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Weakly Coordinating Anions: Crystallographic and NQR Studies of Halogen–Metal Bonding in Silver, Thallium, Sodium, and Potassium Halomethanesulfonates

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^{35}Cl, ^{79,81}Br, and ^{127}I NQR (nuclear quadrupole resonance) spectroscopy in conjunction with X-ray crystallography is potentially one of the best ways of characterizing secondary bonding of metal cations such as Ag^+ to halogen donor atoms on the surfaces of very weakly coordinating anions. We have determined the X-ray crystal structure of $Ag(O_3SCH_2Cl)$ ($a = 13.241(3)$ Å; $b = 7.544(2)$ Å; $c = 4.925(2)$ Å; orthorhombic; space group *Pnma*; $Z = 4$) and compared it with the known structure of $Ag(O_3SCH_2Br)$ (Charbonnier, F.; Faure, R.; Loiseleur, H. *Acta Crystallogr., Sect. B* **1978**, *34*, 3598–3601). The halogen atom in each is apical (three-coordinate), being weakly coordinated to two silver ions. ^{127}I NQR studies on $Ag(O_3SCH_2I)$ show the expected NQR consequences of three-coordination of iodine: substantially reduced NQR frequencies ν_1 and ν_2 and a fairly small NQR asymmetry parameter η. The reduction of the halogen NQR frequency of the coordinating halogen atom in $Ag(O_3SCH_2X)$ becomes more substantial in the series $X = Cl < Br < I$, indicating that the coordination to Ag^+ strengthens in this series, as expected from hard–soft acid–base principles. The numbers of electrons donated by the organic iodine atom to Ag^+ have been estimated; these indicate that the bonding to the cation is weak but not insignificant. We have not found any evidence for the bonding of these organohalogen atoms to another soft-acid metal ion, thallium. A scheme for recycling of thallium halide wastes is included.

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^+, porphyrinatometal cations, (porphyrinato)Fe^+, and various transition metal organometallic cations which are important industrially as catalysts, and which require "vacant" coordination sites. It is now acknowledged that there is no such thing as a noncoordinating anion; the focus is now on seeking very weakly basic, easily dissociated neutral ligands and weakly coordinating anions[1] that act as good leaving groups from latent coordination sites.[2] A symposium on weakly coordinating anions was held at the spring 1998 American Chemical Society meeting in Dallas.[3]

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Weakly coordinating anions should be as nonbasic[4] 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 ($[B(C_6H_5)_4]^-$), and 1-carba-*closo*-dodecaborate $(CB_{11}H_{12})^-$.[5] 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 $CF_3SO_3^-$[6] and $[B(C_6F_5)_4]^-$.[7] For the most important industrial application requiring weakly coordinating anions, the metallocene process of producing stereoregular polymerization of alkenes,[8] the most active catalyst of all is obtained when $(CB_{11}H_6X_6)^-$ (X = Cl, Br, I) anions are present.[9] One might postulate that this is connected with the fact that most weakly coordinating anions now being investigated have fluorinated surfaces, and fluorine is a hard base, more likely to coordinate to the (presumably) hard zirconium(IV) active site in the metallocene catalysts, while the carborane anions have softer surfaces. If this postulate is valid, then the softest carborane anion, the iodinated one, should show the weakest coordination to zirconium and, conversely, the strongest coordination to the (more easily isolated) silver salt. The crystal structures of all six silver salts $Ag(CB_{11}H_6X_6)$ and $Ag(CH_3CB_{11}H_5X_6)$ have been determined,[10] but the varying numbers, types, and bond distances of donors to silver did not present an easily analyzed pattern.

Although X-ray crystallography is the most readily available and most commonly used method of detecting weak secondary bonding[11] of ligands to metal ions, it leaves several important questions unanswered. Secondary bond distances commonly show wide ranges, even in chemically equivalent bonds in the same complex (e.g., from 2.640 to 2.926 Å in $Ag(CB_{11}H_6Cl_6)$). Is there any bonding significance to the differences in contact distances commonly found, or does secondary bonding correspond to such a shallow potential well that the differences merely represent variations in what is needed to achieve good packing at the lowest energy in the solid state?

Table 1. Average Metal−Organohalogen Distances for Halocarbon and Halocarborane Complexes of Silver, Silicon, Thallium, and Cesium

complex	d(M···X)	excess d[a]	CN(Ag)[b]	ref
$Ag(CH_3CB_{11}Cl_{11})$	2.882 Å	0.37 Å	6	*c*
$Ag(CB_{11}H_6Cl_6)$	2.780	0.27 Å	6	*d*
$Ag(CB_{11}H_6Br_6)$	2.824	0.14 Å	6	*d*
$Ag(CB_{11}H_6I_6)$	2.946	0.10 Å	5	*d*
$^iPr_3Si(CB_{11}H_6Cl_6)$	2.323 Å	0.15 Å		*e*
$^iPr_3Si(CB_{11}H_6Br_6)$	2.479 Å	0.16 Å		*e*
$^iPr_3Si(CB_{11}H_6I_6)$	2.661 Å	0.15 Å		*e*
$Tl(CB_{11}H_6Br_6)\cdot 2C_7H_8$	3.469 Å	0.86 Å		*f*
$Cs(HCB_{11}Br_{11})$	3.733 Å	0.24 Å		*c*
$Cs(HCB_{11}I_6Br_5)\cdot THF$	3.89 Å (Br)	0.40 Å		*g*
$Cs(HCB_{11}I_6Br_5)\cdot THF$	4.07 Å (I)	0.39 Å		*g*
$[Ag(Cl_2CH_2)_n]^+$	2.832 Å	0.32 Å	6	*h*
$[Ag(Br_2CH_2)_n]^+$	2.865 Å	0.20 Å	6	*h*
$[Ag(I_2CH_2)_n]^+$	2.851 Å	0.00 Å	4	*h*
$Ag(ClCH_2SO_3)$	2.945 Å	0.43 Å	6	this work
$Ag(BrCH_2SO_3)$	2.971 Å	0.31 Å	6	*i*

[a] Average distance in excess of M−X single bond distance = sum of covalent radii except in the case of Cs^+, for which the single-bonded metallic radius is used. [b] Coordination number of Ag^+. [c] Ref 13a. [d] Ref 10a. [e] Ref 9b. [f] Ref 18. [g] Ref 13b. [h] From sources cited in Table 1 of ref 31. [i] Ref 16.

