

The Weakly Coordinating Trichloromethanesulfonate Anion: NQR Comparison of Its Coordinating Abilities via Oxygen with Those of the Chloroacetate Ions

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Ionic and covalent derivatives of the chlorine analogue of the nonbasic, weakly coordinating triflate ion, $\text{Cl}_3\text{CSO}_3^-$ or “trichlate” ion, have been prepared and compared with the corresponding more strongly coordinated chloroacetates, $\text{Cl}_x\text{CH}_3-x\text{CO}_2\text{M}$ ($x = 1-3$), using ^{35}Cl NQR (nuclear quadrupole resonance) spectroscopy. The ^{35}Cl NQR frequencies of all types of derivatives are sensitive to the nature of the metal ion or Lewis acid and are most sensitive in the case of monochloroacetates. In covalent (including zirconocene) derivatives, the average NQR frequencies fall as the Pauling electronegativity of M falls. The results for ionic derivatives contrast with previous results for ionic hexachlorometalates: the average ^{35}Cl NQR frequencies drop sharply as the ionic radius of the group 1 cation increases. Ab initio Gaussian 98 computations at the B3LYP/6-311++G(3df,3pd) level on isolated $\text{XCH}_2\text{CO}_2\text{M}$ ($\text{M} = \text{Li, Na, K; X} = \text{F, Cl}$) molecules duplicate this trend, showing increasing polarization of the C–Cl bond and smaller electric field gradients for larger group 1 ions; the relevance of this to the solid state polymerization of chloroacetates (Herzberg, O.; Epple, M. *Eur. J. Inorg. Chem.* **2001**, 1395–1406) is discussed. We have prepared the dihydrate and monohydrate of trichlic acid, $\text{Cl}_3\text{CSO}_3\text{H}$. Although trichlates have the highest average NQR frequencies of any of these salts, the NQR frequencies of trichlic acid dihydrate are anomalously lower than those of trichloroacetic acid, which suggests that it is a strong acid, ionized in the solid state to H_3O_2^+ and $\text{Cl}_3\text{CSO}_3^-$ ions.

Introduction

Chemists have long sought “noncoordinating” anions to serve as inert counterions in salts of very elusive, very reactive cations such as silylium ions, R_3Si^+ ,¹ and various transition metal organometallic cations which are important industrially as catalysts, and which require “vacant” coordination sites. It is now acknowledged that there are no noncoordinating anions²; the focus is now on finding easily dissociated weakly coordinating anions³ that act as good leaving groups from latent coordination sites.⁴ Weakly coordinating anions should be as nonbasic⁵ as possible: they should have low charge and a large size over which the charge can be dispersed. Examples of this type of anion

include methanesulfonate (CH_3SO_3^-), tetraphenylborate [$\text{B}(\text{C}_6\text{H}_5)_4^-$], and 1-carba-*closo*-dodecaborate ($\text{CB}_{11}\text{H}_{12}^-$).⁶ Coordinating ability of the anion is further reduced by substituting the outside surface of the anion with weakly coordinating functional groups containing very electronegative atoms such as halogen, to give anions such as [$\text{B}(\text{C}_6\text{F}_5)_4^-$] and CF_3SO_3^- (commonly known as triflate ion and very frequently used as a good leaving group in organic chemistry).⁸ The most important industrial application requiring weakly coordinating anions is the metallocene process of producing stereoregular polymerization of alkenes.⁹ This polymerization has been catalyzed using zirconocene triflates,¹⁰ which are also useful for catalysis of aldol¹¹ and Diels–Alder¹² reactions.

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Most weakly coordinating anions now being investigated have fluorinated surfaces, and organofluorines are hard bases, which have been observed to coordinate to the (presumably) hard zirconium(IV) active site in metallocene catalysts.¹³ One of the least coordinating anions discussed at the Symposium on Weakly Coordinating Anions¹⁴ was not a fluoro anion, but rather $(\text{CB}_{11}\text{H}_6\text{X}_6)^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$),¹⁵ in which the halogen atoms are soft bases, which may have less propensity to bond to hard zirconium(IV).¹⁶

Such anions are appropriately studied spectroscopically, not by NMR, but by ³⁵Cl, ^{79,81}Br, and ¹²⁷I nuclear quadrupole resonance (NQR) spectroscopy. Since NQR studies require gram-scale samples of crystalline solid products, we have begun our investigations, not with the very expensive $(\text{CB}_{11}\text{H}_6\text{X}_6)^-$ salts, but rather with analogues to CH_3SO_3^- and CF_3SO_3^- . Our initial paper focused on the halomethanesulfonate ions $(\text{XCH}_2\text{SO}_3^-)$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$;¹⁷ in this paper we focus on the less basic and presumably more weakly coordinating $\text{Cl}_3\text{CSO}_3^-$ ion (trichloromethanesulfonate), which can be called "trichlate" ion by analogy to the triflate ion. These results are compared with data for the somewhat more basic, more coordinating chlorocarboxylate anions, $\text{Cl}_x\text{H}_{3-x}\text{CO}_2^-$ ($x = 1-3$, Figure 1).

Chloroacetate ions readily coordinate to stronger Lewis acids such as carbonium ions, hydrogen ions, and transition-metal ions to give covalent derivatives (esters, weak acids, and complexes, respectively), among which there are three major structure types (Figure 2).¹⁸ The simplest covalent structure type I is monodentate, as found in esters and some complexes. Other covalent types are found, however, especially for the more basic mono- and dichloroacetate ions.

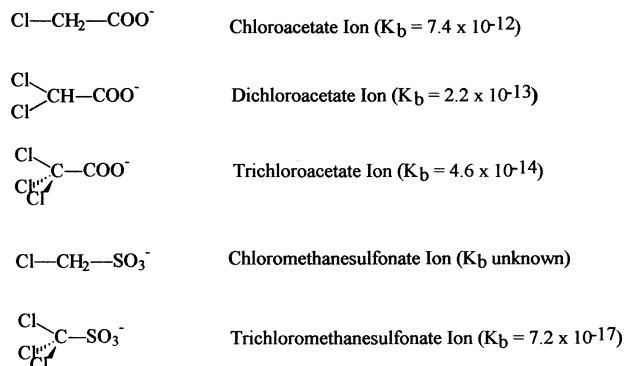
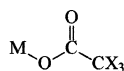
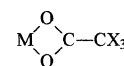


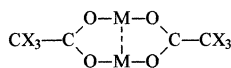
Figure 1. Structures and K_b values for anions involved in this study. Values of K_b are calculated from acid ionization constants from the following references: *CRC Handbook of Chemistry and Physics*, 81st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2000, pp 8–46. Edwards, H. G. M.; Smith, D. N. *J. Mol. Struct.* **1991**, 263, 11–20.



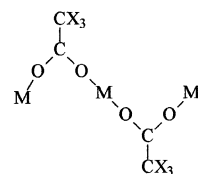
Type I: Monodentate



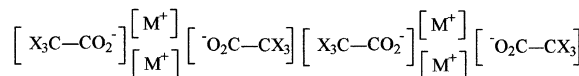
Type II: Chelate



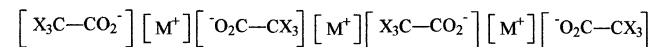
Type III: Bridging Cyclic



Type IIIA: Bridging Polymeric



Type IV: Layer Ionic



Type V: "Normal" Ionic

Figure 2. Bonding types considered for the chloroacetate and chloromethanesulfonate ions in this study (illustrated for trihaloacetate ion). Type V is a largely hypothetical arrangement in which there is a layer of cations alternating with every layer of anions.

On a few occasions the acetate group uses both oxygen atoms to chelate the same metal atom (structure type II). More common are the type III and IIIA bridging acetates; the type III dimeric transition-metal acetates, $\text{M}_2(\text{acetate})_{2x}$, often feature single or multiple metal–metal bonds.

The weakest Lewis acids (the cations of the first two groups) give ionic salts; ionic chloro-, bromo-, and iodoacetates¹⁹ normally adopt layer structures (type IV), in which the haloalkyl groups are far from the metal ions, forming

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layers in which their nearest neighbors in the next layer are also haloalkyl groups. This structure contrasts with that of more “normal” ionic compounds such as NaCl, which alternate layers of cations and anions (type V). Single-crystal structure determinations on layer haloacetates are seldom possible since they tend to form thin, disordered crystals,¹⁹ but NQR spectra are usually obtainable on these crystals.

Soft Lewis acids such as Ag⁺ often additionally coordinate chlorine atoms from chlorocarbons. Silver chloroacetate has a typical type III dimeric structure, but there are also interdimer contacts between each chlorine in one dimer and a silver atom in another;²⁰ such a feature is absent in silver fluoroacetate.²¹ In calcium chloroacetate monohydrate²² conformational changes result in halogen–metal ion contact and a nonlayer overall structure. We have previously shown that organohalogen coordination to metals such as silver profoundly affects their ³⁵Cl NQR frequencies.^{17,23,24} Hence NQR data for soft-acid metal ion salts of chlorinated anions (and calcium chloroacetate) must be analyzed separately; these will be the focus of a separate study.

