Unstable Intermediates. Part CLXII.[1] Electron Spin Resonance Studies of $ClOCl^+$, $FClO^+$, and Cl_4^+

By **Raymond S. Eachus** and **Martyn C. R. Symons**, Department of Chemistry, The University, Leicester LE1 7RH

Fluid and solid-state e.s.r. spectra for the title radicals formed from molecular chlorine and antimony pentachloride are described and approximate orbital populations derived therefrom. The novel radical Cl_4^+, only detected at 77 K, is thought to be planar, being formed from Cl_2^+ and Cl_2 by a weak π^*–π^* interaction. Structural considerations suggest the assignment: $g_x = 2.00$, $g_y = 2.031$, $g_z = 2.125$ and $A_x(^{35}Cl) = 48 G$, $A_y = 0 \pm 4 G$, and $A_z = 0 \pm 4 G$, where x is the principal direction of the combined π^* orbital, z is the direction of the original σ bonds, and y is normal to the plane.

THE discovery that solutions of iodine in oleum contain a paramagnetic species led to the suggestion that this might be the iodine cation in a $^3P_2$ ground state.[2,3] Later, it was shown that this species is not I^+ but I_2^+ which has a $^2\Pi_{3/2}$ ground state.[4,5] A search was made for an e.s.r. spectrum associated with this species,[2,5] but to no avail and it was concluded that the spectrum was dispersed over a wide field range and greatly broadened by spin–orbit–lattice relaxation effects.[5] Edwards *et al.*[6] have isolated salts containing Br_2^+ and have shown that these ions are unique diatomic species with no strong covalent bonding to neighbouring groups in the crystal. Recent work on these and related halogen cations has been reviewed.[7]

Olah and Comisarow [8] detected a paramagnetic species containing two equivalent chlorine atoms in solutions of chlorine in antimony pentafluoride and suggested that this might be Cl_2^+. We stressed [9] that unless the Cl_2^+

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[2] M. C. R. Symons, *J. Chem. Soc.*, 1957, 387.

[3] M. C. R. Symons, *J. Chem. Soc.*, 1957, 2186.

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[6] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1971, 2318.

[7] R. J. Gillespie and M. J. Morton, *Quart. Rev.*, 1971, **25**, 553.

[8] G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, 1968, **90**, 5033.

[9] R. S. Eachus, T. P. Sleight, and M. C. R. Symons, *Nature*, 1969, **222**, 769.

ions were strongly and asymmetrically solvated, a well-resolved liquid-phase e.s.r. spectrum in the free-spin ($g = 2$) region was highly unlikely. The alternative formulation $ClOCl^+$ was suggested. A second species, containing one fluorine atom and one more strongly interacting chlorine atom was also detected,[9] and, by analogy with very similar results for ClO_2, was given the structure $FClO^+$. (In our preliminary note [9] we wrote formulae for these species as Cl_2O^+, $ClOF^+$, and ClO_2, rather than $ClOCl^+$, $FClO^+$, and OClO. However, the context of the note makes it clear that these were not intended as structural representations but simply followed the convention of placing the chlorine first: the postulated structures were unambiguously $ClOCl^+$ and $FClO^+$. It has been assumed by others that our representation $ClOF^+$ had structural significance.[10,11] This was not our intention.) This species was also detected by Olah and Comisarow, who suggested the structure ClF^+.[12]

Christie and Muirhead [13] demonstrated that these paramagnetic species are not formed under conditions of high purity and, in particular, that the Raman line assigned to ClF^+ belongs to ClF_2^+, formed from ClF_3 and SbF_5. Again, Gillespie and Morton [14] gave convincing Raman evidence against the Cl_2^+ and ClF^+ formulations and showed that neither Cl_2^+ nor Cl_3^+ are significant components of these solutions. In addition, the e.s.r. signal assigned by Olah *et al.*[12] to ClF^+ was found to increase rapidly on the addition of water.