The normal criterion for weak secondary bonding is that the metal−donor distance should be greater than the sums of single covalent or ionic radii but less than the sums of van der Waals radii. But van der Waals radii are notoriously hard to determine, because one must first be confident that there is indeed no bonding in the direction in which the contacts are measured. As an illustration of the difficulties, solid halocarbons commonly pack with halogen−halogen distances that are less than the sums of their van der Waals radii. Consequently, one must ask whether the van der Waals radii are incorrect, or differ in different directions around an organohalogen atom, or whether there are hitherto-unsuspected secondary bonding interactions present.[12]

In Table 1, we summarize metal−halogen distances found in silver, silicon, thallium, and cesium salts of weakly coordinating anions and related ligands.[13] We can attempt to analyze these distances by computing the *excess bond distance*: the amount that the observed Ag−X distance is in excess of the distance expected for a normal single bond between Ag and X. For a neutral halogen atom in contact with a cation, the types of radii that should be summed to give the expected distance are not entirely clear, but the most sensible results are obtained from the sums of covalent radii, which are 2.51 Å for Ag−Cl, 2.66 Å for Ag−Br, and 2.85 Å for Ag−I. How much longer than the sums of covalent radii must the metal−halogen contact be before we can decide that it no longer represents coordination? Overall, it may be seen that excess bond distances are broadly similar for Ag, Cs, and Si, although cations of these elements would be expected to bond in quite different ways to halogens.

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Hence, determining whether a long metal−donor atom contact actually signifies coordinate covalent (secondary) bonding requires confirmation by another method. Most spectroscopic methods cannot reliably detect the subtle bonding changes that follow the weak coordination of a halogenated anion or other ligand to a metal ion. We propose that, for ligands or anions in which surface donor atoms are chlorine, bromine, or iodine, the method of choice to supplement X-ray crystallography for characterizing weak bonding may be halogen (^{35}Cl, ^{79,81}Br, ^{127}I) nuclear quadrupole resonance (NQR) spectroscopy.

A limitation of NQR spectroscopy is the requirement for gram-scale samples of polycrystalline solid materials; such quantities are not affordable or even available for Ag($CB_{11}H_6X_6$).[14] Hence, to begin the study of the metal-ion coordinating characteristics of weakly coordinating halogenated anions, we have substituted a much more affordable set of anions, the halomethanesulfonate anions, $ICH_2SO_3^-$ (**1**$^-$), $BrCH_2SO_3^-$ (**2**$^-$), and $ClCH_2SO_3^-$ (**3**$^-$). Fluorinated anions of this type are suggested for use as noncoordinating anions in the "Notice to Authors" of this journal;[15] results on related weakly coordinating anions will be reported elsewhere. Although the oxygen ends of these anions are the main sites of coordination, the crystal structure of Ag(**2**)[16] shows that it has Ag−Br contacts very similar to those found in Ag($CB_{11}H_6Br_6$). In this study, we have determined the X-ray structure of Ag(**3**) and find not only that it is isomorphous and isostructural with Ag(**2**) but also that it shows very similar Ag−Cl contacts to those found in Ag($CB_{11}H_6Cl_6$). Although twinning problems prevented us from determining the structure of Ag(**1**), we shall show that the NQR evidence suggests that it also shows similar characteristics to silver chloro- and bromomethanesulfonate. Study of the NQR spectra of salts of the halomethanesulfonate anions should show what happens when an anion generally expected to be weakly coordinating to typical cations such as Na^+ and K^+ does coordinate to a soft cation such as Ag^+ via halogen atom(s).

The thallium(I) ion is another classical +1-charged soft-acid metal ion which has been found by X-ray crystallography[17] to coordinate to organohalogen atoms of a weakly coordinating ligand and to halogen atoms in the weakly coordinating anion $(CB_{11}H_6Br_6)^-$.[18] This study includes an NQR investigation of the coordinating ability of thallium(I) ion in its halomethanesulfonate salts.

Experimental Section

All reactions involving the photosensitive silver and thallium halomethanesulfonates were carried out with red-light illumination. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN, and are shown in Table 2. It should be noted that in our experience the percent halogen obtained in silver compounds of halocarbons is always somewhat low. TGA measurements were obtained on a Perkin-Elmer TGA-7 thermogravimetric analyzer between ambient temperature and 200 °C. Proton nuclear magnetic resonance (^{1}H) data were obtained in D_2O solution using sodium 3-trimethylsilylpropionate-2,2,3,3-d_4 (TMSP) as internal reference on a Bruker AC 200 MHz spectrometer equipped with a FT Aspect 3000 signal processing system. ^{35}Cl NQR spectra were measured at 77 K on a Decca NQR spectrometer.[19] ^{79}Br, ^{81}Br, and ^{127}I NQR spectra were measured on a Wilks NQR-IA instrument[20] at ambient temperature and then were more accurately recorded at 77 K and room temperature on a pulse IS-3 NQR spectrometer. ^{127}I NQR measurements of ν_1 (~300 MHz) and their temperature dependence were made in Japan on a superregenerative NQR spectrometer with Zeeman modulation, the oscillator of which had a tank circuit with a small Lecher-line in addition to the usual LC parts, or on an ISSH-1-12 pulse NQR spectrometer (SKB IRE, Russia);[21] those obtained above 360 MHz were measured on a homemade pulsed NQR spectrometer.[22] Since doing this work, we have acquired a state-of-the-art RITEC pulse Fourier transform ^{35}Cl NQR spectrometer,[23] which has been built to implement two-dimensional nutation NQR spectra (useful in obtaining asymmetry parameters).[24]

Table 2. Elemental Analyses of Halocarbon Derivatives[a]

compound	%C calcd	%C found	%H calcd	%H found	%hal calcd	%hal found
$AgBrCH_2SO_3$	4.26	4.24	0.72	0.67	28.35	25.91
$KBrCH_2SO_3$	5.64	5.63	0.95	0.93	37.50	37.12
$TlBrCH_2SO_3$	3.17	2.40	0.53	<0.5	21.12	20.91
$KClCH_2SO_3$	7.12	7.05	1.20	1.08	21.02	21.12
$AgClCH_2SO_3$	5.06	5.26	0.85	0.59	14.93	12.73
$TlClCH_2SO_3$	3.60	3.65	0.60	0.59	10.62	10.31
$AgICH_2SO_3$	3.63	2.73	0.61	0.62	38.59	34.01
$TlICH_2SO_3\cdot{}^1/_{12}C_{12}H_{24}O_6$	5.36	5.23	1.12	1.42	28.30	30.34
$KICH_2SO_3$	4.62	4.66	0.78	0.82	48.79	47.66

[a] $NaClCH_2SO_3\cdot{}^1/_3H_2O$ weight loss upon dehydration (between 30 and 131 °C): Calcd, 3.79%. Found by TGA, 3.94%.

Crystallographic Study. The diffraction pattern from a colorless crystal (0.12 × 0.16 × 0.20 mm^3) was studied on a Bruker R3 diffractometer using the Bruker-Nonius XSCANS software. The unit cell constants reported were determined by refinement against the setting angles of 25 widely spread reflections, and the intensity data were measured by $\theta/2\theta$ scans to a maximum in 2θ of 55°. In addition to Lorentz and polarization corrections, a semiempirical absorption correction based on ψ scans of selected reflections over a range of setting angles was performed.