There is limited structural data available for chloromethanesulfonates: silver chloromethanesulfonate¹⁷ and silver bromomethanesulfonate²⁵ show type V ionic structures with silver–halogen coordination. No structural data is available on trichlates, whereas many structures have been done on triflates, so we will assume that the structural types of trichloromethanesulfonates are similar to those of triflates and other organosulfonates. Structure type I is assumed to be found in esters and is found in the metallocene triflate (C₅H₅)₂Ti(O₃SCF₃)₂.²⁶ Covalent or coordinate-covalent triflates of transition, lanthanide, post-transition, and nonmetal elements commonly involve two or three oxygen donor atoms bridging to two or three metal or nonmetal atoms (type IIIA).⁶ Ionic triflates²⁷ and organosulfonates in general²⁸ normally adopt layer structures (type IV).

NQR frequencies are extremely sensitive to the electronic environment of the NQR-active nucleus. If one of these ions were truly noncoordinating, we hypothesize that its average

NQR frequencies would be insensitive to the nature of the Lewis-acid cation, so a plot of NQR frequencies versus an appropriate parameter for the Lewis acid would show zero slope. More plausibly, the plots may show a lower slope for the least basic anion, trichlate, and a higher slope for the most basic anion, chloroacetate.

Theory²⁹

NQR-active nuclei are nonspherical in shape and have nuclear spin $I > 1/2$ with nonzero nuclear quadrupole moments Q . NQR spectra, unlike NMR spectra, are measured without external magnetic fields, because the energy levels of quadrupolar nuclei are determined by the symmetry of their electron environments, specifically their electric field gradients eq. Quadrupolar nuclei in spherical environments, such as ^{35,37}Cl nuclei ($I = 3/2$) in chloride ions in a NaCl lattice, can be flipped with zero input of rf energy, but as the chloride ion forms a covalent bond to an external atom or cation, it becomes nonspherical, and a definite rf energy is required to flip the nucleus between allowed orientations. Hence the NQR frequency responds sensitively to the ionic or covalent character of the bond of the chlorine to the nearby atom or cation.

The electric field gradient is very sensitive to the distance of the electric charges from the nucleus:

$$\text{eq}_{zz} = - \int \Psi^*(3 \cos^2 \theta - 1)r^{-3}\psi \, d\tau \quad (1)$$

External charges can distort the core electrons from spherical symmetry, but this effect is difficult to calculate. Most commonly and generally rather successfully, the Townes–Dailey approximation³⁰ is used, which focuses on the electric field gradient created by imbalances in the valence electron populations of the chlorine atoms. Using this theory, one can derive a relationship of the NQR frequency of a ³⁵Cl atom to the ionic character i or the covalent character σ of the single bond to the unhybridized chlorine atom:

$$\begin{aligned} \nu(^{35}\text{Cl}) &= -1/2(1 - i)e^2Qq_0 = \\ &= -1/2(1 - i)(109.746 \text{ MHz}) = -54.873\sigma \quad (2) \end{aligned}$$

where e^2Qq_0 is the quadrupole coupling constant due to one electron in a chlorine valence 3p orbital. Since in Gordy’s approach³¹ the ionic character of a bond equals one-half of the difference of the Pauling electronegativities of the bonded atom, X_P , and chlorine, 3.16, for chlorines bonded singly to one other atom M, the NQR frequency ν (in MHz) is strongly dependent on the Pauling electronegativity X_P of the other atom M:^{3b}

$$\text{theoretical } \nu(^{35}\text{Cl}) = 27.436(X_P - 1.16) \quad (3)$$

$$\text{empirical best fit}^{3b} \nu(^{35}\text{Cl}) \approx 26.0(X_P - 1.13) \quad (4)$$

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For chlorine bonded to carbon ($X_P = 2.55$), this predicts a frequency of 36.9 MHz, but the NQR frequencies of $R_1R_2R_3C-Cl$ compounds actually span a region of about 33–42 MHz, depending sensitively on the inductive (electron-withdrawing) effects of the R groups.

NQR frequencies are so sensitive to the environments of quadrupolar nuclei that they are affected by charges in neighboring molecules and (especially) ions. Hence, although there is presumably only one kind of C–Cl bond in each of the compounds studied in this paper, there usually is more than one ^{35}Cl NQR signal. Chemically equivalent atoms in crystallographically inequivalent sites give distinct NQR spectra, since they have different intermolecular or interionic contributions to their electric field gradients. If the crystal lattice is complex, the resulting “crystal field effects”³² can cause there to be many signals for the same chemical type of chlorine: $CCl_4(s)$ has 16 frequencies, with a spectral width from the lowest to the highest frequency of 0.351 MHz.

In covalent organochlorine compounds, the spectral widths are normally limited to about 0.8 MHz. Due to the high sensitivity of quadrupolar nuclei to their electronic environments and the presence of point charges in ionic lattices acting to polarize core and valence electrons of the chlorine, crystal field effects can be much larger than 0.8 MHz in ionic compounds; we need to estimate how large they can be in ionic chlorinated organic anions such as chloroacetates and chloromethanesulfonates. To minimize the random influences of crystal field effects, we will first discuss trends in average NQR frequencies, keeping in mind that small deviations of average frequencies from general trends may be due to incomplete averaging of crystal field effects, especially when the compounds are not isomorphous and isostructural.

Substantial sensitivity of average NQR frequencies of anions in salts to the size of the cation has been observed. Brill³³ studied the ^{35}Cl NQR spectra of the type V ionic group I and quaternary ammonium salts of MCl_6^{2-} anions ($M = Sn, Pb, Te, Re, Pt$): the ^{35}Cl NQR frequencies of MCl_6^{2-} salts decrease by up to 2.0 MHz as the counterion radius decreases. Guibé,³⁴ however, has noted that the opposite trend prevails in the NQR frequencies of chloroacetates: average NQR frequencies drop as the ionic radius of the counterion increases. We wish to clarify these effects and seek an explanation of this altered trend.

Experimental Section

^{35}Cl NQR spectra were measured at 77 K on a Decca super-regenerative continuous-wave NQR spectrometer³⁵ or a RITEC pulse Fourier transform ^{35}Cl NQR spectrometer.³⁶ New ^{35}Cl NQR data obtained are reported in Tables 1 and 2. IR spectra were run on KBr pellets on a Nicolet Impact 410 infrared spectrometer; the spectra of all trichlates contained bands very close in position to

Table 1. ^{35}Cl NQR Frequencies^a (MHz) Measured at 77 K for Chloroacetates

compd	frequency	frequency	frequency	av
A. Chloroacetates				
Li(CICH ₂ CO ₂)	35.254(12)			35.254
Hg(CICH ₂ CO ₂) ₂	36.603(> 11)			36.603
Tl(CICH ₂ CO ₂)	33.431(7)			33.431
Pb(CICH ₂ CO ₂) ₂	35.150(15)	33.878(8)		34.514
Ag ₂ (CICH ₂ CO ₂) ₂	33.828(2)	33.700(4)	33.630(4)	33.671
	33.525(2)			
Cu ₂ (CICH ₂ CO ₂) ₄ ·2H ₂ O	36.89(2)	36.84(2)	36.35(2)	36.26
	36.25(2)	36.15(2)	36.07(2)	
	35.82(2)	35.72(2)		
Cu ₂ (CICH ₂ CO ₂) ₄ ·5H ₂ O	37.148(4)	36.905(2)	36.822(1.5)	36.405
	36.580(2)	36.139(3)	35.945(2)	
	35.885(2)	35.813(1.5)		
CICH ₂ CO ₂ Si(CH ₃) ₃	35.814(11)			35.814
B. Trichloroacetates				
Cl ₃ CCO ₂ Si(CH ₃) ₃	39.921(50)	39.583(34)	39.396(50)	39.633
Rb(Cl ₃ CCO ₂)·H ₂ O	39.220(2.5)	39.134(3)	39.089(2)	38.662
	39.000(3)	38.894(3.5)	38.823(2)	
	38.728(3)	38.533(2)	38.476(2.5)	
	38.415(3)	38.374(4)	38.309(4.5)	
	38.225(3)	38.049(3)		

^a Signal-to-noise (S/N) ratios are given in parentheses.

