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The synthesis and characterization of three polyhalogen tetrachloroaluminates

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The synthesis and characterization of three
polyhalogen tetrachloroaluminates

by

Don Jay Merryman

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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Iowa State University
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1972

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Introduction

Investigations of systems containing species in unusual oxidation states have received increased attention during the last several years, particularly those systems involving the dissolution of metals in their molten salts. It has long been known¹ that the mercurous ion is actually the dimer, Hg_2^{2+} , and more recent studies have shown that Cd_2^{2+} ,² Zn_2^{2+} ,³ Pb_2^{2+} ,⁴ Mg_2^{2+} ,⁵ Ca_2^{2+} ,⁶ Sr_2^{2+} ,⁷ and Ba_2^{2+} ⁷ are evidently formed by the addition of the metal to its halide melt.

An early investigation⁸ of the Bi-BiCl₃ system showed that an intermediate phase with the approximate composition BiCl was formed. Later studies of this system suggested the presence of Bi₂ and (BiCl)₂⁹ in the melt at low metal concentrations, and a tetramer, (BiCl)₄ or Bi₃Cl,¹⁰ in the BiCl-BiCl₃ region. However, the complexity of the species formed in this system was not fully realized until the crystal structure of BiCl was determined by Hershafit and Corbett.¹¹ This x-ray study revealed that the correct stoichiometry of this phase was Bi₁₂Cl₁₄ and it consisted of a Bi₉⁵⁺ cation and two kinds of complex chlorobismuthate anions, BiCl₅²⁻ and Bi₂Cl₈²⁻; the Bi₉⁵⁺ cation apparently being stabilized by the large anions.

A later investigation by Corbett¹² of the pseudo-binary system Bi-(BiCl₃+3AlCl₃) resulted in the isolation of two intermediate phases, Bi₅(AlCl₄)₃ and Bi₄AlCl₄. In a related study, Bjerrum, Boston, and

Smith^{13, 14} identified the polycations Bi_5^{3+} and Bi_8^{2+} in melts produced by the dissolution of Bi and BiCl_3 in NaAlCl_4 and NaCl-AlCl_3 or LiCl-ZnCl_2 eutectic mixtures. The stoichiometries of these above phases along with the similarities between the melt and solid state spectra indicated that the solid phases were tetrachloroaluminate salts of Bi_5^+ and Bi_8^+ .

The identification of Bi_5^{3+} and Bi_8^{2+} showed that the occurrence of Bi_9^{5+} was not unique and that other metal polycations might be found in related $\text{M}-(\text{MCl}_x + \text{XAlCl}_3)$ systems. Complexation of the rather basic Cl^- ion by AlCl_3 appears to stabilize reduced polycations (with respect to disproportionation) in acidic AlCl_4^- melts. This process reduces complexation of the more acidic higher oxidation state of the metal with a resultant decrease in its relative stability. The polarizable Cl^- ion complexes cations in both reduced and higher oxidation states although the higher oxidation state is complexed more because of the larger charge density (greater polarizing power), whereas the less polarizable AlCl_4^- ion does not complex cations in either oxidation state appreciably. The larger AlCl_4^- ion also enhances the stability of reduced phases by decreasing the difference in lattice energies of the two oxidation states thus reducing the tendency of the lower state to disproportionate.

In an extension of the bismuth investigations to other systems,

Prince, Corbett and Garbisch¹⁵ determined the phase diagrams of the pseudo-binary systems Se-(SeCl₄+4AlCl₃) and Te-(TeCl₄+4AlCl₃). Two intermediate phases with the empirical compositions Se₂AlCl₄ and Se₄AlCl₄ were found in the selenium system and three phases with the empirical compositions Te₂AlCl_{3.5}, Te₂AlCl₄ and Te₃AlCl₄ were found in the tellurium system. A subsequent crystal structure determination¹⁶ for Se₄AlCl₄ has shown it to be the compound Se₈²⁺(AlCl₄⁻)₂. The Se₈²⁺ ion assumes a puckered eight-member ring conformation that in a formal sense can be viewed as resulting from a two electron oxidation of the Se₈ ring found in elemental selenium.

The crystal structure determination of Te₂AlCl_{3.5} and Te₂AlCl₄ by Couch, Lokken and Corbett¹⁷ revealed the correct formulation for these phases to be Te₄²⁺(Al₂Cl₇⁻)₂ and Te₄²⁺(AlCl₄⁻)₂. The isolation of the Al₂Cl₇⁻ ion meant that intermediate phases formed on reduction in M-(MCl_x+xAlCl₃) systems did not necessarily have to be AlCl₄⁻ salts as had been the case for bismuth.

Concurrent studies of the dissolution of sulfur, selenium and tellurium in fluorosulfuric acid revealed the presence of S₄²⁺, S₈²⁺, S₁₆²⁺,¹⁸ Se₄²⁺, Se₈²⁺,¹⁹ (Te⁺)_n,²⁰ Te₄²⁺,²¹ and (Te₃⁺)_n,²⁰ in solution. The large number of species observed in these investigations indicated polycation formation may be a rather general phenomenon in systems with very low base strength.

An extensive polycation chemistry similar to that exhibited by tellurium, selenium and sulfur has also been found to occur in systems containing iodine or bromine. Conductimetric and cryoscopic studies have shown the presence of I_2^+ , I_3^+ , and I_5^+ in solutions of I_2 in disulfuric acid²² and fluorosulfuric acid.²³ I_2^+ was not completely stable in either acid and partially disproportionated to I_3^+ and $I(SO_4H)_3$ or $I(SO_3F)_3$. In addition, Gillespie, Milne and Morton²⁴ have shown that below -60° I_2^+ is extensively dimerized to I_4^{2+} in HSO_3F . A concurrent investigation has shown²⁵ that the reaction between I_2 and SbF_5 or I_2 , IF_5 and MF_5 ($M = Sb, Ta$) produces solid crystalline compounds with the compositions $I_2Sb_2F_{11}$ and $I_2Ta_2F_{11}$. The similarities between the solid state spectra of these compounds and of the solutions of I_2^+ in HSO_3F ²³ along with the paramagnetism exhibited by the solids and I_2^+ in solution leads to the conclusion that these compounds are salts containing the I_2^+ cation.

In an early study, Ruff et al.²⁶ found that I_2 and SbF_5 react to give two solids $I(SbF_5)_2$ and $ISbF_5$, the product obtained being dependent upon which reagent was in excess. These results were confirmed²⁵ in 1968 and very good spectral evidence was obtained for the presence of I_2^+ in $I(SbF_5)_2$ ⁵ and I_3^+ in $ISbF_5$.⁵ Both solids melt over a temperature range and are thought to be either complex polymeric materials or mixtures rather than discreet phases.

The bromine polycations Br_2^+ and Br_3^+ have been identified and found to be less stable than the analogous iodine species. Gillespie and Morton²⁷ found Br_3^+ to be stable in HSO_3F ; however, the lower basicity of the "superacid", $\text{HSO}_3\text{F} \cdot 3\text{SO}_3 \cdot \text{SbF}_5$, was required to stabilize the Br_2^+ cation. Even in the superacid Br_2^+ is extensively disproportionated to Br_3^+ and BrOSO_2F . Br_4^{2+} and Br_5^+ were not found to occur in either acid which further illustrates the lower stability of bromine polycations compared with iodine polycations.

Glemser and Smalc²⁸ have prepared $\text{Br}_3^+\text{AsF}_6^-$ by reaction of Br_2 with $\text{O}_2^+\text{AsF}_6^-$ and by the reaction of BrF_5 or BrF_3 with Br_2 and AsF_5 . Characterization of this compound was accomplished primarily by chemical analyses and spectral studies. A similar reaction between BrF_5 , Br_2 and SbF_5 resulted in the formation of $\text{Br}_2^+\text{Sb}_3\text{F}_{16}^-$. A crystal structure determination²⁹ for this compound has shown the definite presence of the Br_2^+ cation. The Br-Br bond length was found to be significantly shorter than in elemental bromine³⁰ (2.13 Å compared with 2.27 Å); no significant covalent interaction between cationic bromine and fluorine in anions was observed (Br-F distances were ≥ 2.85 Å).

Evidence for the existence of chlorine polycations has been minimal although Gillespie and Morton³¹ have reported the preparation of $\text{Cl}_3^+\text{AsF}_6^-$ at low temperatures and have identified the compound

by its Raman spectrum. In a related study³² these authors found no evidence of Cl_2^+ in $\text{HSO}_3\text{F}-3\text{SO}_3-\text{SbF}_5$ superacid in contrast with the conclusion by Olah and Comisarow³³ that Cl_2^+ was formed in the reaction between ClF and $\text{HSO}_3\text{F}-\text{SbF}_5$.

In addition to the homopolyatomic cations of iodine, bromine and chlorine, several interhalogen cationic species have been identified. Garret, Gillespie and Senior³⁴ found that the addition of ICl or IBr and I_2 to solutions of HIO_3 in H_2SO_4 resulted in the formation of ICl_2^+ , I_2Cl^+ and I_2Br^+ . ICl_2^+ has also been identified³⁵ in the compounds $\text{ICl}_2^+\text{AlCl}_4^-$ and $\text{ICl}_2^+\text{SbCl}_6^-$ prepared from the reaction of ICl_3 with AlCl_3 or SbCl_5 . X-ray studies of these compounds have shown the ICl_2^+ ion is bent with Cl-I-Cl angles of 97° and 92° , respectively. Interionic distances suggest there is apparently some interaction between the iodine atom and anionic chlorine in both but the extent of this interaction is difficult to determine because of the large standard deviations in I-Cl , Sb-Cl and Al-Cl distances.

The observation that polycations of selenium and tellurium were stable both in HSO_3F and AlCl_4^- melts indicated iodine polycations might also be stable in AlCl_4^- media. The formation of I^+ by the autoionization reaction



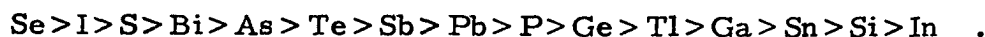
has been postulated³⁶ in order to explain the observed conductivity of

molten ICl. However, Gillespie and Malhotra²² have found that the addition of ICl to disulfuric acid results in the complete disproportionation of unipositive iodine into I_2^+ , I_3^+ and $I(SO_4H)_3$. In view of this result, the ionic species present in molten ICl are more reasonably formulated as I_2Cl^+ and ICl_2^- produced by the reaction



Since it appears that complexation of Cl^- by a relative weak Lewis acid (ICl) imparts a certain measure of stability to I_2Cl^+ , the addition of $AlCl_3$ (strong Lewis acid) should greatly increase the stability of I_2Cl^+ and also iodine polycations.

The formation and stability of polyiodine cations is also predicted by the large $5s - 5p$ promotion energy of a gaseous I^+ ion. Grossaint³⁷ has shown a correlation between polycation formations and the $ns - np$ promotion energy of the gaseous ions (+1 oxidation state) of the heavier post-transition elements; the +1 oxidation state being chosen because it approximates the average charge density on each atom in many polycations. Arranging the heavier elements in order of decreasing $ns - np$ separation results in the series:



All of the elements known to form polycations are on the left side of the series (large $ns - np$ separation) and on this basis iodine polycations should be quite stable.

The study reported here was an investigation of the $I_2-(ICl + AlCl_3)$ pseudo-binary system which resulted in the isolation and partial characterization of two reduced phases, $I_3^+AlCl_4^-$ and $I_5^+AlCl_4^-$. The presence of I_2Cl^+ in the previously known³⁸ phase $2ICl \cdot AlCl_3$ has also been demonstrated. An added reward of this investigation has been the emergence of nuclear quadrupole resonance spectroscopy as a useful technique for identifying $AlCl_4^-$ in solid phases of unknown structure.

Experimental

Materials - The iodine used was Fisher Certified Reagent Grade and was sublimed once under dynamic vacuum to remove iodine oxide and other nonvolatile impurities.

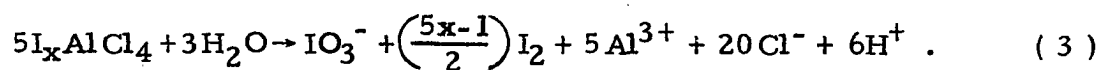
Iodine monochloride of 99% purity was purchased from Research Organic/Inorganic Chemical Corp. and used without further purification. The specifications show ICl_3 to be the main impurity ($\leq 1\%$) along with 0.001% Br_2 .

Commercial anhydrous aluminum chloride was sublimed once under dynamic vacuum to remove Al_2O_3 and AlOCl , then resublimed under 30 mm argon to remove FeCl_3 . The resultant AlCl_3 was a white crystalline solid.

The sensitivity of the salts to moisture necessitated the use of dry box and vacuum techniques throughout this investigation. The dry box was filled with argon which was continuously circulated through a column of Linde molecular sieve and over a tray of P_2O_5 to insure a minimum pressure of H_2O . Entry to the dry box was accomplished through an evacuable port. Iodine transfers were carried out in a nitrogen-filled glove bag so that the dry box would not be contaminated with iodine vapor. Aluminum chloride was stored in a stoppered glass bottle in the dry box while I_2 and ICl were stored in evacuable glass (Pyrex) containers equipped with a glass stopcock and Teflon needle

valve, respectively. Aluminum chloride was weighed in the dry box using a single pan triple beam balance accurate to 5 mg. Weights of iodine were determined in a glove bag using a double pan single beam balance accurate to 2 mg. Iodine monochloride was weighed in a pre-weighed evacuable container using a Mettler single pan balance accurate to 0.05 mg.

