Iodine-127 Mössbauer Study of Iodine(III) Interhalogen Cations and Related Compounds

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The ^{127}I Mössbauer spectra of a number of iodine(III) cations and related molecules having four ligands and two non-bonding electron pairs about the central iodine have been recorded at 4.2 K. The Mössbauer parameters are dominated by the primary bonds to the iodine which are largely of *p* character.

We have recently reported ^{127}I Mössbauer data for a series of linear $[XIY]^-$ anions of iodine(I) where X and Y can be F, Cl, Br, or I.[1] We found that the Mössbauer parameters could be correlated with the sum of the electronegativities of the ligands X and Y, except when X and/or Y were fluorine. In these latter cases the lack of correlation was attributed to the propensity for fluorine to be involved in bridging interactions to adjacent anions. This destroys the symmetry about iodine through weak I $\cdots$ F interactions which are off the $[X-I-Y]^-$ axis. These data were used to check the relationship between the isomer shift and the population parameters for the *s* and *p* iodine atomic orbitals. This relationship has since been modified as a result of a careful examination of some potential single-line absorbers and we have made the recommendation that KI be the preferred choice as the substance against which all iodine Mössbauer isomer shifts be referred.[2,3]

In order further to test these empirical relationships we decided to extend the range of compounds of iodine(III) that have already been studied by Mössbauer spectroscopy.[4,5] Here we present data for a number of compounds of iodine(III) which have been characterised by *X*-ray crystallography and which all have four ligands in a near planar environment about the iodine. The Mössbauer data are discussed in terms of the bond distances and the electronegativities of the ligands bound to iodine.

Experimental

The compounds were prepared by established procedures,[6-10] while $[I_3][AsF_6]$ was supplied by Professor Passmore,[11] and their authenticity verified by *X*-ray crystallography and/or Raman spectroscopy and melting point.

Iodine-127 Mössbauer spectra were recorded as described earlier with all samples and the source immersed in liquid helium at 4.2 K.[1,7] The Zn^{127m}Te (20 mCi) source was purchased from New England Nuclear Corporation. Spectra were calibrated by using an iron-foil absorber and a ^{57}Co/Rh source. All spectra were computer fitted using a program previously described which incorporates full transmission-integral procedures.[12] In cases where the compound contained two iodine sites the linewidths of the two overlapping spectra were constrained to be equal; the relative intensities of the two sites were fixed at their atomic ratios and it was assumed that the Debye temperatures for the two sites would be the same. The possibility of crystallite orientation was also allowed for in the fitting procedure: this effect was found to be small.

Results and Discussion

The data obtained are summarized in Table 1. Included in this Table are literature data for $K[ICl_4]\cdot H_2O$ [4] and for I_2Cl_6 and $I_2Cl_4Br_2$,[5] the isomer shifts for these latter compounds having been converted from ^{129}I data to their ^{127}I equivalents by multiplying by -0.345.[13] Only for I_2Cl_6 and $[ICl_4]^-$ are there literature data with which we can compare our results. For I_2Cl_6 our data are in good agreement with the values of Pasternak and Sonnino,[5] considering the errors involved in converting ^{129}I results into their ^{127}I equivalents. The agreement between our data for the $[ICl_4]^-$ ion and those of Perlow and Perlow [4] are also reasonable considering that our material was anhydrous whereas the earlier data were reported for the hydrated salt. A typical spectrum is shown in Figure 1, with the line due to the $\frac{5}{2}$ (ground) — $\frac{5}{2}$ (excited) transition in the energy level scheme being at high negative velocity.[14] This situation applies to all of the compounds examined in this work and indicates that the quadrupole coupling constant, $e^2q^{127}Q_g/h$, is positive for all of them. Since $e^{127}Q_g$ is negative, the sign of the electric-field gradient must therefore also be negative and hence the values are those expected for a central iodine bonded to four ligands in the *xy* plane, with the non-bonded electron pairs along the *z* axis.

Examination of the data in Table 1 reveals that the interhalogen cations with the same terminal I–X interactions, *i.e.*