Table 2. ^{35}Cl NQR Frequencies^a (MHz) Measured at 77 K for Chloromethanesulfonates

compd	frequency	frequency	frequency	av
A. Trichloromethanesulfonates				
Cs(Cl ₃ CSO ₃)	39.200(32)	38.970(23)	38.724(20)	38.965
Rb(Cl ₃ CSO ₃)	40.258(4)	40.027(2)	39.990(3)	39.438
	39.822(4)	39.528(4)	39.063(4)	
	38.830(5)	38.766(3)	38.656(3)	
K(Cl ₃ CSO ₃)·H ₂ O	39.941(17)	39.637(10)	39.560(6)	39.740 ^b
	39.419(7)			
K(Cl ₃ CSO ₃)	40.133(1.5)	39.822(2.2)	39.766(2.2)	39.759 ^b
	39.244(1.5)			
Na(Cl ₃ CSO ₃)·H ₂ O	40.143(7)	40.079(7)	39.376(7)	39.866
Na(Cl ₃ CSO ₃)	40.997(4)	40.636(4)	40.300(3)	40.016
	39.825(2)	39.225(2)	39.111(2)	
H ₅ O ₂ (Cl ₃ CSO ₃)	40.240(17)	40.202(17)	39.563(12)	40.002
H ₃ O(Cl ₃ CSO ₃)	40.321(30)	40.199(40)	40.126(30)	40.215
Ag(Cl ₃ CSO ₃)·H ₂ O	40.287(36)	40.009(34)	39.577(34)	39.958
Ba(Cl ₃ CSO ₃) ₂ ·3H ₂ O	40.331(2.5)	40.151(4)	40.037(4)	40.173
Ba(Cl ₃ CSO ₃) ₂	40.402(8)	40.183(8)	40.053(8)	40.213
Cl ₃ CSO ₃ CH ₂ CF ₃	41.050(35)	40.944(26)	40.702(21)	40.899
B. Chloromethanesulfonate				
Na(CICH ₂ SO ₃)	37.026(4)			37.026

^a Signal-to-noise (S/N) ratios are given in parentheses. ^b Weighted average, taking into account S/N ratios and unexpected numbers of signals; where possible confirmed by studies at other temperatures.

those previously assigned to the trichlate anion.³⁷ Melting points were measured and dehydration behavior was observed on an Electrothermal melting-point apparatus. CCl_3SO_2Cl and $Cl_3CCO_2Si(CH_3)_3$ were obtained from Aldrich, $CICH_2CO_2Si(CH_3)_3$ was obtained from Fluka, and $Cl_3CSO_3CH_2CF_3$ was obtained from Lancaster Syntheses; all were used as received. Elemental analyses were performed by Galbraith Laboratories and are reported in Supporting Information Table 1. Water percentages are also included in Supporting Information Table 1 and were obtained by Karl Fischer titration, TGA, or vacuum dehydration. Dehydrations

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of salts were done on weighed samples under vacuum using either desiccation over P₂O₅ or heating with a hot water bath or a tube furnace. TGA measurements were obtained on a Perkin-Elmer TGA-7 thermogravimetric analyzer between ambient temperature and 200 °C. Karl Fischer titrations were carried out using a Mettler DL18 Karl Fischer titrator. Representative syntheses of Ba(Cl₃CSO₃)₂, Ag(Cl₃CSO₃)₂·H₂O, and Tl(ClCH₂CO₂) are included in the Supporting Information.

Cesium Trichloromethanesulfonate. Trichloromethanesulfonyl chloride (5.026 g, 23.07 mmol), ca. 17 g (57 mmol) of 50% aqueous CsOH solution, and 100 mL water were stirred at room temperature for 5 days, the amount of time it took for the Cl₃CSO₂Cl to dissolve. The volume of the solvent was reduced by rotary evaporation, and the solution was cooled in a refrigerator overnight. After filtration, a second crop of crystals was similarly obtained; the total yield of the cesium salt was 7.133 g (21.53 mmol; 93.1% yield). The crystals were recrystallized from hot water to give 3.513 g (10.60 mmol, 46.0% yield) of purified product; the salt decomposed at 268–270 °C.

Trichloromethanesulfonic Acid Dihydrate and Monohydrate. In a 250 mL round-bottom flask, 5.61 g (19.9 mmol) of Cl₃CSO₃CH₂CF₃, 40 mL of deionized water, and 80 mL of ethanol were refluxed for 4 days, until titration of an aliquot with strong base indicated nearly complete hydrolysis of the ester to the acid. The solution was then reduced to a small volume by rotary evaporation and placed in a vacuum desiccator over phosphorus pentoxide to remove water from the solution, giving 3.44 g (14.6 mmol, 73% yield) of large crystals. These crystals gradually lost further water over several months in vacuo over phosphorus pentoxide to give the monohydrate.

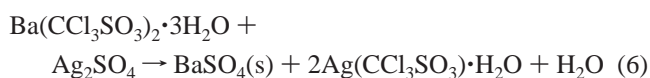
Results and Discussion

Synthesis of Compounds. Kolbe³⁸ first prepared the potassium and monohydrated sodium, barium, and silver salts of the trichloromethanesulfonate ion (“trichlate” ion) by the reaction of metal hydroxides with Cl₃CSO₂Cl:



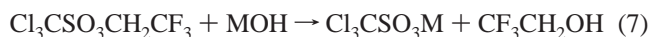
Other workers have also described this preparation of the monohydrated sodium salt.³⁷ Kolbe also prepared the monohydrated acid; Edwards^{37a} prepared the anhydrous acid by reacting the sodium salt with HCl in acetonitrile.

In contrast to our previous experience with monohalomesulfonates,¹⁷ we find the group 1 trichlates to be sufficiently less soluble than the group 1 halides that they can be easily separated, and are pure after one recrystallization (from water, methanol, or ethanol). The barium salt is best prepared from Ba(OH)₂·8H₂O and Cl₃CSO₂Cl in methanol, from which BaCl₂·2H₂O precipitates; the product can be obtained on evaporation. The monohydrated silver salt could not be prepared from insoluble Ag₂O by analogy with eq 5; it can be prepared from the barium salt and Ag₂SO₄:



At the present time, the ester 2,2,2-trifluoroethyl trichloromethanesulfonate is more readily available than is

Cl₃CSO₂Cl; we found that metal salts could also be readily produced from this ester by warming for a few hours, without any separation from MCl being required.



The dihydrated acid can be obtained as large crystals by refluxing this ester for 4 days with a 1:2 mixture of water and ethanol, and then allowing the aqueous solution to evaporate over H₂SO₄ or P₂O₅:



This hydrated acid can be dehydrated slowly over phosphorus pentoxide in vacuo to a monohydrate. The hydrated acid can be used for an easier preparation of the silver salt, by dissolution of Ag₂O.

Acid–base neutralization was used to prepare lithium chloroacetate, lithium and cesium dichloroacetates, and potassium, rubidium, and tetraethylammonium trichloroacetates, but most of these compounds failed to give NQR spectra (both hydrated and anhydrous forms were checked). The chloroacetates of silver,³⁹ lead,⁴⁰ thallium(I), mercury(II),⁴¹ and copper(II)⁴¹ were synthesized by acid–base reactions in water or ethanol. Calcium chloroacetate monohydrate was synthesized both from ethanol and water and gave the NQR spectrum reported earlier by Guibé; TGA analysis confirmed that the product obtained was actually the monohydrate, the crystal structure of which has been determined.²² Silver chloroacetate was also prepared by precipitation⁴² and homogeneous precipitation,²² although the largest crystals were produced by the latter method, there was little difference in NQR signal strength. Cu₂(ClCH₂CO₂)₄·5H₂O dissolved in methanol was reacted with the chemical dehydrating reagent 2,2-dimethoxypropane for 2 days: the crystals that were obtained still showed the IR bands of water and analyze approximately to be the known dihydrate.⁴³

NQR Results: General. The large amount of literature data available for chloroacetates, dichloroacetates, and trichloroacetates (including those of the zirconocene and hafnocene cations) are summarized in Supporting Information Tables 2, 3, and 5, respectively; we give our new data in Tables 1 and 2 and summarize average frequencies for these compounds in Tables 3–6.

The NQR frequencies of chloroacetates (Table 3) are lowest, followed by dichloroacetates and chloromethanesulfonates (Table 4), trichloroacetates (Table 5), and then

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Table 3. Summary of 77 K NQR Parameters (MHz) of Chloroacetates