Analysis - Samples were added to small glass weighing bottles which were capped while in the dry box, and weighed in air on an analytical balance. The sample container was then cooled to $\sim 0^\circ$ in an ice bath (to minimize loss of I_2 and ICl by volatilization), the cap removed and the sample and weighing bottle dropped into 200 ml. of 0.5N H_2SO_4 which had previously been cooled to 0° . This solution was immediately capped with a ground glass stopper and kept in an ice bath until all reaction had ceased and no purple iodine vapor was visible above the solution. The solution was then decanted into a volumetric flask. A solution of KI was added to the original flask containing the bulk of the elemental iodine liberated in the initial reaction between the sample and water according to the equation:



When all of the I_2 had dissolved, the KI-KI₃ solution was also added to the solution in the volumetric flask after which it was made up to

volume. The empty weighing bottle was washed and weighed and the weight of sample determined by difference corrected for the buoyancy of argon. (This correction was the difference in weights of a weighing bottle containing argon and then air as determined experimentally.)

Iodine was determined volumetrically using a standard sodium thiosulfate solution and starch indicator.

Chloride was determined gravimetrically as AgCl from a 50:50 water-acetone mixture. Interference from I^- was eliminated by diluting an aliquot five fold, adding $NaNO_2$ to oxidize I^- to I_2 , and heating to expell I_2 .

Physical Measurements - A Cary 14 spectrophotometer was used to record the ultraviolet-visible spectra. The samples were mulled with Halocarbon oil or grease and pressed between two optical grade silica plates. In addition, spectra of thin films of the sample alone (as a liquid or paste) with no mulling agent present were obtained. The edges of the quartz plates were coated with Halocarbon grease to provide a seal against air and moisture.

Far infrared spectra were obtained using a Beckman Model IR-11 with the assistance of Mr. A. deSilva of the Ames Laboratory Analytical Services Group II. The samples were either mulled with Fluorolube or ground into a paste with no mulling agent present and placed between two sheets of Teflon film which were positioned in a

cell equipped with a rubber O-ring seal.

X-ray powder patterns were obtained using a Phillips Debye-Sherrer camera with a diameter of 114.59 mm and nickel filtered copper K_{α} radiation. Because of their paste-like consistency, the samples were ground together with an equal volume of powdered Pyrex glass before loading into 0.3 mm Lindemann glass capillaries. The capillaries were sealed with Apiezon Q wax while in the dry box and later sealed permanently with a gas-oxygen torch. Intensities were estimated visually with a maximum value of 10.

Thermal analysis containers were made from 50 mm lengths of 10 mm i. d. quartz tubing. The containers were connected to a ball joint through 7 mm i. d. tubing at the top and had a 10 mm length of 3 mm i. d. tubing sealed inwardly at the bottom for a thermocouple well. The containers were filled with four to six grams of sample, sealed under vacuum, and placed in a double wall evacuated jacket with the thermocouple in the well. Temperatures were regulated with an Elektronik Indicating Proportionating Controller (Minneapolis-Honeywell) accurate to $\pm 1^{\circ}$. The thermocouple junction potentials were recorded on a Bristol Model 560 Dynamaster strip chart recorder and measured with a Rubican potentiometer.

The ^{35}Cl and ^{127}I nuclear quadrupole resonance (nqr) spectra were obtained using a Wilks NQR-1A super-regenerative nqr

spectrometer and a wide line induction spectrometer described previously by Torgeson.³⁹ The spectra were measured by Mr. Paul Edwards of Physical and Inorganic Chemistry Group X.

The Wilks spectrometer was used for the collection of most of the ^{35}Cl nqr data and all of the ^{127}I nqr data. Basically, this instrument imposes a variable frequency on the sample until resonance occurs. At the resonance frequency, the sample absorbs energy creating an imbalance in the circuitry which is recorded on a strip chart recorder as the nqr spectrum. A more detailed description of the design and operation of super-regenerative nqr spectrometers is given in the text by Das and Hahn.⁴⁰

The wide line induction spectrometer was used to resolve closely spaced ^{35}Cl resonances which occurred for several samples. The spectrometer scanned repeatedly through a narrow frequency range (100-150 KHz) centered on the approximate resonance frequency of interest. Data from repeated scans were stored in a 400 channel analyzer and continuously averaged for six to eight hours to insure reasonable signal-to-noise values.

Sample containers for ^{35}Cl nqr spectroscopy were prepared from 18 cm lengths of 15 mm o. d. Pyrex tubing with a rounded bottom. The top of the container was connected to a ball joint with 10 mm o. d. tubing. Twenty to twenty-five grams of sample were placed into the

container which was then sealed under vacuum. Sample containers for ^{127}I nqr spectroscopy were similar except 22 mm o.d. Pyrex tubing was used. The different diameters of sample containers were necessitated by the design of the Wilks spectrometer which used a 5/8 inch (15.9 mm) diameter sample coil for the 0-300 MHz range and a 7/8 inch (22.2 mm) diameter coil for the 300-650 MHz range.

The samples were melted and recrystallized to insure the presence of a dense crystalline mass in a minimum volume. The tendency of the samples to melt at frequencies > 100 MHz was circumvented by directing a stream of air from a fan onto the bottom of the sample container.

The ^{27}Al broadline nuclear magnetic resonance (nmr) spectra were measured by Mr. Paul Edwards using a spectrometer designed by D. R. Torgeson.³⁹ Data were collected from samples used previously for ^{35}Cl nqr spectroscopy. Frequency probes of 5 MHz and 10 MHz were used during the investigation. Data from repetitive scans were stored in a 400 channel analyzer and continuously averaged over 6-8 hours to insure reasonable signal-to-noise ratios.

Synthesis - Most of the samples used during this investigation were prepared by the addition of stoichiometric amounts of I_2 to an equimolar mixture of ICl and AlCl_3 (1:1 mole ratio), this ratio being chosen so that all of the chloride present would potentially be converted

to AlCl_4^- upon reduction of ICl with I_2 . Other samples were prepared by the addition of I_2 to 1:2 mole ratio mixtures of ICl and AlCl_3 which would theoretically result in the formation of heptachlorodialuminate (Al_2Cl_7^-) salts of iodine polycations upon reduction; and by the addition of I_2 to 2:1 mole ratio mixtures of ICl and AlCl_3 which would give incomplete conversion of Cl^- to AlCl_4^- upon reduction. The preparation of samples that do not lie on the pseudo-binary $\text{I}_2-(\text{ICl} + \text{AlCl}_3)$ was prompted by the fact that the compound $(\text{Te}_4^{2+})(\text{Al}_2\text{Cl}_7^-)_2$ has been found¹⁷ to exist in the Te- $(\text{TeCl}_4 + 4\text{AlCl}_3)$ system and a phase with the stoichiometry $2\text{ICl} \cdot \text{AlCl}_3$ has been reported³⁸ to exist in the ICl- AlCl_3 system.

The apparatus used for the preparation of samples is shown in Figure 1. A Pyrex glass container of ICl (A) and a preweighed evacuated transfer container (B) which were both equipped with a Teflon needle valve were attached to a vacuum manifold with ball and socket joints lubricated with Halocarbon grease. After evacuation, the Teflon needle valve (C) was closed and ICl was sublimed slowly from A at 0° to B which had been cooled to -196° in a dewar of liquid nitrogen. The needle valves at A and B were closed, and B was removed and weighed after warming to room temperature, the weight of ICl present being determined by difference. The proper amounts of I_2 and AlCl_3 were then computed (based on the weight of

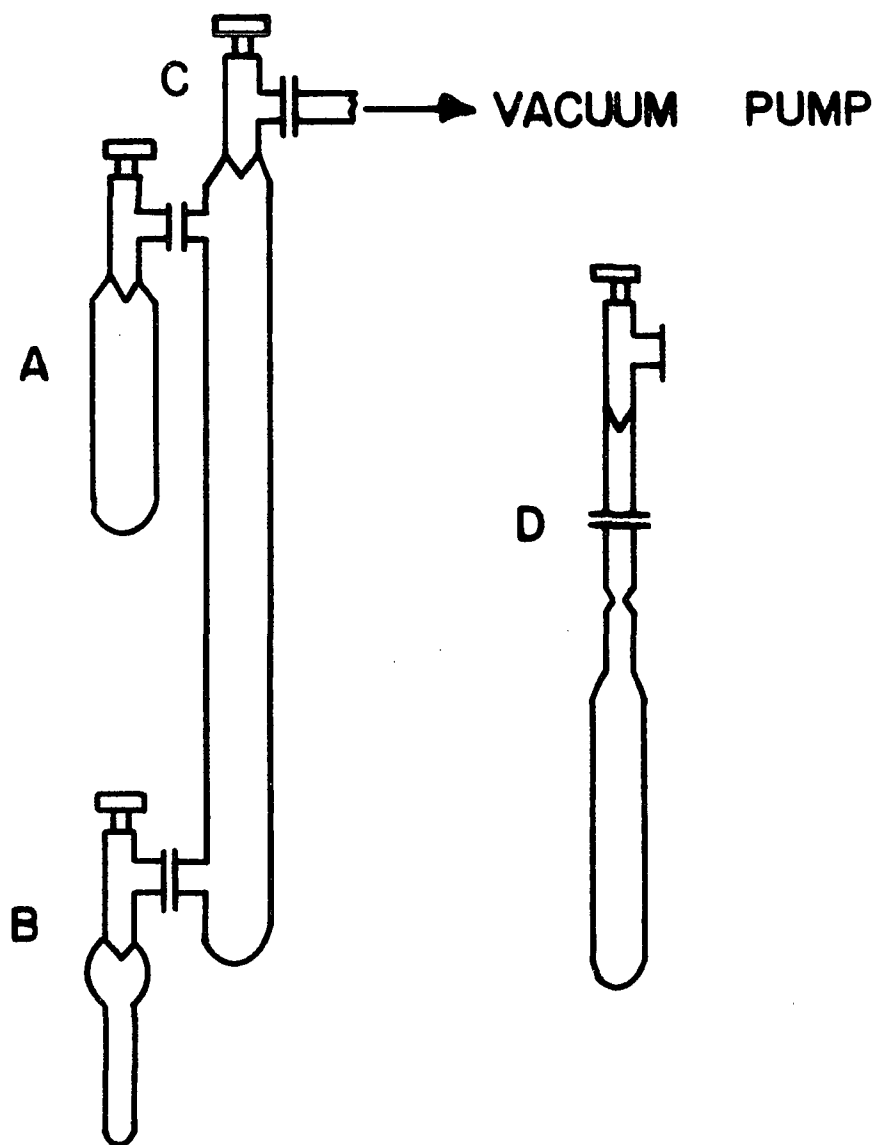


Figure 1. Apparatus for the preparation of reduced compositions in the $I_2-(ICl + AlCl_3)$ system.

ICl) to give a sample of the desired stoichiometry. A one mole percent excess of AlCl_3 and of I_2 were taken to allow for loss of AlCl_3 by hydrolysis and I_2 by volatilization during transfer.

Aluminum chloride was added to the sample container (D) in an argon filled dry box and iodine added in a nitrogen filled glove bag to prevent contamination of the dry box with iodine vapor. The container of ICl (A) was removed from the vacuum manifold and B and D were attached. The known weight of ICl was sublimed from B to D using the same sublimation procedure as before after which the sample container was sealed under vacuum.

The initial cooling of the ICl (0°) and slow rate of sublimation minimized the disproportionation into ICl_3 and I_2 . The occurrence of this reaction could be easily monitored by the appearance of bright yellow ICl_3 at B (ICl is red-brown). Using the sublimation conditions just described, the amount of ICl_3 (deposited as a very thin film on the upper wall of B) was visually estimated to be $< 2\%$ of the total sample weight.

Heating the samples to $\sim 150^\circ$ resulted in a black homogeneous melt. When cooled to room temperature, the samples remained a black viscous liquid and cooling the samples to -196° did not initiate crystal growth as the samples liquified when warmed to room temperature. However, the thermal shock produced by quenching the

samples in liquid nitrogen and partially melting them in hot water did cause nucleation, after which ~ 15 minutes were required for complete crystallization of the samples at room temperature.

Results and Discussion

Preliminary Studies and Phase Equilibria - Preliminary

investigations of the I_2 -(ICl + $AlCl_3$) system consisted of the preparation of several samples with the general formula I_xAlCl_4 ($x = 1, 2, \dots, 7$). The samples were equilibrated at 140-160° for 1-2 hours and then cooled to room temperature. The composition $IAlCl_4$ ($ICl \cdot AlCl_3$) was composed of a black viscous liquid and a rather large amount (~ 50 % by volume) of colorless platelets which appeared to be free $AlCl_3$. I_2AlCl_4 (33 mol % I_2 in ICl + $AlCl_3$) was also composed of a similar black liquid with a smaller amount of $AlCl_3$ floating on the surface. Samples with the composition I_xAlCl_4 ($x = 3, 4, 5, \text{ and } 6$) corresponding to 50-71.4 mol % I_2 in ICl + $AlCl_3$ were homogeneous black viscous liquids with no evidence of free $AlCl_3$ while I_7AlCl_4 was composed of a black liquid and crystals of elemental iodine. No free ICl was observed in any of the samples.

