

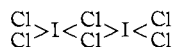
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Chlorine Nuclear Quadrupole Coupling in Iodine Trichloride and in Its Adduct with Aluminum Trichloride

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Nuclear quadrupole coupling data have yielded much knowledge of the nature of chemical bonding in the interhalogen compounds. Cornwell and Yamasaki¹ showed that, in the ions ICl_2^- and ICl_4^- , the attainment of higher valencies by the iodine is due more to transfer of charge to chlorine atoms than to promotion to higher iodine orbitals, the previously favored supposition. The same authors also considered the available coupling data for the chlorine² and the iodine³ nuclei of iodine trichloride which had earlier been shown by X-ray methods to possess a planar, dimeric, bridged structure in the solid phase⁴



with all angles close to 90° . Two observed resonances near 34 Mc/sec, which had been initially assigned to the terminal and to the bridging chlorine atoms,² were reassigned to the terminal nuclei only; these fall into two sets which differ slightly in their crystalline environments. The bridging chlorine resonance was predicted to occur near 11 Mc/sec. This prediction has apparently not yet been tested and this was one of the purposes of the present study; the expected resonance was indeed observed near 13.7 Mc/sec. The second purpose was to determine the coupling constant for the Cl atoms in the ICl_2^+ ion. An assumed value for this quantity was used in interpreting the observed resonances of ICl_4^- and I_2Cl_6 in terms of resonance hybrid structures.¹ X-Ray studies have established the presence of this cation in $\text{ICl}_2^+\text{AlCl}_4^-$.⁵ Although it appears that the considerable cation-anion interaction which exists in this solid will modify the electronic structure of the cation, in the absence, at present, of a better example of an ICl_2^+ salt, this was chosen for study.

Experimental Section

Iodine trichloride was prepared by treating solid I_2 with excess liquid Cl_2 at approximately -70° ; the yellow mixture was kept at this temperature for 1 hr after which the excess Cl_2 was distilled away at *ca.* -25° . The resulting orange solid, I_2Cl_6 , was sealed in the nqr sample tube. The frequency range 10–40 Mc/sec was scanned, with the sample held at $24 \pm 0.2^\circ$, using a superregenerative spectrometer constructed in this laboratory under

W. O. Swan's direction; the design is similar to that described by Petersen and Bridenbaugh.⁶ Frequencies were measured with a BC-221 AA frequency meter. The detection and measurement of the corresponding, weaker Cl^{37} resonance provided, in each case, an additional independent check. The observed resonances are tabulated and assigned in Table I.

TABLE I
OBSERVED RESONANCES FOR I_2Cl_6 AT 24°

Frequency, Mc/sec ^{a-c}	Nucleus	Location of nucleus
34.918	Cl^{35}	Terminal (set I)
33.413	Cl^{35}	Terminal (set II)
27.528	Cl^{37}	Terminal (set I)
26.338	Cl^{37}	Terminal (set II)
13.740	Cl^{35}	Bridging (both nuclei) ^d
10.82	Cl^{37}	Bridging (both nuclei) ^d

^a Uncertainty in frequencies ± 0.003 Mc/sec. ^b The first two resonances were detected previously, at a different temperature,² but the remaining four were not. ^c The I^{127} data³ were interpreted to yield a value of +2989.3 Mc/sec for the coupling constant (at 20°). ^d The observation of only one resonance for the two bridging Cl^{35} atoms shows that they are equivalent.

$\text{ICl}_2^+\text{AlCl}_4^-$ was prepared by treating a mixture of I_2 and AlCl_3 , in the appropriate ratio, with excess Cl_2 at approximately -70° . After 1 hr the excess Cl_2 was distilled away at *ca.* -25° and the resulting dark red solid was sealed in the nqr sample tube at room temperature. It was examined over the frequency range 10–52 Mc/sec. Two adjacent resonances were observed at 38.690 and at 39.086 Mc/sec and these are assigned to the ICl_2^+ ion. Several resonances were also observed near 11.4 Mc/sec; these are assigned to the AlCl_4^- ion (Table II).

