis of the nqr data in Table II depends principally on the absence of several iodine transitions, but the observation of an evidently complete set of strong transitions in $I_2Cl^+SbCl_6^-$ [15] provides much stronger evidence for this cation.

The only known structures for compounds of these types involve ICl_2^+ with both $AlCl_4^-$ and $SbCl_6^-$,[20] and although the results are quite imprecise, they do suggest that chlorine atoms in the anion which are 0.6 Å further away than the bonded chlorine complete a roughly rectangular arrangement of chlorine about iodine. Such bridging does appear to be weak according to the $AlCl_4^-$ nqr data, however. A simple interpretation of the shifts observed in average *terminal* chlorine resonances in I_2Cl^+ and ICl_2^+ salts with variation in anion can be made in terms of the expected inductive effect of such weak anion coordination to the central halogen, assuming an approximately constant geometry at that atom. Thus the data suggest slightly stronger coordination to I_2Cl^+ occurs with $AlCl_4^-$ than with $SbCl_6^-$ (38.02 *vs.* 38.28[15] MHz) and a relatively stronger coordination to ICl_2^+ occurs with SO_3F^- than with $AlCl_4^-$ (38.12[14] *vs.* 38.89 MHz, respectively) presuming a normal (negative) temperature coefficient of the former datum at 77°K. The down-frequency shift of terminal chlorine with stronger coordination of the anion to the central atom indeed may be extended to encompass the larger effects observed in the planar I_2Cl_6 (34.16 MHz[22]) and ICl_4^- (22.37 MHz[24]). Continuing this model, the average and extreme ^{35}Cl data in the $AlCl_4^-$ anion also show a plausible progression with increasing acidity expected for iodine in the cation, averaging 10.74, 10.83, and 11.09 MHz in β-I_3^+, I_2Cl^+, and ICl_2^+ salts, respectively.

Sufficient resonance data are available for some cations that calculations can be made using a simple bonding model developed for such systems with C_{2v} symmetry, namely, that two equivalent bonding orbitals on the central atom generated from the s, p_x, and p_y atomic orbitals overlap pure p orbitals from the terminal atoms, the remaining orbitals on the central iodine atom and all other ao's being considered filled and nonbonding.[25]

In the case of α-$I_3^+AlCl_4^-$ the observation of both transitions for the central iodine first allows a direct computation of 0.373 for the asymmetry parameter (η). The relationship $\eta = -3 \cos \theta$ then leads to what would seem to be a very plausible interorbital (bond) angle of 97.1° for I_3^+. The model gives a reasonable account of total electron population in the molecule as well. The molecular coupling constant on the central iodine is known from η and ν_Q, and with the atomic value of that constant (2292.8 MHz[26]) the bonding orbital populations on the central iodine are calculable.[25] Likewise the nqr frequencies for each terminal atom lead directly to the molecular coupling constant and hence its σ-bonding population with the assumption of axial symmetry for the electric field gradient and the use of only p orbitals for bonding by that atom. The σ-bond population sum in I_3^+ thus obtained separately from the central and terminal atom transitions averages about 1.89 electrons per bond rather than the expected 2.0. When eight nonbonding electron pairs are included, 19.78 of the 20 electrons present in the cation are accounted for by this simple model.

An interesting test of the model may also be made with $ICl_2^+AlCl_4^-$ when the crystallographically known angle (96.7°) is used to compute the asymmetry parameter (0.350). σ-Bond populations on the central atom can be calculated by difference

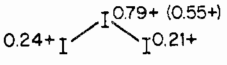
Table III. Stability of Some Solid Polyhalide Salts[a]