Solidifying the black liquids proved to be rather difficult; cooling the samples to -196° resulted in the formation of a solid glass which liquified upon warming to room temperature. However, by trial and error it was found that alternately quenching the samples in liquid N_2 and partially remelting them in hot water (this cycle repeated five to ten times) did initiate crystallization at room temperature for all the samples except I_2AlCl_4 . Samples of this composition were impossible

to solidify (at room temperature) even with prolonged quenching. The ease with which the samples crystallized varied with composition; in general, crystal growth was easier to initiate in more reduced compositions. The visual appearance of the samples after quenching is described in Table I.

The crystalline solid formed in samples of composition $IAlCl_4$ was purplish-black in bulk but thin sections were brownish-yellow. Because of the unreacted $AlCl_3$ present, the composition of this solid must correspond to $ICl \cdot nAlCl_3$ where $n < 1$. Fialkov and Shor³⁸ have reported the existence of an intermediate phase $2ICl \cdot AlCl_3$ (33 mol % $AlCl_3$) in the $ICl-AlCl_3$ binary system together with a eutectic composition containing 42 mol % $AlCl_3$. Therefore, it was assumed that the solid isolated here from the 1:1 composition consisted of a mixture of the two phases $2ICl \cdot AlCl_3 + AlCl_3$.

I_3AlCl_4 appeared to be a single crystalline phase with no free ICl or $AlCl_3$ present. This solid was a shiny black color although thin sections were brownish-red. Microscopic examination revealed the presence of several small black platelets on the wall of the sample container. The bulk solid was composed of similar crystals with a small amount of black liquid trapped in the solid matrix partially coating the crystals. The heat from the microscope light tended to melt the individual crystals in about 2 minutes indicating a rather low

Table I

Physical Appearance of Reduced Compositions
in the I_2 -(ICl + AlCl₃) System

Empirical Composition	Physical Appearance
$IAlCl_4$	Equal volumes of AlCl ₃ and purple-black crystalline solid.
I_2AlCl_4	Black liquid with AlCl ₃ floating on the surface.
I_3AlCl_4	Shiny black solid; traces of black liquid present in the crystal matrix.
I_4AlCl_4	Two crystalline solids present that solidify independently. The first has a green-black metallic luster; the second is shiny black similar to I_3AlCl_4 .
I_5AlCl_4	Crystalline solid with a green-black metallic luster; traces of black liquid present in the crystal matrix.
I_6AlCl_4	Same as I_5AlCl_4 .
I_7AlCl_4	Same as I_5AlCl_4 with small crystals of I_2 on the container walls and in the solid matrix.

melting point.

Samples containing 60 mol % I_2 (I_4AlCl_4) were unique in that the quenching cycle resulted in only partial crystallization of the sample, the rest of the sample remaining a black liquid. The liquid was poured off the solid (greenish-black metallic luster) to the other end of the tube and again repeatedly quenched, the result being complete crystallization of the remaining liquid (shiny black solid resembling I_3AlCl_4).

I_5AlCl_4 , I_6AlCl_4 , and I_7AlCl_4 all formed a dark crystalline mass with a very definite green metallic luster although thin sections were brown-red as in I_3AlCl_4 . Small greenish needles were observed growing from the container walls and from the bulk sample surface. In addition to the green-black solid, small crystals of I_2 were present on the walls of the sample container of I_7AlCl_4 (no free I_2 visible in I_5AlCl_4 or I_6AlCl_4). These samples also appeared to be "wet" and melted rather easily from the heat generated by the microscope light.

On the basis of these preliminary visual observations, it appeared that two intermediate phases were formed in the I_2 -($ICl + AlCl_3$) binary section, the first phase containing 50 to 60 mol % I_2 and the second containing 60 to 75 mol % I_2 (in $ICl + AlCl_3$).

In order to define the composition limits of the reduced phases more accurately, a phase equilibrium study of the I_2 -($ICl + AlCl_3$)

pseudo-binary section was undertaken using a combination of thermal analysis and x-ray powder pattern methods. Because of the severe supercooling exhibited by the system cooling data could not be obtained. Heating data were not completely satisfactory either; the samples had to be vigorously shaken while being heated to give even marginally reproducible liquidus halts ($\pm 3-4^\circ$ for most compositions). For samples with I/Cl ratios ≥ 4 , the liquidus could only be determined accurately by equilibrating the sample with a small amount of solid present and then gradually increasing the temperature ($1-2^\circ$) at hourly intervals until visual inspection revealed the sample to be completely liquid.

The resultant phase diagram for $I_2-(ICl + AlCl_3)$ is shown in Figure 2. The presence of two intermediate phases is indicated with the stoichiometries being limited to $I_{3.0 \pm 0.15} AlCl_4$ (50 ± 2 mol % I_2) and $I_{5.0 - 0.2, +1.0} AlCl_4$ ($67 - 1.2, +4.4$ mol % I_2). The lower phase melts congruently at $45 \pm 1^\circ$ and the upper phase melts slightly incongruently at $50.0 - 50.5^\circ$. The rather small temperature range bracketing the peritectic is thought to be valid for two reasons. First, samples containing 66.7, 68.2, and 71.4 mol % I_2 were almost completely liquid with only a very small amount of solid remaining undissolved when equilibrated at $50.0 - 51.0^\circ$. The solid looked like elemental iodine and the amount of solid present increased as the

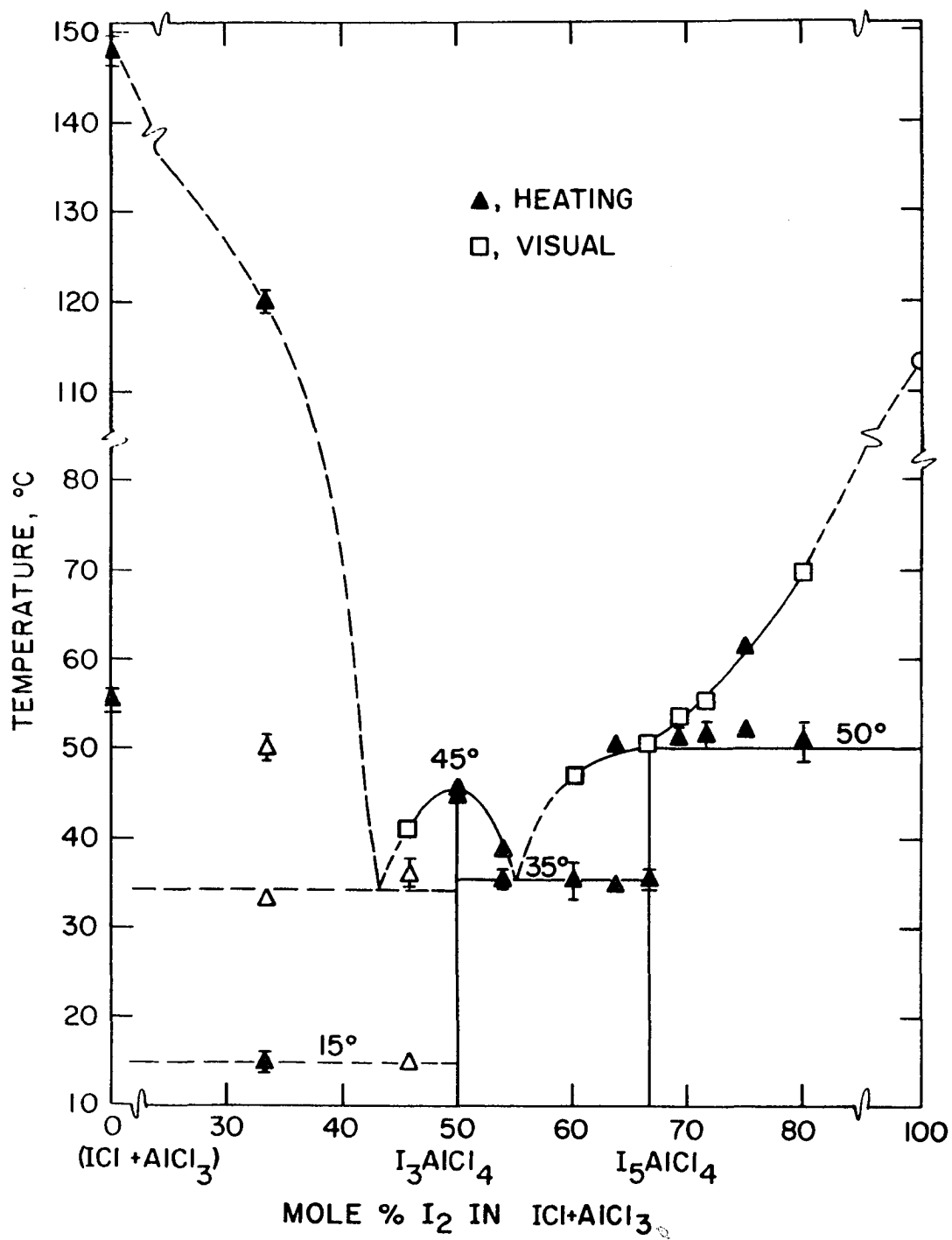


Figure 2. Phase diagram for the I_2 - $(ICl + AlCl_3)$ system.

extent of reduction increased (more iodine present initially). Second, heating the samples to just over 50° and then equilibrating for 5-6 hours at $47.0 - 49.5^{\circ}$ usually resulted in the growth from the melt of large greenish acicular crystals which sometimes reached 1.5 cm. in length. These crystals were present as long as the sample temperature remained $< 50.0^{\circ}$ but disappeared completely if heated above 50° .

Powder patterns of I_3AlCl_4 and I_5AlCl_4 are shown in Figure 3 along with powder patterns of I_2 , $AlCl_3$, and $2ICl \cdot AlCl_3$ for comparison. The patterns are unique and contain no lines that may be attributed to I_2 , $AlCl_3$ or $2ICl \cdot AlCl_3$. Powder patterns of 71.4 mol % I_2 in $ICl + AlCl_3$ (I_6AlCl_4) were the same as those obtained for I_5AlCl_4 .

Samples containing 75 and 80 mol % I_2 in $ICl + AlCl_3$ gave powder patterns which were a superposition of the patterns obtained for I_5AlCl_4 and I_2 which indicated $67 - 72 \pm 1$ mol % I_2 to be the probable composition of the most reduced phase in agreement with the thermal analysis data.

Composition limits for I_3AlCl_4 were impossible to ascertain from powder pattern data because of the low melting points for samples in the composition range of 50 - 67 % I_2 . It was rather surprising that any powder patterns were obtained since the solids have a consistency approximating paste shoe polish and had to be ground together with an equal volume of powdered glass before

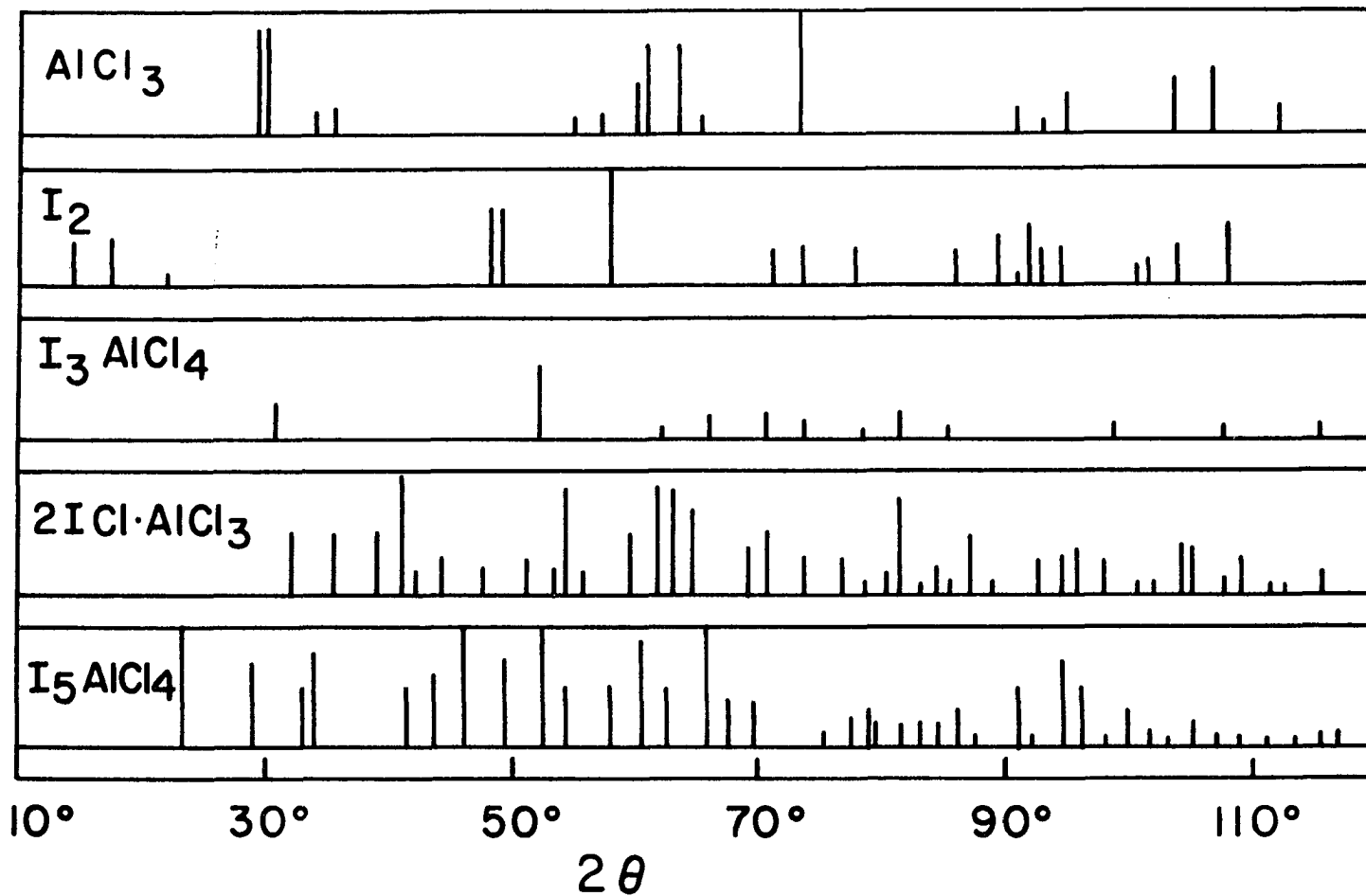


Figure 3. X-ray powder pattern data for I_3AlCl_4 and I_5AlCl_4 . Data for $2\text{ICl}\cdot\text{AlCl}_3$, I_2 , and AlCl_3 also presented for comparison.