A. Covalent Esters, Acids, Complexes						
compd	structure type ^a	av frequency (MHz)	no. NQR signals	largest splitting ^b	spectral width ^c	χ_P^d
CICH ₂ CO ₂ CH ₃		36.116	2	0.033	0.033	2.44
CICH ₂ CO ₂ C ₆ H ₅		36.471	4	0.467	0.725	2.46
CICH ₂ CO ₂ C ₆ H ₂ Cl ₃		36.856	1	0	0	2.57
CICH ₂ CO ₂ Si(CH ₃) ₃		35.814	1	0	0	1.76
(C ₅ H ₅) ₂ Zr(CICH ₂ CO ₂) ₂	I + II ^e	35.045	2	0.550	0.550	1.33
(C ₅ H ₅) ₂ Hf(CICH ₂ CO ₂) ₂	I + II ^e	35.145	2	0.570	0.570	1.30
CICH ₂ CO ₂ H phase I	III ^f	36.280	2	0.298	0.298	2.20
CICH ₂ CO ₂ H phase II	III ^g	36.45	1	0	0	2.20
CICH ₂ CO ₂ H phase III		36.14	1	0	0	2.20
Cu ₂ (CICH ₂ CO ₂) ₄ ·5H ₂ O	III ^h	36.405	8	0.441	1.335	2.00
Cu ₂ (CICH ₂ CO ₂) ₄ ·2H ₂ O	III ^h	36.26	8	0.49	1.17	2.00
B. Ionic Structures						
compd	structure type ^a	av frequency (MHz)	no. NQR signals	largest splitting ^b	spectral width ^c	r^d
Rb(CICH ₂ CO ₂)		33.82	1	0	0	166
K(CICH ₂ CO ₂)		34.11	1	0	0	152
Na(CICH ₂ CO ₂)	IV ⁱ	34.794	1	0	0	116
Li(CICH ₂ CO ₂)	IV ^j	35.254	1	0	0	90
Ba(CICH ₂ CO ₂) ₂ ·H ₂ O		33.310	2	0.227	0.227	149
C. Soft-Acid or Cl-Coordinated Structures						
compd	structure type ^a	av frequency (MHz)	no. NQR signals	largest splitting ^b	spectral width ^c	
Ag ₂ (CICH ₂ CO ₂) ₂	III-Cl ^k	33.671	4	0.128	0.303	
Ca(CICH ₂ CO ₂) ₂ ·H ₂ O	V-Cl ^l	34.58	2	0.38	0.38	
Hg(CICH ₂ CO ₂) ₂		36.603	1	0	0	
Tl(CICH ₂ CO ₂)		33.431	1	0	0	
Pb(CICH ₂ CO ₂) ₂		34.514	2	1.272	1.272	

^a Structure type (see Figure 1) and source of structural information; for literature sources of NQR data see Supporting Information Table 2. ^b Equal to largest separation in MHz between any two signals in NQR spectrum. Splittings greater than 0.8 MHz are shown in bold. ^c Equal to highest NQR frequency in spectrum minus lowest frequency (in MHz). ^d χ_P = Pauling electronegativity, from Wulfsberg, G. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000, Table A, or as calculated from eq 4 and NQR frequency of corresponding alkyl or trimethylsilyl chloride. For corresponding ionic salts, r = cation radius (in pm) from Wulfsberg, G. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000, Table C. ^e Based on infrared criteria: Brainina, É. M.; Bryukhova, E. V.; Lokshin, B. V.; Alimov, N. S. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1973**, 860–863. ^f Source: Kalyanaraman, B.; Atwood, J. L.; Kispert, L. D. *J. Chem. Soc., Chem. Commun.* **1976**, 715–716. ^g Source: Kanters, J. A.; Roelofsen, G.; Feenstra, T. *Acta Crystallogr., Sect. B* **1976**, B32, 3331–3333. ^h Based on infrared criteria: Yamada, S.; Nishikawa, H.; Tsuchida, R. *Bull. Chem. Soc. Jpn.* **1960**, 33, 1278–1284. Shi, Q.; Cao, R.; Hong, M. C.; Wang, Y. Y.; Shi, Q. Z. *Transition Met. Chem. (Dordrecht, Netherlands)* **2001**, 26, 657–661. ⁱ Source: Elizabé, L.; Kariuki, B. M.; Harris, K. D. M.; Tremayne, M.; Epple, M.; Thomas, J. M. *J. Phys. Chem. B* **1997**, 101, 8827–8831. ^j Source: Ehrenberg, H.; Hasse, B.; Schwarz, K.; Epple, M. *Acta Crystallogr., Sect. B* **1999**, B55, 517–524. ^k Source: Epple, M.; Kirschnick, H. *Chem. Ber./Recl.* **1997**, 130, 291–294. ^l Source: Karipides, A.; Peiffer, K. *Inorg. Chem.* **1988**, 27, 3255–3256.

trichlates (Table 6); this order correlates with the presence of increasing numbers of more electron-withdrawing substituents.

The anion in this study that is most sensitive to the nature of the cation or Lewis acid is the most basic one, chloroacetate (Table 3): its average frequencies span 3.546 MHz, from 33.310 MHz in Ba²⁺(CICH₂CO₂)₂ to 36.856 MHz in the 2,4,6-trichlorophenyl ester. By contrast, the total range for the least basic anion, trichlate (Table 6), is only 1.934 MHz, from 38.965 MHz for the Cs⁺ salt to 40.899 MHz for the 2,2,2-trifluoroethyl ester.

Covalent Esters, Acids, and Complexes. In Figure 3 we plot the average NQR frequencies of these covalent derivatives as a function of the Pauling electronegativity of the Lewis acids; since these solids are not all isomorphous and isostructural, there is scatter in the plots due to crystal field effects. For esters, group electronegativities of the alkyl, aryl, and silyl groups are obtained from the NQR frequency of the corresponding chlorocarbon RCl and silane R₃SiCl using eq 4. In principle the slope would be zero for a totally

nonbasic, noncoordinating anion; in fact the slopes are positive as expected for weakly coordinating anions. There is no statistically significant difference in the slopes of the least basic (chloroacetate) and most basic (trichloroacetate) ions: whatever difference may be present is smaller than the random crystal field effects. Likewise, although there could in principle be a difference in frequencies depending on whether the bonding to the metal atom is of type I, II, IIIA, or IIIB, the difference (if any) is so small that it is masked by crystal field effects.

Ionic Salts. In Figure 4 we plot the average ³⁵Cl NQR frequencies of the anhydrous group 1 and tetramethylammonium chloroacetates and chloromethanesulfonates as a function of the cation radii. The dichloroacetates, trichloroacetates, and trichlates of these ions cannot be isomorphous, since the number of NQR signals varies in each series; consequently there is some crystal-field scatter in each plot. All group 1 monochloroacetates give one NQR signal each and give a very good correlation in Figure 4, even though the Li⁺ and Na⁺ salts are not isomorphous or isostructural.¹⁹

Table 4. Summary of 77 K NQR Parameters (MHz) of Dichloroacetates and Chloromethanesulfonates

A. Covalent Esters, Acids, Complexes						
compd	structure type ^a	av frequency (MHz)	no. NQR signals	largest splitting ^b	spectral width ^c	χ_P^d
Cl ₂ CHCO ₂ CH ₃		37.865	6	0.507	1.388	2.44
Cl ₂ CHCO ₂ C ₆ H ₄ Cl ₃		38.477	4	0.489	0.702	2.57
(C ₅ H ₅) ₂ Zr(Cl ₂ CHCO ₂) ₂	I + II ^e	37.495	4	0.76	1.33	1.33
(C ₅ H ₅) ₂ Hf(Cl ₂ CHCO ₂) ₂	I + II ^e	37.580	4	0.83	1.33	1.30
Cl ₂ CHCO ₂ H		38.393	2	0.828	0.828	2.20
B. Ionic Structures						
compd	structure type ^a	av frequency (MHz)	no. NQR signals	largest splitting ^b	spectral width ^c	r^d
Cl ₂ CHCO ₂ Na		~37.0	>12	<i>f</i>	2.075	116
Cl ₂ CHCO ₂ K		36.512	2	0.240	0.240	152
Cl ₂ CHCO ₂ Rb		36.400	1	0	0	166
(Cl ₂ CHCO ₂) ₂ Ba		37.039	4	1.275	2.130	149
Cl ₂ CHCO ₂ N(CH ₃) ₄		35.8	8	<i>f</i>	3.135	215
C. Chloromethanesulfonates						
compd	structure type ^a	av frequency (MHz)	no. NQR signals	largest splitting ^b	spectral width ^c	r^d
ClCH ₂ SO ₃ Na·1/3H ₂ O		37.060	3	1.120	1.182	116
ClCH ₂ SO ₃ Na		37.026	1	0	0	116
ClCH ₂ SO ₃ K		36.311	3	0.239	0.329	152
ClCH ₂ SO ₃ Tl		35.915	1	0	0	
ClCH ₂ SO ₃ Ag	V-Cl ^g	34.545	1	0	0	

^a Structure type (see Figure 1) and source of structural information; for literature sources of NQR data see Supporting Information Table 3. ^b Equal to largest separation in MHz between any two signals in NQR spectrum. Splittings greater than 0.8 MHz are shown in bold. ^c Equal to highest NQR frequency in spectrum minus lowest frequency (in MHz). ^d χ_P = Pauling electronegativity, from Wulfsberg, G. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000, Table A, or as calculated from eq 4 and NQR frequency of corresponding alkyl or trimethylsilyl chloride. For corresponding ionic salts, r = cation radius (in pm) from Wulfsberg, G. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000, Table C. ^e Based on infrared criteria: Brainina, É. M.; Bryukhova, E. V.; Lokshin, B. V.; Alimov, N. S. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1973**, 860–863. ^f Not reported. ^g Source: Wulfsberg, G.; Parks, K. D.; Rutherford, R.; Jackson, D.; Jones, F. E.; Derrick, D.; Ilsley, W.; Strauss, S.; Miller, S.; Anderson, O. P.; Babushkina, T. A.; Gushchin, S. I.; Kravchenko, E. A.; and Morgunov, V. G. *Inorg. Chem.* **2002**, *41*, 2032–2040.