	Cation					
Anion	I_3^+	I_5^+	I_7^+	I_2Cl^+	ICl_2^+	Br_3^+
$AlCl_4^-$	Yes	Yes	No	Yes	Yes[b]	No
$FeCl_4^-$	No	No	No[c]	No		
$HfCl_6^{2-}$	No[c]	No	No[c]	No		
$TaCl_6^-$	No	No[c]	No[c]	No		
$SbCl_6^-$	No[d]	No[c]	No[d]	Yes[d]	Yes[b]	No
FSO_3^-	Yes[e]	No[f]	Yes[f]	Yes[g]	Yes[g]	No[h]

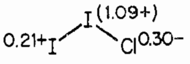
[a] This work unless otherwise referenced. [b] Reference 20. [c] The nonexistence of this compound can be reasonably inferred from observations made in the attempts to synthesize neighboring phases. [d] Reference 15. [e] Reference 12. [f] Reference 13. [g] Reference 14. [h] Reference 27.

from those on the terminal atoms using the observed resonances together with the atomic coupling constant for chlorine and $\eta = 0$ for the latter. The central atom populations in the same bonding model give a calculated molecular coupling constant of 2650.7 MHz, corresponding to a transition frequency of 447 MHz, in remarkably good agreement with the observed value of 458 MHz. As expected from this close agreement, the use of the observed frequencies together with the known bond angle to gain η on iodine gives total σ-bond populations of 1.97 electrons, very close to the expected 2.0.

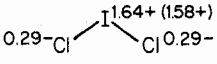
Charge distributions calculated as above are given as follows, in each case the additional value in parentheses for the central atom being that calculated by difference from the terminal charges and the total ionic charge of 1+, thus allowing the inclusion of the lower symmetry I_2Cl^+ ion as well.



($AlCl_4^-$)



($SbCl_6^-$)



($AlCl_4^-$)

The differences found for the central atom by the two approaches presumably reflect both the limitations of the model, including the presumed absence of any s contribution to bonding of the terminal atoms, and any real effects of anion coordination to the central atom.

Dependence of Stability on Anion. The stabilities of the polyiodine compounds as well as those of I_2Cl^+, ICl_2^+, and Br_3^+ as a function of anion are summarized in Table III.[12-15,20,27] The differences appear to be rather remarkable and not entirely explicable. Polybismuth cations are known to be stabilized as solid phases by $HfCl_6^{2-}$ [4] and $TaCl_6^-$ [28] as well as by $AlCl_4^-$,[2] with differences in the cation obtained appearing to depend at least in part on a numerical anion:cation ratio given a series of anions of adequate stability (high pCl).[4] These same anions are much more selective in stabilizing polyiodide cations, $AlCl_4^-$ being the only one which yields stable products. It may be inferred that a higher chloride ion activity established by $HfCl_6^{2-}$ and $TaCl_6^-$ destabilizes the desired cation by stabilizing molecular ICl. The $SbCl_6^-$ ion might well serve the same role as $AlCl_4^-$ except that it is known to oxidize iodine to the I_2Cl^+ cation.[15]

One quantity which to a first approximation should serve as a relative measure of the chloro complex stability or pCl in these systems is the chloride ion affinity of the neutral gaseous chloro acid, that is, $-\Delta H°$ for the reaction

$$Cl^-(g) + MCl_n(g) \rightarrow MCl_{n+1}^-(g) \qquad (6)$$

Unfortunately this quantity is not known in many instances and so phase diagram criteria have been employed to judge relative stabilities.[4] One well-established affinity value is that for $AlCl_4^-$, 83 ± 7 kcal,[29,30] and it was the estimate[31] of an impressive 120 kcal for the analogous reaction leading to $FeCl_4^-$ which prompted the unproductive application of the $FeCl_3$–$FeCl_4^-$ couple to the stabilization of iodine cations (Table III). An explanation of the discrepancy between experiment and prediction for $FeCl_4^-$ was not at all obvious until it was pointed out to us[32] that the prior calculation of the chloride ion affinity of $FeCl_3$ had incorrectly applied the Kapustinskii equation in estimating the lattice energy of $NaFeCl_4$ and $KFeCl_4$ by employing the spherical crystallographic radius of 4.00 Å for $FeCl_4^-$ rather than the empirical and smaller "thermochemical" radius.[33] About a 25% reduction in the observed anion radius has been found appropriate for comparable $AlCl_4^-$ and $GaCl_4^-$ salts,[32] and the application of a like adjustment in a recalculation for $FeCl_4^-$ (together with small subsequent changes in standard thermodynamic data[34]) gives about 88 kcal for the chloride ion affinity of $FeCl_3(g)$, comparable to the affinity of $AlCl_3$.

