^{29}Si-^{19}F coupling constant pairwise parameters have recently been reported for the mixed tetrahalosilanes.[18] The chemical shift parameters are plotted against the corresponding boron compound parameters in Figure 4. Separate straight lines are formed by the fluorine-containing and nonfluorine-containing parameters. The difference between the two lines corresponds to about 4 ppm in either the boron or the silicon compound parameters. This seems to confirm that fluorine has anomalous effects when compared to the other halogens. The anomaly is probably related to different degrees of multiple bonding from fluorine to boron and to silicon. The results obtained would be consistent with better fluorine-to-central-atom multiple bonding in the boron compounds than in the corresponding silicon compounds, consistent with the better correspondence in orbital sizes in the boron case.

Our tetrahedral-boron ^{11}B chemical shift parameters correlate well with corresponding tetrahedral-carbon parameters,[3b] tetrahedral-^{27}Al parameters,[4a] and trigonal-boron parameters,[2] as can be shown by smooth-curve plots. A previously noted anomaly of the ^{13}C Br,Br parameter[3b] recurs in our work. Unfortunately no pairwise terms involving fluorine are available for the ^{13}C or ^{27}Al systems.

Adequate interpretation of trends in pairwise parameters awaits the availability of more data. Nevertheless it seems that corresponding parameters relating to different central nuclei can be related to differences in bonding, so that the parameters should be of value in chemical bonding studies as well as of empirical use.

Acknowledgments. We wish to thank the National Research Council of Canada for financial support and McMaster University for use of heteronuclear nmr facilities.

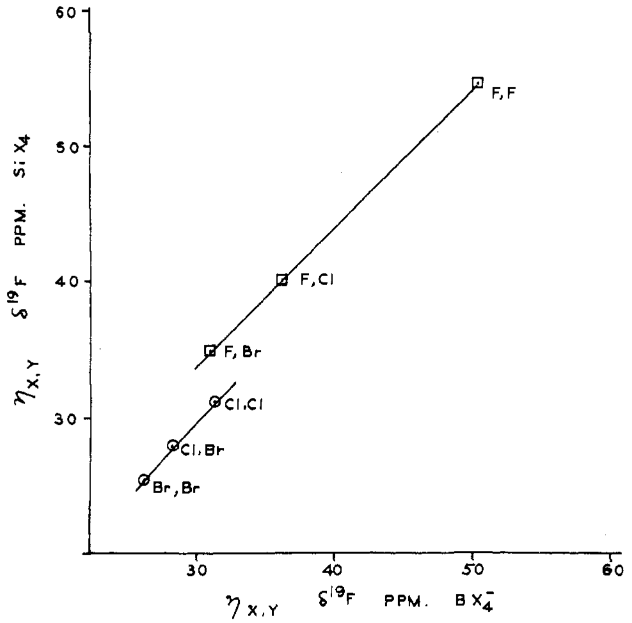

Figure 4. δ ^{19}F pairwise interaction parameters for SiX$_4$ species *vs.* BX$_4^-$ species.

Registry No. BCl$_3$, 10294-34-5; BF$_3$, 7637-07-2; BBr$_3$, 10294-33-4; BI$_3$, 13517-10-7; ^{11}B, 14798-13-1.

Supplementary Material Available. Table I, showing observed and calculated chemical shifts and coupling constants, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche referring to code number INORG-74-1467.

---

(18) F. Hofler and H. D. Pietka, *Monatsh. Chem.*, 104, 1 (1973).