The structure was solved by direct methods (Bruker-Nonius SHELXTL) and refined by full matrix least squares techniques on F. The final model employed anisotropic displacement coefficients to model motion of all non-hydrogen atoms. The single crystallographically unique hydrogen atom was placed in an idealized position and allowed to ride on the carbon atom to which it was attached. The final electron density map was reasonably flat, with the only significant peak (1.89 e Å^{-3}) being due to residual electron density from the Ag(I) cation.

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Materials. Insoluble silver(I) sulfite was precipitated upon reaction of solutions of $AgNO_3$ and Na_2SO_3. Slightly soluble thallium(I) sulfite was synthesized from waste thallium halides, which were first boiled with ethanol and concentrated HCl to convert any soluble thallium compounds to insoluble TlCl, while leaving organic contaminants in the ethanol. The mixed halides were filtered off, dried, and then heated with concentrated H_2SO_4 to drive off HCl(g), HBr(g), and I_2(g), while producing soluble Tl_2SO_4 and perhaps some $TlHSO_4$. Yellow Tl_2SO_3 in good purity was precipitated using an excess of 1.0 M freshly opened Na_2SO_3.[25] Calcd % SO_3^{2-} in Tl_2SO_3: 16.4%. Found: 15.4% iodimetrically.[26] Because thallium sulfite and sulfate have similar solubilities, the sulfate contaminates product made from older, air-oxidized Na_2SO_3.

Tl(1). Freshly prepared Tl_2SO_3 (4.53 g, 9.28 mmol) was dissolved in 50 mL of deionized water in a Schlenk flask under Ar in an ~85 °C hot water bath. This solution was stirred with CH_2I_2 (4.00 g, 14.9 mmol); a yellow precipitate of TlI gradually formed during the first hour. After 2 h, 3.01 g (9.09 mmol) of TlI was filtered off and washed with 30 mL of hot water. The volume of the combined filtrate was reduced in a vacuum desiccator, producing at first 0.693 g mixed yellow and white crystals (possibly including some unreacted Tl_2SO_3). After filtering these off, the volume was reduced nearly to dryness to give 3.06 g (7.19 mmol, 77.5% yield) of white $Tl^+(\mathbf{1})^-$, which was washed with 1.5 mL of cold deionized water. The product was characterized successfully by ^1H NMR in D_2O and NQR.

Tl(1)·$^1/_n$$C_{12}H_{24}O_6$ ($n \approx 12$). Tl_2SO_3 (4.89 g, 10.0 mmol) in 20 mL of deionized water in a Schlenk flask under Ar was mixed with CH_2I_2 (4.02 g, 15.0 mmol) and 18-crown-6 (0.13 g, 0.49 mmol); the mixture was stirred in the absence of light for 2 days. However, no reaction was observed until the solution was heated to about 85 °C in a hot water bath for about 1 h, whereupon TlI precipitated, was filtered off, and was washed with 20 mL of hot deionized water. The filtrate was allowed to evaporate; the 2.90 g of air-dried crystals were then rinsed with 10 mL of ethanol and then with 50 mL of hot methanol to give 2.00 g of the final product. The washed product gave two ^1H NMR peaks of roughly equal intensity at δ 4.41 (methylene) and at at δ 3.70 (crown ether) in D_2O solution**.** Elemental analysis (Table 2) also confirmed the presence of a small amount (about $^1/_{12}$ mol) of 18-crown-6. This product gave very strong ^{127}I NQR signals, which were different from those of crown ether-free Tl(**1**), and which were too strong to be due to the small possible yield of the crown ether adduct for which $n = 1$.

Ag(1). Solutions of 2.68 g (16.8 mmol) of $AgNO_3$ in 20 mL of hot ethanol and of 4.11 g (15.7 mmol) of Na(**1**)·H_2O in 165 mL of hot ethanol were mixed and then allowed to cool to room temperature. The solution was filtered to remove precipitated $NaNO_3$, and the filtrate was placed in a vacuum desiccator. After 12 h, crystals had appeared; the mother liquor was decanted from 1.62 g (4.9 mmol, 31% yield) of product which gave a single ^1H NMR peak in D_2O at δ 4.44. Evaporation of the mother liquor gave an additional 3.34 g of product, the ^1H NMR of which indicated some contamination.

Ag(3). Chloromethanesulfonyl chloride (Alfa, 2.55 g, 17.1 mmol) was placed in 40 mL of dry methanol in a Schlenk flask under Ar. Ag_2O (3.97 g, 17.1 mmol) was added. Stirring overnight caused the dark color of the Ag_2O to disappear. The solution was then filtered, and the precipitate was washed with five 20-mL portions of dry methanol, leaving behind the expected amount of AgCl. Evaporation of the combined filtrate in a vacuum desiccator gave a total of 3.01 g (12.7 mmol, 74% yield) of crystalline product.

Results

Preparation of Compounds. Halomethanesulfonates are usually prepared by refluxing solutions of sulfite ion with dihalomethanes:

$$SO_3^{2-} + CH_2X_2 \rightarrow XCH_2SO_3^- + X^- \qquad (1)$$

We synthesized Na(**1**)·H_2O and K(**1**) in this manner using the procedure of Ossenbeck.[27] We also prepared the thallium salt from Tl_2SO_3 and CH_2I_2 using 5 mol % of 18-crown-6 as a phase transfer catalyst, but purer product was obtained almost as quickly by omitting the crown ether. The corresponding reaction using Ag_2SO_3 and 18-crown-6 gave very low yields, presumably because of the low solubility of Ag_2SO_3. Although Ag(**1**) has previously been prepared by the neutralization of Ag_2CO_3 with ICH_2SO_3H (obtained by ion-exchange from Na(**1**)),[28] we found it more convenient to react Na(**1**) with $AgNO_3$ in hot ethanol, filtering off the precipitated $NaNO_3$ and allowing crystallization of the product as the filtrate evaporated. All iodomethanesulfonates were characterized by ^1H NMR peaks at δ 4.39−4.41 in D_2O.

Na(**2**) was synthesized by refluxing aqueous Na_2SO_3 and CH_2Br_2 for 4 days,[29] but we could find no satisfactory way to separate it from the byproduct NaBr by fractional crystallization. Refluxing aqueous K_2CO_3, CH_2Br_2, and 3 mol % 18-crown-6 for 2 days produced K(**2**); fractional crystallization from water produced first KBr crystals and then the product, which was recrystallized from water. Tl(**2**) was similarly produced by refluxing CH_2Br_2 and aqueous Tl_2SO_3 and was easily separated from insoluble TlBr and unreacted, slightly soluble Tl_2SO_3; more complete reaction but less pure product resulted from the addition of catalytic amounts of 18-crown-6. Our synthesis of Ag(**2**) was a modification of the procedures of Charbonnier[16] and Senning:[28] we passed our unseparated NaBr−Na(**2**) mixture through a strongly acidic cation-exchange resin to give a mixture of HBr and $BrCH_2SO_3H$. This was reacted with Ag_2O, AgBr was filtered off, and the filtrate was slowly evaporated to give crystalline Ag(**2**). The reaction of this salt with KBr was used to prepare analytically pure K(**2**). All bromomethanesulfonates were characterized by ^1H NMR peaks at δ 4.43−4.44 in D_2O.