intromission into capillaries could be effected.

The left hand portion of the phase diagram ($I_2 < 50$ mol %) was not determined very well. Samples with compositions in this region could not be completely solidified at room temperature and free $AlCl_3$ was usually visible although the amount of $AlCl_3$ present decreased as the extent of reduction increased. A fairly reproducible halt (~ 60 % of the runs) occurred at $\sim 15^\circ$ in compositions containing 33 mol % I_2 . This halt is thought to correspond to the melting point of the ternary eutectic composition in the 3-phase region, $AlCl_3 - 2ICl \cdot AlCl_3 - I_3AlCl_4$. Since this halt occurs below room temperature, the inability to obtain completely solid samples at room temperature is understandable. The low temperature of this halt also explains its partial lack of reproducibility. Samples in this region were prepared for thermal analysis by repeatedly quenching them in liquid N_2 and then equilibrating at 0° for 5 - 6 hours. At 0° , the samples appeared to be solid but it was impossible to tell if they were crystalline or solid glasses. If they were glasses, the halt at 15° would not be observed since no melting process would have taken place.

The phase diagram shows that a possible I_2^+ in a phase I_2AlCl_4 is not stable in this system. This is not surprising in view of the fact that I_2^+ is partially disproportionated into I^{3+} species and I_3^+ in $H_2S_2O_7$ ²² and HSO_3F ²³ and almost completely disproportionated

in H_2SO_4 .³⁴ These studies indicate highly acidic systems are necessary for the stabilization of I_2^+ ; this suggests that AlCl_4^- may not be sufficiently acidic to allow I_2^+ formation. Similar results have been obtained for reduced tellurium systems; $(\text{Te}^+)_n$ has been identified²⁰ in HSO_3F solution whereas the +1 oxidation state does not exist as a solid in the $\text{Te}-(\text{TeCl}_4+4\text{AlCl}_3)$ system.¹⁵

The thermal halts observed in samples with the composition 1AlCl_4 did not agree with the results obtained by Fialkov and Shor in the investigation of the $\text{ICl}-\text{AlCl}_3$ binary system. Their phase diagram shows a low melting eutectic (2°) at 13 mol % AlCl_3 , one intermediate phase with the approximate composition $2\text{ICl}\cdot\text{AlCl}_3$ (33 mol % AlCl_3) melting congruently at 110° , and a second eutectic (42 mol % AlCl_3) melting at 105° . Only the liquidus halt at $\sim 142^\circ$ was reported for equimolar mixtures of ICl and AlCl_3 although the 105° eutectic halt should also have been observed.

The 142° liquidus temperature agrees with the liquidus temperature ($146 - 149^\circ$) observed for $\text{ICl}+\text{AlCl}_3$ (1:1) in this study; however, the melting point of the supposed peritectic eutectic composition was found to be $54 - 56^\circ$ rather than 105° . This inconsistency indicated that other portions of the $\text{ICl}-\text{AlCl}_3$ phase diagram may also be incorrect; namely, $2\text{ICl}\cdot\text{AlCl}_3$ may not be a single phase as had previously been assumed.

Thermal analysis of $2\text{ICl}\cdot\text{AlCl}_3$ samples showed a single transition at $53 \pm 1^\circ$ which was visually determined to be the liquidus. An extremely small amount of AlCl_3 crystals were observed floating on the surface of the melt but they may have resulted from the 1 mol % excess of AlCl_3 added in sample preparation. Again, this melting point does not agree with the results obtained by Fialkov and Shor. The lower halts observed in $2\text{ICl}\cdot\text{AlCl}_3$ and $\text{ICl}\cdot\text{AlCl}_3$ were almost at the same temperature which indicated the same energy absorbing process was probably occurring in both compositions. This process may be the melting point of an eutectic composition (in which case $2\text{ICl}\cdot\text{AlCl}_3$ could not be a single phase) or it may be the incongruent melting point of $2\text{ICl}\cdot\text{AlCl}_3$.

In an attempt to clarify the situation, samples with the ICl/AlCl_3 ratios of 5.0, 3.0 and 2.5 were also studied. The visible appearances of these samples after reaction and quenching along with those of $2\text{ICl}\cdot\text{AlCl}_3$ and $\text{ICl}\cdot\text{AlCl}_3$ are shown in Table II. Free ICl was visibly present in all samples with ICl/AlCl_3 ratios ≥ 2.5 , the amount of free ICl increasing as the ICl/AlCl_3 ratio increased. At room temperature, $5\text{ICl}\cdot\text{AlCl}_3$ and $3\text{ICl}\cdot\text{AlCl}_3$ could not be solidified and $5\text{ICl}\cdot 2\text{AlCl}_3$ only partially solidified. These results suggest the presence of mixtures in the region $2.5 \leq \text{ICl}/\text{AlCl}_3 \leq 5$. Samples of $2\text{ICl}\cdot\text{AlCl}_3$ were purplish-black crystalline solids (thin sections were

Table II

Physical Appearance of Samples Containing Different Ratios
of ICl and AlCl₃

Empirical Composition	Physical Appearance
ICl · AlCl ₃	Equal volumes of AlCl ₃ and purple-black crystalline solid.
2ICl · AlCl ₃	Purple-black crystalline solid. No free ICl or AlCl ₃ visible.
5ICl · 2AlCl ₃	Sample only partially solidified. Black liquid and free ICl present.
3ICl · AlCl ₃	Sample could not be solidified at room temperature. Free ICl visibly present.
5ICl · AlCl ₃	Sample could not be solidified at room temperature. Large quantity of free ICl present.

brownish-yellow) and were indistinguishable from the dark solid present in $\text{ICl} \cdot \text{AlCl}_3$ when viewed through a microscope. Also no free ICl or AlCl_3 was visibly present in the 2:1 composition and powder patterns contained no lines which could be attributed to AlCl_3 (Figure 3).

The $\text{ICl} \cdot \text{AlCl}_3$ phase diagram is shown in Figure 4. Fialkov and Shor were unable to solidify (at room temperature) compositions containing 20 - 28 mol % AlCl_3 (liquidus curve extrapolated in this region) and were able to solidify compositions containing 28 - 50 mol % AlCl_3 only with extreme difficulty. These solidification problems were probably the partial cause of the erroneous liquidus curve obtained from 20 - 40 mol % AlCl_3 although the 53° melting point of $2\text{ICl} \cdot \text{AlCl}_3$ should still have been observed. No mention was made of composition limits on samples used in the investigation; however, if the samples containing 30 - 40 mol % AlCl_3 were actually 2 - 3 mol % richer in AlCl_3 than assumed, liquidus halts $15 - 30^\circ$ higher than the true liquidus would have been observed resulting in an incorrect liquidus curve. The present investigation has verified the existence of the phase $2\text{ICl} \cdot \text{AlCl}_3$ although the observation of this phase in the previous study appears to have been rather fortuitous.

This research was concerned mainly with the formation of AlCl_4^- salts of polyiodine cations; however, the compound $2\text{ICl} \cdot \text{AlCl}_3$ was of interest since the observed stoichiometry suggested the correct

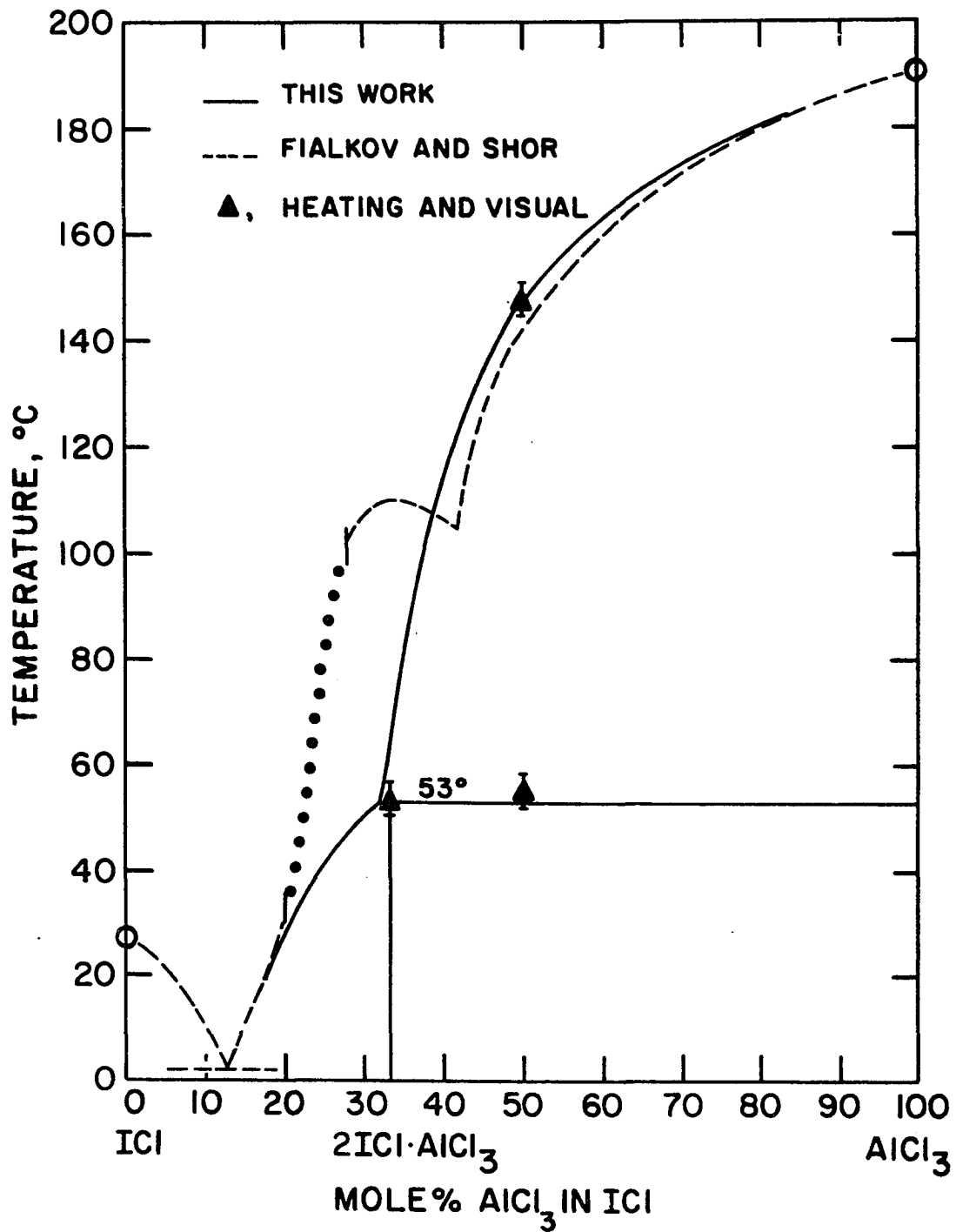


Figure 4. Phase diagram for the ICl-AlCl₃ system.

formulation might be either $I_2Cl^+AlCl_4^-$ or the double salt $(ICl_2^+)(I_3^+)(AlCl_4^-)_2$. The I_2Cl^+ cation has not previously been identified in the solid state although it has been shown³⁴ to exist in H_2SO_4 solution.