Some doubt was passed on our proposals by an apparent failure to incorporate ^{17}O into these species,[14] but recently Morton and Preston [11] have shown that, in fact, ^{17}O can be incorporated and their results strongly support our original formulations of $ClOCl^+$ and $FClO^+$. In the light of these positive results we considered it worth reporting our solid-state data in full. We also report results for a species containing four equivalent chlorine atoms, only detected in frozen solutions. This is tentatively described as Cl_4^+.

EXPERIMENTAL

Materials.—Antimony pentafluoride, used as solvent throughout, kindly supplied by Professor R. D. Peacock, was purified by fractional distillation *in vacuo*. Chlorine was reagent grade. Pyrex apparatus was pre-heated *in vacuo* to remove absorbed water, but this was never sufficient to prevent some formation of $ClOCl^+$. (We note, however, that using ClF_3 in copper apparatus Morton and Preston [11] were able to eliminate the formation of $ClOCl^+$, which could then be formed by controlled addition of water.)

Sample Preparation.—Freshly distilled antimony pentafluoride was condensed into quartz e.s.r. tubes at 77 K. Chlorine was deposited onto the surface at this temperature. The mixture was warmed to generate radicals and recooled to 77 K for measurement. On re-warming, liquid-state spectra identical with those originally described by Olah *et al.* were obtained.[8] On standing at room temperature the $FClO^+$ radical features grew in, and the samples were re-cooled to 77 K. Samples that gave the spectrum assigned to Cl_4^+ were warmed only to a small extent. Further warming gave solid-state spectra containing features for both Cl_4^+ and $ClOCl^+$. We were unable to detect any features assignable to Cl_4^+ in the liquid phase.

E.s.r. Spectra.—Spectra at *X*-band were measured on a Varian V4502 spectrometer. *Q*-Band spectra were measured on an instrument constructed by Mr. J. A. Brivati in these laboratories.

RESULTS AND DISCUSSION

Our results, together with those of Morton and Preston, are summarised in Table 1 and typical spectra are shown in Figures 1—3. Some derived orbital populations are given in Table 2. In all cases, the analyses indicated were checked with spectra at *X*-band and *Q*-band frequencies. The average values estimated from the solid-state spectra agree well with the solution values provided the relative signs are taken as indicated in Table 1.

TABLE 1

E.s.r. data for various 19-electron AB_2 radicals

	Hyperfine coupling (G) [a] ^{35}Cl or ^{19}F			^{17}O	
Radical	$\parallel$	$\perp$	iso	iso	*g*-Values
$ClOCl^+$	(77 K) 8.5	0 ± 3	2.25	20.6 [b]	2.003, 1.991, 2.001
	(4.2 K) 14.3	0 ± 3			
$FClO^+$	(77 K) 66.3	−19.5	12.9 (Cl)	18.0 [b]	2.002, 2.008, 2.008
	(4.2 K) 77.0	−13.8			
	96.4	−17.6	20.4 (F)		
OClO	79.9	−12.5 −13.4	17.9	11.5 [b]	2.0036, 2.0183, 2.0088
FOO [c]			12.8	14.5 (1) 22.2 (1)	2.0038
Cl_4^+	48	0 ± 4	16		2.000, 2.031, 2.125

[a] 1 G = 10^{-4}T. [b] Ref. 11. [c] Ref. 20.

TABLE 2

Unpaired electron populations

Radical	Central atom	Ligand atoms
$ClOCl^+$	0.76 [a] (*ca.* 1.0) [b]	0.12
$FClO^+$	0.64	(F) 0.07
OClO	0.62	0.32 [e]
O_3^-	0.58	0.32
ClSS		(Cl) 0.04 [c]
PCl_2	*ca.* 1.0	0.12 [d]

[a] By difference. [b] Allowing approximately for overlap effects. [c] F. G. Herring, C. A. McDowell, and J. C. Tait, *J. Chem. Phys.*, 1972, **57**, 4564. [d] M. S. Wei, J. H. Current, and J. Gendell, *J. Chem. Phys.*, 1972, **57**, 2431. [e] Ref. 16.