The 7 day reaction of aqueous Tl_2SO_3 and CH_2Cl_2 in the presence of 18-crown-6 did not prove a satisfactory method of preparing Tl(**3**) although reaction occurred and NMR spectra suggested the formation of the crown ether adduct [Tl(18-crown-6)](**3**). The thallium salt is produced instead by the reaction of $ClCH_2SO_2Cl$ (Alfa) with Tl_2CO_3 in

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methanol overnight.

$$ClCH_2SO_2Cl + Tl_2CO_3 \rightarrow TlCl(s) + Tl(\mathbf{3}) + CO_2(g) \quad (2)$$

Silver salt Ag(**3**) was similarly prepared using Ag_2O in place of Tl_2CO_3; this synthesis was simpler than that earlier used by Senning.[28] The sodium salt was similarly prepared using Na_2CO_3 and Ag_2O and was extracted from insoluble AgCl using methanol.

$$2ClCH_2SO_2Cl + Ag_2O + Na_2CO_3 \rightarrow 2AgCl(s) + 2Na(\mathbf{3}) + CO_2(g) \quad (3)$$

Potassium salt K(**3**) was prepared from the silver salt by reaction with aqueous KCl, or in the same manner as the sodium salt. Chloromethanesulfonates were characterized by ^1H NMR peaks at δ 4.50−4.52 in D_2O.

The use of 3 mol % of the phase transfer catalyst 18-crown-6 seemed to speed up the reaction of aqueous sulfite with dihalomethanes. The catalyst gave trouble in the case of thallium salts, which seem to form substantial amounts of crown-ether adducts of stoichiometry $Tl(XCH_2SO_3)\cdot{}^1/_n(C_{12}H_{24}O_6)$, which give distinctive NQR spectra and which are difficult to separate from uncomplexed $Tl(XCH_2SO_3)$. Both NMR spectra and elemental analysis suggested that n could be as high as 12, although the results were not definitive because this product was not obtained pure. Using 1 mol of 18-crown-6, the pure, more normal crown ether adduct $Tl(\mathbf{2})\cdot C_{12}H_{24}O_6$ (i.e., $n = 1$) was produced; this did not give the NQR spectrum of the product for which n was about 12 (^{81}Br $\nu = 236.9$ MHz at rt).

Crystal Structure of Ag(3). The crystal structure of Ag(**3**) was determined at 173 K so that it could be compared with the previously published structure of Ag(**2**);[16] the two compounds are isomorphous and isostructural. Unfortunately, the crystals of Ag(**1**) were twinned, so their crystal structure could not be determined; later in the paper, we present evidence from ^{127}I NQR spectroscopy which suggests that it at least has a very similar structure.

Table 3 presents a summary of the crystallographic data for Ag(**3**); Table 4 summarizes the bond lengths and bond angles. Figure 1 shows the labeling of the atoms and the thermal ellipsoids. Figure 2 illustrates the coordination environment of Ag^+ in the salt. The silver(I) ion is approximately octahedrally coordinated by four oxygen donor atoms from sulfonate groups at distances of 2.367 and 2.436 Å and two chlorine donor atoms from chloromethane groups at a distance of 2.945 Å. All bond angles at Ag^+ are within 5° of the ideal angles. The primary bond lengths are unremarkable. As is commonly the case, there is no significant lengthening of the primary C−Cl bond upon formation of the secondary bonds to Ag^+. The structure is in striking contrast to the layer type of structure commonly found for halogenated and nonhalogenated organosulfonates of the hard-acid group 1 and 2 cations, which feature a layer of metal ions surrounded exclusively by hard-base oxygen donor atoms from two layers of sulfonate groups (and sometimes water), leaving the organic group (and terminal halogens if present) in a layer far from the metal ion, but nearer to a layer of organic groups (and terminal halogen atoms) from the next set of (anion)(cation)(anion) layers.[30]

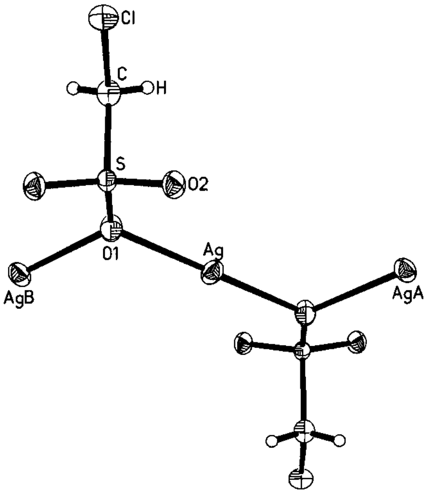

Figure 1. Thermal ellipsoid plot (50% probability) of the structure of compound Ag(**3**), with atom labeling indicated. Hydrogen atoms are drawn as spheres of arbitrary radius. Bond lengths and angles are given in Table 4.

Table 3. Crystallographic Data for $Ag(O_3SCH_2Cl)$

chemical formula	$Ag(O_3SCH_2Cl)$
a	13.241(3) Å
b	7.544(2) Å
c	4.925(2) Å
V	492.0(3) Å^3
Z	4
fw	237.4
space group	*Pnma* (No. 62)
T	173 K
λ	0.7107 Å
D_{calcd}	3.20 g cm^{-3}
μ	0.49 cm^{-1}
R1	0.058 (observed reflections)[a]
wR2	0.084 (all data)[b]

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 4. Bond Lengths (Å) and Angles (deg) with esd's

Ag(1)−O(1)	2.436(4)	Ag(1)−O(1A)	2.436(4)
Ag(1)−O(2A)	2.367(4)	Ag(1)−O(2B)	2.367(4)
Ag(1)−Cl(1)	2.9454 (15)	Cl(1)−C	1.799(8)
S−O(1)	1.465(6)	S−O(2)	1.499(4)
S−O(2C)	1.449(4)	S−C	1.764(9)
O(2)−Ag(1A)	2.367(4)	O(1)−Ag(1B)	2.436(4)

