**SHORT PAPER**

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# The radicals $F_3\bullet$ and $F_3^{\bullet 2-}$[†]

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Exposure of a range of alkali-metal fluorides to ionising radiation gives, in addition to the expected F- and $V_k$-centres, a radical identified as $F_3^{\bullet 2-}$; the aim of this study is to offer an alternative, namely, the radical $F_3\bullet$, and to offer a tentative explanation for its formation.

When alkali-halides are exposed to ionising radiation, electron-injection gives halogen atoms, which normally bond to a neighbour to give $hal_2^{\bullet -}$ radicals called $V_k$ centres. The ejected electrons are trapped at anion vacancies, giving F-centres.[1] However, in some cases, such as LiF, another anion bonds to the $V_k$ centre to give $hal_3^{\bullet 2-}$ radicals. These have been extensively studied by EPR spectroscopy.[2–5]

Halogen molecules readily add halide ions to give $hal_3^-$ anions, which are quite stable. The $hal_3^{\bullet 2-}$ centres represent the limit of bonding. A further electron leads to 3 $hal^-$ anions. Loss of an electron to give $hal_3\bullet$ radicals should increase the strength of the σ- bonding rather than reduce it. All three of these centres are expected to be linear, in the absence of any constraints.

Again, in the absence of major constraints, the SOMO for $hal_3^{\bullet 2-}$ radicals is expected to have high spin-density in the $p_z$ orbital of the central atom and relatively low spin-density on the two outer atoms. This agrees well with one of the species studied in fluoride salts.[2–4]

On the other hand, for $hal_3\bullet$ radicals, the spin-densities on the two outer halogens should increase and that on the central atom should fall the SOMO for $hal_3\bullet$ radicals is also sigma-antibonding but the electrons now favour the two outer atoms rather than the central one. This seems to accommodate the other set of data.

## Discussion

These results are given in Table 1 and the derived spin-densities are given in Table 2. These have been derived from data for $F_2^{\bullet -}$, rather than using calculated parameters, since the spin-densities must be equal to 50% on each fluorine. These data strongly support the present postulate since for $F_3^{\bullet 2-}$ (i) the estimated spin-density on the central fluorine ($F_2$) is 103%. However, if the values of 17% each for the outer atoms ($F_{1,3}$) represent real spin-densities, the total spin-density is 137%. I suggest that there is a considerable contribution from spin-polarisation from the near spin-density on $F_2$ which will place extra positive spin-density on $F_2$ and negative spin-densities on $F_1$ and $F_3$.

For species (ii), thought to be $F_3\bullet$, the total spin-density on $F_1$ and $F_3$ is 150%. Again, some of this will stem from positive spin-polarisation of $F_1$ and $F_2$. Since spin-density on $F_2$ is probably close to zero, the calculated value is taken to be negative. However, although $F_3^{\bullet 2-}$ radicals are an expected product, it is hard to see why $F_3\bullet$ radicals should be formed.

**Table 1** EPR parameters assigned to $F_3^{\bullet 2-}$ radical-anions (i) with major spin-density on F(2), (ii) with major spin-density on F(1,3)

| Radical | Hyperfine coupling to $^{19}F^a$/G | | | Host crystal | Ref. |
|---|---|---|---|---|---|
| | $A_x$ | $A_y$ | $A_z$ | | |
| (i) | ($F_2$) 1153.4 | 184.5 | 121.6 | $KAsF_6$ | 7 |
| | ($F_{1,3}$) 85.0 | 19.2 | 34.0 | | |
| (i) | ($F_2$) 1122 | 212 | 268 | LiF | 5 |
| | ($F_{1,3}$) 378 | 142 | 80 | | |
| (ii) | ($F_2$) 106 | 25 | 25 | NaF | 6 |
| | ($F_{1,3}$) 843 | 150 | 70 | | |

$^a$G = $10^{-4}$T.

**Table 2** Estimated total spin-densities (s- + p- character) for the $F_3^{\bullet 2-}$ centres listed in Table 1

| Radical | Spin-densities | Matrix |
|---|---|---|
| (i) | ($F_{1,3}$) 0.17 | |
| ($F_3^{\bullet 2-}$) | ($F_2$) 1.03 | LiF |
| | Total 1.37 | |
| (ii) | ($F_{1,3}$) 0.75 | |
| ($F_3\bullet$)$^a$ | ($F_2$) (-) 0.21$^b$ | NaF |
| | Total 1.29 | |

The total spin densities are for the hypothetical linear radicals, since some are slightly bent. They are based on the A and 2B values for $F_2^{\bullet -}$, for which the spin-density must be 50% on each atom. However, for the 3F centres there will be significant contributions for spin polarisations)

$^a$Present proposal.

$^b$Negative if spin-polarisation dominates.

I suggest that the difference may be in the extent of exposure to the radiation. It is difficult to see how the F-centres can be responsible, since electron-loss is required. At high doses, the $F_3^{\bullet 2-}$ centres may be close enough to react together:

$$2F_3^{\bullet 2-} \rightarrow F_3^- + 3F^-$$

Since $F_3^-$ is stable, this is not expected to be reversible. The $F_3^-$ ions would not be detected by EPR spectroscopy, so the signal intensity should fall. However, on further exposure, the same type of reaction could again occur:

$$F_3^- + F_3^{\bullet 2-} \rightarrow F_3\bullet + 3F^-$$

Other possibilities include matrix effects or hyperfine coupling from matrix nuclei. However, as shown in Table 1, apart from the rather strange case of $AsF_6$,[7] the matrices are very similar, so this is unlikely. Also, a triplet of doublets is required, and $^7$Li nuclei have $I = 3/2$, so there is no way in which these can be contributing.

I conclude that the second species is the previously unknown radical, $F_3\bullet$.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*