Remarkably, the total ranges of average NQR frequencies within the group I ionic salts of a given anion (Figure 4) are as large as the ranges for the corresponding group I–14 covalent esters, acids, and complexes (Figure 3). The slope of the correlation for chloroacetate ions, (-0.019 ± 0.002) MHz/pm, is slightly steeper than the slope for trichlates, (-0.016 ± 0.004) MHz/pm.

It may be seen that the trend previously noted by Guibé³⁴ holds here: Frequencies drop as the ionic radius of the counterion increases. This is opposite to the trend observed earlier by Brill³³ among typical type V ionic salts, (M⁺)₂(MCl₆²⁻) (M⁺ = group I cation or (CH₃)₄N⁺). Computations by Brill^{33,44} and Borchers⁴⁵ suggest that a variety of opposing effects may be involved in that trend, but that the dominant effect is due to anion–anion repulsions that occur when the M⁺ cations are too small to keep MCl₆²⁻ anions, which are attracted together by the intervening small cations in the type V lattice, from compressing and polarizing each other. In contrast, the known group I chloroacetates have type IV layer structures with no intervening cations attracting the chlorine ends of the anions to each other. Hence the dominant feature in the NQR trend in the (M⁺)₂(MCl₆²⁻) salts has been removed, leaving the other, opposing features.

We carried out computations to determine whether the NQR trends might be reproduced without invoking these

complex type V lattice effects. For computational feasibility, simple monomeric chloroacetates of Li⁺, Na⁺, and K⁺ were modeled by symmetric type II monomers. To explore the polarization effect of the metal on the halogen–carbon bond of halogenoacetates, ab initio calculations were performed on the CH₂XCOO–M systems (X = Cl, F and M = K, Na, and Li), including the free anions, at the B3LYP/6-311++G(3df,3pd) level of theory using the Gaussian98 program package.⁴⁶ The geometry of each molecule was optimized at the same level starting with a structure of type II and imposing C_s symmetry. The assumption that the conformations corresponding to the energy minima are symmetric was justified with frequency calculations. X-ray diffraction studies¹⁹ also show that the anion adopts the symmetric conformation. The topology of the electron densities was analyzed with the AIMPAC program suite.⁴⁷

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Table 5. Summary of 77 K NQR Parameters (MHz) of Trichloroacetates

A. Covalent Esters, Acids, Complexes						
compd	structure type ^a	av frequency (MHz)	no. NQR signals	largest splitting ^b	spectral width ^c	χ_P^{*d}
Cl ₃ CCO ₂ Si(CH ₃) ₃		39.633	3	0.338	0.525	1.76
Cl ₃ CCO ₂ CH ₃		39.918	6	0.280	0.515	2.44
Cl ₃ CCO ₂ C ₆ H ₅		40.202	6	0.337	0.884	2.46
Cl ₃ CCO ₂ C ₆ H ₂ Cl ₃		40.450	3	0.296	0.572	2.57
Cl ₃ CCO ₂ CH ₂ CF ₃		40.270	9	0.132	0.529	2.57
(C ₃ H ₅) ₂ Zr(Cl ₃ CCO ₂) ₂	I ^e	38.86	3	1.17	1.52	1.33
Cu(Cl ₃ CCO ₂) ₂ ·3H ₂ O	IV ^f	39.575	24	0.144	1.557	2.00
Co(Cl ₃ CCO ₂) ₂ ·4H ₂ O		39.25	6	0.373	1.874	1.88
Ni(Cl ₃ CCO ₂) ₂ ·4H ₂ O		39.25	6	0.357	1.994	1.91
Cu(Cl ₃ CCO ₂)		40.198	3	0.448	0.528	1.90
Cu(Cl ₃ CCO ₂) ₂		39.765	3	0.301	0.301	2.00
Co(Cl ₃ CCO ₂) ₂		39.146	3	0.224	0.224	1.88
Cl ₃ CCO ₂ H	III ^g	40.120	3	0.196	0.272	2.20
Cl ₃ CCO ₂ H·H ₂ O		40.058	9	0.338	1.148	2.20
B. Ionic Structures						
compd	structure type ^a	av frequency (MHz)	no. NQR signals	largest splitting ^b	spectral width ^c	r^d
Me ₄ N(Cl ₃ CCO ₂)		37.673	4	0.118	0.337	215
Cs(Cl ₃ CCO ₂) _n ·nH ₂ O		38.111	6	0.463	0.996	181
Rb(Cl ₃ CCO ₂) _n ·H ₂ O		38.662	14	0.195	1.171	166
(NH ₄) _n (Cl ₃ CCO ₂) _n	IV ^h	38.785	9	0.388	1.567	151
Na(Cl ₃ CCO ₂) _n ·3H ₂ O		38.906	6	0.560	1.400	116
Na(Cl ₃ CCO ₂) _n ·CH ₃ OH		38.686	12	0.490	1.722	116
Na(Cl ₃ CCO ₂) _n		38.892	3	0.560	1.120	116
Li(Cl ₃ CCO ₂) _n		39.648	2	1.067	1.067	90
Li(Cl ₃ CCO ₂) _n ·H ₂ O	VI ⁱ	38.906	9	0.639	1.474	90
Ba(Cl ₃ CCO ₂) _n		38.883	6	0.354	1.307	149
Ca(Cl ₃ CCO ₂) _n ·4H ₂ O		39.09	6	0.171	0.596	114
Mg(Cl ₃ CCO ₂) _n ·6H ₂ O		39.17	6	0.735	1.269	86
C. Soft-Acid or Cl-Coordinated Structures						
compd	structure type ^a	av frequency (MHz)	no. NQR signals	largest splitting ^b	spectral width ^c	
Hg(Cl ₃ CCO ₂) ₂ ·THF		39.655	9	0.616	1.351	
Ag(Cl ₃ CCO ₂) ₂		39.067	3	1.484	1.834	
Hg ₂ (Cl ₃ CCO ₂) ₂		39.715	6	1.078	1.925	

^a Source of structural information; for literature sources of NQR data see Supporting Information Table 5. ^b Equal to largest separation in MHz between any two signals in NQR spectrum. Splittings greater than 0.8 MHz are shown in bold. ^c Equal to highest NQR frequency in spectrum minus lowest frequency (in MHz). ^d χ_P = Pauling electronegativity, from Wulfsberg, G. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000, Table A, or as calculated from eq 4 and NQR frequency of corresponding alkyl or trimethylsilyl chloride. For corresponding ionic salts, r = cation radius (in pm) from Wulfsberg, G. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000, Table C. ^e Based on infrared criteria: Brainina, É. M.; Bryukhova, E. V.; Lokshin, B. V.; Alimov, N. S. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1973**, 860–863. ^f Source: Kiriya, H.; Hashimoto, M.; Okuno, N. *Bull. Chem. Soc. Jpn.* **1987**, 60, 2983–2988. ^g Source: Jonsson, P. G.; Hamilton, W. C. *J. Chem. Phys.* **1972**, 56, 4433–4439. Rajagopal, K.; Mostad, A.; Krishnakumar, R. V.; Nandhini, M. Subha; Natarajan, S. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, E59, o316–o318. ^h Source: Kiriya, H.; Doi, T.; Yamagata, Y. *Acta Crystallogr., Sect. C* **1987**, C43, 1175–1177. ⁱ Source: Tuomi, D. Structure of Crystalline Lithium Trichloroacetate Monohydrate. Ph.D. Dissertation, Ohio State University, Columbus, OH, 1958; *Dissertation Abstr.* **1958**, 18, 839–843.

Table 7 summarizes the results in terms of the C–X bond distances and bond topological indices; the density ($\rho(\mathbf{r}_{\text{BCP}})$) and its Laplacian ($\nabla^2\rho(\mathbf{r}_{\text{BCP}})$), the sum of principal curvatures of ρ at the bond critical point (\mathbf{r}_{BCP}) where $\nabla\rho(\mathbf{r})$ vanishes. These parameters provide a topological classification of atomic interactions.⁴⁸ For covalent interactions charge is both accumulated (measured by $\rho(\mathbf{r}_{\text{BCP}})$) and concentrated (measured by $\nabla^2\rho(\mathbf{r}_{\text{BCP}})$) along the bond path. The latter is a result of perpendicular contractions of ρ toward the bond and yields a continuous region of space over which the Laplacian is negative. In this region the local potential energy dominates over the total energy. Thus, higher $\rho(\mathbf{r}_{\text{BCP}})$ and more negative $\nabla^2\rho(\mathbf{r}_{\text{BCP}})$ values indicate greater covalent character of a bond.

As expected, the cation–anion charge separation increases in the Li, Na, and K sequence. The M–O distances change from 1.85 to 2.51 Å (on average) in the above order. The C–X and C–C bonds are weakened with increasing negative charge on the anion (and on the halogen atom), while the opposite trend is observed for the carbonyl bonds. The data clearly show that the C–X bond is the most polarized (as C^{δ+}–Cl^{δ-}) in the free anion and is least polarized in the Li⁺ complex.