O(1)−Ag(1)−O(1A)	180.0(1)	O(1)−Ag(1)−O(2A)	85.7(2)
O(1A)−Ag(1)−O(2A)	94.3(2)	O(1)−Ag(1)−O(2B)	94.3(2)
O(1A)−Ag(1)−O(2B)	85.7(2)	O(2A)−Ag(1)−O(2B)	180.0(1)
O(1)−S−O(2)	112.6(2)	O(1)−S−C	103.3(4)
O(2)−S−C	105.9(2)	O(1)−S−O(2C)	112.6(2)
O(2)−S−O(2C)	115.2(3)	C−S−O(2C)	105.9(2)
Ag(1)−O(1)−S	129.3(1)	Ag(1)−O(1)−Ag(1B)	101.5(2)
S−O(1)−Ag(1B)	129.3(1)	S−O(2)−Ag(1A)	131.9(3)
Cl(1)−C−S	109.4(4)	C−Cl(1)−Ag(1)	105.62(19)
Ag(1)−Cl(1)−Ag(1B)	79.6(2)		

Figure 3 shows the coordination environment of the chlorine atom (crosshatched) in the chloromethanesulfonate ion. It is three-coordinated by its carbon atom at 1.799 Å and two silver ions at 2.945 Å. The bond angles C−Cl−Ag and Ag−Cl−Ag are 105.6° and 79.6°, respectively. In our

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(30) Shubnell, A. J.; Kosnic, E. J.; Squattrino, P. J. *Inorg. Chim. Acta* **1994**, *216*, 101−112. Jansen, M.; Korus, G. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1625−1632.

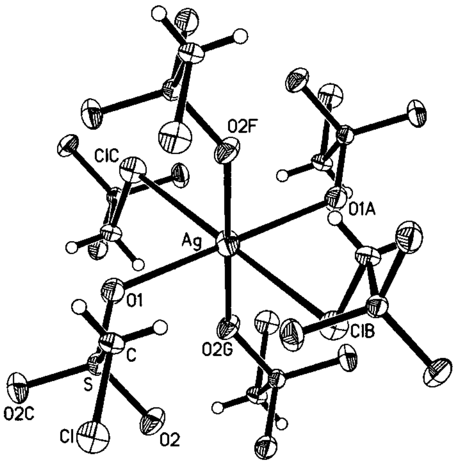

Figure 2. Thermal ellipsoid drawing showing the coordination environment of Ag(**3**).

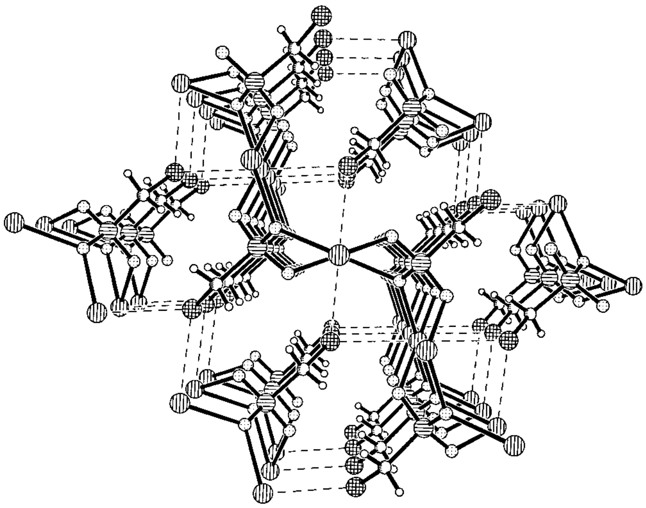

Figure 3. Packing diagram of the structure of Ag(**3**) showing the pseudooctahedral AgO_4Cl_2 coordination spheres. An Ag atom is shown at the center of the diagram; Cl atoms are crosshatched (⊗). The Ag−Cl bonds, at 2.9454(15) Å, are shown as dashed lines. The C−Ag−Cl and Ag−Cl−Ag(1B) angles are 105.62 (19)° and 79.6 (2)°.

earlier NQR study of complexes of neutral halocarbons with silver ions,[31] the complexes featured two-coordinate halogen atoms *bridging* between carbon and silver. In this study, we have three-coordinate *apical* halogen atoms, each halogen atom being bonded to carbon through the primary covalent bond and to two different silver ions through two secondary bonds.

Apically coordinated organohalogen atoms are rather unusual; crystallographic data for these atoms are summarized in Table 5. Only 1 of the 12 coordinated organochlorine atoms reported[32] in the dichloromethane and dichloroethane adducts of silver(I), Cl(3) in $[Ag(1,2\text{-}C_2H_4Cl_2)OTeF_5]_2$, was an apical chlorine atom. Only 2 of the 31 crystallographically different coordinated halogen atoms found in 7 silver(I) hexahalocarborane salts by Xie et al.,[9,10,33] Br(12) in $Ag(CB_{11}H_6Br_6)$ and Br(12) in $Ag(CH_3CB_{11}H_5Br_6)$, are apical. Only 2 (or perhaps 3) apical organoiodine atoms were found among the over 50 examples of coordinated organoiodine atoms in Powell's[34] extensive studies of iodocarbon ligands coordinated to Ag^+.

In Table 1, we note the following average excess bond distances for two-coordinate halogen atoms: (a) in dihalomethanes CH_2X_2 coordinated to silver ions, 0.32 Å for X = Cl, 0.20 Å for X = Br, and 0.00 Å for X = I; (b) in halogenated carborane anions $(CB_{11}H_6X_6)^-$ coordinated to silver ions, 0.27 Å for X = Cl, 0.14 Å for X = Br, and 0.05 Å for X = I; and (c) in $(CB_{11}H_6X_6)^-$ coordinated to $(i\text{-Pr})_3Si^+$ ions, 0.15−0.16 Å regardless of the halogen involved. For halocarbons and halocarboranes bonded to the soft acid Ag^+, the excess bond distance decreases as the halogen atom becomes softer, while for halocarbons bonded to the hard siliconium cation, there is no such trend.

We find (Table 5) that the Ag···Cl secondary bond distances in $Ag(XCH_2SO_3)$ are 2.945 Å for X = Cl (this study) and 2.971 Å for X = Br.[16] These give excess bond distances of 0.43 Å for X = Cl and 0.31 Å for X = Br. These excess bond distances are quite comparable to those previously found for the apical halogen atoms in $[Ag(1,2\text{-}C_2H_4Cl_2)OTeF_5]_2$ and $Ag(CB_{11}H_6Br_6)$, respectively. They are, however, on the order of 0.1 Å longer than the excess bond distances found for the same halogen atoms acting as bridging ligands to silver. The same is true of the apical iodine atoms of the first two iodotoluene and iodobenzene adducts listed in Table 5, but the third one is anomalous: It has two Ag−I contacts, one with zero excess bond distance (as is found with bridging iodine atoms) and one with a very large 0.46 Å excess bond distance. This suggests that possibly this iodine atom is more nearly bridging than apical, so it will not be included in this analysis of apical halogen atoms.

