Weakly Coordinating Ligands: Nuclear Quadrupole Coupling Constants and Asymmetry Parameters of Iodocarbons Coordinated to Metal Ions

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NQR (nuclear quadrupole resonance) spectroscopy is potentially one of the best ways of characterizing the bonding of metal cations such as zirconocene cations and Ag^+ to halogen donor atoms in weakly coordinating anions and neutral ligands such as halocarbons. Known coordination of organoiodine atoms to silver ions was studied by ^{127}I NQR spectroscopy in $[Ag(p\text{-}C_6H_4I_2)](PO_2F_2)$, $[Ag(o\text{-}C_6H_4I_2)]NO_3$, $[Ag(CH_2I_2)_2]PF_6$, and the explosive $[Ag(CH_2I_2)]NO_3$; a possible case of iodocarbon coordination to a mercury atom in $C_5Cl_5HgCl{\cdot}CH_2I_2$ was also investigated. Both the low-frequency (*ca.* 300 MHz) and the high-frequency (*ca.* 500 MHz) NQR signals were detected for each compound, and, for the first time, the quadrupole coupling constants e^2Qq_{zz}/h and asymmetry parameters η of coordinated organohalogen atoms were obtained. As compared to the free iodocarbons, substantial (4 - 12%) reductions of e^2Qq_{zz}/h and substantial increases in η (to about 20 - 40%) were found in the iodocarbon complexes of silver, but not of mercury. From approximate theoretical analysis of the data, it appears that the electronic interaction of silver and iodine is quite substantial.

Key words: Nuclear Quadrupole Interaction; ^{127}I NQR; Asymmetry Parameter; Weakly Coordinating Ligands; Iodocarbon Complexes.

Introduction

The catalysts used in the major new "metallocene" industrial process for stereoregular polymerization of alkenes [1] are cations such as $[Zr(C_5H_5)_2CH_3]^+$ ("zirconocene") which must be able to coordinate very weak ligands such as ethylene in order to polymerize them. Catalytic activity is critically affected by the coordinating ability of the anion of the catalyst, which may coordinate to Zr in place of the ethylene. So polymer chemists are seeking very weakly coordinating anions [2] to pair with the zirconocene cations in catalysts.

Weakly coordinating anions are large and of low charge; examples include $CH_3SO_3^-$, $[B(C_6H_5)_4]^-$, and $(CB_{11}H_{12})^-$, but these coordinate too strongly to zirconocene cations. So the coordinating ability of these anions has been reduced by covering their surfaces with very electronegative fluorine to give anions such as $CF_3SO_3^-$ and $[B(C_6F_5)_4]^-$. However, the surface fluorine atoms make these hard Lewis bases still able to coordinate fairly well to hard Lewis acids such as the zirconocene cation and the elusive tris(isopropyl)silylium cation. The most active zirconocene catalysts employ anions with surfaces covered with less electronegative but softer halogen atoms: $(CB_{11}H_6X_6)^-$ (X = Cl, Br, I) [3]. These soft Lewis bases coordinate well to soft Lewis acids such as Ag^+ but less readily to hard acids. The crystal structures of the $(CB_{11}H_6X_6)^-$ salts of the soft silver [4]

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Table 1. Average Crystallographic Results for Halo-carbon and -carborane Complexes of Metals (M = Ag, Si).