The eigenvalues eq₁, eq₂, and eq₃ of the electric field gradients at the chlorine atoms in these molecules were also calculated, as were the asymmetry parameters $\eta = (eq_2 - eq_3)/eq_1$ (Table 8). The asymmetry parameters, if zero, indicate axial symmetry at the chlorine atoms, and these computed values are quite close to zero. The trend in values of eq₁ obtained are consistent with the trend in NQR

(48) Bader, R. F. W. *Atoms in Molecule—A Quantum Theory*; Oxford University Press: Oxford, 1990.

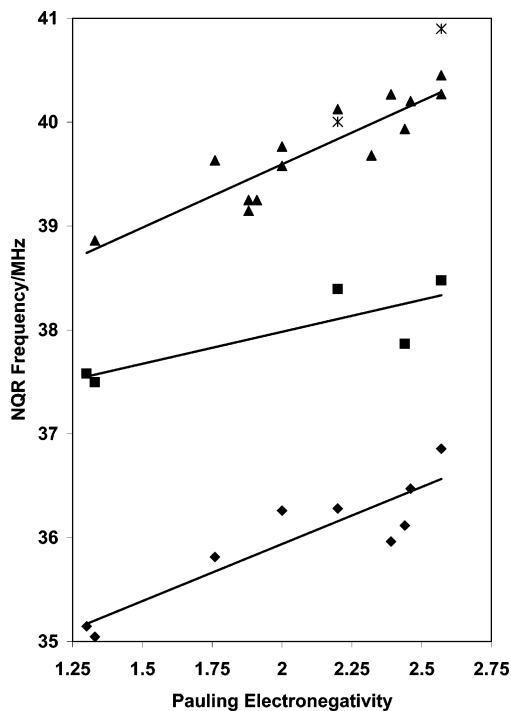


Figure 3. Average ^{35}Cl NQR frequencies of covalent esters, acids, and complexes of the anions $\text{Cl}_3\text{CSO}_3^-$ (indicated with *), $\text{Cl}_3\text{CCO}_2^-$ (indicated with ▲), $\text{Cl}_2\text{HCCO}_2^-$ (indicated with ■), and $\text{ClCH}_2\text{CO}_2^-$ (indicated with ◆), as a function of the Pauling electronegativity of the nonmetallic element to which the oxygen atom is bonded.

Table 6. Summary of 77 K NQR Parameters (MHz) of Trichloromethanesulfonates

compd	av frequency (MHz)	no. NQR signals	largest splitting ^a	spectral width ^b	r^c
$\text{Cs}(\text{Cl}_3\text{CSO}_3)$	38.965	3	0.246	0.476	181
$\text{Rb}(\text{Cl}_3\text{CSO}_3)$	39.438	9	0.465	1.602	166
$\text{K}(\text{Cl}_3\text{CSO}_3)\cdot\text{H}_2\text{O}$	39.740 ^d	4	0.304	0.522	152
$\text{K}(\text{Cl}_3\text{CSO}_3)$	39.759 ^d	4	0.522	0.889	152
$\text{Na}(\text{Cl}_3\text{CSO}_3)\cdot\text{H}_2\text{O}$	39.866	3	0.703	0.767	116
$\text{Na}(\text{Cl}_3\text{CSO}_3)$	40.016	6	0.600	1.886	116
$\text{H}_3\text{O}_2(\text{Cl}_3\text{CSO}_3)$	40.002	3	0.639	0.677	
$\text{H}_3\text{O}(\text{Cl}_3\text{CSO}_3)$	40.215	3	0.122	0.195	
$\text{Ag}(\text{Cl}_3\text{CSO}_3)\cdot\text{H}_2\text{O}$	39.958	3	0.432	0.710	
$\text{Ba}(\text{Cl}_3\text{CSO}_3)_2\cdot 3\text{H}_2\text{O}$	40.173	3	0.118	0.294	149
$\text{Ba}(\text{Cl}_3\text{CSO}_3)_2$	40.213	3	0.219	0.349	149
$\text{Cl}_3\text{CSO}_3\text{CH}_2\text{CF}_3$	40.899	3	0.242	0.328	

^a Equal to largest separation in MHz between any two signals in NQR spectrum. ^b Equal to highest NQR frequency in spectrum minus lowest frequency (in MHz). ^c r = cation radius (in pm) from Wulfsberg, G. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000, Table C. ^d Weighted average, taking into account differing signal-to-noise ratios and unexpected numbers of signals; where possible, confirmed by studies at other temperatures.

frequencies:⁴⁹ These values drop in magnitude by 3.46% from the Li^+ to the K^+ salt, while the NQR frequencies drop by 3.24%. Hence complex lattice interactions are not needed to explain the NQR frequency trend among group I chloroacetates (and presumably chloromethanesulfonates).

The computations and the NQR data suggest the possibility that (particularly) the chloroacetate ion is not exactly the

(49) We find that the computed eq_1 values are not quite linear in cation radius, so it is probable that the NQR correlations in Figure 4 should not be linear either, but should ultimately reach limiting values for anions with infinitely large cations, e.g., about 30 MHz for chloroacetate ion.

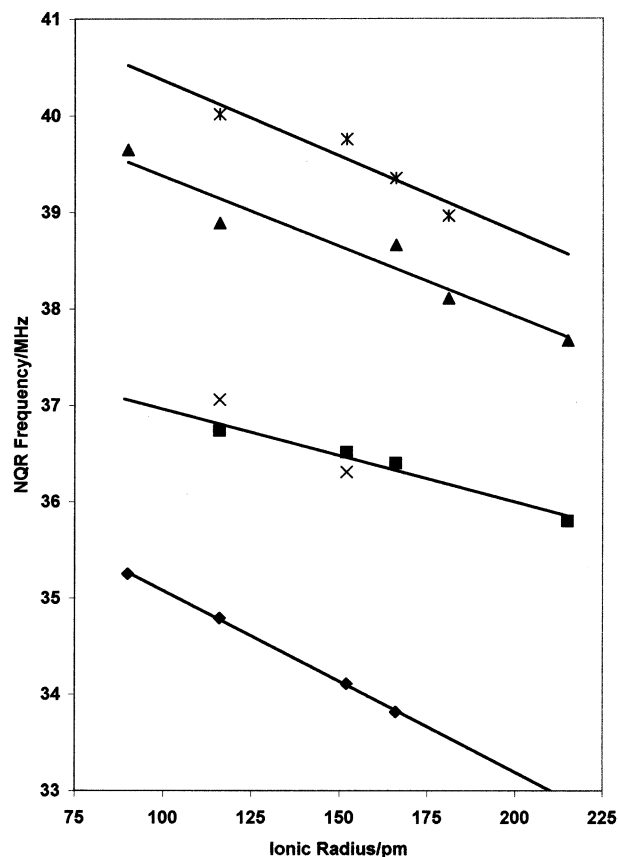


Figure 4. Average ^{35}Cl NQR frequencies of ionic salts of the anions $\text{Cl}_3\text{CSO}_3^-$ (indicated with *), $\text{ClCH}_2\text{CSO}_3^-$ (indicated with x), $\text{Cl}_3\text{CCO}_2^-$ (indicated with ▲), $\text{Cl}_2\text{HCCO}_2^-$ (indicated with ■), and $\text{ClCH}_2\text{CO}_2^-$ (indicated with ◆), as a function of the Shannon–Prewitt ionic radius of the group 1 or $(\text{CH}_3)_4\text{N}^+$ cation of the salt.

Table 7. Bond Distances, Topological Indices ρ_{BCP} and $\nabla^2\rho_{\text{BCP}}$ for the C–X Bonds, Net Anion Charges, and Dipole Moments in $\text{CH}_2\text{XCOO}-\text{M}$ Molecules (Units Are Ångstroms, Electrons, and Debyes)

	C–X bond distance	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	anion charge	dipole moment
	CH_2FCOO				
K	1.4097	1.528	−2.856	−1.000	4.30
Na	1.3854	1.635	−3.040	−0.918	8.57
Li	1.3827	1.650	−3.149	−0.629	7.05
	CH_2ClCOO				
K	1.8383	1.094	−4.263	−1.000	4.98
Na	1.7958	1.219	−5.807	−0.922	9.06
Li	1.7924	1.223	−5.941	−0.621	7.46
	1.7870	1.247	−6.134	−0.397	5.07

^a ρ_{BCP} is the density at the bond critical point where all three components of the spatial derivatives of ρ vanish. For a covalent bond ρ_{BCP} is relatively large (more charge is accumulated in the bond); for an ionic bond ρ_{BCP} is relatively small (less charge is accumulated in the bond). ^b $\nabla^2\rho_{\text{BCP}}$ is the Laplacian at the bond critical point. For a covalent bond $\nabla^2\rho_{\text{BCP}}$ is negative (charge is concentrated along the bond path); for an ionic bond $\nabla^2\rho_{\text{BCP}}$ is positive (charge is depleted along the bond path).

same ion in the different group 1 solid salts. Cesium chloroacetate is quite difficult to prepare and is unstable in the solid state,⁵⁰ decomposing even below room temperature to give $\text{MCl}(\text{s})$ and the polymer polyglycolide, $(\text{CH}_2\text{CO}_2)_n$,⁵¹

(50) Pokorny, J. Z. *Chem.* **1975**, *15*, 238–239. Pokorny, J. *Sb. Vys. Sk. Chem.-Technol. Praze, B: Anorg. Chem. Technol.* **1972**, *B14*, 127–152.