Some theoretical treatments of NQR parameters predict a great sensitivity to bond angles at the halogen atom. Apical halogen atoms, like bridging ones, generally show C−X−Ag angles between 90° and 109° (Table 5). In addition, there is a Ag···X···Ag angle, which in contrast shows wide variability (between 61.4° and 144.5°); this angle is 79.6° in Ag(**3**) and 79.1° in Ag(**2**).

NQR Spectra: Theory.[35−37] The two fundamental properties of a quadrupolar nucleus in a compound or ion are its *quadrupole coupling constant*, e^2Qq_{zz}/h (in MHz), which measures the deviation of the electronic environment of the nucleus from spherical symmetry, and its *asymmetry pa-*

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[35] Buslaev, Yu. A.; Kravchenko, E. A.; Kolditz, L. *Coord. Chem. Rev.* **1987**, *82*, 1−237; (a) p 52−58.

[36] Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants*; Academic Press: London, 1969; (a) p 39; (b) Chapter 7; (c) p. 139.

[37] Semin, G. K.; Babushkina, T. A.; Yakobson, G. G. *Nuclear Quadrupole Resonance In Chemistry*; Wiley: New York, 1975; (a) pp 202−204; (b) Chapter 5.

Table 5. Average Crystallographic Results for Apically-Coordinated Halocarbons and Halo Anions

compound	ref	r(C−X)	r(Ag−X)	excess	∠C−X−Ag	∠Ag−X−Ag
$Ag(ClCH_2SO_3)$		1.799	2.945	0.43	105.6	79.6
$[Ag(Cl_2C_2H_4)OTeF_5]_2$, apical Cl only	*a*	1.75	2.915, 3.000	0.40 0.49	98.9, 106.3	119.2
$Ag(BrCH_2SO_3)$	*b*	1.938	2.971	0.31	103.6	79.1
$Ag(CB_{11}H_6Br_6)$			2.940	0.28		
$Ag_4(O_2CCF_3)_4(H_2O)_2$- (p-$IC_6H_4CH_3)_2$	*c*	2.119	2.920, 2.933	0.07, 0.08	102.2, 101.2	144.53
$Ag_2(O_2CCCl_3)_2$- $(HO_2CCCl_3)(IC_6H_5)$	*c*	2.093	2.927, 2.970	0.08, 0.12	102.3, 94.4	61.4
$Ag_2(O_2CCF_3)_2(IC_6H_5)$	*c*	2.082	2.853, 3.309	0.00, 0.46	99.0, *d*	*d*

[a] Ref 34. [b] Ref 17. [c] Ref 36. [d] Not reported.

rameter η (a dimensionless fraction that ranges from 0.00 to 1.00), which measures the deviation of the electronic environment from axial symmetry. Neglecting the asymmetry of the solid-state crystalline environment or the effects of distant substituents, a singly bonded organohalogen atom has axial symmetry but does not have spherical symmetry, so has a nonzero e^2Qq_{zz}/h but an (approximately) zero η. On forming a secondary bond at a bond angle other than 180°, the halogen atom also loses its axial symmetry, so it also has a nonzero η. In our earlier study of secondary-bonded iodocarbons coordinated to one Ag^+ ion, we found values of η ranging from 0.20 to 0.42.[31]

An NQR experiment measures not these fundamental parameters, but the *NQR frequencies* ν. For a spin $I = {}^5/_2$ nucleus such as ^{127}I, there are two NQR frequencies for each crystallographically inequivalent atom. If it is known or can be assumed that these two frequencies come from the same iodine atom, then it is possible to determine e^2Qq_{zz}/h and η based on the relationships[38]

$$\nu_1 = {}^3/_{20}(e^2Qq_{zz}/h)(1 + {}^5/_{54}\eta^2) \tag{4}$$

$$\nu_2 = {}^6/_{20}(e^2Qq_{zz}/h)(1 - {}^{11}/_{54}\eta^2) \tag{5}$$

For $I = {}^3/_2$ nuclei such as ^{35}Cl, ^{79}Br, and ^{81}Br, there is only one ν, which is related to the two fundamental parameters e^2Qq_{zz}/h and η by the equation

$$\nu = {}^1/_2(e^2Qq_{zz}/h)(1 + \eta^2/3)^{1/2} \tag{6}$$

If η is zero or even close to zero it has a negligible effect on ν (an η of 0.17 raises the value of ν by only 0.5%). Thus, as long as η does not exceed 0.17, it is often assumed that the fundamental property, e^2Qq_{zz}/h, is 2 times ν. However, it is possible to obtain η and therefore e^2Qq_{zz}/h by the Fourier analysis of the slow beats in the spin-echo envelope of the pulse NQR signal of polycrystalline samples;[39] this was done in external magnetic fields of 32 Œ at 300 K for polycrystalline Ag(**2**) and 48 Œ at 77 K for polycrystalline K(**2**).

The potential value of the fundamental NQR parameters is that they are readily computable in principle. Rigorous computations on the ionic compounds in this study would in practice be quite formidable, because of the heavy atoms involved and because the compounds are ionic, and the quadrupole parameters are sensitive to the long-range ionic forces present in the lattice. Fortunately, the NQR parameters can be fairly directly related to the populations of the valence orbitals of the halogen atom through simple Townes−Dailey computations[35,36b] that often give reasonable estimates of valence orbital populations, particularly in molecular species. This theory assumes that core electron shells, which are filled and have spherical symmetry, contribute nothing to e^2Qq_{zz}/h or ν. It also assumes that external charges can be neglected as well. In practice, this is a rough approximation, particularly in ionic compounds, where the external ionic charges can change the polarization of the halogen core electrons. Thus, the NQR frequencies of group 1 salts of halo anions (in which cations are very close to halogen atoms) can increase by as much as 10% as the cation is increased in radius from K^+ through Cs^+ to $(CH_3)_4N^+$,[35a] while the NQR frequencies of layered group 1 metal chloroacetates (in which cations are close only to oxygen atoms)[40] decrease by about 3% from Na^+ to Rb^+.[41] Hence, we have taken care in this study to emphasize data for ions of comparable six-coordinate Shannon−Prewitt radii: Na^+ (1.16 Å), Ag^+ (1.29 Å); K^+ (1.52 Å); Tl^+ (1.64 Å). We do not know, however, whether these are isomorphous and isostructural; if not, changes in structure type could produce additional shifts of NQR frequencies. Under these circumstances, the Townes−Dailey model only gives us an estimate of what more sophisticated computations might be able to tell us.