A more direct estimate of this chloride ion affinity appears feasible since $NaAlCl_4$ and $NaFeCl_4$ are isostructural,[35] and a careful calculation of the lattice energy of the former has been made.[8] For this purpose the thermochemical radius sum for $NaAlCl_4$ calculated from its U_0 was simply increased by the 0.07-Å difference known between the iron–chlorine[35] and aluminum–chlorine[16] bond lengths in these anions for the U_0 calculation for $NaFeCl_4$. The affinity value obtained utilizing this approximation is substantially the same, 85 kcal/mol.

Although this revision indicates that $FeCl_4^-$ should be comparable to $AlCl_4^-$ in stability, the chloride ion affinity of MCl_3 in the gaseous state probably represents only the principal portion of the quantities appropriate for the comparison of the condensed-state reactions such as studied here. Under conditions where MCl_3 is molecular, the species M_2Cl_6 would be expected and this favors $FeCl_3$ over $AlCl_3$ (and destabilizes $FeCl_4^-$) by 5.4 kcal/mol. Of greater significance in the present study is the fact that $FeCl_4^-(g)$ is relatively destabilized by 6 kcal when *solid* MCl_3 is involved instead, a factor which accounts for the major portion of the difference between the enthalpies of formation of solids $NaFeCl_4$ and $NaAlCl_4$ from solid NaCl and MCl_3, −0.2[36] and −8.0 kcal,[30,34] respectively. The formation of $Al_2Cl_7^-$ is well established in acidic systems through dissociation of $AlCl_4^-$, and a comparable $FeCl_4^-$–$Fe_2Cl_7^-$ equilibrium has been inferred.[37] Although the formation of $M_2Cl_7^-$ presumably involves a higher chloride ion affinity than for MCl_4^-, these species are known only in systems containing major amounts of MCl_4^-, and so $M_2Cl_7^-$ properties are not critical in cases of borderline stability. Finally in the condensed state there may be appreciable differences in the strength of coordination of the two MCl_4^- ions to I_3^+, etc., though obviously this is not very large for stable phases. On balance a somewhat lesser stability of the $FeCl_4^-$ salts indicated by the present investigation appears qualitatively plausible in the above terms, but the difference is not large and stabilization by this anion probably can be accomplished in somewhat more favorable situations.

Unfortunately sufficient data do not exist to judge the hafnium and tantalum anions. Clearly little is known about the chloride ion affinity of I_n^+, the other part of the decomposition couple, but it is worth noting that the chloride ion affinity of $I^+(g)$ (to ICl(l)) is ~205 kcal/mol,[34] meaning that a considerable stabilization of I^+ through bonding to I_2 (ICl or Cl_2) must be involved in I_n^+ and related ions.

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Registry No. I_3AlCl_4, 39019-01-7; I_5AlCl_4, 39019-02-8; $I_2ClAlCl_4$, 39019-00-6; ICl_2AlCl_4, 42813-30-9; ICl, 7790-99-0; $AlCl_3$, 7446-70-0; I_2, 7553-56-2; ^{35}Cl, 13981-72-1; ^{27}Al, 7429-90-5; $FeCl_3$, 7705-08-0.