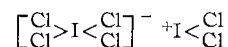
TABLE II
OBSERVED RESONANCES FOR IAlCl_6 AT 24°

Frequency, Mc/sec	Nucleus	Location of nucleus
39.086	Cl^{35}	ICl_2^+
38.690	Cl^{35}	ICl_2^+
11.42	Cl^{35}	AlCl_4^-
11.40		
11.31		

^a The complex resonance observed was, somewhat arbitrarily, resolved into three separate resonances.

Discussion

The experimental data for I_2Cl_6 confirm the earlier observations of two terminal Cl^{35} resonances near 34 Mc/sec² and also Cornwell and Yamasaki's prediction of the approximate frequency of the bridging Cl^{35} resonance. This prediction was based on the expectation that the molecule is well presented as a hybrid of two equivalent structures of the type



in which the $[\text{ICl}_4]^-$ group is similar to the ICl_4^- ion. The coupling constant for the terminal Cl^{35} should then be the average of the values for the ICl_4^- ion (-44.6 Mc/sec, observed) and for ICl_2^+ (-89.2 Mc/sec, estimated¹), or -66.9 Mc/sec; the resonance should appear near 33.5 Mc/sec. The presently obtained data for ICl_2^+ —the mean value of the two observed resonances which are assigned to the two Cl^{35} atoms in slightly different crystalline environments yields a

(1) C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, **27**, 1060 (1957); **30**, 1265 (1959).

(2) P. J. Bray, *ibid.*, **23**, 703 (1955).

(3) S. Hagiwara, K. Kato, Y. Abe, and M. Minematsu, *J. Phys. Soc. Japan*, **12**, 1166 (1957).

(4) K. H. Boswijk and E. H. Wiebenga, *Acta Cryst.*, **7**, 417 (1954).

(5) C. G. Vonk and E. H. Wiebenga, *ibid.*, **12**, 859 (1959).

(6) G. E. Petersen and P. M. Bridenbaugh, *Rev. Sci. Instr.*, **35**, 698 (1964).

coupling constant of 77.8 Mc/sec—do not significantly change this expectation; the expected value is lowered to 30.7 Mc/sec.

For the bridging chlorine atoms the unique symmetry axis is normal to the molecular plane and the coupling constant along this axis should be the same as that of the chlorine nuclei in ICl_4^- in *this same* direction, +22.3 Mc/sec. The resonance should then appear near 11.2 Mc/sec for the Cl^{35} atoms; the observation of the resonance at 13.7 Mc/sec shows that the postulated contributing structures provide a fairly reasonable approximation to the molecular structure.

A refinement of this description is possible now that quadrupole coupling data are available for all of the nuclei in the molecule. The procedures devised by Townes and Dailey⁷ yield the electric field gradient q at the nucleus of interest as a sum of contributions by the valence p electrons only

$$q = q_0[N_z - \frac{1}{2}(N_x + N_y)]$$

where N_i is the electron population of the valence p_i orbital and eq_0Q/h is the known contribution of one p electron to the coupling constant. The z axis is the unique principal axis for the field gradient tensor at the nucleus of interest, and it lies along the I-Cl bond for each terminal Cl atom but perpendicular to the molecular plane for the bridging Cl atoms and the iodine atoms.

Substitution of $eqQ/h = -68.34$ Mc/sec (mean of observed), $eq_0Q/h = +109.74$ Mc/sec,⁷ and $N_x = N_y = 2$ electrons in the expression given above yields a value of $N_z = 1.38$ for the number of electrons in the bonding orbitals of each terminal Cl atom. This is a gain of 0.38 electron at each terminal Cl atom over the electron population of this orbital in the unbonded atom.