The stoichiometries of the reduced phases present in the I_2 - $(ICl + AlCl_3)$ system suggested that $AlCl_4^-$ salts of I_3^+ and I_5^+ had been isolated. Admittedly, the rather large range of uncertainty in the composition limits for the lower phase gives equal probability to the existence of I_6^+ ; however, subsequent analytic work eliminates this possibility. The I_6^+ species would have an odd number of electrons and be expected to be paramagnetic (or I_{12}^{2+}) as opposed to I_5^+ (and I_3^+) which should be diamagnetic. I_5AlCl_4 , I_3AlCl_4 , and $2ICl \cdot AlCl_3$ were all found to be qualitatively diamagnetic by placing the sample between the poles of an electromagnet and observing whether the sample was pulled into the magnetic field (paramagnetic) or pushed out of the field (diamagnetic). The physical properties of the reduced phases and $2ICl \cdot AlCl_3$ are collected in Table III.

Samples with the stoichiometries $I_2 \cdot ICl \cdot 2AlCl_3$ ($I_3Al_2Cl_7$) and $2I_2 \cdot ICl \cdot 2AlCl_3$ ($I_5Al_2Cl_7$) were prepared so that the possible formation of heptachlorodialuminate salts might be determined. After fusion both samples contained free $AlCl_3$ and a homogeneous black liquid. Quenching the samples caused the liquids to crystallize

Table III

Properties of Polyiodine and -Iodochlorine Tetrachloroaluminates

Empirical Composition	Melting Pt. ° C	Color	Magnetic Character	Crystal Shape
I_3AlCl_4	45 ± 1	Black, thin sections brown-red	diamagnetic	square platelets
I_5AlCl_4	50.50-50.5 incongruent	Green-black metallic luster, thin sections brown-red	diamagnetic	needles
$2ICl \cdot AlCl_3$	53 ± 1 incongruent	Purple-black, thin sections brown- yellow	diamagnetic	irregular 3-dimensional crystals

into solids which visually appeared to be identical to I_3AlCl_4 and I_5AlCl_4 , respectively. Powder patterns of these solids were identical with those previously obtained for I_3AlCl_4 and I_5AlCl_4 . Therefore, it was concluded that $Al_2Cl_7^-$ salts do not form in the I_2 - ICl - $AlCl_3$ ternary system.

The possible formation of I_4Cl^+ was also investigated by preparing samples containing 50 mol % I_2 in $(2ICl + AlCl_3)$, i. e., " $I_4Cl^+AlCl_4^-$ ". Samples with this composition could not be solidified at room temperature and free ICl was still visible. These results indicate that solid $I_4Cl^+AlCl_4^-$ probably does not exist although the cation may be present in the melt. The next cation in the series, $I_3Cl_2^+$, also does not exist (at least in the solid state) since it should be present in samples with the stoichiometry $3ICl \cdot AlCl_3$ ($I_3Cl_2^+AlCl_4^-$). Previous observations have shown samples with this composition were not a single phase. The related species $I_2Cl_3^+$ and ICl_4^+ were not considered since they can not be formed directly in this system.

Chemical Analysis - Samples containing two reduced phases were fractionated and analyzed in order to determine the composition limits more accurately. The samples prepared for analysis initially contained 55.6 mol % I_2 in $ICl + AlCl_3$ (" $I_{3.5}AlCl_4$ ") and 69.2 mol % I_2 in $ICl + AlCl_3$ (" $I_{5.5}AlCl_4$ "). Approximately 80% of each sample was solidified and the remaining liquid decanted. This process was

repeated two or three times until about 50 % of the original samples had been decanted; the solids that remained after this procedure were analyzed for iodine and chloride. The crystalline solids still appeared to be "wet" when examined microscopically and some of the mother liquor was still present in the solid matrix. The analytical results are presented in Table IV.

Accurate stoichiometries of the reduced phases could not be determined because the total weight of sample in both cases recovered was only 97 - 98 % of the original sample weight. The chief source of error causing these low values was probably the loss of ICl by volatilization during transfers and the initial reaction of the samples with H₂O. However, the analytical data did establish upper limits of reduction for both reduced phases. Assuming that the low sample weight obtained were caused only by the loss of I₂, the reduced phase stoichiometries would be I_{3.38}AlCl₄ and I_{5.27}AlCl₄. Even with this assumption, the I/Cl ratios are less than for the initial compositions (i. e., $\frac{3.38}{4} < \frac{3.5}{4}$ and $\frac{5.27}{4} < \frac{5.5}{4}$).

Establishing an absolute upper reduction limit for the less reduced phase was not particularly helpful since thermal analysis data and visual observations had already indicated the probable stoichiometry to be close to I₃AlCl₄. However, this upper limit of reduction for the more reduced phase bracketed the composition in a much

Table IV

Analytical Results for I_3AlCl_4 and I_5AlCl_4

	I_3AlCl_4	I_5AlCl_4
Sample weight	0.7179 g	1.6156 g
I ($Na_2S_2O_3$ titration)	0.4933 g	1.2568 g
Cl (AgCl ppt.)	0.1703 g	0.2737 g
Al (as $AlCl_4^-$ based on the amount of Cl found)	0.0324 g	0.0521 g
Weight recovered	0.6960 g	1.5826 g
Percent recovery	96.9 %	98.0 %
Empirical composition based on recovery weight	$I_{3.23}AlCl_4$	$I_{5.13}AlCl_4$
Empirical composition assuming low recovery weight the result of iodine loss ^a	$I_{3.38}AlCl_4$	$I_{5.27}AlCl_4$

^a Iodine rich composition limit.

narrower range than had been possible using only thermal analysis and powder pattern data. Using thermal analysis data for the lower limit of reduction and analytical data for the upper limit, the composition was established as $I_{5.0 - 0.2, +0.3}AlCl_4$ which strongly suggests the correct composition to be I_5AlCl_4 . Since the observed stoichiometries suggested these phases to be $AlCl_4^-$ salts of I_3^+ and I_5^+ , attention was turned to methods of identifying the presence of these cations.

Ultraviolet-Visible Spectra - The spectral data obtained from mulls of $2ICl \cdot AlCl_3$, I_3AlCl_4 , and I_5AlCl_4 were reproducible although the peaks observed were rather broad and not well resolved. Representative spectra of the three compounds are shown in Figure 5 and the peaks observed are listed in Table V along with values for I_3^+ and I_5^+ in HSO_3F solution. The peaks observed for I_3AlCl_4 mulls do not agree very well with those found for I_3^+ in HSO_3F with the possible exception of the peak at $490\ m\mu$ (mull) and $470\ m\mu$ (solution).

The similarity between the spectra of I_5AlCl_4 (mull) and I_5^+ (solution) was much more pronounced since three of the four peaks observed for I_5^+ in solution were also present in the spectrum of I_5AlCl_4 . The absence of a peak in the mull spectrum corresponding to the $270\ m\mu$ peak observed for I_5^+ in solution was not particularly disquieting since the $270\ m\mu$ absorption in solution was relatively weak compared to those at $345\ m\mu$ and $240\ m\mu$ and consequently may not be

Figure 5. Ultraviolet-visible spectra of (a) I_3AlCl_4 , (b) I_5AlCl_4 , and (c) $2ICl \cdot AlCl_3$.

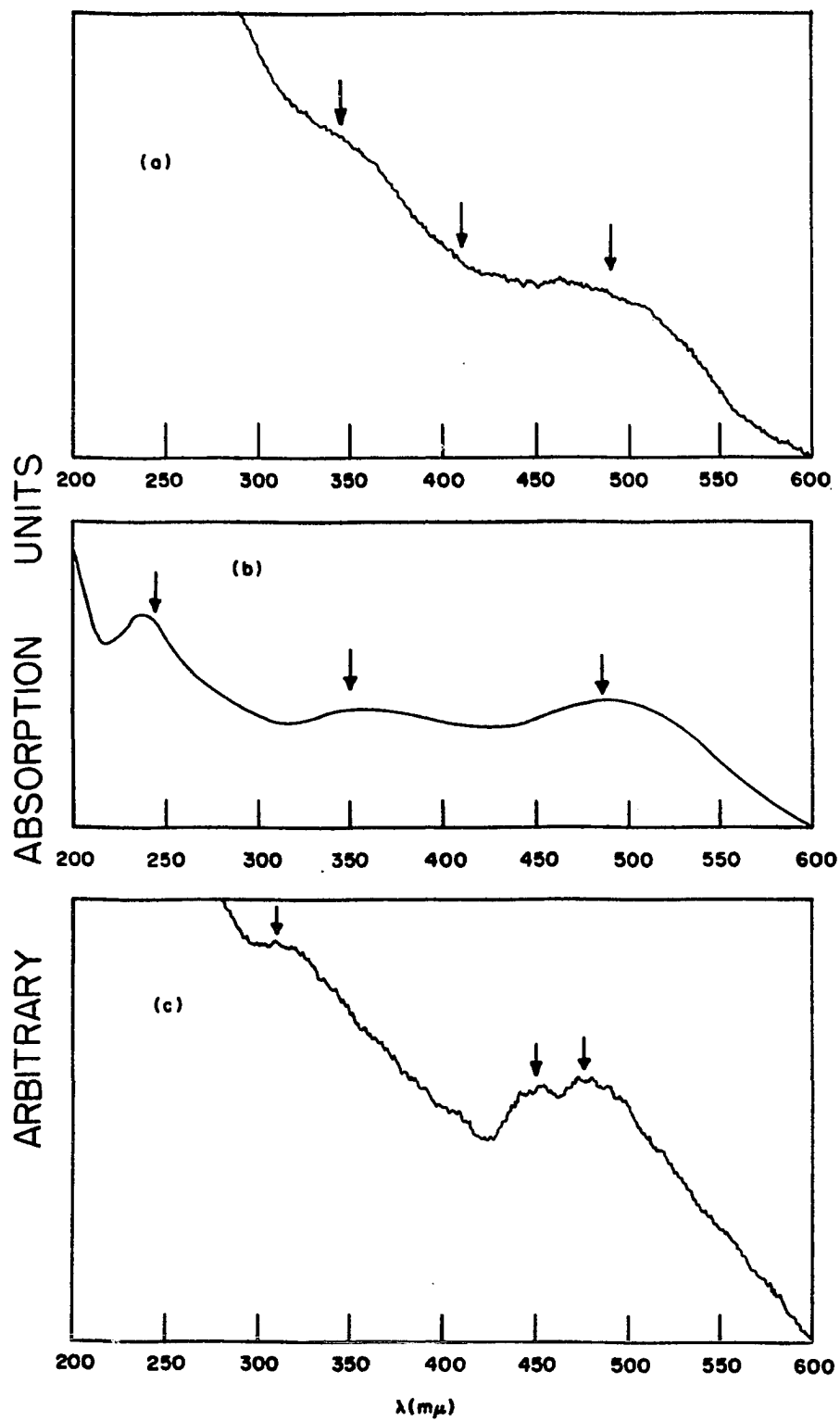


Table V

Ultraviolet-Visible Spectra of I_3AlCl_4 , I_5AlCl_4 , and $2ICl \cdot AlCl_3$ in the Solid State

Compound	Wavelength ($m\mu$)			
I_3AlCl_4	490m, br ^b	410w, sh	345s, br	
I_3^+ ^a	470m		305s	
I_5AlCl_4	485m, br		350m, br	245s
I_5^+ ^a		450m	345s	270m 240s
$2ICl \cdot AlCl_3$	475m, br	450m, br	310s	

^a In HSO_3F solution, ref. 23.^b s = strong, m = medium, w = weak, sh = shoulder, br = broad.

sufficiently resolved in the mull spectrum to allow observation.

The electronic spectrum of I_2Cl^+ has not been previously recorded which prevented the identification of I_2Cl^+ in $2ICl \cdot AlCl_3$ by spectral comparison. However, the similarity between the spectrum of $2ICl \cdot AlCl_3$ and I_3^+ (solution) was rather pronounced which may indicate the presence of I_3^+ (and equal amount of ICl_2^+) in $2ICl \cdot AlCl_3$ but this possibility was not consistent with nuclear quadrupole resonance data (discussed more completely in the last section of this thesis).

Far Infrared Spectra - The infrared spectra of $2ICl \cdot AlCl_3$, I_3AlCl_4 , and I_5AlCl_4 contained no peaks between 90 and 500 cm^{-1} , the region for iodine-iodine vibrations is expected to be $< 250\text{ cm}^{-1}$ based on the known vibration frequency of I_2 ⁴¹ and the frequencies assigned¹⁵ to Te-Te vibrations in $[Te_4^{2+}][AlCl_4^-]_2$ and Te_3AlCl_4 .

The $AlCl_4^-$ ion has two infrared active vibrations, ν_3 and ν_4 , (both of t_2 symmetry in an unperturbed ion) which occur at 183 cm^{-1} and 495 cm^{-1} , respectively.⁴² The absence of observable peaks from this region was attributed to the consequences of extreme reactivity and low melting points exhibited by these compounds. The reduced phases and $2ICl \cdot AlCl_3$ reacted instantaneously with polyethylene and Nujol which necessitated the use of Teflon film for cell windows and Fluorolube as a mulling agent. Teflon is one of the few materials

available (other than polyethylene) that is transparent below 250 cm^{-1} which is the main region of interest.