Complex	M...X *d* [Å]	Excess *d* [Å]	Angle at X [°]	Conform.	CN (Ag)
$Ag(CB_{11}H_6Cl_6)$	2.780	0.27	105.0	Chelate	6
$Ag(CB_{11}H_6Br_6)$	2.824	0.14	92.6	Chelate	6
$Ag(CB_{11}H_6I_6)$	2.946	0.10	94.2	Chelate	5
$i Pr_3Si(CB_{11}H_6Cl_6)$	2.323	0.15	122.6	Monodentate	
$i Pr_3Si(CB_{11}H_6Br_6)$	2.479	0.16	114.7	Monodentate	
$i Pr_3Si(CB_{11}H_6I_6)$	2.661	0.15	110.3	Monodentate	
$[Ag(Cl_2CH_2)_n]^+$	2.832	0.32	93	Chelate	6
$[Ag(Br_2CH_2)_n]^+$	2.865	0.20	90	Chelate	6
$[Ag(I_2CH_2)]^+(NO_3)^-$ (**1**)	2.843	–0.01	100.4	Bridging	4
$[Ag(I_2CH_2)_2]^+(PF_6)^-$ (**2**)	2.859	0.01	101.5	Bridging	4
$[Ag(o\text{-}I_2C_6H_4)]^+(NO_3)^-$ (**3**)	2.835	–0.01	104.8	Bridging	4
$[Ag(p\text{-}I_2C_6H_4)]^+$-$(PO_2F_2)^-$ (**4**)	2.821	–0.03	103.0	Bridging	4

Excess d: distance in excess of M-X single bond distance; *Conform* = conformation of ligand; *CN*(Ag) = coordination number of Ag^+. For references see text.

and the hard tris(isopropyl)silylium cations have been determined [5]. In all cases, as befits weak coordination, there are metal-halogen contacts of distances in excess of the sums of the covalent radii but well within the sums of van der Waals radii (Table I, "Excess *d*"). The soft silver ion appears to have the closest to a normal covalent bond distance with the softest halogen atom, iodine; while the hard silicon cation does not show any preference for the iodinated anion.

To date, the metal-bonding abilities of few other chlorinated, brominated, or iodinated anions have been studied, while the coordination chemistry of neutral chloro-, bromo,- and iodocarbons have been much more extensively studied. Strauss [6] and Powell [7] have made and crystallographically characterized over two dozen of their Ag^+ complexes. As shown in the bottom half of Table 1, similar trends are shown in the bonding of these ligands to Ag^+: the excess of the bonding distance over the sums of covalent radii diminishes as the halogen becomes softer. Indeed, the Ag-I distance becomes about equal to the sums of Ag and I covalent radii, which suggests strong coordination of iodocarbon ligands. However, the series of dihalomethane complexes is not properly controlled. Dichloro- and dibromomethane chelate the silver ion, which puts geometric constraints on the bond distances and angles, while diiodocarbons bridge silver ions, avoiding the constraints. The coordination number of the silver ion also drops in the iodocarbon complexes, which should allow iodocarbon ligands to approach the metal ion more closely. Hence the crystallographic data do not unambiguouly characterize the degree to which the ligands are weakly coordinating; data from other types of physical measurements are needed to determine this.

When polymer chemists begin producing zirconocene catalysts with chlorinated, brominated, and iodinated anions, instead of using ^{19}F NMR spectroscopy, they will want to study weak coordination using ^{35}Cl, $^{79,81}Br$ and ^{127}I NQR spectroscopy. Halogen NQR is potentially capable of giving useful information such as the number of electrons actually donated by the halogen atoms to the zirconium cation, if both the NQR quadrupole coupling constant, e^2Qq_{zz}/h, which measures the deviation of the electronic environment of the nucleus from spherical symmetry, and the NQR asymmetry parameter, η, which measures the deviation of the electronic environment from axial symmetry, can be obtained. This is most easily done for iodine, since this spin-5/2 nucleus gives two measurable NQR frequencies from which e^2Qq_{zz}/h and η can be computed [8]. In this work we report the first measurements of e^2Qq_{zz}/h and/or η for any coordinated halocarbons or halogenated organic anions.

Experimental

The syntheses [7] of $[Ag(CH_2I_2)]NO_3$ (**1**), $[Ag(CH_2I_2)_2]PF_6$ (**2**), $[Ag(o\text{-}C_6H_4I_2)]NO_3$ (**3**), and $[Ag(p\text{-}C_6H_4I_2)](PO_2F_2)$ (**4**) were scaled up to give gram yields of products.