Contribution from Ames Laboratory–USAEC and
the Department of Chemistry, Iowa State University, Ames, Iowa 50010

Structural Diagnosis of Chloroaluminate Compounds by Chlorine-35 Nuclear Quadrupole Resonance Spectroscopy

DON J. MERRYMAN, PAUL A. EDWARDS, JOHN D. CORBETT,* and ROBERT E. McCARLEY

Received October 29, 1973 AIC307972

The ^{35}Cl nqr spectra at room temperature are reported for chloroaluminate groups in Te$_4$(AlCl$_4$)$_2$, ICl$_2$AlCl$_4$, Bi$_5$(AlCl$_4$)$_3$, Co(AlCl$_4$)$_2$, Hg$_3$(AlCl$_4$)$_2$, and Te$_4$(Al$_2$Cl$_7$)$_2$. These and the literature data for NaAlCl$_4$, GaAlCl$_4$, and SCl$_3$AlCl$_4$ are compared for known and probable structures. The transitions of relatively free AlCl$_4^-$ groups in "ionic" compounds are found to average 10.6–11.3 MHz with a range of $\leq$1 MHz for the individual compounds. Strong coordination of AlCl$_4^-$ to the cation (*e.g.*, Co^{2+}, Hg$_3^{2+}$) or the formation of Al$_2$Cl$_7^-$ anions is reflected in an elongation of the bridging aluminum-chlorine bonds and in appreciable increases in both the range and the average frequency of the chlorine transitions. The effects of bridging on the halogen nqr transitions are considered and compared with those for the aluminum and gallium halide dimers M$_2$X$_6$.

Introduction

The need for a convenient method for determining the identity and bonding character of the anions in chloroaluminate compounds that is quicker than an X-ray study has been made more apparent by the increased utilization of AlCl$_4^-$ anions in compounds with unusual cations. The problem was brought to a head by the recent preparation of a series of apparently ionic tetrachloroaluminate compounds of some polyhalogen cations[1] which had particularly unfavorable properties for crystallographic study. The classical technique of infrared spectroscopy is inconclusive (and hence misleading) in some practical situations, for example,

---

(1) D. J. Merryman, P. A. Edwards, J. D. Corbett, and R. E. McCarley, *Chem. Commun.*, 779 (1970).

in its inability to distinguish between $AlCl_4^-$ and $Al_2Cl_7^-$ anions in salts with the Te_4^{2+} cation.[2] In addition, there is an increasing need to be able to diagnose a strong coordination of the normally "inert" $AlCl_4^-$ group to the cation. The present study of the ^{35}Cl nqr spectra of a number of chloroaluminate compounds of known or probable structure demonstrates that this technique does well in distinguishing most ionic $AlCl_4^-$ structures from those containing either $Al_2Cl_7^-$ ions or $AlCl_4^-$ anions which have strong coordination and the concomitant distortion.

Experimental Methods

Commercial $AlCl_3$ was sublimed first under vacuum and then under 30 Torr of argon to remove $FeCl_3$. All sublimed reactants and products were transferred in the usual drybox or, in the case of ICl and its compounds, in a polyethylene glove bag. Following the reported preparation of ICl_2AlCl_4,[3] purified ICl was slowly sublimed from an evacuated storage flask into an evacuated, preweighed container which was then closed and weighed on an analytical balance. The ICl was then transferred by sublimation to a reaction vessel containing the appropriate amount of $AlCl_3$, a slight excess of dry Cl_2 was added, and the contents were slowly heated over a period of several hours to ~70°. Teflon needle valves (Fischer-Porter) were used as closures in all such handlings.

The tetrachloroaluminate salts of Co^{2+}, Hg_3^{2+}, and Bi_5^{3+} were prepared by fusion of the appropriate quantities of $CoCl_2$ and $AlCl_3$; $HgCl_2$, Hg, and $AlCl_3$; or $BiCl_3$, Bi, and $AlCl_3$ in evacuated, sealed Pyrex containers, the sublimed component salts being weighed in the drybox to ±20 mg on a triple-beam balance. The Te_4^{2+} salts came from a previous study.[2] Samples of 20–30 g each were sealed under vacuum in 18-cm lengths of 15-mm o.d. Pyrex tubing for the spectroscopic study. Each sample was usually fused and annealed just below the melting point before study in order to obtain a maximum density and crystallinity; all the phases are thought to melt congruently.