For the bridging chlorine atoms in the ideal, square configuration—to which the molecule approximates rather closely—the in-plane p_x and p_y orbitals are completely equivalent so that $N_x = N_y$; the p_z orbital contains a lone pair so $N_z = 2$. With $eqQ/h = +27.48$ Mc/sec, the total electron population of the two planar p orbitals is $N_x + N_y = 3.50$ electrons. Since the unbonded Cl atom has 3 electrons in these orbitals, this represents a gain of 0.5 electron at each bridging Cl atom.

The iodine atoms are equivalent⁸ and for these also, $N_x = N_y$ and $N_z = 2$. The observed coupling constant of +2989 Mc/sec and the value¹ +2640 Mc/sec for eq_0Q/h yield $N_x + N_y = 1.74$ electrons, *i.e.*, a loss of 1.26 electrons at each iodine atom.

The total electron population in the molecular orbitals which are formed by combinations of the valence p atomic orbitals is thus given by the nqr data as

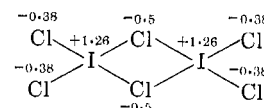
$$(4 \times 1.38)_{\text{Cl}} + (2 \times 3.50)_{\text{Cl}} + (2 \times 1.74)_{\text{I}} = 16.0 \text{ electrons}$$

These same atomic orbitals in the unbonded atoms contain

$$(4 \times 1)_{\text{Cl}} + (2 \times 3)_{\text{Cl}} + (2 \times 3)_{\text{I}} = 16 \text{ electrons}$$

(7) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949); **23**, 118 (1955).

The exact agreement is, of course, fortuitous, and, as soon as refinements are introduced, the bonding electron population calculated from the nqr data will fall below the quoted total; for example, the use of sp hybrid orbitals instead of the pure p orbitals considered for the terminal chlorine atoms would reduce the total bonding population by about 0.4 electron if the usual assumption of 15% s character for the Cl orbitals were used. For our present, qualitative purpose, the approximation of using p orbitals suffices to yield estimates of the formal charges at each atom



These values show that considerable transfer of charge from the iodine to the chlorine atoms occurs.

IAlCl_6

An X-ray study of this material⁵ revealed a structure containing distinct ICl_2^+ , with I-Cl bonds of length 2.26 and 2.29 Å and Cl-Cl angle of 96.7° , and approximately tetrahedral AlCl_4^- ions. The nqr data, Table II, are in accord with this structure. The Cl^{35} resonances near 39 Mc/sec are compatible with the ICl_2^+ structure¹ while those near 11.4 Mc/sec are reasonably assigned to the Cl^{35} nuclei of AlCl_4^- . The only reported observation for this ion is that by Segal and Barnes⁸ for GaAlCl_4 ; the mean of four resonances was 10.6 Mc/sec. An additional check with a salt known from X-ray studies to contain the AlCl_4^- ion seemed desirable, and $\text{Na}^+\text{AlCl}_4^-$ ⁹ was prepared by fusing equimolar quantities of dried NaCl and AlCl_3 together in an evacuated tube. It gave, at 24° , four resonances at 11.583, 11.385, 11.272, and 11.009 Mc/sec, which are assigned to the four Cl^{35} nuclei of AlCl_4^- ; the mean value is 11.312 Mc/sec.

(8) S. L. Segal and R. G. Barnes, USAEC Report IS-520, 1962.

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

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Tris(π -allyl)iridium(III)

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Wilke and co-workers¹ have recently reported on tris(π -allyl)cobalt and Powell and Shaw² on tris(π -allyl)rhodium, while the analogous tris(π -allyl)iridium has not yet been reported. We have now obtained this compound, in yield of about 20%, by the reaction of $\text{Ir}(\text{acac})_3$ or IrCl_3 with allylmagnesium chloride in THF.

Tris(π -allyl)iridium(III) is a white crystalline sub-

(1) G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmermann, *Angew. Chem.*, **5**, 151 (1966).

(2) J. Powell and B. L. Shaw, *Chem. Commun.*, 323 (1966).