Caution: Aged samples of $[Ag(CH_2I_2)]NO_3$ were found to be *moderately explosive* upon mild heating (by RF fields in an NQR spectrometer).

The synthesis of **4** involves the hydrolysis of the PF_6^- ion in an intermediate to give its $PO_2F_2^-$ salt; the elemental analysis suggests that some unhydrolyzed PF_6^- was still present. *Anal.* Calcd. for $AgC_6H_4I_2PO_2F_2$: C 13.38%, H 0.75%, F 7.05%. Found: C 11.49%, H 1.13%, F 9.88%. The new compound $C_5Cl_5HgCl.CH_2I_2$ (**5**) was prepared by dissolving 0.30 g (0.6 mmol) C_5Cl_5HgCl in 0.36 g (1.3 mmol) CH_2I_2 plus 0.2 ml CH_2Cl_2, followed by the addition of 1.0 ml pentane. Cooling in a freezer gave 0.32 g of **5**. *Anal.* Calcd. for $C_5Cl_5HgCl.CH_2I_2$: C 9.72%, H 0.27%, I 34.24%; Found: C 9.45%, H <0.5%; I 36.43%.

Table 2. ^{127}I NQR Frequencies ν_1, ν_2, Signal-to-Noise Ratios (S/N) and Parameters at 77 K.

Compound	ν_1 (S/N)[a]	ν_2(S/N)[a]	$\frac{-e^2Qq_{zz}}{h}$[a]	η[a]
CH_2I_2[b]	286.88	568.36	1897.37	0.0858
$[Ag(CH_2I_2)]$-	289.26(20)[d]	574.53(10)[d]	1917.4	0.07
NO_3 (**1**)	284.26(30)[c]	535.37(20)	1800.9	0.22
		516.65(10)	1749.71	0.28
$[Ag(CH_2I_2)_2]$-	305.48(10)	536.75(5)	1826.96	0.335
PF_6 (**2**)	302.63(5)	531.93(10)	1810.39	0.335
	292.76(15)	523.33(20)[c]	1776.1	0.31
	291.98(15)		1776.6	0.30
C_5Cl_5HgCl	284.27	568.36(10)	1894.6	0.015
$\cdot CH_2I_2$[e] (**5**)	276.36(5)	551.29(10)	1838.4	0.045
o-$C_6H_4I_2$[b]	286.92	566.33	1888.3	0.088
$[Ag(o$-$C_6H_4I_2)]$-	282.92(40)	535.85(40)	1802.5	0.20
NO_3 (**3**)	282.51(40)	522.35(40)	1763.1	0.25
	275.31(25)	518.26(25)	1744.6	0.21
	274.50(25)	490.72(25)	1665.4	0.30
p-$C_6H_4I_2$[b]	280.15	559.10	1864.3	0.04
$[Ag(p$-$I_2C_6H_4)]^+$-	291.47(~2)	481.92(2)	1659.0	0.42
$(PO_2F_2)^-$ (**4**)	285.79(~2)	478.95(3)	1643.1	0.40

[a] Units of ν and e^2Qq_{zz}/h are MHz; signal-to-noise ratios (S/N) are given in parentheses. Errors in ν are ±0.01 MHz except for weak signals, for which the errors are ±0.02 MHz. Values of ν_1 and ν_2 have been arbitrarily associated with each other in numerical order for a given compound. Different associations (such as of the two S/N 5 and the two S/N 10 signals in **2**) would result in different e^2Qq_{zz}/h (1817.1 and 1823.4 MHz) and η values (0.35 and 0.31) with similar average values. [b] Source: G. K. Semin, T. A. Babushkina, and G. G. Yakobson, Nuclear Quadrupole Resonance in Chemistry, Wiley, New York 1975, pp. 423, 425. The data for *ortho*-$C_6H_4I_2$ is an average for four very closely-spaced sets of signals. [c] Signal of doubled intensity, therefore likely due to two iodine nuclei. [d] Seen only on a discolored sample that subsequently exploded, so possibly due to a decomposition product. [e] Chlorine-35 NQR signals also seen at 38.76, 37.20, 36.87 (double intensity), and 36.415 MHz.