The general instrumental techniques employed for the spectroscopy have been described elsewhere.[4] Initial spectra and the approximate frequencies of observed resonances (±10–20 kHz) were recorded on a Wilks NQR-1A superregenerative spectrometer. Precise frequency measurements were obtained and the resolution of overlapping resonances (separation >20 kHz) was accomplished at room temperature on a wide-line spectrometer previously described by Torgeson.[5] This spectrometer was set to scan a 50–125-kHz region for 3–18 hr, the data being collected on a 400-channel analyzer. Proper data for ^{37}Cl were observed accompanying all but the weakest ^{35}Cl resonances; the former were checked quantitatively whenever other assignments were conceivable, as with the compounds of Co, Hg, and Bi.

Results and Discussion

In Table I are collected ^{35}Cl resonance frequencies (ν_Q) for the anions in the six chloroaluminate compounds studied, [$Te_4(AlCl_4)_2$, ICl_2AlCl_4, $Bi_5(AlCl_4)_3$, $Co(AlCl_4)_2$, $Hg_3(AlCl_4)_2$, and $Te_4(Al_2Cl_7)_2$], together with literature data for three more [$NaAlCl_4$, $GaAlCl_4$, SCl_3AlCl_4].[6-8] Also tabulated are the number of independent chlorine atoms expected for known structures.[3,9-12] The illustration of data in Figure 1 gives a better comprehension of the gross differences. The resonance region shown should of course be viewed in the perspective of the much greater range known for ^{35}Cl transitions, from a few megahertz in "ionic" chlorides to 54.5 MHz in (solid) "covalent" Cl_2.[13]

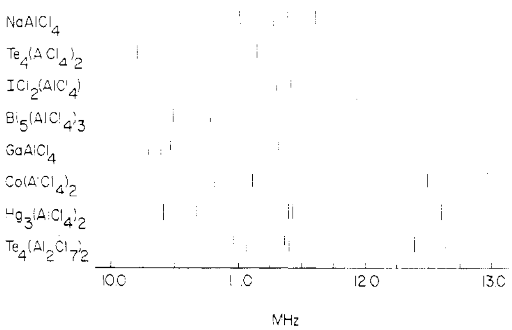

Figure 1. Frequencies of the nqr transitions for ^{35}Cl in the indicated chloroaluminates at room temperature.

Nqr transition frequencies for chlorine which can be measured to five significant figures clearly contain much more information on field gradients and the intertwined asymmetry parameters at the chlorine nucleus than can be accounted for in any quantitative detail with the present understanding of these factors. Nonetheless, the simple correlation of gross changes in the ^{35}Cl data for chloroaluminate groups with the strength of the greater chlorine–cation interactions when the latter are judged in terms of just the elongation of the aluminum–chlorine bonds is demonstrably successful. All other effects (except perhaps asymmetry corrections in the case of strong bridging of chlorine to the cation) are apparently much less important at this level of interpretation. This correlation is aided by the relative ease with which chlorine resonances may be observed in these compounds with present instrumentation; of all the compounds studied only $Se_8(AlCl_4)_2$[14] did not give any detectable resonances.

The first five compounds listed and plotted appear to be ionic $AlCl_4^-$ compounds. A more detailed consideration of this judgment and of the spectra will lead to the conclusion that an array of ^{35}Cl resonances ranging between about 10.2 and 11.7 MHz is typical for tetrachloroaluminate compounds in which the $AlCl_4$-cation interactions are substantially only coulombic in nature. In these examples the resonances average between 10.6 and 11.3 MHz[15] and in each compound show a range of 1 MHz or less. After these generalities are discussed, data for the last group of compounds in Table I will be considered as exceptions, that is, as containing a strongly coordinated $AlCl_4^-$ group or the different anion $Al_2Cl_7^-$ both of which exhibit ^{35}Cl transitions with appreciably higher averages and with wider ranges.