Table 8. The Eigenvalues eq_1 , eq_2 , eq_3 , and the Asymmetry Parameters $\eta = (eq_2 - eq_3)/eq_1$ of the Electric Field Gradient Tensor for the Chlorine Atoms in $\text{CH}_2\text{XCOO}-\text{M}$ Molecules

	eq_1	eq_2	eq_3	$(eq_2 - eq_3)/eq_1$
anion	-3.158	1.542	1.615	0.023
K	-3.572	1.757	1.815	0.016
Na	-3.623	1.784	1.838	0.015
Li	-3.700	1.829	1.871	0.011

which is of interest as a biodegradable polymer for medical applications.⁵² This reaction does not occur in the solid state for the lithium salt but occurs at progressively lower temperatures in the heavier solid group 1 salts of the monohaloacetate ions. This contrasts with the group 1 hexachlorometalates, which decompose to group 1 halides most readily in the case of lithium salts; such reactions eliminate many weakly coordinating anions from being useful counterions for catalyst cations such as zirconocenes. Eppler found a connection between this reaction tendency of chloroacetates and the lattice energies of the group 1 halides formed.⁵³ Our computations and the NQR data suggest that the increasing ease of loss of chloride ion from chloroacetate with larger group 1 cations may be in part connected with the increasing polarization of the chloroacetate ion to produce more partial negative charge on the chlorine atom.

Effects of Waters of Hydration and of Cation Charge.

Hydrogen bonding to the oxygen atom could in principle alter the average NQR frequencies of haloacetate ions; the effects of strong hydrogen bonding to haloacetate ions are marked and have been extensively studied.⁵⁴ Comparison of the data in Table 2 and the Supporting Information tables for the corresponding hydrates and anhydrous salts of these anions show that the NQR frequencies and their averages are little altered by dehydration; the only exception is lithium trichloroacetate, the monohydrate of which may have an anomalous type V structure.⁵⁵ Evidently, the effects of weak hydrogen bonding three bonds removed from the carbon-chlorine bond do not stand out above crystal field effects. NQR data for trichloroacetates is available often only for hydrated salts, which are also included in Figure 4.

There are now data on several salts involving nonhydrated or partially hydrated group 2 cations, which allows us to make a preliminary assessment of the effect of cation charge on the NQR frequency of an anion. In Figure 5 we add data for Ba^{2+} and Ca^{2+} salts to the graph and correlations of Figure 4. The four Ba^{2+} salts shown at $r = 149$ pm fall at +0.6, +0.3, +0.6, and -0.6 MHz from the respective original correlations; the two Ca^{2+} salts shown at $r = 114$ pm fall at -0.04 and -0.2 MHz from the respective original

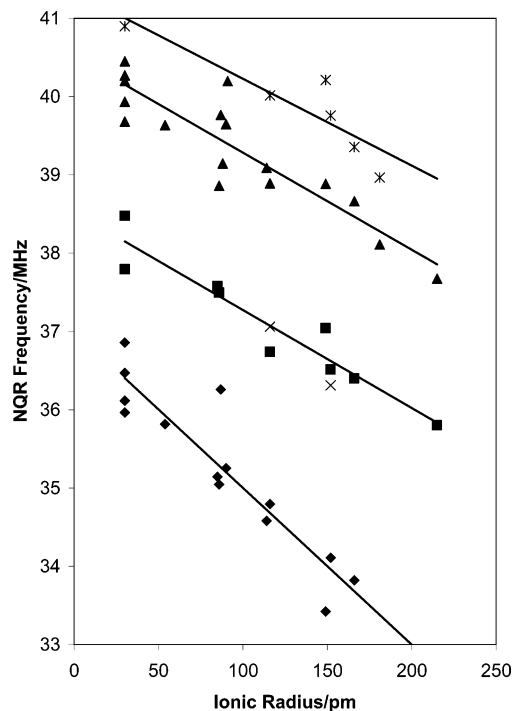


Figure 5. Average ^{35}Cl NQR frequencies of ionic and covalent compounds of the anions $\text{Cl}_3\text{CSO}_3^-$ (indicated with *), $\text{ClCH}_2\text{CSO}_3^-$ (indicated with x), $\text{Cl}_3\text{CCO}_2^-$ (indicated with ▲), $\text{Cl}_2\text{HCCO}_2^-$ (indicated with ■), and $\text{ClCH}_2\text{CO}_2^-$ (indicated with ◆), as a function of the Shannon-Prewitt ionic radius of the element to which the oxygen atom is bonded.

correlations. All in all, there is little evidence for the charge of the cation having much of an effect on the frequency of the anion, when its radius has been taken into account. Perhaps this preliminary result reflects the fact that, in a solid salt of a +2 cation, there can only be half as many cations near the oxygen atoms of the anion as in a solid salt of a similar +1 cation.

For many lighter and earlier elements, approximately the same average frequency is predicted by the covalent model of Figure 3 and the ionic model of Figure 4: i.e., if we use Figure 4 and the ionic radius of Zr^{4+} (86 pm), we predict an average NQR frequency for a noncoordinated zirconocene chloroacetate ($\text{C}_5\text{H}_5)_2\text{Zr}^{2+}(\text{OOCCH}_2\text{Cl})_2$ of about 35.15 MHz, which is not significantly different from the average frequency found for covalent zirconocene chloroacetate, 35.045 MHz. Likewise, we can plot the data for esters $\text{R}_3\text{-EOOCCl}_3$ versus the ionic radii of C^{4+} and Si^{4+} (30 and 54 pm, respectively) along with the data for genuinely ionic chloroacetates in Figure 5 and still keep virtually the same linear plots as in Figure 4; the slopes in Figure 5 confirm that chloroacetate ion (slope of -0.0200 ± 0.0024 MHz/pm; trichlate slope -0.0111 ± 0.0027 MHz/pm; other ions similar to trichlate) is the most affected by changing its counterion or associated Lewis acid. There is no discontinuity in this plot of NQR frequencies versus radius that can be taken as evidence for an abrupt change in character of the bonding to the chloro anion as it moves from a layer ionic structure to a covalent structure. But it is possible that the absence of a discontinuity is fortuitous.

Since the ionic radii of the group 1 elements vary strongly while their Pauling electronegativities scarcely vary at all,

- (51) Herzberg, O.; Eppler, M. *Eur. J. Inorg. Chem.* **2001**, 1395–1406.
 (52) Eppler, M.; Herzberg, O. *J. Mater. Chem.* **1997**, *7*, 1037–1042.
 (53) Lagoa, A. L. C.; Diogo, H. P.; Minas da Piedade, M. E.; Schwarz, K.; Eppler, M. *J. Phys. Chem. B* **2002**, *106*, 10764–10770.
 (54) For example: Lynch, R. J.; Waddington, T. C.; O'Shea, T. A.; Smith, J. A. S. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1980–1990. Ratajczak, H.; Orville-Thomas, W. J.; Chollniewska, I. *Chem. Phys. Lett.* **1977**, *45*, 208–210. Markworth, A.; Paulus, H.; Weiden, N.; Weiss, A. *Z. Phys. Chem. (Munich)* **1991**, *173*, 1–19.
 (55) Tuomi, D. Structure of Crystalline Lithium Trichloroacetate Monohydrate. Ph.D. Dissertation, Ohio State University, Columbus, OH 1958; *Dissertation Abstr.* **1958**, *18*, 839–843.

it follows that the NQR frequencies of type IV ionic and type I covalent salts of these anions cannot share the same linear relationship to Pauling electronegativities of the cation elements. Hence a general linear relationship of NQR frequencies to Pauling electronegativities, analogous to that of eq 4, has not been found.

Trichlic acid dihydrate has an anomalously low average NQR frequency, lower than that of the dimeric covalent trichloroacetic acid; its average frequency overlaps those of the ionic trichlates (see next section). The tetra-, di-, and monohydrates of triflic acid are known to have ionic structures (i.e., to be hydronium triflates);⁵⁶ we propose that dihydrated and monohydrated trichlic acid are also H_3O_2^+ and H_3O^+ salts of the trichlate ion. This result fits the status of trichlic acid as a strong acid: Its hydrates appear to be completely ionized, even in the solid state.