^{127}I NQR measurements of ν_1 (~300 MHz) as functions of temperature 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. Then the samples were sent to Russia where frequencies below 360 MHz were measured on an ISSH-1-12 pulsed NQR spectrometer (SKB IRE, Russia); those obtained above 360 MHz were measured on a homemade pulsed NQR spectrometer. Except as noted below, agreement within ±0.5 MHz (and often much better) was found for measurements on the superregenerative and pulsed NQR spectrometers; the frequencies obtained on the pulsed NQR spectrometers at 77 K are given in Table 2.

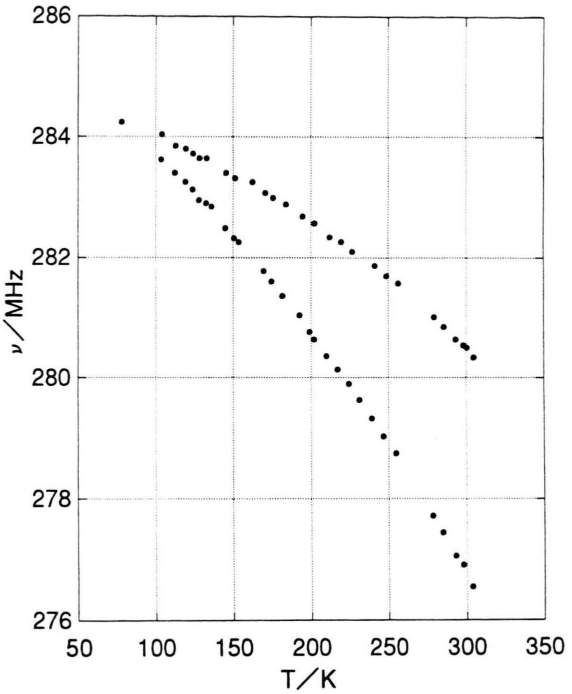

Fig. 1. Temperature dependence of the ^{127}I NQR frequency ν_1 of **1**.

Results

The room-temperature X-ray studies [7] found two crystallographically-distinct iodine atoms in the structure of **1**, four in the structures of **2** and **3**, and one in the structure of **4**; in the absence of phase transitions between 294 K and 77 K this should be the number of ^{127}I NQR frequency pairs (ν_1 and ν_2) seen at 77 K. There are clearly four frequencies of each type in the case of **3**. Since unexpected numbers of ν_1 frequencies were detected in Japan for **1** and **2**, studies were made of their temperature dependence.

Freshly-prepared samples of **1** gave only one ν_1 signal at 77 K, at 284.26 MHz; as seen in Fig. 1, this is due to the accidental coincidence of two signals. The later Russian measurements on this sample of **1**, which had turned explosive and greenish in color by this time (several months later), showed in addition weak extra signals for free CH_2I_2 and a fairly strong pair of signals from an unknown compound at higher frequencies than those of CH_2I_2. We speculate that this unknown compound might be a substitution product such as $CH_2I(NO_3)$, which is likely to be explosive.

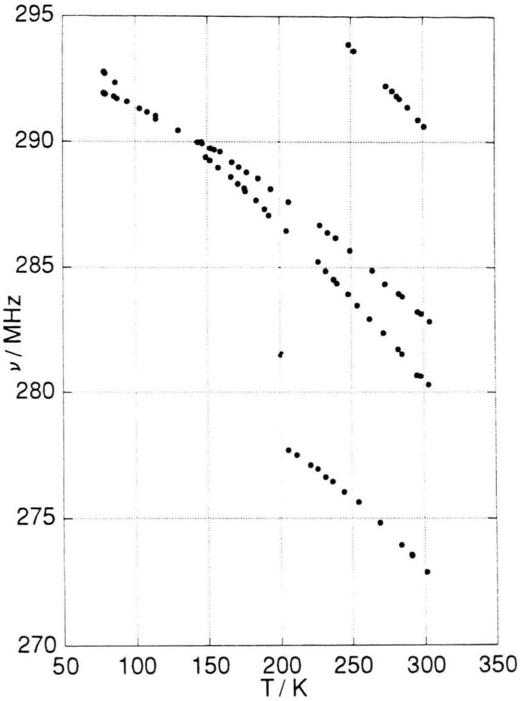

Fig. 2. Temperature dependence of ^{127}I NQR frequency ν_1 of **2**.