The $ClOCl^+$ *Cation.*—From the resolved parallel features and the isotropic coupling of ±2.25 G we deduce $2B$ values of 12.05 or 16.55 G. ($2B$, the parallel component of the dipolar coupling, is related to $A_{\parallel}$ and $A_{\perp}$ by $A_{iso} + 2B = A_{\parallel}$ and $A_{iso} - B = A_{\perp}$.) The latter value gives an unacceptably large perpendicular coupling. The former, divided by $2B^{\circ}$, the computed value for unit

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[10] A. Hudson and K. D. J. Root, *Adv. Magnetic Resonance*, 1971, **5**, 1.

[11] J. R. Morton and K. F. Preston, *Inorg. Chem.*, 1974, **13**, 1786.

[12] G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, 1969, **91**, 2172.

[13] K. O. Christie and J. S. Muirhead, *J. Amer. Chem. Soc.*, 1969, **91**, 777.

[14] R. J. Gillespie and M. J. Morton, *Inorg. Chem.*, 1972, **11**, 591.

3*p* population of ^{35}Cl(100 G),[15] gives an orbital population $(Cp)^2$ of *ca.* 0.12 for each chlorine ligand (Table 2). If we assume that the sum of the values for chlorine and oxygen should be unity, then the oxygen population is *ca.* 0.76. However, this sum is expected to be greater, since overlap contributes a negative term usually amounting to between 0.1 and 0.2, in which case $(Cp)^2$ for oxygen is *ca.* 1.0 (Table 2).

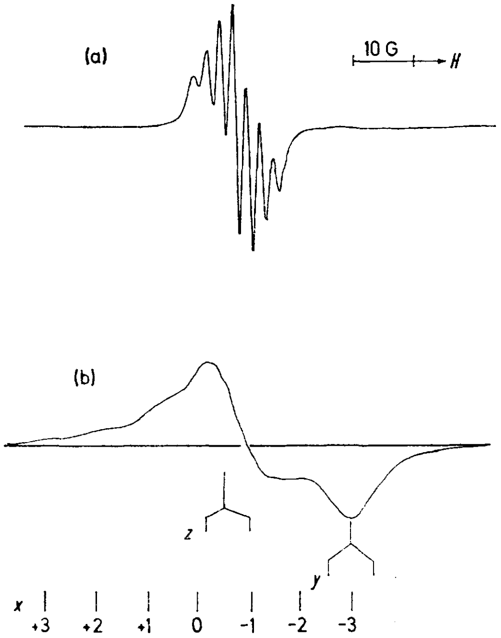

FIGURE 1 First derivative *X*-band e.s.r. spectra assigned to ClOCl$^+$ in SbF$_5$ (a) at room temperature, (b) at 77 K

This distribution of spin is surprising when compared with those for O_3^- [16] and ClO_2 (Table 2). In fact, it is remarkably close to that for PCl_2. On electronegativity arguments we would have predicted a decrease in the central-atom spin-density on going from OClO to ClOCl$^+$ since the electronegativity of chlorine (3.0) is less than that of oxygen (3.5). The change in the $A_{\parallel}(^{35}Cl)$ coupling on cooling from 77 to 4.2 K (Table 1) is almost certainly due to a quenching of librationary movements at 77 K that partially average the parameters. It is most unlikely that the radicals librate significantly at 4.2 K and, hence, our estimated spin-densities should not be seriously in error. We suggest that the unexpectedly small spin-densities on the chlorine ligands in ClOCl$^+$ arise partly because of the unfavourable overlap between 2*p* and 3*p* orbitals. Thus it is reasonable to compare spin-density trends in AO_2 species and these are fairly linear,[15] but attempts to extend this correlation to AL_2 species with second or third row ligands may be less successful. Reuveni *et al.* have also drawn attention to the fact that electronegativity trends are only clear cut for elements with the same valence shell.[17] It is interesting that the isotropic ^{17}O hyperfine coupling to the central oxygen atoms in O_3^- and ClOCl$^+$ (22.2G [17] and 20.6G [11] respectively) are almost equal. This would suggest very similar spin-densities so, again, the magnetic data do not seem to provide a very reliable guide. The only alternative to this conclusion would be that the species is not ClOCl$^+$. One possible alternative is ClOOCl$^+$. This is, however, unlikely since Morton and Preston [11] used 25 atom-% enriched ^{17}O and would surely have detected satellite lines from Cl–^{17}O–^{17}O–Cl radicals if this formulation were correct.