Within this simple model, e^2Qq_{zz}/h is a function of the imbalance in population of the valence orbitals of a halogen atom:

$$e^2Qq_{zz}/h = -e^2Qq_{at}/h(N_z - {}^1/_2(N_x + N_y)) \tag{7}$$

where e^2Qq_{at}/h is the atomic quadrupole coupling constant (+109.746 MHz for ^{35}Cl, −643.032 MHz for ^{81}Br, −769.756 MHz for ^{79}Br, and +2292.712 MHz for ^{127}I)[36c] and N_z, N_x,

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(39) Sapozhnikov, Yu. E.; Yasman, Ya. A. *Bull. Acad. Sci. USSR, Phys. Ser. (Engl. Transl.)* **1978**, *42*, 120−123. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1978**, *42*, 2148−2151. Current modifications described in: Morgunov, V. G.; Kravchenko, E. A. *Prib. Tekh. Eksp.* **1988**, *6*, 199−200. Kravchenko, E. A. *Russ. Chem. Rev.* **1999**, *68*, 787−805. Additional modifications to be described elsewhere.

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(41) David, S.; Guibé, L.; Gourdji, M. *New J. Chem.* **1995**, *19*, 37−46.

and N_y are the populations of the valence p orbitals indicated. For a single-bonded halogen atom, N_x and N_y are 2.00 each, so N_z (which is less than 2) is easily computed from

$$e^2Qq_{zz}/h = -e^2Qq_{\mathrm{at}}/h(N_z - 2) \qquad (8)$$

The Townes−Dailey expression for η shows that it arises from an imbalance in the populations of the valence p_x and p_y orbitals:

$$\eta = (e^2Qq_{xx} - e^2Qq_{yy})/e^2Qq_{zz} \cong {}^3/_2(N_x - N_y)(e^2Qq_{\mathrm{at}}/e^2Qq_{zz}) \qquad (9)$$

For three-coordinate (apical) halogen atoms, the population of all valence p orbitals of the halogen atom are different from 2.00; potentially, there are more unknowns than measurables.[42] Fortunately, the two secondary bonds in most of the compounds listed in Table 5, including the silver chloro- and bromomethanesulfonates, are identical by symmetry. We will assume that they are in the iodomethanesulfonate as well, so we take $N_y = N_x$.

If the secondary-bonding orbitals are pure unhybridized valence p orbitals bonding at 90° angles to the main bonding orbital and at 90° angles to each other, then by eq 9, because $N_x = N_y$, $\eta = 0$. Equation 7 then becomes

$$e^2Qq_{zz}/h = -e^2Qq_{\mathrm{at}}/h(N_z - N_y) \qquad (10)$$

Because N_y is between 2.00 and N_z, it can be seen by comparing eqs 10 and 8 that e^2Qq_{zz}/h moves closer to zero for apical halogen atoms, and (applying eqs 4−6) the halogen NQR frequencies of apical halogens are reduced as compared to those of the original terminal halogen atoms.

The crystallographic data show that the angles at the apical halogen atoms in Ag(**3**) and Ag(**2**) are not equal to 90°. Under these conditions, η becomes greater than zero, because the valence p_x and p_y orbitals can no longer be equally involved in the bonding. It should also be noted that asymmetry parameters are also very sensitive to the polarizing effects of external charges (ions).

It is important, in assessing the effects of coordination of a halocarbon or a halogenated anion to a metal ion such as Ag^+, to have a reference set of NQR parameters of that species when it is not coordinated. Because K^+ is a hard acid likely to coordinate only to the sulfonate oxygen atoms, and because K^+ has the same charge as Ag^+ and has about as similar a size as is possible, we take it as the best reference salt. The suitability of K^+ salts as reference compounds will be supported by the observation that, for these and several other halogenated anions that we will describe elsewhere, it is observed that solid halogenated compound X−C_nH_m−R has about the same halogen NQR frequency when R = X as when R = $SO_3^-K^+$. Thus, although the various potassium salts are undoubtedly not isostructural or isomorphous either with the Ag^+ salt or with each other, and thus have diverse crystal lattices, this makes relatively little difference in their spectra: they are all similar to the corresponding halocarbon in their electronic effects as measured by NQR. We could then use either the K^+ salt or the neutral dihalomethane as the reference with very similar results.

Table 6. ^{127}I NQR Frequencies and Parameters at 77 K[a]

compound	ν_1, rt	ν_1	ν_2	$-e^2Qq$[b]	η
CH_2I_2[c]		286.88	568.36	1897.37	0.086
$K(ICH_2SO_3)$		286.95	573.19(2)	1911.0	0.03
		288.19	576.24(4)	1920.1	0.01
		288.90[d]	577.53(4)	1925.2	0.02
$Na(ICH_2SO_3)\cdot H_2O$		300.32	599.80(4)	1999.9	0.03
		301.81[d]	602.29(8)	2008.4	0.04
$Tl(ICH_2SO_3)\cdot {}^1/_n$(18-crown-6)		300.28	599.76(25)	1999.7	0.03
$Tl(ICH_2SO_3)$	281.44(8)	287.51(20)			
	279.85(30)	286.52(40)			
	277.85(8)	284.81(20)			
$Ag(ICH_2SO_3)$	262.28(30)	264.85(42)	527.54	1759.7	0.05

[a] Signal-to-noise (S/N) ratios are given in parentheses. [b] By theory, the quadrupole coupling constants should have negative values, although this is not determined in the experiment. [c] Sources: Biryukov, I. P.; Voronkov, M. G.; Safin, I. A. *Tables of Nuclear Quadrupole Resonance Frequencies*; Israel Program for Scientific Translations: Jerusalem, 1969; p 105. Semin, G. K.; Babushkina, T. A.; Yakobson, G. G. *Nuclear Quadrupole Resonance In Chemistry*; Wiley: New York, 1975; p 423. [d] Signal of doubled intensity, therefore likely due to two iodine nuclei.

NQR Spectra: Results and Discussion. We begin with the results and analysis of the ^{127}I NQR spectra (Table 6); these are the most valuable because e^2Qq_{zz}/h and η can be obtained directly from them. As expected, η for the free ligand CH_2I_2 is close to zero (0.086). In the K^+, Na^+, Ag^+, and crown-complexed Tl^+ salts of this anion, η is found to range from 0.01 to 0.04, which suggests the absence of two-coordinated (bridging) halogen atoms[31] and either the absence of any metal coordination to the iodine or, if it is present, that it is apical with bond angles close to 90°. The two NQR frequencies and the quadrupole coupling constant of each iodine atom have similar values in CH_2I_2 and in all of the metal iodomethanesulfonates except that of silver, suggesting the absence of metal−iodine coordination. Applying eq 8, we can estimate N_z, the population of the iodine $5p_z$ orbital involved in σ bonding to carbon, to be 1.16−1.17 electrons in CH_2I_2 and the potassium (and likely the crown-free thallium) salts and 1.13 electrons in the sodium and crown-complexed thallium salts.