The temperature-dependence measurements made in Japan on **2** (Fig. 2) show that two of the four ν_1 signals fade out in intensity at lower temperatures. When this sample was shipped to Russia, somewhat different four-signal spectra were obtained at 77 K (Table 2) and room-temperature, which suggests that the compound may have undergone a phase transition. We do not know which NQR spectrum belongs to the phase for which the crystal structure was determined.

The 77 K NQR spectrum of **4** gave two weak pairs of iodine NQR frequencies, not the one expected from the room-temperature crystal structure (no NQR spectrum could be detected at room temperature). There may also be a phase transition in **4**, or possibly the signals are due to remnants of $[\mathrm{Ag}(p\text{-}C_6H_4I_2)_n](PF_6)$. Hence it is not safe to correlate fine details of the crystal structures and NQR parameters for compounds **2** and **4**.

Discussion

Due to the presence of a strong covalent sigma bond to carbon, an iodocarbon iodine atom has a high value of e^2Qq_{zz}/h, since the iodine is far from having the spherical symmetry that it has in the iodide ion. Coordination to a metal ion *via* a second (coordinate) covalent bond is expected to reduce the e^2Qq_{zz}/h of the iodocarbon, since upon coordination electrons are being donated (to carbon and to the metal) from two of the three *5p* orbitals of the iodide ion. In accord with these expectations, the quadrupole coupling constants we obtained [9] for silver-coordinated diiodomethane range from 1826.96 to 1749.7 MHz, from 3.7% to 7.8% below the 1897.37-MHz value for CH_2I_2 itself. The values for coordinated *ortho*-diiodobenzene range from 1802.5 to 1665.4 MHz, from 4.5% to 11.8% below the average 1888.3-MHz value for free o-$C_6H_4I_2$; the values for coordinated *para*-diiodobenzene, 1659-1643 MHz, fall 11.0 - 11.8% below the 1864-MHz value for free p-$C_6H_4I_2$.

The asymmetry parameter η of the iodine atom in a normal iodocarbon is quite small, since it has approximate axial symmetry. Formation of a bond to *one* metal ion breaks the axial symmetry and should result in an increased value of η. Iodide ions coordinated strongly and equally to two metal ions can have η values as large as 1.00 (0.18 in Al_2I_6, 0.24 in Ga_2I_6, 0.24 in In_2I_6; and 0.53 in polymeric red HgI_2) [8]; the bridging iodine atoms in diphenyliodonium halides show η values from 0.37 to 0.47 [10]. By way of comparison, when a halide ion is strongly coordinated to one metal ion and is weakly coordinated to another, η values are smaller: between 0.057 and 0.182 in fifteen Hg-I···Hg, Sn-I···Sn, and Group 15-I···Group 15 inorganic two-coordinate bridged systems [11]. The 0.2 to 0.4 values of η in Table 2, the first ever measured for coordinated halocarbons, fall between these ranges.

In theory, iodine orbital populations can be obtained using the Townes-Dailey theory as applied to two-coordinate quadrupolar nuclei. However, this theory manifests itself differently depending on whether the two bonding interactions are equal (as in Al_2I_6 or diphenyliodonium ion) or are unequal in strength (strong to carbon, weak to metal). In the former case [12], the Townes-Dailey treatment allows the calculation of N, the populations of the two bonding orbitals of the bridging iodine atom:

$$(2 - N) = (e^2Qq_{zz}/e^2Qq_{\mathrm{at}})(1 + \eta/3), \qquad (1)$$

where e^2Qq_{at}/h is the quadrupole coupling constant of a free iodine atom, –2292.712 MHz.