The "shoe polish" consistency of the compounds prevented the preparation of satisfactory mulls since the solids tended to clump together in large particles with very little surface area rather than forming a suspension of very fine particles in the Fluorolube as desired. This problem was further compounded by the tendency for the sample particles in the mull to melt when exposed to the incident radiation of the spectrometer and then coalesce into droplets which sank to the bottom of the cell. The Teflon windows were not sufficiently rigid to prevent this and using thicker Teflon windows or backing the Teflon film with rigid polyethylene sheets resulted in zero percent transmission of the incident radiation.

Crystallographic Studies - Samples of $2\text{ICl}\cdot\text{AlCl}_3$, I_3AlCl_4 , and I_5AlCl_4 usually contained discreet crystals that appeared to be of good quality under microscopic examination. No particular attempts were made to grow these crystals; they form in the solidification process and also grow (or disappear) over a period of several months as a result of the slight temperature differential in the sample tubes caused by the ambient air currents. However, all attempts to mount these crystals for x-ray diffraction studies proved to be unsuccessful. The microscope light caused the crystals to melt if they were held in the

beam for more than three or four minutes. Also, when attempting to place a crystal in a capillary, the crystal usually adhered to the top of the tube and smeared into a liquid streak when pushed farther down.

The lifetime of all three compounds in the dry box or glove bag was only about twenty minutes; crystals of $2\text{ICl}\cdot\text{AlCl}_3$ actually appeared to boil and were completely decomposed in one or two minutes. The reduced phases I_3AlCl_4 and I_5AlCl_4 appeared to melt rather easily when the sample containers were opened in the dry box. The presence of eutectics at 15 and 35° account for this since both phases suffer ready loss of I_2 and ICl . In addition, all three of the compounds were found to be extremely reactive toward air and moisture. Cooling the samples by means of an ice bath under the glove bag, cooling the N_2 atmosphere by routing the inlet hose through a copper coil immersed in liquid N_2 , and attempting to saturate the glove bag atmosphere with iodine were all tried in an effort to solve these problems with no success. Attempts to grow crystals inside capillaries (by placing the capillaries inside sample tubes prior to reaction) were also unsuccessful.

Nuclear Quadrupole Resonance and Nuclear Magnetic Resonance Spectroscopy Data - Characterization of the reduced phases and $2\text{ICl}\cdot\text{AlCl}_3$ was hampered by the low melting points and extremely

reactive nature of these compounds. However, these problems were avoided to a large extent by using nuclear quadrupole resonance (nqr) and nuclear magnetic resonance (nmr) spectroscopy for investigative tools. No transfers of the samples were required after preparation which eliminated any possibility of reaction with air or moisture and usually the samples were not heated sufficiently during data collection to cause melting problems.

In general, nqr spectroscopy allows one to obtain information about the electronic charge distribution on the various atoms in a molecule and the relative covalent-ionic character of the bonds from the number and frequency of the resonances observed. The frequency at which a quadrupole transition(s) occurs for a given nucleus is determined by the quadrupole moment (eQ) of the nucleus, the electric field gradient (eq) at the nucleus produced by the electron distribution in the molecule, the nuclear spin (I) of the nucleus, and the asymmetry parameter (η). The asymmetry parameter is related to the three components of the field gradient q_{xx} , q_{yy} , and q_{zz} by the equation:⁴³

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} \quad (4)$$

If $q_{xx} = q_{yy} = q_{zz}$, the field gradient is zero and the quadrupole levels are degenerate. If $q_{xx} = q_{yy} \neq q_{zz}$ the field gradient is axially symmetric and $\eta = 0$, and when $q_{xx} \neq q_{yy} \neq q_{zz}$ η will have a value

between zero and one.

For a nucleus with spin $3/2$ (^{35}Cl) the observed resonance frequency (ν_Q) for the $\pm 1/2 \rightarrow \pm 3/2$ transition is given by the equation:⁴⁴

$$\nu_Q = \left(\frac{e^2 Q q}{2h} \right) \left(1 + \eta^2/3 \right)^{1/2} \quad (5)$$

The coupling constant ($e^2 Q q$) cannot be obtained directly from a single measured frequency since eq and η are both unknown (unless $\eta = 0$).

For a nucleus with spin $5/2$ (^{127}I) two transitions are observed ($\pm 1/2 \rightarrow \pm 3/2$, $\pm 3/2 \rightarrow \pm 5/2$) and the frequencies are given by⁴⁵

$$\nu_{Q_1} = \frac{3e^2 Q q}{20h} (1 + 1.0926\eta^2 - 0.6340\eta^4) \quad (6)$$

$$\nu_{Q_2} = \frac{3e^2 Q q}{10h} (1 - 0.2037\eta^2 + 0.1621\eta^4) \quad (7)$$

If both ν_{Q_1} and ν_{Q_2} are experimentally observed, η and $e^2 Q q$ can both be calculated⁴⁶ from the ratio ν_{Q_1}/ν_{Q_2} .

For ^{35}Cl ($I = 3/2$) in a polycrystalline sample only one resonance corresponding to the transition $\pm 1/2 \rightarrow \pm 3/2$ will be observed. This resonance will occur at a different frequency for each kind of ^{35}Cl present in the sample, i. e., crystallographically or chemically nonequivalent chlorine atoms. For example, two resonances should be present in the ^{35}Cl nqr spectrum of a compound

which has two nonequivalent chlorine lattice positions even though all the chlorine atoms are chemically similar.

It is unfortunate that ^{35}Cl has a $3/2$ spin since the ^{35}Cl coupling constant cannot be obtained from the measured resonance frequency unless the chlorine atom is terminally bonded (η assumed to be zero). This limitation does not exist for ^{127}I ; however in molecules with a large field gradient at the ^{127}I nucleus the $\pm 3/2 \rightarrow \pm 5/2$ transition may occur above the accessible frequency range of the spectrometer (650 MHz).

The original purpose of the nqr investigation was to identify the I_3^+ , I_5^+ , and I_2Cl^+ cations in I_3AlCl_4 , I_5AlCl_4 and $2\text{ICl}\cdot\text{AlCl}_3$ by means of their ^{127}I nqr spectra. However, only the completely unambiguous identification of I_3^+ was possible on this basis because of spectrometer limitations on accessible frequency ranges and a tendency for the samples to melt in the $\sim 175 - 300$ MHz region. Quadrupole transitions cannot be observed if the sample melts because molecular rotation in a liquid averages the field gradient so that the quadrupole energy levels are degenerate. In order to overcome these problems ^{35}Cl nqr data and ^{27}Al nmr data were collected on the three compounds since the identification of AlCl_4^- would strongly indicate the presence of I_5^+ and I_2Cl^+ in I_5AlCl_4 and $2\text{ICl}\cdot\text{AlCl}_3$, respectively.

Table VI

Pure Quadrupole Resonance Data for ^{35}Cl (Anion) in $\text{I}_2\text{ClAlCl}_4$,
 I_3AlCl_4 , I_5AlCl_4 , and Related Compounds at Room Temperature

Compound	ν_Q (MHz)	Assignment
$\text{I}_2\text{ClAlCl}_4$	10.297 ± 0.001	^{35}Cl in AlCl_4^-
	10.474	
	11.265	
	11.283	
I_3AlCl_4	10.129	^{35}Cl in AlCl_4^-
	10.590	
	11.093	
	11.452	
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	
$\text{ICl}_2\text{AlCl}_4^a$	11.31	^{35}Cl in AlCl_4^- complex resonance arbitrarily resolved
	11.40	
	11.42	

(continued)

^a Ref. 47.

Table VI (continued)

Compound	ν_Q (MHz)	Assignment
GaAlCl ₄ ^b	10.296 ± 0.001	³⁵ Cl in AlCl ₄ ⁻
	10.382	
	10.460	
	11.312	
Hg ₃ (AlCl ₄) ₂	10.676	³⁵ Cl in AlCl ₄ ⁻
	10.812	
	11.383	
	11.433	
	11.843	
Co(AlCl ₄) ₂	10.813	³⁵ Cl in AlCl ₄ ⁻
	11.115	
	12.491	
	12.959	
Te ₄ (Al ₂ Cl ₇) ₂	10.965	³⁵ Cl in Al ₂ Cl ₇ ⁻
	11.368	
	11.390	
	11.976	
	12.391	
	12.633	

^b Ref. 48.

The ^{35}Cl and ^{127}I nqr data have been divided into two parts; anionic ^{35}Cl (AlCl_4^-) data will be presented first followed by cationic ^{35}Cl (I_2Cl^+) and ^{127}I data. Representative ^{35}Cl nqr spectra for I_3AlCl_4 , I_5AlCl_4 and $\text{I}_2\text{ClAlCl}_4$ are shown in Figure 6 and the ^{35}Cl frequencies are given in Table VI. Resonance frequencies (^{35}Cl) observed for other AlCl_4^- compounds and $(\text{Te}_4^{2+})(\text{Al}_2\text{Cl}_7^-)_2$ have been included in Table VI for comparison. The data presented in Table VI is also shown graphically in Figure 7 so that the ^{35}Cl nqr frequencies obtained for the different compounds may be more readily compared.

The number (4) and location (10-12 MHz) of the ^{35}Cl resonances observed for I_3AlCl_4 , I_5AlCl_4 and $2\text{ICl}\cdot\text{AlCl}_3$ strongly suggest the presence of AlCl_4^- group in these compounds. In particular, the extremely good agreement between the ^{35}Cl resonances observed for I_5AlCl_4 and NaAlCl_4 is striking. The frequency spread of the four ^{35}Cl resonances observed in I_3AlCl_4 and $\text{I}_2\text{ClAlCl}_4$ (1.32 and 1.00 MHz, respectively) is larger than for I_5AlCl_4 (0.46 MHz) but compares well with the frequency spread in GaAlCl_4 (1.02 MHz). The mean of the four frequencies in I_3AlCl_4 (10.82 MHz), $\text{I}_2\text{ClAlCl}_4$ (10.83 MHz), and GaAlCl_4 (10.61 MHz) is also rather similar. By comparison, the frequency spread of the four ^{35}Cl resonances in $\text{Co}(\text{AlCl}_4)_2$ is much larger (2.15 MHz) even though the presence of AlCl_4^- groups has been shown by a crystal structure determination.⁴⁹ Therefore, the

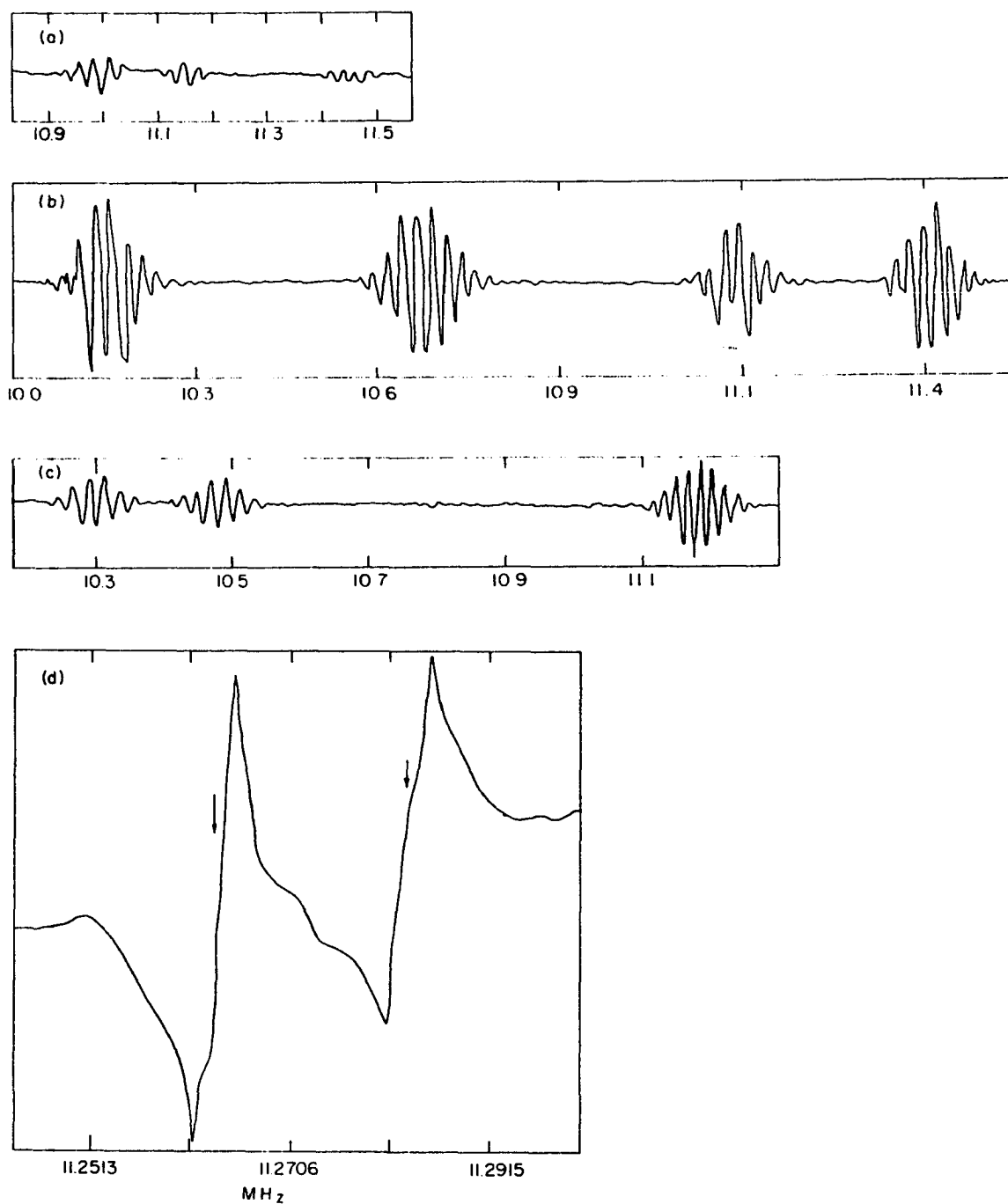


Figure 6. Representative ^{35}Cl nqr spectra (super-regenerative spectrometer) of (a) I_5AlCl_4 , (b) I_3AlCl_4 , and (c) $\text{I}_2\text{ClAlCl}_4$; (d) resolution of the strong resonance at ~ 11.2 MHz in (c) into two resonances (wide line induction spectrometer).