The necessary data regarding d(Al–Cl) in pertinent known structures are given in Table II,[3,9-12,16,17] sorted according to normal (terminal) and bridging chlorine functions where appropriate and including the angle at chlorine for some of the latter examples. Probably the best behaved of

---

(2) D. J. Prince, J. D. Corbett, and B. Garbisch, *Inorg. Chem.*, 9, 2371 (1970).

(3) C. G. Vonk and E. H. Wiebenga, *Acta Crystallogr.*, 12, 859 (1959).

(4) P. A. Edwards, R. E. McCarley, and D. R. Torgeson, *Inorg. Chem.*, 11, 1185 (1972).

(5) D. R. Torgeson, *Rev. Sci. Instrum.*, 38, 612 (1967).

(6) J. C. Evans and G. Y-S. Lo, *Inorg. Chem.*, 6, 836 (1967).

(7) S. L. Segel and R. G. Barnes, USAEC Report IS-512, Ames Laboratory, Iowa State University, 1962.

(8) H. E. Doorenbos, J. C. Evans, and R. O. Kogel, *J. Phys. Chem.*, 74, 3385 (1970).

(9) N. C. Baenziger, *Acta Crystallogr.*, 4, 216 (1951).

(10) T. W. Couch, D. A. Lokken, and J. D. Corbett, *Inorg. Chem.*, 11, 357 (1972).

(11) J. A. Ibers, *Acta Crystallogr.*, 15, 967 (1962).

(12) R. D. Ellison, H. A. Levy, and K. W. Fung, *Inorg. Chem.*, 11, 833 (1972).

(13) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, London, 1969.

(14) R. K. McMullan, D. J. Prince, and J. D. Corbett, *Inorg. Chem.*, 10, 1749 (1971).

(15) The results of semiempirical calculations of ^{35}Cl nqr frequencies in normal $AlCl_4^-$ ions using SAVE-CNDO theory also fall in this experimentally observed range: P. A. Edwards and M. A. Whitehead, unpublished research.

(16) A. C. Hazell and R. G. Hazell, *Acta Chem. Scand.*, 26, 1987 (1972).

(17) N. C. Baenziger and A. D. Nelson, *J. Amer. Chem. Soc.*, 90, 6002 (1968).

Table I. Quadrupole Transitions for ^{35}Cl in Chloroaluminate Compounds at Room Temperature

	^{35}Cl resonance data				Structure	
Compd	Obsd ν_Q,[a] MHz	Intens	Av ν_Q, MHz	Source	No. of indep Cl	Source
$NaAlCl_4$	11.009 11.272 11.385 11.583	m	11.31	Ref 6[b]	4	Ref 9
$Te_4(AlCl_4)_2$	10.201 11.138	w	10.67	This work	4	Ref 10
ICl_2AlCl_4	10.802 10.843 11.297 11.413	w w m m	11.09	This work	4	Ref 3
$Bi_5(AlCl_4)_3$	10.479 10.779	s	10.63	This work		See text
$GaAlCl_4$	10.296 10.382 10.460 11.312		10.61	Ref 7		See text
$Co(AlCl_4)_2$	10.813 11.115 12.491 12.959	s	11.84	This work	4	Ref 11
$Hg_3(AlCl_4)_2$	10.417 10.676 10.812 11.383 11.433 11.843 12.568 12.597	w	11.47	This work	8	Ref 12
$Te_4(Al_2Cl_7)_2$	10.965 11.058 11.368 11.390 11.976 12.391 12.633	mw	11.68	This work	7	Ref 10
SCl_3AlCl_4	9.91 10.18 10.46 11.04		10.40	Ref 8		

[a] ±1 kHz except ±30 kHz and ±3 kHz for data from SCl_3AlCl_4 and $NaAlCl_4$, respectively. [b] ν_Q values given in literature for $NaAlCl_4$ were all confirmed semiquantitatively and the first two listed to ±3 kHz in the course of the present study.