Assuming hybridization at the iodine is fixed by the bond angle θ, the equation $\eta = -3 \cos \theta$ can also be derived [12]. This equation fits known bond angles at iodine in diphenyliodonium halides and Group 13 metal iodides fairly well, but fails seriously for these iodocarbon complexes: in **1**, the average η is 0.25 but the average $(-3 \cos \theta)$ is 0.54; in **3** these are 0.24 and 0.76 respectively.

In the case of unequal bonding, (1) also results for the calculation of the population of the strong bond (the C-I bond), but a different equation results for the population N_y of the iodine $5p_y$ orbital engaged in weak coordination to the metal [11]:

$$(2 - N_y) = (e^2Qq_{zz}/e^2Qq_{\mathrm{at}})(2/3\eta). \qquad (2)$$

The quantity $(2-N_y)$ is the *covalent bond order* of the Ag-I bond. Taking the average values of e^2Qq_{zz}/h and η for **1** and applying (1), we compute $N = 1.16\ e^-$ for the population of the iodine orbital engaged in bonding with carbon, which is virtually unchanged from $N = 1.15\ e^-$ for free diiodomethane. This fits with the observation that the C-I bond length (average of 2.11 Å for compounds in this study [7]) is insignificantly longer than the sum of the covalent radii of C and I, 2.10 Å. If the bonding to silver is equivalent, then the I-C and I-Ag bonds are both nearly full nonpolar covalent bonds, and the iodine atom should resemble that in diphenyliodonium ion, i. e. to be positively charged. But if we apply the weak-bonding model and (2), we compute an average Ag-I covalent bond order of 0.13, and the iodine atom is virtually neutral; it has donated to Ag^+ nearly all of the $-0.15\ e^-$ charge it had in free CH_2I_2. Very similar values are computed for **2**, **3**, and **4**.

In contrast, e^2Qq_{zz}/h of one of the iodines of **5** is virtually the same as that of the free CH_2I_2 ligand, suggesting that this iodine atom is not coordinated to mercury. The e^2Qq_{zz}/h value of the other iodine atom is 3.1% below that of the free ligand, which is probably more than can be accounted for from solid-state crystal field effects [13]. And the average ^{35}Cl NQR frequency of its non-coordinated vinylic chlorines [14], 36.98 MHz, falls between the corresponding averages in C_5Cl_5HgCl (β-form 37.158 MHz, γ-form 37.118 MHz) and in $C_5Cl_5HgCl \cdot$diglyme (36.592 MHz) [15]. This would be expected if CH_2I_2 were acting as an electron donor, but one which is weaker than diglyme. The small value of η is consistent either with coordination of this iodine atom to *two* mercury atoms, a situation with approximate axial symmetry, or with no coordination of the iodine atoms. If a crystal structure determination were to establish the former environment for this iodine atom, **5** would provide a good example of the NQR characteristics of an extremely weakly coordinated ligand, such as is desired in metallocene catalysts.

Conclusions

Coordination of even so weak a ligand as an iodocarbon produces very marked changes in the quadrupole interaction parameters: the quadrupole coupling constant is significantly lowered and, if only one metal coordinates to the iodine, the asymmetry parameter is greatly raised. Two Townes-Dailey estimations of the numbers of electrons donated to the metal ion give quite different results, so more sophisticated calculations should be carried out. Computations involving such heavy atoms are non-trivial, but have been carried out on rhenium complexes of iodocarbons [16], for which no NQR data exist. Both simple Townes-Dailey calculations indicate that weakly coordinating ligands such as iodocarbons can donate significant electron density to silver ion. Since the general crystallographic parameters of iodocarbons and iodocarborane anions complexed to Ag^+ are similar, we anticipate similar results for silver salts of halogenated anions, and will report results on these later, followed by results for hard-acid cations similar to silylium or zirconocene cations.

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