We have analysed the spectra for ClOCl$^+$ in the manner adopted in our studies of $R_2\dot{C}Cl$ and $R\dot{C}Cl_2$ radicals.[18] Thus the large hyperfine coupling is taken to lie along the $P(\pi)$ axis on chlorine (x). This is certainly to be expected unless the spin-density on chlorine is negligibly small, in which case the major coupling would lie along the O–Cl bonds (z, z') as a result of spin polarisation. We do not consider this to be probable, but just this situation is envisaged for the radical ClOO.[19] In this case, the major coupling to ^{35}Cl(±17.9G) was taken to be along z because the maximum g-value was expected to fall along the Cl–O bond direction and because the four hyperfine components were fairly evenly disposed, and no quadrupole shifts are expected along the z direction. However, the quadrupole shifts for $R_2\dot{C}$–Cl radicals along x were small and, unless the value of Q is very much greater for ClOO, the shifts should still be small in this case. Also the g-shifts were small and need not involve chlorine predominantly. Thus it seems possible that the value of 17.9 G is really A_x not A_z. We should add that using normal values for spin-polarisation effects, we have been unable to predict hyperfine coupling constants as large as those reported for ClOO and, hence, we conclude that π-delocalisation must be significant. In that case, the values for ^{35}Cl in ClOCl$^+$ and ClOO are quite similar, thus adding weight to our identification.

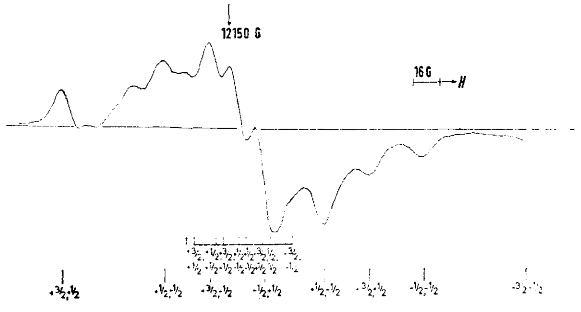

FIGURE 2 First derivative *Q*-band e.s.r. spectrum assigned to FClO$^+$ in SbF$_5$ at 77 K

The FClO$^+$ *Radical*.—Although the solid-state spectra are difficult to interpret, the 'parallel' features are clearly defined, and using the isotropic data, together with *X*- and *Q*-band spectra, it has been possible to derive a

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[15] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

[16] S. Schlick, *J. Chem. Phys.*, 1972, **56**, 654.

[17] A. Reuveni, R. Poupko, and Z. Luz, *J. Magnetic Resonance*, 1975, **18**, 358.

[18] S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1973, 1425.

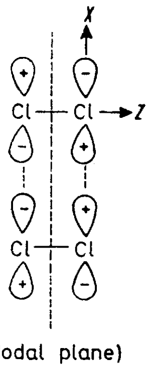
[19] F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, 1972, **56**, 6251.

reasonable spectral analysis (Figure 2). If the species is $FClO^+$, the unpaired electron should again be in the $2b_1(\pi^*)$ orbital and the principal values of the ^{19}F and ^{35}Cl tensor components should be co-directional. Hence the powder spectra should give good values for the hyperfine interactions and these can be used to derive approximate π spin-densities.[15] This gives, by the procedure outlined above, a spin-density of *ca.* 0.64 on the central chlorine atom. This value is very close to the value of *ca.* 0.62 estimated by the same method for ClO_2 (Table 1). Thus, in this case, replacing oxygen by the far more electronegative fluorine has made very little difference to the spin-density on chlorine.