Table II. Aluminum-Chlorine Distances and Angles in Some Chloroaluminate Structures

	d(Al-Cl), Å		Al-Cl-M	
	Terminal	Bridge	Bridged angle, deg	Ref
$(S_5N_5)(AlCl_4)$	2.093 (5)-2.126 (3) (eight)			16
$(CH_3)_7C_6(AlCl_4)$	2.105 (3)-2.128 (4) (four)			17
$NaAlCl_4$	2.11-2.16[a] (four)			9
$Te_4(AlCl_4)_2$	2.110 (7) 2.093 (6)	2.149 (6)[b] 2.130 (6)[b]	98	10
ICl_2AlCl_4	2.05 (6) 2.08 (6)	2.20 (6) 2.10 (6)		3
$Te_4(Al_2Cl_7)_2$	2.081 (8) 2.094 (7) 2.097 (7) 2.099 (7)	2.128 (7)[b] 2.115 (7)[b] 2.262 (7)[c] 2.222 (7)[c]	110.8 (3)	10
$Co(AlCl_4)_2$	2.105 (19)	2.188 (18) 2.183 (14) 2.151 (16)	87 87 127	11
$Hg_3(AlCl_4)_2$	2.106 (6)-2.131 (5) (six)	2.185 (5) 2.181 (5)	105.7 (2) 103.4 (2)	12

[a] Errors of 0.03-0.05 Å estimated by Ibers.[11] [b] A weak bridging function is suggested by d(Al-Cl) and by chlorine-to-cation distances.[10] [c] Intraionic bridge.

the known structures in exhibiting unperturbed Al-Cl bonds to serve as reference values are $S_5N_5{}^+AlCl_4{}^-$ and $(CH_3)_7C_6{}^+AlCl_4{}^-$, where the bond averages [and ranges] are 2.119 (2) [0.033 (6)] and 2.120 (2) Å [0.023 (5) Å], respectively. Substantially the same average [2.120 (4) Å] occurs in $Te_4{}^{2+}(AlCl_4{}^-)_2$, even though a weak bridging of the edges of the $Te_4{}^{2+}$ square by chlorine has been deduced[8] and is reflected in the range of distances within the anion [0.056 (8) Å]. The remaining examples are either less adequately determined or show markedly larger variations and ranges because of either coordination to the cation or a change in the nature of the anion.

Returning to Table I and Figure 1, $NaAlCl_4$ should be a good example of a well-behaved tetrachloroaluminate salt insofar as an "inert" cation is concerned (though the coulombic effect of the small cation may actually have caused a general increase in the net electric field gradients at chlorine and a concomitant shift of all resonances to higher frequencies). Only two weak transitions out of four possible are observed for $Te_4^{2+}(AlCl_4^-)_2$, and these only after extensive annealing, but if they are representative of the two types of chlorine (Table II), the compound is reasonably "ionic," as also suggested by the intraionic distances. The same is indicated by the nqr data for ICl_2AlCl_4 even though the reported structure[3] is not sufficiently well-determined to confirm this in terms of *d*(Al–Cl). (The iodine has an approximately rectangular environment with a second pair of chlorine neighbors from $AlCl_4^-$ groups 26% (0.6 Å) further away than those bonded in the cation.) An earlier nqr study on ICl_2AlCl_4[6] was inadequate in both resolution and sensitivity. The $AlCl_4^-$ compounds of Bi_5^{3+} and Ga^+ give every indication of being ionic phases[18,19] though complete crystal structural data are presently not available for either. Solid $Bi_5(AlCl_4)_3$ exhibits a normal ir spectrum for $AlCl_4^-$,[20] and the Bi_5^{3+} species exhibits a negligible change in its electronic spectrum in the melt when the anion is altered from chloroaluminate to chlorozincate.[21] The ir and Raman spectra of solid $Ga^+AlCl_4^-$ support an ionic constitution,[22] while the crystal structure[23] of the very similar[19] $Ga^+GaCl_4^-$ indicates no significant or specific interactions of Ga^+ with the anion; in fact, the volume available to the cation seems unusually large. The compounds which prompted this study, $I_2ClAlCl_4$, I_5AlCl_4, and I_3AlCl_4, also appear to be "normal" salts as judged by both the average and the range of ν_Q for ^{35}Cl in the anion,[1] although the 1.32-MHz range for the last suggests a wider variety of chlorine environments and therewith perhaps some deviation from this classification.