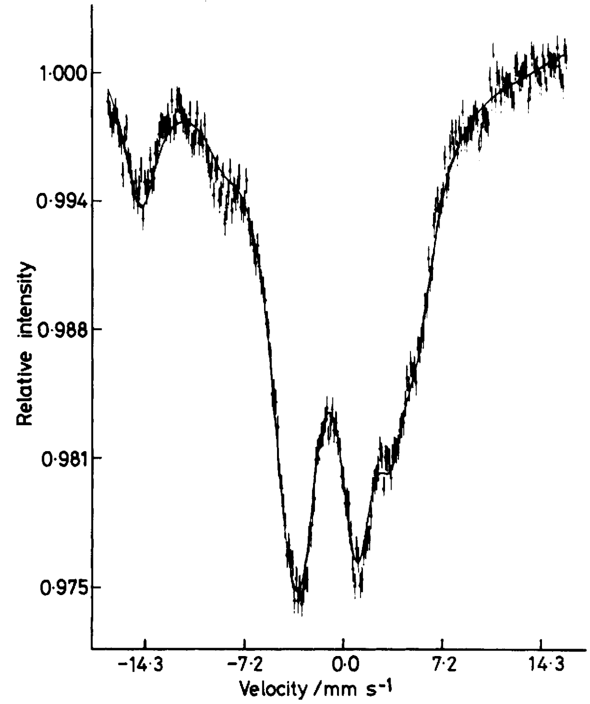


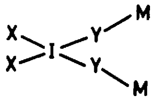
Figure 1. The ^{127}I Mössbauer spectrum of $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ measured at 4.2 K. The solid line is the best fit to the data

Table 1. Iodine-127 Mössbauer data for iodine(III) cations and related species

Compound	Isomer shift mm s^{-1}	$e^2q^{127}Q_g/h$ MHz	η	Γ mm s^{-1}	T_A [a]	χ^2/ degrees of freedom	$\lvert U_p \rvert$	h_p (h_s = 0)	h_s (h_p = $2U_p$)
$[ICl_2][SbCl_6]$	−1.28(5)	3 066(30)	0.08(6)	2.02(18)	1.47(10)	0.83	1.34	1.90	0.13
$[ICl_2][SbF_6]$	−1.27(5)	3 066(30)	0.25(2)	1.59(14)	0.85(8)	0.96	1.34	1.89	0.13
$[IBr_{0.75}Cl_{1.25}][SbCl_6]$	−1.24(1)	2 860(9)	0.22(1)	1.82(5)	1.36(2)	1.54	1.25	1.83	0.11
$[IBr_2][Sb_2F_{11}]$	−1.09(8)	2 758(13)	0.31(1)	2.54(8)	1.55(2)	1.74	1.20	1.59	0.13
$[I_3][AsF_6]$	−0.59(11)	2 267(54)		2.31(18)	1.53(11)	1.03	0.99	0.77	0.20
	−0.87(5)	−2 880(26)					1.26	1.23	0.00
I_2Cl_6	−1.41(3)	3 028(19)	0.09(3)	2.68(15)	0.44(1)	1.28	1.32	2.11	0.09
	−1.39(2) [b]	3 060(10)	0.06(2)				1.33		
$I_2Cl_4Br_2$ [b]	−1.37(1)	3 040(10)	0.06(2)				1.33		
	−1.14(1)	2 916(10)	0.06(2)				1.27		
$K[ICl_4]$	−1.44(2)	3 097(8)	0.02(1)	2.37(5)	1.37(2)	4.16	1.35	2.16	0.09
$K[ICl_4]\cdot H_2O$ [c]	−1.53	3 094(20)							
$(Ph_2ICl)_2$	−0.54	2 044(19)	0.31(2)	2.13(13)	0.32(1)	0.98	0.89	0.69	0.18
$(Ph_2IBr)_2$	−0.68(2)	1 970(13)	0.36(1)	1.81(8)	0.81(3)	1.15	0.86	0.92	0.13
$(Ph_2I_2)_2$	−0.71(5)	1 951(33)		2.08(13)	0.51(2)	1.60	0.85	0.97	0.12
	0.04(4)	−780(33)					0.34	−0.26	0.10
KI	0								
$Na_2[H_3IO_6]$	0.89(2)								

[a] See ref. 12 for definition. [b] Ref. 5; data have been converted from ^{129}I results. [c] Ref. 4.

Table 2. Geometry around iodine in $[IX_2][MY_6]$ and related compounds



Compound	Ref.	I–X/Å	I···Y/Å	$[IX_2Y_2]$ [a]
$[ICl_2][SbF_6]$	7	2.268(2)	2.650(6)	13.9
$[ICl_2][SbCl_6]$	15	2.33(4) 2.29(4)	2.85(4) 3.00(4)	7.9 [b]
$[ICl_2][AlCl_4]$	15	2.29(4) 2.26(4)	2.86(4) 2.88(4)	4.1 [b]
I_2Cl_6	16	2.38(3) 2.39(3)	2.72(3) 2.68(3)	0
$[IBr_2][Sb_2F_{11}]$	8	2.424(3) 2.422(3)	2.845(12) 2.782(12)	4.7
$[IBr_{0.75}Cl_{1.25}][SbCl_6]$	8	2.427(2) 2.373(3)	2.927(3) 2.976(3)	0.9
$[I_3][AsF_6]$	11	2.660(2) 2.669(2)	3.01(1) 3.07(1)	11.1 [c]
$K[ICl_4]$	17	2.34		

[a] $[IX_2Y_2]$ represents the angle in degrees between the two planes defined by IX_2 and IY_2. [b] Calculated here from atomic positions in ref. 15. [c] Calculated here from atomic positions in ref. 11.