Turning to the data for the Ag^+ salt, we observe that its quadrupole coupling constant is substantially (7.3%) lower than that of the reference CH_2I_2 and is similarly lower than the coupling constants of the other metal salts. We also note that η for the Ag^+ salt is close to zero. These two findings taken together suggest that the iodine atom in this salt is apical and is coordinated to two Ag^+ ions with bond angles close to 90°. Hence, eq 10 ought to apply to this salt, giving us the result that $N_z - N_y = -0.77$ electrons. This does not allow us to solve for N_y unless we make an additional assumption, that N_z remains about 1.16 electrons after complexation (which is supported in general by observations that carbon−iodine bond lengths are unaltered upon complexation).[31] Then, we estimate that $N_x = N_y = 1.92$ electrons, that is, that the iodine atom has donated 0.08 electrons to each of the two coordinated silver ions, for a total of 0.16

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[42] Because of the lower symmetry of a pyramidal apical halogen atom, the z direction of the quadrupole coupling tensor may not coincide exactly with the direction of the C−X bond, in which case the right side of eq 9 does not apply exactly.

Table 7. ^{81}Br and ^{79}Br NQR Frequencies (MHz)[a]

compound	^{81}Br, 298 K	^{81}Br, 77 K	^{79}Br, 77 K	e^2Qq, 77 K	η
CH_2Br_2[b]		236.18	282.72		
$K(BrCH_2SO_3)$	230.36(13)	236.60(25)		472.07	0.12 ± 0.03[c]
$Tl(BrCH_2SO_3)$	229.64	233.82	279.86		
$Ag(BrCH_2SO_3)$	218.21(30)	220.80(100)	264.36	438.08	0.22 ± 0.05[d]

[a] Signal-to-noise (S/N) ratios are given in parentheses. [b] Source: Semin, G. K.; Babushkina, T. A.; Yakobson, G. G. *Nuclear Quadrupole Resonance In Chemistry*; Wiley: New York, 1975; for the α phase, p 402. The value for ^{81}Br was computed from the listed value for ^{79}Br. [c] At 77 K. [d] At 300 K.

Table 8. ^{35}Cl NQR Frequencies (MHz)[a]

compound	298 K	77 K
CH_2Cl_2[b]		35.991
$Na(ClCH_2SO_3)\cdot{}^1/_3H_2O$		37.827(3)
		36.707(3)
		36.645(3)
$Ag(ClCH_2SO_3)$	34.151(3)	34.545(4)
$K(ClCH_2SO_3)$	36.026(2)[c]	36.500(4)
	35.699(2)[c]	36.261(2)
		36.171(3)
$Tl(ClCH_2SO_3)$	34.690(7)	35.915(17)

[a] Signal-to-noise (S/N) ratios are given in parentheses. [b] Source: Semin, G. K.; Babushkina, T. A.; Yakobson, G. G. *Nuclear Quadrupole Resonance In Chemistry*; Wiley: New York, 1975; p 314. [c] Measured at 195 K.

electrons donated. This is virtually the same total as is donated by the two-coordinated iodine atoms in silver complexes of iodocarbons.[31] But each of the two secondary bonds in Ag(**1**) has only half the bond order that is found with a two-coordinated iodine atom, which goes along with the observation that secondary bond distances are longer with three-coordinate iodine atoms.

Table 6 also lists some NQR frequencies recorded at room temperature. NQR frequencies are almost always lower at room temperature than at 77 K, but we have previously noted that this is less so when intermolecular (or in this case, interionic) coordination is involved.[43] Thus, ν_1 drops by about 6 MHz (2%) in the thallium salt (no coordination) but only by about 2.5 MHz (1%) in the silver salt (interionic coordination present).

Bromine NQR frequencies are shown in Table 7. The frequencies of the two bromine isotopes were detected as shown and found to be in the ratio of their atomic quadrupole coupling constants, as expected. We found the NQR frequencies of K(**2**) and Tl(**2**) to be very similar to that of the parent bromocarbon CH_2Br_2, while the frequencies of Ag(**2**) are substantially (6.5%) lower than that of the reference CH_2Br_2 or of the other metal salts.

The measured η of K(**2**) is relatively small (0.12 ± 0.03) but is not so small (0.22 ± 0.05) in Ag(**2**), which may be connected with the bond angles C−Br−Ag and Ag−Br−Ag being substantially different than 90°. Hence, eq 10 probably cannot be applied to this salt. The temperature dependence of the ^{81}Br NQR frequencies is, as expected, less in the silver salt (2.6 MHz or 1.2%) than in the potassium and thallium salts (6.3 MHz or 2.7% and 4.18 MHz or 1.8%, respectively).

Chlorine NQR frequencies recorded at 77 K and either 195 K or room temperature are shown in Table 8. We found the NQR frequencies of K(**3**) and Tl(**3**) are close to that of CH_2Cl_2, while the frequency of Ag(**3**) is substantially (4.0%) lower than that of the reference CH_2Cl_2 or of the other metal salts. Again, the temperature dependence for the silver salt is much less (0.4 MHz or 1.2%) than that in the thallium salt (1.2 MHz or 3.3%).

Conclusions. We have determined the crystal structure of a silver salt of a weakly coordinating anion, Ag(**3**), and found it to be isostructural and isomorphous with Ag(**2**). Crystals of Ag(**1**) were twinned, so the crystal structure could not be determined, but analysis of the NQR spectrum suggests that it has, in common with the other salts, an unusual feature: a three-coordinate organohalogen donor atom which is coordinated to two Ag^+ ions by weak secondary covalent bonds. The bond lengths and bond angles indicate that these salts are good models for very weakly coordinating carborane anions in $Ag(CB_{11}H_6X_6)$ and for weakly coordinating halocarbons in salts of $[Ag(CH_2X_2)_n]^+$ (X = Cl, Br, I). The NQR frequencies of the three silver salts are lower than those of the other salts and of the parent dihalomethanes; the degree of frequency lowering grows as the halogen becomes softer (Cl, 4.0% < Br, 6.5% < I, 7.3%). Even though thallium(I) is also a soft acid and has been found capable of coordinating chlorocarbons, our evidence indicates that it does not coordinate the halogen atoms in the thallium halomethanesulfonates. For the first time, the fundamental NQR parameters, the quadrupole coupling constant e^2Qq_{zz}/h and the asymmetry parameter η, have been obtained for halogenated weakly coordinated organic anions, in the silver halomethanesulfonates. Asymmetry parameters so far tend to be smaller for three-coordinated (apical) organohalogen atoms (0.05 and 0.22) than two-coordinate (bridging) organohalogen atoms (0.20−0.42), but they are not necessarily close to zero. We have used the simple Townes−Dailey analysis of NQR frequencies to estimate that there is indeed a significant degree of covalent bonding between the Ag and organohalogen atoms in Ag(**1**): a total of about 0.16 electrons are donated by the iodine atom to its neighbor silver ions. This suggests that although the coordination of such an anion to silver ion may be weak, it is by no means negligible.

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Supporting Information Available: Four X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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