Still stronger coordination of anion chlorine to a second center and the concomitant elongation of that aluminum-chlorine bond is well illustrated by the structures of the compounds $Co(AlCl_4)_2$, $Hg_3(AlCl_4)_2$, and $Te_4(Al_2Cl_7)_2$, and all three show unusual arrays of nqr transitions. A working hypothesis for the effects of strong interactions of this sort is as follows: (1) polarization of and partial removal of negative charge from the entire anion by the electrophilic partner would appear to cause a general up-frequency shift of the resonance family; (2) an appreciable bridging role for some chlorine atoms causes their transitions to shift to relatively lower frequencies. The first is a rationalization for the observations (Table I) as well as for $AlBr_4^-$ [24] *vs.* Al_2Br_6[13] whereas precedent for the latter is already available.

Studies of M_2X_6 compounds for both aluminum and gallium (save of course for the unknown dimer Al_2Cl_6(s)) clearly indicate that the bridging halogens, with bond elongations of 4–11% and angles at the bridging halogen in the neighborhood of 90°, exhibit nqr transitions which are at 75–85% of the frequencies shown by the terminal halogens.[7,13] (This is in contrast to the dimers of heavy transition metal halides where the larger effects of π bonding to terminal atoms leave the bridging atoms at higher frequencies.[25]) The same appears true for the dimers of the less polar $RAlCl_2$,[26] where the presumed transitions of the bridging chlorine atoms occur at 91.5–92.5% of the values for the terminal atoms.

In general a relative downward shift of the transition frequency for a chlorine atom in $AlCl_4^-$ which acts in a bridging role and forms a second σ bond can be rationalized in terms of a reduction of the net electric field gradient at that chlorine associated with lengthening of the aluminum-chlorine bond plus the cancelation of components of the field gradients accompanying the formation of a second, albeit weak, bond by that chlorine. The asymmetry parameter η for the bridging atom, nonzero values for which are reflected in a slow increase in the observed frequency according to $(1 + \eta^2/3)^{1/2}$, should have only a relatively small effect with the asymmetric bridging (small Al–Cl bond lengthening) associated with all examples save probably with $Al_2Cl_7^-$. Therefore, the lowest ν_Q values are tentatively attributed to the bridging chlorine atoms from $AlCl_4^-$ anions, consistent with the "high-low" pattern seen with $Te_4(AlCl_4)_2$, $ICl_2(AlCl_4)$, $I_2Cl(AlCl_4)$, and $Co(AlCl_4)_2$.

In the structure[11] of $Co(AlCl_4)_2$ two chlorine atoms in each anion participate in relatively strong bridging to a single cobalt, with 87° angles at the chlorine and the Al–Cl bond elongated by 0.06–0.08 Å (Table II). Following earlier discussion, these atoms presumably give rise to the lowest two resonance frequencies. A third chlorine in each anion bridges more weakly to another cobalt to form chains, with a bond lengthening of about 0.03 Å relative to the normal distance and a bridging angle of 127°. The combined inductive effect of the three bridging chlorine atoms causes the fourth terminal chlorine to have a somewhat shortened aluminum-chlorine bond, and this atom is likely responsible for the highest transition at 12.96 MHz. The ratio of the average of the lower two frequencies to that of the higher pair is 0.86, very close to that which may be extrapolated from ν(bridging)/ν(terminal) in known M_2X_6 species with similar halogen-bonding arrangements.