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Spectra and Structure of Phosphorus–Boron Compounds. IX.[1] Vibrational Analysis and Molecular Symmetry of Solid $B_2Cl_4{\cdot}2PH_3$ and $B_2Cl_4{\cdot}2PD_3$

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The Raman (25–2500 cm^{-1}) and infrared (90–2500 cm^{-1}) spectra of solid $B_2Cl_4{\cdot}2PH_3$ and $B_2Cl_4{\cdot}2PD_3$ have been recorded. The vibrational data have been interpreted on the basis of a trans (C_{2h}) molecular conformation in the solid state. This structure requires that the principle of mutual exclusion holds, and this is seen to be the case since the P–B stretching frequencies observed in the infrared and Raman effect are 651 and 713 cm^{-1}, respectively, in $B_2Cl_4{\cdot}2PH_3$ and 620 and 658 cm^{-1}, respectively, in $B_2Cl_4{\cdot}2PD_3$. Differences in frequencies between the adducts and the parent molecule are attributed to phosphorus–boron coordination. The assignments of torsional fundamentals give 2.92 ± 0.18 kcal/mol for the periodic barriers to internal rotation about the P–B bonds.

Introduction

The symmetries of molecules having the general formula X_2Y_4 have been under investigation in this laboratory over the past few years.[3-15] These investigations have involved compounds which have group Va elements as the central atoms as well as studies on the diboron tetrahalides. More recently, the effects upon symmetry resulting from the coordination of the lone-pair electrons on nitrogen in hydrazine and phosphorus in diphosphines have been investigated.[16-18] The results have been identical in that for the solid phases, the molecules of tetramethyldiphosphine–bis(borane)[16] and hydrazine–bis(borane)[17] have both been found to exist as one conformer, the C_{2h} (trans) form. For these trans molecules, the differences between the infrared and Raman frequencies as required by symmetry were most pronounced for the skeletal and bending motions.

To continue our studies of the effects of adduct formation in relation to structure, we have undertaken the vibrational analysis of diboron tetrachloride–bis(phosphine). This molecule differs from previously examined adducts in that the symmetry must change from D_{2h} (crystalline solid) in the parent B_2Cl_4 molecule to either or both of the likely forms, C_{2h} (trans) and C_2 (gauche). The possible symmetries of the bis(borane) adducts of hydrazine[17] and tetramethyldiphosphine[16] are the same as those possible for the parent molecules. No previous structural work has been reported for $B_2Cl_4{\cdot}2PH_3$ and no vibrational data are available for this molecule.

Experimental Section

With the exception of the phosphine syntheses, all preparative work was carried out in a high-vacuum system employing greaseless stopcocks. All ground-glass apparatus was lubricated with Kel-F 90 grease to prevent decomposition of halogen-containing species. Boron trichloride was obtained commercially (Matheson) and was purified by trap-to-trap fractionation or by distillation on a variable-temperature vacuum fractionation column[19] followed in either case by exposure to mercury until the vapor pressure was 476 Torr at 0°.[20] The diboron tetrachloride was prepared either by a slightly modified method of that reported by Wartik, *et al.*,[21] or by the method of Brennan.[22] Purification was by high-vacuum column distillation.

Phosphine was prepared under a stream of gaseous nitrogen in a well-ventilated fume hood as described in the literature.[23] Phosphine-d_3 was prepared in a similar manner using D_2O and D_2SO_4. All phosphine species were purified by passing them through a trap at −131° (*n*-pentane slush) into a trap at −196°. Purity was monitored by vapor pressure measurements[24] and infrared spectra.[25]

Diboron tetrachloride–bis(phosphine) was prepared by allowing B_2Cl_4 and PH_3 in a 1:2 mole ratio, respectively, to react at −80°.[26] The reaction tube was immersed in a −22° bath (CCl_4 slush) and pumped under dynamic vacuum to remove any $H_3P{\cdot}BCl_3$ which may have been formed or any traces of unreacted B_2Cl_4 or PH_3.

Raman spectra were recorded on a Cary Model 82 Raman spectrophotometer equipped with a Coherent Radiation Model 53