$[ICl_2][SbCl_6]$ and $[ICl_2][SbF_6]$, have the same value for their quadrupole coupling constants despite the fact that the bridging I···Y interactions are not the same, *i.e.* I···Cl in $[ICl_2][SbCl_6]$ and I···F in $[ICl_2][SbF_6]$. The constancy in these coupling constants is at first somewhat surprising since we have found that for a series of linear $[X\text{–}I\text{–}Y]^-$ (X,Y = Cl, Br, or I) anions the quadrupole coupling constant increased as the electronegativity of both X and Y ligands increased. Apparently this behaviour does not seem to carry over to bridging interactions, although it should be pointed out that the secondary I···Cl interactions in $[ICl_2][SbCl_6]$ have been shown to be of approximately the same strength as the secondary I···F interactions in $[ICl_2][SbF_6]$.[7] The implication is that the total electron density in the *xy* plane does not change significantly in these two compounds. Indeed this would appear to be the case for all the compounds containing I–Cl bonds examined in their series, except for the disordered cation. All of these species have rather invariant quadrupole coupling constants in the range 3 028—3 097 MHz suggesting that as the strength of one interaction in the *xy* plane increases, the interaction directly opposite in the same plane decreases in strength. This is apparent in the crystallographic data summarised in Table 2 where the average I–Cl bond length of 2.31 Å in $[ICl_2][SbCl_6]$ [15] lengthens to 2.39 Å in I_2Cl_6 [16] as the average secondary I···Cl contact shortens from 2.93 Å to 2.70 Å. In $[ICl_4]^-$ all I–Cl bonds have the same length at 2.34 Å.[17] de Waard *et al.*[18] noticed a similar effect on the ^{129}Xe quadrupole coupling constants in a series of Xe–F compounds.

However, as the terminal halogen bonded to the central iodine of the cations is varied the magnitude of the quadrupole coupling constant changes and $e^2q^{127}Q_g/h$ values are in the order $[ICl_2]^+ > [IBr_{0.75}Cl_{1.25}]^+ > [IBr_2]^+ > [I_3]^+$, which follows the order of decreasing halogen electronegativity. Since

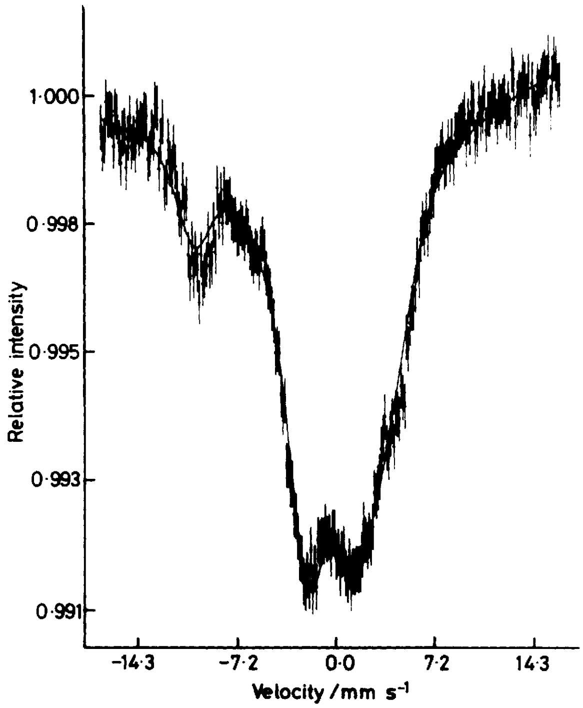


Figure 2. The ^{127}I Mössbauer spectrum of $(Ph_2ICl)_2$ measured at 4.2 K. The solid line is the best fit to the data

the disordered cation $[IBr_{0.75}Cl_{1.25}]^+$ has, on average, both chlorine and bromine bonded to the central iodine, $e^2q^{127}Q_g/h$ lies between that for the $[IBr_2]^+$ and $[ICl_2]^+$ cations. The ^{127}I Mössbauer spectrum of $[IBr_{0.75}Cl_{1.25}][SbCl_6]$ (Figure 1) was computed incorporating only one iodine site. Attempts were made to fit the spectrum to two sites, which might arise from, for example, a mixture of $[ICl_2]^+$ and $[IBr_2]^+$ species or one of these and $[IBrCl]^+$ but the fits were inferior to that shown and the parameters unreasonable. On the basis of Mössbauer spectroscopy it seems likely that the cation $[IBr_{0.75}Cl_{1.25}]^+$ is indeed a truly disordered mixture of the $[ICl_2]^+$ and $[IBr_2]^+$ and $[IBrCl]^+$ cations.