The different types of chlorine atoms in $Co(AlCl_4)_2$ cannot be distinguished according to the temperature dependencies of their nqr transitions, each showing a negative dependence of about 1% per 100°. Interestingly, the intensity of the 12.491-MHz transition is enhanced appreciably by cooling whereas the other three diminish so that they cannot be observed below about −60°.

The cobalt in $Co(AlCl_4)_2$ achieves a sixfold coordination that is fairly regular in Co–Cl distances but substantially distorted in angles. Judging from its electron spectrum Co^{2+} maintains remarkably specific and well-defined coordination polyhedra in chloroaluminate melts.[27] The distorted octahedral species observed in molten $KAlCl_4$ containing ~5–25% excess $AlCl_3$ may be most related spectroscopically to the solid tetrachloroaluminate. Aluminum-chlorine distances found in the isostructural $Ti(AlCl_4)_2$[28] are within the uncertainties of the known cobalt structure but have less than 0.01 Å distinguishing between the two types of bridging chlorines, while the terminal chlorine is only 2.079 Å from aluminum. The strength of the coordination is demonstrated by the formation of melt polymers which have the same spectrum as $Ti(AlCl_4)_2$(s).[29]

The general increase in the ^{35}Cl resonance frequencies and

---

(18) J. D. Corbett, *Inorg. Chem.*, **7**, 198 (1968).

(19) R. K. McMullan and J. D. Corbett, *J. Amer. Chem. Soc.*, **80**, 4761 (1958).

(20) D. J. Prince and J. D. Corbett, unpublished data.

(21) H. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967).

(22) F. J. Brinkmann and H. Gerding, *Inorg. Nucl. Chem. Lett.*, **7**, 667 (1971).

(23) G. Garton and H. M. Powell, *J. Inorg. Nucl. Chem.*, **4**, 84 (1957).

(24) Data for ^{79}Br in $NaAlBr_4$ at room temperature are (±20 kHz) 87.44, 90.99, and a very distorted resonance centered at 96.96 MHz which is presumed to be a doublet.

(25) P. A. Edwards and R. E. McCarley, *Inorg. Chem.*, **12**, 900 (1973), and references therein.

(26) M. J. Dewar, D. B. Patterson, and W. K. Simpson, *J. Amer. Chem. Soc.*, **93**, 1030 (1971).

(27) H. A. Oye and D. M. Gruen, *Inorg. Chem.*, **4**, 1173 (1965).

(28) J. Brynestad and G. P. Smith, private communication, 1973.

(29) J. Brynestad, S. von Winbush, H. L. Yakel, and G. P. Smith, *Inorg. Nucl. Chem. Lett.*, **6**, 889 (1970).

particularly in the range observed with $Hg_3(AlCl_4)_2$ befit this remarkable structure. As with $Co(AlCl_4)_2$, the strongly bridging atoms are presumed to give rise to lower frequencies; an opening of the bridge angle to ~104° has probably resulted in some up-frequency shift relative to that predicted by distance alone. The spectrum is not without its complications; the highest pair of resonances is very weak and could just be verified by wide-line techniques on a well-annealed sample. The compound's spectrum actually results from the overlap of transitions for two rather different $AlCl_4$ tetrahedra which differ by 0.045 Å in the shortest Hg-Cl approach, by 0.006 (2) Å in average Al-Cl distance, and by almost 2° in maximum angular distortions, the shortest Hg-Cl approach accompanying the larger Al-Cl average and the greater distortion. Specific assignments do not seem at all feasible.

The compound $Te_4(Al_2Cl_7)_2$ is related in the sense that the anion represents the extreme in $Cl_3Al\text{-}Cl\cdots M$ interactions when M is the $AlCl_3$ monomer rather than a cation. Interestingly, the range of d(Al-Cl) in $Al_2Cl_7^-$ is closely comparable to that in $Al_2Cl_6(g)$[30] with the distances uniformly about 0.03 Å larger in $Al_2Cl_7^-$.