The spin-density on fluorine, estimated from the anisotropic hyperfine coupling using $2B^\circ = 1\,084$ G[15] is *ca.* 0.07. This very small value is quantitatively unreliable because of the many corrections to be made. However, we can conclude that the majority of the ligand spin-density is to be found on oxygen rather than on fluorine, which seems to be largely excluded from this π^* orbital. This is probably also true for FOO[20] (Table 1).

These results for the ligands (Table 2) suggest that when one ligand is more electronegative than the other there is a relatively large migration of spin-density onto the least electronegative atom.

The Cl_4^+ *Radical.*—As we have stressed before,[9] the radical Cl_2^+ is likely to have a very diffuse e.s.r. spectrum, with a large down-field shift for some features and a smaller up-field shift for others. The extent of these shifts is dependent upon the environment and, until Cl_2^+ can be doped dilutely into some well-defined crystal site, its e.s.r. spectrum is unlikely to be detected. However, in the presence of an excess of chlorine the complex Cl_4^+, thought to have structure (I), could be formed at least at low temperatures. In this case, the orbital levels are largely governed by intramolecular forces and the magnetic properties should be far less environmentally dependent.



(I)

Our spectra assigned to this species (Figure 3) comprised thirteen reasonably well-defined features for one direction, which must be x in terms of structure (I). The other two features appear as broad singlets, which is not unreasonable for such a species. Thus, the high g-value feature must be g_z since, for relatively weak bonding, orbital motion coupling π_x^* and π_y^* should still give rise to a positive g-shift.

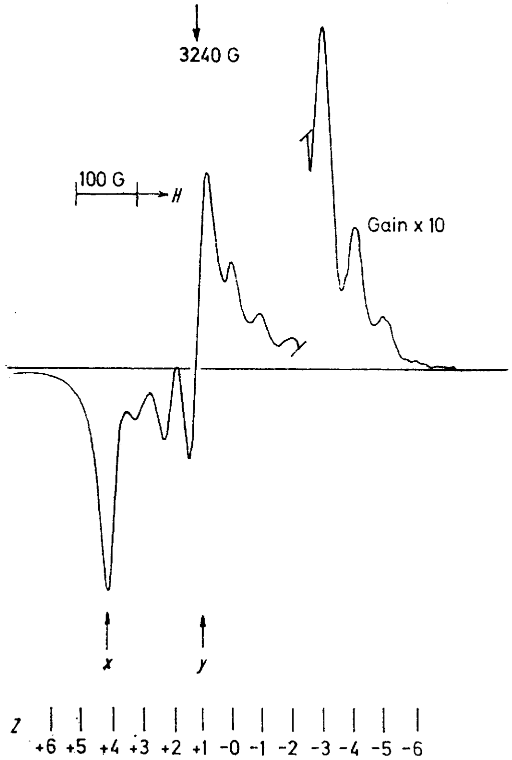


FIGURE 3 First derivative X-band e.s.r. spectrum assigned to Cl_4^+ in SbF_5 at 4.2 K

These hyperfine parameters have been used to derive the approximate spin-density of 0.32 on each atom. This gives a total apparent density of 1.28. This is not an unexpected result since overlap has been neglected. Indeed, results for various V_K-centres such as Cl_2^- generally lead to values in excess of unity.

There is some precedent for postulating a weak planar complex of this type since N_2^- is thought to give a similar species, N_4^-, with a nitrogen molecule.[21] In this case, the bonding orbital contains only one electron rather than three, but the strength of the interactions could well be comparable.

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[21] M. C. R. Symons, *J. Chem. Soc.*, 1963, 570.