^{35}Cl NQR

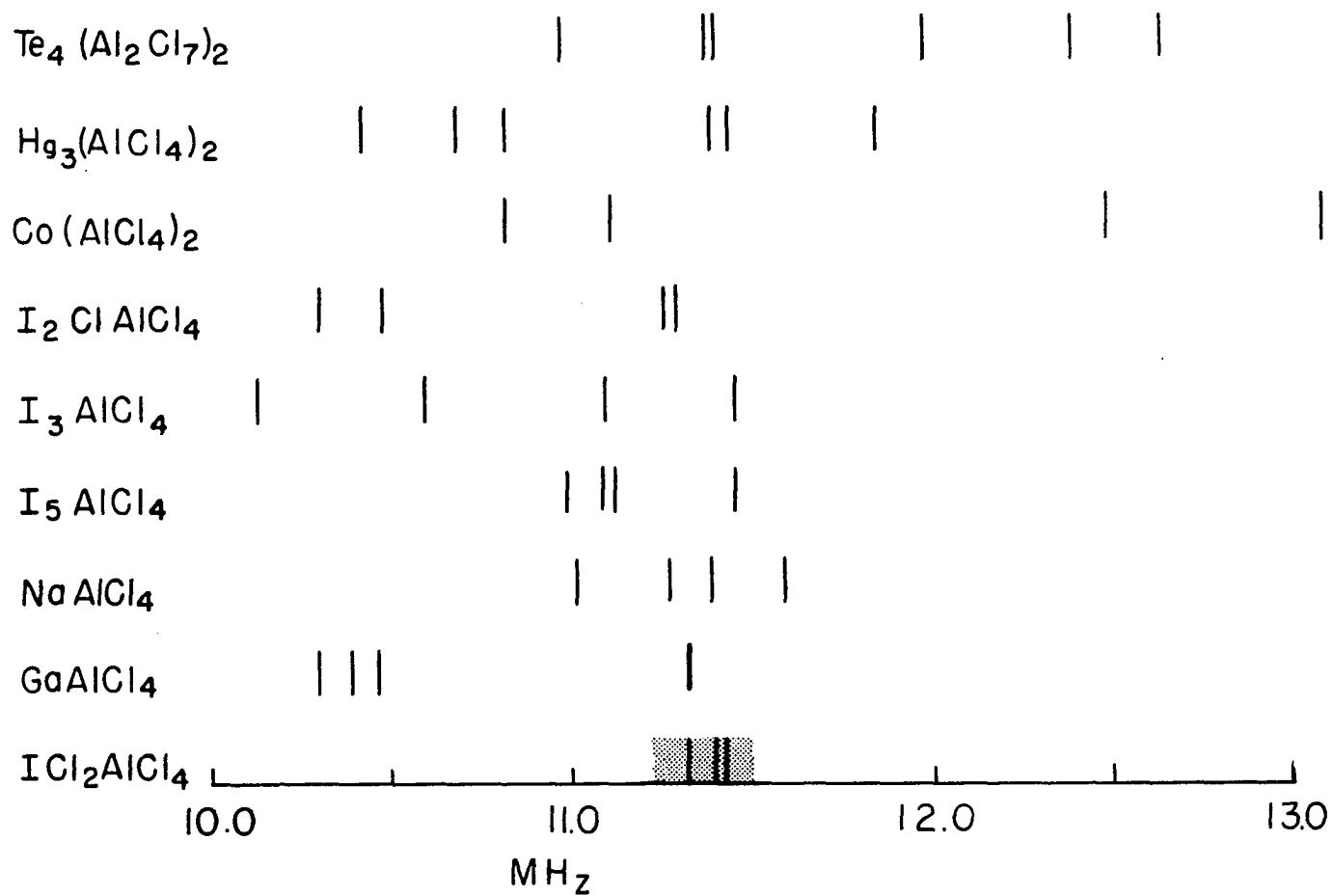


Figure 7. Pure quadrupole resonance data for ^{35}Cl (anion) in $\text{I}_2\text{ClAlCl}_4$, I_3AlCl_4 , I_5AlCl_4 , and related compounds at room temperature.

assignment of the four ^{35}Cl resonances (~ 11 MHz) observed in I_3AlCl_4 and $\text{I}_2\text{ClAlCl}_4$ to crystallographically nonequivalent chlorine atoms in AlCl_4^- is very reasonable.

The cation present in the AlCl_4^- salts obviously influences the frequency spread and location of the ^{35}Cl resonances. Thus some of the ^{35}Cl resonances for $\text{Co}(\text{AlCl}_4)_2$ and $\text{Hg}_3(\text{AlCl}_4)_2$ have been shifted to higher frequencies relative to NaAlCl_4 indicative of a larger degree of covalent character for chlorine in the mercury and cobalt compounds than in NaAlCl_4 . In $\text{Co}(\text{AlCl}_4)_2$ each cobalt atom is surrounded by a distorted octahedron of chlorine atoms with the average Co-Cl distance $\approx 2.46\text{\AA}$. This distance is longer than the sum of the cobalt octahedral radius and chlorine radius (2.3\AA)⁵⁰ but compares favorably with the distance found in α -cobalt dipyrindine dichloride (2.49\AA).⁵¹

$\text{Co}(\text{AlCl}_4)_2$ was expected to give four ^{35}Cl resonances with a frequency grouping of 2:1:1. The AlCl_4^- group has two chlorine atoms bridging to cobalt atom A, one chlorine bridging to cobalt atom B, and one terminal chlorine atom. However, as can be seen from Table VI, the frequencies exhibit a 2:2 grouping. This result can tentatively be explained by a closer examination of the $\text{Co}(\text{AlCl}_4)_2$ structure in which the chlorine atom bridging to cobalt B has an Al-Cl-Co angle of 127° and the two chlorine atoms bridging to cobalt A have an Al-Cl-Co angle of 87° . The 87° angle is very similar to the chlorine bridge

angles ($M-X-M = 82-90^\circ$) found in the dimeric group IIIb halides.^{52, 53}

Halogen nqr data for the group IIIb halides usually show a 1:2 frequency distribution in which resonance at lower frequency is assigned to the bridging halogens and the resonances at high frequencies are assigned to the terminal halogens.⁵⁴⁻⁵⁸ The ratio of average terminal frequency to average bridging frequency for AlI_3 and $AlBr_3$ ($AlCl_3$ not known) is 1.21 and 1.17, respectively; gallium and indium trihalides also follow this same pattern of decreasing ratios from iodine to bromine to chlorine. Therefore, if the Al_2Cl_6 dimer existed in the solid state, one would expect a terminal to bridge ratio < 1.17 (Al_2Br_6). For $Co(AlCl_4)_2$ the ratio of the average of high frequencies to the average of low frequencies is 1.16 which is consistent with the expected ratio for hypothetical solid Al_2Cl_6 . Since the location of the resonance frequency for a bridging atom is very dependent on the bridge angle, it is thought that the two ^{35}Cl frequencies at ~ 11 MHz arise from the chlorine atoms bonded to cobalt A (double halogen bridge as in group IIIb halides) and the two ^{35}Cl frequencies at ~ 12.5 MHz arise from the chlorine bonded to cobalt B and the terminal chlorine atom. No assignment of the two higher frequencies to terminal and bridging chlorines is possible. The small frequency range between these two ^{35}Cl resonances is probably an accidental result of the particular Al-Cl-Co angle

(127°) that is found in $\text{Co}(\text{AlCl}_4)_2$; if this angle were different the frequency range would be expected to change as a result of the change in the asymmetry parameter (η) for the bridging chlorine. Admittedly, this assignment is somewhat tenuous; however, the location of a bridging chlorine nqr frequency seems to be quite dependent on the bridging chlorine angle. Similarly, a structural determination⁵⁹ of $\text{Hg}_3(\text{AlCl}_4)_2$ has shown each AlCl_4 group to be bonded to the Hg_3 trimer through a single bridging chlorine atom. The Hg-Cl distances are $\approx 2.54\text{\AA}$ which are not much longer than the sum of the covalent radii (2.47\AA).⁵⁰ The formation of this bond will decrease the electron density available to each chlorine atom in AlCl_4^- (relative to nonbonded AlCl_4^-) causing the ^{35}Cl resonances to occur at higher frequencies as observed.

This same argument can be used to explain the shift to higher frequencies (relative to NaAlCl_4) observed for ^{35}Cl resonances in $\text{Te}_4^{2+}(\text{Al}_2\text{Cl}_7^-)_2$. However, rather than being strongly bonded to the cation, AlCl_4^- has bonded to an AlCl_3 group through a chlorine atom forming an Al_2Cl_7^- ion. The net result is the same, i. e., the single negative charge is now distributed over seven chlorine centers rather than four which means each chlorine atom in Al_2Cl_7^- is less ionic (more covalent) than in AlCl_4^- .

Originally it was thought that nqr spectroscopy might be a useful technique for unambiguously identifying the Al_2Cl_7^- ion in compounds of unknown structure. However, the crystal structure¹⁷ of $\text{Te}_4^{2+}(\text{Al}_2\text{Cl}_7^-)_2$ shows all seven chlorine atoms to be nonequivalent but only six of the seven expected ^{35}Cl resonances were observed. Likewise, the crystal structure of $\text{Hg}_3(\text{AlCl}_4)_2$ indicates eight non-equivalent chlorine atoms but again only six resonances were observed. The fact that the number of unobserved resonances corresponds to the number of bridging chlorine atoms in each compound may be coincidental but it is apparent that the anionic species could not have been determined unequivocally using only ^{35}Cl nqr data. However, $\text{Hg}_3(\text{AlCl}_4)_2$ was the only AlCl_4^- compound investigated for which more than four ^{35}Cl resonances were expected; four ^{35}Cl resonances were predicted and observed for the other AlCl_4^- compounds with known structure. Therefore, if the ^{35}Cl nqr spectrum of a supposed AlCl_4^- compound showed four resonances in the 10-12 MHz range the presence of AlCl_4^- (and absence of Al_2Cl_7^-) would be strongly indicated. If five or six resonances were observed the anion could not be definitely determined but the possible presence of Al_2Cl_7^- would be recognized. Even this partial identification of Al_2Cl_7^- would be valuable since we have found the infrared mull spectra of Al_2Cl_7^- and AlCl_4^- to be very similar which makes the identification of Al_2Cl_7^-

extremely difficult.

The ^{27}Al ($I = 5/2$) nmr spectra of I_3AlCl_4 , I_5AlCl_4 and $2\text{ICl} \cdot \text{AlCl}_3$ ($\text{I}_2\text{ClAlCl}_4^-$) also indicated the presence of relatively unperturbed AlCl_4^- groups therein. Since ^{27}Al has a quadrupole moment, a single resonance corresponding to the $+1/2 \rightarrow -1/2$ transition will probably not be observed unless the field gradient at the nucleus is zero (cubic symmetry) which causes the quadrupole levels to be degenerate. The net field gradient at the aluminum atom in an undistorted AlCl_4^- ion (T_d symmetry) is zero and a single nmr signal is expected assuming the quadrupole moment of ^{35}Cl does not cause extremely rapid spin-lattice relaxation.

The ^{27}Al nmr spectra of I_3AlCl_4 , I_5AlCl_4 and $\text{I}_2\text{ClAlCl}_4$ were obtained and compared with the ^{27}Al nmr spectrum of $\text{Te}_4^{2+}(\text{Al}_2\text{Cl}_7^-)_2$. The line width of the $+1/2 \rightarrow -1/2$ transition and the ^{27}Al coupling constant e^2Qq for each of the four compounds is given in Table VII. The Al_2Cl_7^- salt was chosen for comparison because the crystal structure has been determined and the effect of known distortions from T_d symmetry on the ^{27}Al nmr spectrum can be observed. The Cl-Al-Cl angles and Al-Cl bond lengths in $\text{Te}_4^{2+}(\text{Al}_2\text{Cl}_7^-)_2$ vary between $102.5 - 116.5^\circ$ and $2.115 - 2.262\text{\AA}$, respectively,¹⁷ indicating a moderate degree of distortion in the electron distribution around the aluminum atoms.