It would appear then that in these compounds it is mainly the primary bonding interactions to the central iodine atom which determine the magnitude of the quadrupole coupling constant. There is however a correlation between terminal ligand electronegativity and quadrupole coupling constant similar to that found for the linear $[X{-}I{-}Y]^-$ anions. In order to test the influence of bridging groups upon the Mössbauer parameters of the central iodine we examined the $(Ph_2IX)_2$ (X = Cl, Br, or I) series of compounds whose structures have been determined by Alcock and Countryman.[19] Each iodine is in a planar arrangement with two bonds to carbon and two bridging bonds to the X halogen. These compounds are described as $([Ph_2I]^+[X]^-)_2$ systems held together by secondary bonds.[19]

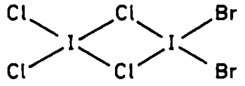
The Mössbauer spectrum of $(Ph_2ICl)_2$ is shown in Figure 2. The quadrupole coupling constants found for these diphenyliodonium halides $(Ph_2IX)_2$ (X = Cl, Br, or I) are significantly smaller than those of the other compounds in Table 1, where the quadrupole coupling constants are mainly influenced by the strong primary iodine–halogen bonds. In the $(Ph_2IX)_2$ series the primary bond is from iodine to carbon which is much less electronegative than the halogens. The bridging iodine–halogen bonds are less significant in determining the magnitude of the quadrupole coupling constant since they are longer, weaker bonds. For example, the bridging $I \cdots Cl$ interactions in $(Ph_2ICl)_2$ average 3.085 Å, a distance which is longer than the bridging $I \cdots Cl$ interactions in $[ICl_2][SbCl_6]$[15] and $[ICl_2][AlCl_4]$,[15] which average 2.90 Å. Again it is noted that the quadrupole coupling constants decrease with decreasing electronegativity of the bridging halogen although the effect is less dramatic (2 044—1 951 MHz) than when the terminal halogens are varied (~3 060—2 267 MHz). It is the primary bonds to iodine which mainly determine the magnitude of the quadrupole splitting although the bridging or secondary contacts modify the final value. These secondary interactions are however extremely important in determining the sign of the quadrupole coupling constant at the iodine nucleus.

Most of the compounds studied have a significant η value so that although the principal axis of the electric-field gradient is along the direction of the non-bonded electron pairs perpendicular to the IX_2Y_2 plane there is some degree of asymmetry in the x and y directions. In I_2Cl_6, $[ICl_4]^-$, and $[ICl_2][SbCl_6]$ where all the halogen ligands about the iodine are the same, and where the $[ICl_4]$ rectangular unit is nearly planar, the value of η is small. However, in $[ICl_2][SbF_6]$ where the bridging chlorines have been replaced by bridging fluorines, and the ICl_2F_2 rectangular unit is no longer planar, $\eta = 0.25$. Similarly in the remaining compounds, if X and Y in the IX_2Y_2 rectangular unit are not the same the value of η ranges from 0.25 to 0.36. Large asymmetry parameters for the central iodine atoms in $[I_3]^+$ and $(Ph_2I_2)_2$ would also have been expected, but it was not possible to extract reliable η values from these spectra because of the complexity caused by two overlapping iodine absorption envelopes.

The chemical isomer shifts of all of the compounds examined are all more negative than KI which was used as the reference substance. Since $\delta R/R$ is negative for ^{127}I[14] this means that the total s electron density at the iodine in these compounds is greater than in the iodide ion. These isomer shifts appear to be dominated by the primary interactions as were the quadrupole coupling constants. In the $[IX_2]^+$ cationic series the isomer shifts become more positive as the electronegativity of X becomes smaller, *i.e.* the iodine in $[ICl_2]^+$ has the highest s electron density while $[I_3]^+$ has the lowest. The terminal iodines in $[I_3]^+$ have Mössbauer parameters expected for an iodine with one strong covalent interaction with the principal component of the electric-field gradient tensor lying along the iodine–iodine bond, as in I_2. The geometry around the iodine in these species could be viewed, in valence bond terms, either as sp^3 or sp^3d^2 hybridized depending upon the extent of cation–anion interaction. However, the Mössbauer data suggest that the s character of the bonds in these compounds is low and that the bonds are largely of p, with perhaps some d, character.