NQR Crystal Field Effects:³² Spectral Widths and Frequency Splittings. The NQR spectral width for chemically equivalent but crystallographically inequivalent chlorine atoms may be up to about 0.8 MHz ($\pm 1\%$ of the average) in organic halogen compounds. The average nonzero spectral widths found among the esters and acids in Tables 3–5 are the least in chloroacetates (average 0.3 MHz), still less than 0.8 MHz in trichloroacetates (average 0.6 MHz), but are decidedly larger in dichloroacetates (average 1.0 MHz).⁵⁷ Crystal field effects are compounded in ionic compounds, since charged ions have greater effects on their neighbor's electronic environment than do molecules. We note, in this small sample, the average nonzero spectral widths are about twice as large in ionic salts and complexes: averages are 0.8 MHz in chloroacetates, chloromethanesulfonates, and trichloromethanesulfonates, 1.2 MHz in trichloroacetates, and 1.7 MHz in dichloroacetates (spectral widths of up to 3.135 MHz were noted by Guibé³³ among dichloroacetates). The large spectral widths of these chlorinated organic salts and complexes do not seem to produce significant distortions in the averaged NQR frequencies for these compounds, which fall reasonably close to the trends of Figures 3–5.⁵⁸ Eighteen of the 30 complexes and salts with spectral widths from 0.8 to 2.0 MHz have from 6 to 24 NQR signals each, so that in the majority of cases, the large spectral widths do not result in unusually large frequency splittings between adjacent signals.

In covalent chlorinated organic compounds, any frequency difference (“splitting”) of two adjacent chlorine NQR signals that exceeds about 0.8 MHz may signify a chemical difference between the two chlorines: for example, in neutral chlorocarbon complexes of metals, a splitting of over 0.8 MHz between two chlorines that are equivalent in the neutral

chlorocarbon is strongly suggestive of the presence of organochlorine–metal coordination involving the lower-frequency chlorine atom(s).⁵⁹ In all of the NQR spectra summarized in this study (Tables 3–6), there are well over 200 different frequency splittings. Only nine of these largest splittings (shown in bold in Tables 3–6) exceed 0.8 MHz; they range from 0.83 MHz in dichloroacetic acid and hafnocene dichloroacetate to 1.484 MHz in silver trichloroacetate. These large splittings could signify the presence of metal–chlorine coordination of some of the otherwise equivalent chlorines. It is tempting to explain the large splittings by invoking coordination of the relatively soft chlorine to the soft acids Ag^+ , Hg_2^{2+} , and Pb^{2+} found in three of these salts. Large splittings are also found in a few salts and complexes of the hard acids Li^+ , Na^+ , H^+ , Ba^{2+} , $(\text{C}_5\text{H}_5)_2\text{Zr}^{2+}$, and $(\text{C}_5\text{H}_5)_2\text{Hf}^{2+}$. Such hard acid–soft base interactions are found in calcium chloroacetate monohydrate²² and in two recently reported complexes of dihaloalkanes with $[\text{Cs}(\text{tetrabenzocrown-8})]^+$.⁶⁰ But the large splittings could alternately be due to some other chemical difference: for example, the presence of both free and coordinated anions in the same structure. And in view of the large spectral widths found in ionic compounds, it is clearly not impossible for only two crystallographic sites with very different crystal field effects to be occupied, resulting in a large NQR frequency splitting which does not signify any chemical differences between the two chlorines.

One test of the chemical significance of these large splittings over 0.8 MHz is to recompute the average NQR frequency of the salt omitting the split-off NQR signal, then determine whether the adjusted average gives a better or worse fit to the correlations of Figure 4. In all seven cases in which we can clearly apply this criterion (lead chloroacetate, barium and hafnocene dichloroacetates, sodium chloromethanesulfonate· $\frac{1}{3}\text{H}_2\text{O}$, lithium, silver, and zirconocene trichloroacetates), worse fits result. This result is not conclusive, but it tends to suggest that the splittings in these ionic compounds and complexes, even the 1.484 MHz splitting in $\text{Ag}(\text{Cl}_3\text{CCO}_2)$, may not signify any chemical differences, but may only be manifestations of the large spectral widths due to large crystal field effects that can be found in ionic compounds and their metal complexes. This is verified in the case of sodium chloromethanesulfonate· $\frac{1}{3}\text{H}_2\text{O}$ by remeasuring the NQR frequency after dehydration (Table 4): The large splitting disappears, but the average NQR frequency is virtually unchanged. Hence, when chlorinated organic ions (rather than molecules) show large NQR frequency splittings of 0.8–1.4 MHz, it will be desirable to use other means (such as X-ray crystallography or measure-

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(57) An anomalous spectral width of almost 1.8 MHz in $\text{Cl}_3\text{CCOOC}(\text{CH}_3)_3$ has been attributed to interactions caused by the bulky *t*-butyl group: Hashimoto, M.; Watanabe, M.; Takada, H. *J. Magn. Reson.* **1979**, *34*, 553–558.

(58) Semín, G. K.; Babushkina, T. A.; Yakobson, G. G. *Nuclear Quadrupole Resonance In Chemistry*; Wiley: New York, 1975; pp 315, 317, 337, 332.

(59) Richardson, M.; Zaghoni, S.; Wulfsberg, G.; Shadid, K.; Gagliardi, J.; McCorkle, D.; Farris, B. *Inorg. Chem.* **1993**, *32*, 1913–19. Wulfsberg, G.; Jackson, D.; Ilsley, W.; Dou, S.-q.; Weiss, A.; Gagliardi, J., Jr. *Z. Naturforsch.* **1992**, *47a*, 75–84. Wulfsberg, G.; Yanisch, J.; Meyer, R.; Bowers, J.; Essig, M. *Inorg. Chem.* **1984**, *23*, 715–9. Meyer, R.; Gagliardi, J., Jr.; Wulfsberg, G. *J. Mol. Struct.* **1983**, *111*, 311–6. Wulfsberg, G.; West, R.; Rao, V. N. M. *J. Organomet. Chem.* **1975**, *86*, 303–19.

(60) Levitskaia, T. G.; Bryan, J. C.; Sachleben, R. A.; Lamb, J. D.; Moyer, B. A. *J. Am. Chem. Soc.* **2000**, *122*, 554–562. Bryan, J. C.; Kavallieratos, K.; Sachleben, R. A. *Inorg. Chem.* **2000**, *39*, 1568–1572.

ment of the NQR asymmetry parameter)¹⁷ to confirm that metal–chlorine coordination is involved.

Conclusions

1. In this study we have compared a series of weakly basic, weakly coordinating anions, ranging from the feebly basic chloroacetate ion ($K_b = 7.4 \times 10^{-12}$) to the virtually nonbasic trichlate ion ($K_b = 7.2 \times 10^{-17}$), and have paired them with a series of Lewis acids and cations, ranging from the nonacidic $(\text{CH}_3)_4\text{N}^+$ to the very strongly acidic R_3C^+ (which in fact forms covalent esters with all of these anions). Even though the chlorine atoms in chloroacetates and chloromethanesulfonates are generally quite far away from the cations or Lewis acids (which associate with the oxygen atoms), ³⁵Cl NQR is able to show differences in interactions in the solid state; the average frequencies increase with increasing electronegativity and decreasing radius of the acceptor atom (cation). The total range of average frequencies among chloroacetates is found to be 3.546 MHz; for the less polarizable, more weakly coordinating trichlates the total range is only 1.934 MHz. Although none of the anions are noncoordinating, the trichlate ion is closest to this ideal.

2. The average NQR frequencies of ionic chloro anions are very sensitive to the radius of the cation (but not its charge or degree of hydration). The NQR frequencies of the type IV layer ionic salts in this study increase with decreasing radius, while those of type V “normal” ionic salts studied earlier decrease with decreasing radius. Computations on model monomeric haloacetates $\text{M}^+(\text{XCH}_2\text{COO}^-)$ ($\text{M} = \text{Li}, \text{Na}, \text{K}; \text{X} = \text{F}, \text{Cl}$) exhibit more polarized C–Cl bonds and electric field gradients of smaller magnitudes with larger cations. These calculations could explain the observed trend in NQR frequencies without having to invoke solid-state lattice effects and may partly explain the trends observed by Epple⁴⁹ for the heavier group 1 monochloroacetates to decompose more readily to chlorides and poly(glycolide).

These effects are apparently minimized in trichlates, which are much more stable to heat than chloroacetates.

3. For a common cation and lattice type, the order of average NQR frequencies is (unsurprisingly) chloroacetate < dichloroacetate \approx chloromethanesulfonate < trichloroacetate < trichloromethanesulfonate (trichlate). However, dihydrated trichlic acid deviates from this pattern, falling below trichloroacetic acid. This suggests a structural difference: trichloroacetic acid is a weak acid that has a dimeric (type III) structure, while trichlic acid dihydrate is a strong acid, fully ionized as dihydronium trichlate. (The monohydrate is probably hydronium trichlate.)

4. Although quite large spectral widths (up to 2–3 MHz) can be found in ionic salts with many crystallographically inequivalent but chemically equivalent chlorines, these large widths do not seem to distort the average frequencies of these salts, which fit the observed correlations of Figures 3–6 well. Ionic salts also can show unusually large (0.8–1.5 MHz) splittings of adjacent NQR frequencies, but these large splittings do not necessarily indicate that the chlorines involved are chemically inequivalent.

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Supporting Information Available: Additional tables, synthetic details, and figure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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