The obvious effect of diminished charge per chlorine in $Al_2Cl_7^-$ relative to $AlCl_4^-$ is a greater covalency (shorter Al-Cl distances) and a general shift of the transitions to higher frequencies (Figure 1). The effect of the weak bridging to Te_4^{2+} is presumably small [compare $Te_4(AlCl_4)_2$]. Although no particular assignments seem obvious, the chlorine bridging within the ion is presumably responsible for one of the lower frequency transitions.[31] The resonances at about 10.96 and 11.98 MHz are the strongest while that at 11.06 MHz is the weakest, about one-third as intense and thus not obviously resolved from the 10.96-MHz neighbor on the Wilks instrument. The pair near 11.37 MHz would of course not have been deduced without the wide-line capabilities. The temperature dependencies of the chlorine transitions reveal nothing unique, ranging between −1.0 and −2.0% per 100° with ν_2 and ν_6 showing the smallest change.

The data for $SCl_3(AlCl_4)$ included in Table I for completeness[32] are a little surprising in the frequency of the lowest (9.91 MHz) transition. However, the lack of a crystal structure determination precludes further interpretation. The spectral data would be incomplete, however, should the compound be isostructural with $SeCl_3(AlCl_4)$ since the latter solid contains two independent anions.[33] Difficulties in assigning the observed Raman data to a simple $SeCl_3^+$ ion[34] are in line with the structural complexities found in the latter.

Among the original objectives of this study, the means by which simple tetrachloroaluminate salts could be diagnosed have been met. In general, the observation of one, two, four, or some multiple of four resonances with a range of about 1 MHz and an average of 10.6-11.3 MHz would be considered sufficient to judge the compound as reasonably saltlike, particularly if strong transitions gave some assurance that the data were complete. Observations of other numbers of resonances would probably mean the data set was incomplete, thereby allowing only less certain conclusions. Conversely, the observation of data at higher frequencies, especially with a wider range, would appear to implicate clearly either $Al_2Cl_7^-$ ($Al_3Cl_{10}^-$, etc.) anions or $AlCl_4^-$ groups which are strongly bound to the cations. More well-determined chloroaluminate structures will obviously be necessary to explore many and more subtle factors that give rise to differences within these rather wide "normal" ranges.

Acknowledgments. This work would not have been possible without the assistance and advice of Dave Torgeson in the use of the wide-line spectrometer. This service and the use of some instruments were generously provided by Professor R. G. Barnes.

Registry No. $Te_4(AlCl_4)_2$, 36632-67-4; ICl_2AlCl_4, 16040-08-7; $Bi_5(AlCl_4)_3$, 12301-55-2; $Co(AlCl_4)_2$, 12296-86-5; $Hg_3(AlCl_4)_2$, 36554-82-2; $Te_4(Al_2Cl_7)_2$, 36645-21-3.

(30) K. J. Palmer and N. Elliott, *J. Amer. Chem. Soc.*, **60**, 1852 (1938).

(31) Interestingly, the ^{27}Al nmr spectrum for $Al_2Cl_7^-$ herein shows a single $+^1/_2 \rightarrow -^1/_2$ transition with no satellites. The coupling constant calculated from the line width has an upper limit of 1.6 MHz—compare 25.5 and 13.86 MHz for $EtAlCl_2$ and Al_2Br_6.[26] The intraionic distortions and second neighbor chlorine atoms at ~3.7 Å in this structure[10] evidently do an effective job of reducing the field gradient at aluminum in spite of the approximately trigonal distortion of the tetrahedral geometry about aluminum.

(32) A thoroughly reasonable ^{35}Cl transition of 11.23 MHz in $(C_6H_5)_4P^+(AlCl_4^-)$ at 77°K has also been reported: D. Scaife, *Aust. J. Chem.*, 23, 2205 (1970).

(33) B. A. Stork-Blaisse and C. Romers, *Acta Crystallogr., Sect. B.*, 27, 386 (1971).

(34) H. Gerding and H. Houtgraaf, *Recl. Trav. Chim. Pays-Bas*, 73, 759 (1954).