Table VII

Nuclear Magnetic Resonance Data for

 ^{27}Al in $\text{I}_2\text{ClAlCl}_4$, I_3AlCl_4 , I_5AlCl_4 , and $\text{Te}_4(\text{Al}_2\text{Cl}_7)_2$

Compound	Linewidth ($\Delta\nu$) of $+1/2 \rightarrow -1/2$ (Oe) ^a	^{27}Al Coupling Constant e^2Qq (MHz)
$\text{I}_2\text{ClAlCl}_4$	3.4	0.7
I_3AlCl_4	9.7	1.9
I_5AlCl_4	6.0	1.1
$\text{Te}_4(\text{Al}_2\text{Cl}_7)_2$	9.0	1.6

^a No side bands observed in the ^{27}Al nmr spectrum of all four compounds.

Coupling constants for ^{27}Al were calculated with the aid of equations (6) and (8)⁶⁰ where $\Delta\nu$ = the line width of

$$\Delta\nu = \frac{25\nu_Q^2}{144\nu_0} [I(I+1) - 3/4] \quad (8)$$

the observed $+1/2 \rightarrow -1/2$ transition, ν_0 = the probe frequency, and $I = 5/2$. The asymmetry parameter, η , was assumed to be zero.

The line widths and ^{27}Al coupling constants obtained for $\text{I}_2\text{ClAlCl}_4$ and I_5AlCl_4 are smaller than those obtained for $\text{Te}_4^{2+}(\text{Al}_2\text{Cl}_7^-)_2$ which is interpreted as less distortion in the tetrahedral arrangement of chlorine atoms around aluminum in $\text{I}_2\text{ClAlCl}_4$ and I_5AlCl_4 than in $\text{Te}_4^{2+}(\text{Al}_2\text{Cl}_7^-)_2$. This interpretation agrees reasonably well with the ^{35}Cl nqr data previously discussed which shows a smaller frequency spread in $\text{I}_2\text{ClAlCl}_4$ (1.00 MHz) and I_5AlCl_4 (0.46 MHz) than in $\text{Te}_4^{2+}(\text{Al}_2\text{Cl}_7^-)_2$ (1.67 MHz). The ^{27}Al nmr data for I_3AlCl_4 and $\text{Te}_4^{2+}(\text{Al}_2\text{Cl}_7^-)_2$ imply that nearly the same degree of distortion in the chlorine tetrahedra is present in both compounds which is consistent with the larger spread of ^{35}Cl nqr frequencies observed in I_3AlCl_4 (1.32 MHz) compared with $\text{Te}_4^{2+}(\text{Al}_2\text{Cl}_7^-)_2$ (1.67 MHz).

The extent to which the ^{27}Al nmr data reflects minor distortions in the AlCl_4^- groups cannot be determined from the limited data available; however, the ^{27}Al coupling constants obtained are all quite small (<2MHz) which does rule out the possibility of large

distortions in AlCl_4^- . By comparison, the ^{27}Al coupling constant in $\text{Al}_2\text{Br}_6(\text{s})$ is 13.86 MHz⁶¹ and as expected, the tetrahedral array of bromine atoms is quite distorted (Br-Al-Br angles = 93 - 115°, Al-Br bond lengths = 2.23 - 2.42 Å).⁶² On the basis of the ^{35}Cl nqr data and ^{27}Al nmr data the most likely formulations of the two reduced phases and $\text{I}_2\text{ClAlCl}_4$ are $\text{I}_3^+\text{AlCl}_4^-$, $\text{I}_5^+\text{AlCl}_4^-$ and $\text{I}_2\text{Cl}^+\text{AlCl}_4^-$ since other formulations such as five coordinate aluminum adducts or compounds with chlorine bridging between aluminum and iodine groups are not indicated.

The experimental nqr data for ^{35}Cl (cationic) and ^{127}I in $\text{I}_2\text{Cl}^+\text{AlCl}_4^-$, $\text{I}_3^+\text{AlCl}_4^-$, and $\text{I}_5^+\text{AlCl}_4^-$ are given in Table VIII. The ^{35}Cl nqr frequencies in ICl_2^+ and I_2Cl^+ (chlorine assumed to be terminal) are 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 MHz in I_2Cl^+ and 38.7 and 39.1 MHz in ICl_2^+ . The data are not consistent with the presence of ICl_2^+ in $2\text{ICl} \cdot \text{AlCl}_3$ which refutes the formulation as $(\text{I}_3^+)(\text{ICl}_2^+)(\text{AlCl}_4^-)_2$. Also, no ^{127}I resonance was observed in the 300-320 MHz region although such a resonance would be expected if I_3^+ were present. The reason for two ^{35}Cl resonances being observed in I_2Cl^+ is not known but is assumed to be the result of crystallographically nonequivalent chlorine atoms.

Table VIII

Pure Quadrupole Resonance Data for ^{35}Cl (Cation) and ^{127}I in $\text{I}_2\text{ClAlCl}_4$, I_3AlCl_4 , I_5AlCl_4 and Related Compounds at Room Temperature

Compound	ν_Q (MHz)	Assignment
$\text{I}_2\text{ClAlCl}_4$	37.912 ± 0.001	^{35}Cl in I_2Cl^+
	38.127 "	
	417. ± 1	^{127}I , ν_1 - central
I_3AlCl_4	415. ± 1	^{127}I , ν_1 - terminal
	428. ± 1	ν_1 - terminal
	308.6 ± 0.1	ν_1 - central
	527. ± 1	ν_2 - central
ICl^a	37.202 ± 0.001	^{35}Cl
	440.9 ± 0.1	^{127}I , ν_1
	451.46 ± 0.01	
	902.46 ± 0.01	^{127}I , ν_2
$\text{ICl}_2\text{AlCl}_4^b$	38.690 ± 0.001	^{35}Cl in ICl_2^+
	39.086	
	458. ± 1	^{127}I , ν_1 - central
I_5AlCl_4	400. ± 5	^{127}I , tentatively assigned to ν_1 - terminal

^a Chlorine datum at -196° , Ref. 63; iodine data from Ref. 64.

^b Chlorine data from Ref. 47.

The ^{127}I resonance observed at 417 MHz was assigned to the ν_1 transition of the central iodine atom in I_2Cl^+ by comparison with the ^{127}I resonances observed for I_3^+ and ICl_2^+ . The ν_1 transition for the terminal iodine atom was expected to occur at $\sim 530\text{-}550$ MHz; however, spectrometer malfunction prevented investigation above ~ 510 MHz.

The ^{127}I nqr data obtained for $\text{I}_3^+\text{AlCl}_4^-$ was very complete and the presence of I_3^+ was definitely indicated. Fortunately, the resonance at 527 MHz (ν_2 - central iodine) was observed before the spectrometer malfunction at high frequencies occurred. From the ratio of ν_2/ν_1 , η was calculated to be 0.35.

The resonance frequency of the central iodine in the ICl_2^+ cation and the geometry of the I_3^+ cation can be predicted using established equations relating the observed ^{127}I frequencies to bonding and structural parameters. In the coordinate system chosen for the bridging iodine atoms the z axis is perpendicular to the X-I-X plane, the x axis is parallel to the X-X axis, the y axis points from the center iodine perpendicular to the X-X axis, and the X-I-X angle is defined as 2θ . With this coordinate system, the following equations and hybrid orbitals (for the bridging iodine) are valid:⁶⁵

$$\phi_1 = \psi_{p_z} \quad (9)$$

$$\phi_2 = \psi_s \cot \theta + \psi_{p_y} (1 - \cot^2 \theta)^{1/2} \quad (10)$$

$$\phi_3 = \frac{1}{\sqrt{2}} [\psi_s (1 - \cot^2 \theta)^{1/2} + \psi_{p_x} - \psi_{p_y} \cot \theta] \quad (11)$$

$$\phi_4 = \frac{1}{\sqrt{2}} [\psi_s (1 - \cot^2 \theta)^{1/2} - \psi_{p_x} - \psi_{p_y} \cot \theta] \quad (12)$$

$$\eta = -3 \cos 2\theta \quad (13)$$

$$\left(e^2 Q q_{\text{mol}} / e^2 Q q_{\text{atm}} \right) [1 + \eta/3] = 2-a \quad (14)$$

The population of ϕ_1 and ϕ_2 (N_1 and N_2) is assumed to be two ($N_1 = N_2 = 2$) and the population of ϕ_3 and ϕ_4 (N_3 and N_4) is defined as a ($N_3 = N_4 = a$). The atomic coupling constant for ^{127}I ($e^2 Q q_{\text{atm}}$) = 2298.8 MHz⁶⁶ and $e^2 Q q_{\text{mol}}$ is the molecular coupling constant.

The ^{35}Cl nqr data for ICl_2^+ allow one to determine the population of the bonding orbitals on the chlorine atoms and by difference, N_3 and N_4 of the bridging iodine. Using this value for a , 0.35 for η (calculated using the crystallographically determined³⁵ 96.7° bond angle for ICl_2^+) and $e^2 Q q_{\text{atm}} = 2298.8$ MHz, ν_1 for the central iodine in ICl_2^+ is found to be 433.2 MHz which compares well with the observed frequency of 458 MHz. A similar interpretation of the data obtained for I_3^+ , assuming $\eta=0$ for the terminal iodine atoms, gives a charge distribution of +0.21 and +0.24 for the terminal iodine atoms, +0.76 for the central atom, and an angle of 97° between the bonding orbitals ϕ_3 and ϕ_4 . Of the 20 valence electrons in I_3^+ , 19.79 are accounted for in this treatment which is very reasonable in view of the model

limitations, i. e., overlap of the bonding orbitals is assumed to be zero (Huckel approximation) and cation-anion bonding is neglected.

Further support for the presence of I_3^+ and I_2Cl^+ in $I_3^+AlCl_4^-$ and $I_2Cl^+AlCl_4^-$ is obtained from the resonance data for the central iodine atom in the series I_3^+ , I_2Cl^+ , and ICl_2^+ . An entirely reasonable progression on increasing substitution of chlorine for iodine is observed, namely, 308.6, 420 and 457 MHz.

Only one ^{127}I resonance at ~ 400 MHz in the 300 - 500 MHz range was observed for I_5AlCl_4 and consequently no structural information about I_5^+ could be obtained. Some of the expected ^{127}I resonances may fall below 300 MHz as a result of the average positive charge on each iodine atom being less in I_5^+ than in I_3^+ ($\nu_1 = 308.6$ MHz for central iodine in I_3^+). However, for reasons unknown the samples always melted while collecting data between $\sim 175 - 300$ MHz and no resonances could be observed.

On the basis of the ^{35}Cl and ^{127}I nqr data and the ^{27}Al nmr data the formulation of these compounds as $I_3^+AlCl_4^-$, $I_5^+AlCl_4^-$ and $I_2Cl^+AlCl_4^-$ is well justified. As such, they are the first demonstrated examples of I_3^+ , I_5^+ , and I_2Cl^+ in the solid state.

Future Work

The ^{127}I ν_1 resonance for the terminal iodine atom in $\text{I}_2\text{Cl}^+\text{AlCl}_4^-$ should be obtained to confirm the assignment (ν_1 - central iodine) of the ^{127}I resonance observed at 420 MHz. This would allow a calculation of the charge distribution in I_2Cl^+ as was done for I_3^+ . If suitable nqr spectrometers become available, an extension of the ^{127}I nqr investigation to ~ 900 MHz should allow the ^{127}I ν_2 transitions of the terminal iodine atoms in I_3^+ and the central iodine in I_2Cl^+ to be obtained. The observation of the ν_2 resonances would allow the bond angle in I_2Cl^+ and a more accurate charge distribution in I_3^+ to be calculated. Also the magnitude of the asymmetry parameters of the terminal iodine atoms in $\text{I}_3^+\text{AlCl}_4^-$ should give some information about the extent of bonding interactions between the terminal iodine atoms in I_3^+ and the AlCl_4^- anion.

Raman spectral data for $\text{I}_2\text{Cl}^+\text{AlCl}_4^-$, $\text{I}_3^+\text{AlCl}_4^-$ and $\text{I}_5^+\text{AlCl}_4^-$ would be very useful and hopefully would confirm the results of the nqr investigation. However, some means of cooling the samples during data collection will be necessary to prevent decomposition.

An investigation of the bromine tetrachloroaluminate system may be profitable since the Br_2^+ and Br_3^+ cations have been identified in "superacid" and HSO_3F solution²⁷ and the compounds,

$\text{Br}_2^+ \text{Sb}_2\text{F}_{11}^-$ ²⁹ and $\text{Br}_3^+ \text{AsF}_6^-$ ²⁸ have been prepared. The Br_2^+ cation will probably not be present in the AlCl_4^- system since it is less stable with respect to disproportionation than I_2^+ . However, Br_3AlCl_4 and possibly $\text{Br}_2\text{ClAlCl}_4$ may be sufficiently stable to allow their preparation.

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