In I_2Cl_6 and $[ICl_4]^-$ the s electron density at the iodine is even higher, implying a negligible s participation in the bonds to chlorine. On going from $[ICl_2][SbCl_6]$ through I_2Cl_6 to $K[ICl_4]$, a series in which the iodine is bonded only to chlorine atoms, there is a gradual increase in s electron density which parallels the decrease in average I–Cl bond length. These range from 2.618 Å for $[ICl_2][SbCl_6]$, through 2.54 Å for I_2Cl_6, to 2.34 Å for $K[ICl_4]$. Presumably the shorter, stronger I–Cl bond results in the withdrawal of more p electrons from the central iodine thereby reducing the shielding effect on the s electrons and giving a more negative isomer shift. In this series of three compounds one might have expected that the formal charge on the ions would have strongly influenced the isomer shift such that the positive charge on the $[ICl_2]^+$ cation would result in a contraction of the s orbitals and thereby increase the s electron density, while the negative charge on the $[ICl_4]^-$ anion would have the opposite effect. This does not happen and one is led to the conclusion that these charges are not localised on the central iodine atom.

Data obtained by Pasternak and Sonnino [5] on $I_2Cl_4Br_2$ are included in Table 1 for comparison purposes. Their measurements were made using the ${}^{129}I$ isotope [5] and these have been converted to their ${}^{127}I$ equivalents. Based on a comparison with data for I_2Cl_6 and IBr they concluded that the molecule had the asymmetric structure shown below. The Mössbauer



parameters for this molecule follow very well the trends discussed above for these interhalogen molecules and confirm the postulated structure.

The isomer shifts of the diphenyliodonium halides are much less negative that the other compounds. Because of the difficulty of fitting the $(Ph_2I_2)_2$ spectrum, due to the presence of two iodine sites whose individual absorption envelopes strongly overlap, the isomer shift values for this compound may not be very reliable. The apparent trend from −0.54 to −0.71 mm s^{-1} on going from $(Ph_2ICl)_2$ to $(Ph_2I_2)_2$ may then not be significant. It is apparent that there is much less withdrawal of *p* electron density by the phenyl group than by a terminal halogen. This results in a greater shielding of the *s* electrons from the nuclear charge and an effective lowering of the *s* electron density.

In Table 1 we have calculated values for U_p, the imbalance in the *p* orbitals, and h_p and h_s, the magnitude of the electron holes in the iodine 5*s* and 5*p* orbitals relative to the closed shell of the iodide ion, where $U_p = -e^2q_{\text{mol}}{}^{127}Q_g/h$ divided by 2 293 MHz and h_p and h_s are obtained from equation (1) (in

$$ {}^{127}\delta(\text{mm s}^{-1}) = 3.74\, h_s - 0.61\, h_p - 0.12 \qquad (1) $$

an earlier publication [3] we reported this equation incorrectly). It is obvious from the data that there is not very good agreement between U_p and h_p calculated from equation (1) assuming that there is no participation of *s* electrons in the bonds (*i.e.* $h_s = 0$). Either equation (1), which was derived from data on the linear $[X\text{–}I\text{–}Y]^-$ series of compounds,[1,3] is not of general applicability or there is some *s* participation and h_s cannot be zero. Calculations of h_s from equation (1), assuming that $h_p = 2U_p$, gives values for h_s which are all *ca.* 0.13. This appears rather high in view of the trends in Mössbauer parameters discussed above. However when these empirical relationships are used to calculate orbital-occupation numbers the lattice contribution to the quadrupole coupling constant is always neglected and this may lead to considerable error in the h_s and h_p values obtained. Grodzicki *et al.*[20] have recently used a self-consistent field approach with charge molecular-orbital calculations to estimate the various contributions to the electric-field gradient with some success. However none of the compounds reported in this investigation was included.

Conclusions

A number of compounds of iodine(III) have been examined by ${}^{127}I$ Mössbauer spectroscopy. Agreement with literature data for $K[ICl_4]$ and for I_2Cl_6, the latter after conversion from ${}^{129}I$ data, is good. The Mössbauer parameters are consistent with largely *p* character for the ligand–iodine bonds. The central iodine in all of the compounds has a positive quadrupole coupling constant indicating that the principal component of the electric-field gradient is along an axis perpendicular to the near planar ligand arrangement. These changes in Mössbauer parameters are dominated by the two primary bonding interactions and the bridging ligands which complete the arrangement about the iodine have only a minor, although significant, effect on the data.

Acknowledgements

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