Inorganica Chimica Acta, 17 (1976) 125–128

The Electronic Structures of Some Aluminium Fluoride Compounds

D. R. ARMSTRONG

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow Gl 1XL, Scotland, U.K.

Received July 24, 1974

The electronic structures of AlF, AlF_3, AlF_4^- and AlF_6^{3-} are reported. Comparison of the electronic structures of the monofluorides of B, Al, Ga and In reveals that the heavier element fluorides have a greater ionic character and a lower bond population. AlF_3 is calculated to be a better fluoride-ion acceptor than BF_3 due to the formation of a stronger donor–acceptor bond while the reorganisation energies of BF_3 and AlF_3 are similar. From the calculations on AlF_6^{3-} and AlF_4^- it is postulated that in molten cryolite the AlF_6^{3-} ion is more likely to dissociate to AlF_4^- and $2F^-$ ions than to AlF_3 and $3F^-$ ions. It is found in all the compounds that (1) the aluminium possesses a substantial positive charge, (2) the d-orbital population of aluminium is ca. 0.4–0.5e except for AlF where it is 0.13, and (3) the d-orbital bonding contribution is significant. Reasons are presented for the non-formation of the BF_6^{3-} ion.

Introduction

Since the era of large-scale molecular orbital calculations dawned, the realm of boron chemistry has been well served by the results from this mode of investigation. In particular, the electronic structures of the boron halides[1–3] and hydrides[4–6] have been detailed, enabling a comprehensive picture of the bonding in these boron compounds to be ascertained. However, there has been no theoretical examination of the compounds of aluminium. This is rather surprising, as these compounds are commercially important.[7] In this publication we attempt to provide some information in this previously barren area by reporting the electronic structures of some fluorides of aluminium.

In contrast to BF_3, AlF_3 exists not as a discrete species but as a polymeric solid in which the aluminium is surrounded by an octahedral array of fluorines and the octahedra are connected to each other by their vertices. It has been conjectured that this structural difference is due to the contribution of the 3*d* orbitals on aluminium and also to presence of the weaker π bonding associated with second-row atoms. An examination of the electronic structure of monomeric AlF_3 would therefore be of interest.

Further species of interest are the fluoro anions AlF_4^- and AlF_6^{3-}, which are important in the electrolytic production of aluminium.[7] Controversy has recently arisen, however, over the composition of molten cryolite used in the electrolysis. Holm[8] suggested that thc AlF_6^{3-} anions present in the melt are dissociated to AlF_3 and F^- ions, whereas other workers[9] propose a dissociation into AlF_4^- and F^-, hence, calculations on these systems might help to resolve this contentious issue.

Method

The calculations were performed within a non-empirical version of the LCAO–MO–SCF framework. Each *s* and *p* atomic orbital was represented by two Slater orbitals, while the 3*d* orbital of aluminium was simulated by a single Slater orbital. This ensured that the role of the *d* orbital, a formally vacant orbital, was not overemphasised when compared to the behavior of the occupied orbitals. Each Slater orbital was constructed from a linear combination[10] of four Gaussian orbitals. The molecular geometries were obtained from references 7 and 11, while the orbital exponents were extracted from the work of Clementi.[12]

Results and Discussion

Initially we examined the structure of monomeric AlF_3. It was necessary to obtain an optimum 3*d* orbital exponent and this was procured by minimisation of the total energy. The acquired value, 1.6, was then used for all subsequent calculations. The atomic and overlap populations are presented in Table I. These values show that there is a net flow of electrons towards the fluorine atoms resulting in a substantial charge (+1.6) on the aluminium, despite a considerable back-donation of electrons (0.58) into the $3p_\pi$ and 3*d* orbitals of aluminium. The majority of these back-donated electrons resides in the 3*d* orbitals of aluminium. Combination with three fluorine atoms causes considerable denuding of the aluminium 3*s*-orbital population. The overlap population data indicates that the π character of

TABLE I. The Atomic and Overlap Populations of the Aluminium Fluoride Species.

	AlF	AlF$_3$	AlF$_4^-$	AlF$_6^{3-}$
Electron density				
Al s	5.882	4.306	4.328	4.283
p_σ	2.365	4.504	6.767	6.886
p_π	4.132	2.164		
d_σ	0.050	0.275	0.419	0.273
d_π	0.082	0.143		0.223
Total	12.451	11.392	11.514	11.665
F s	3.952	3.954	3.961	3.960
p_σ	1.810	3.684	5.660	1.857
p_π	3.788	1.898		3.905
Total	9.550	9.536	9.621	9.722
Overlap Population				
Al s–F	−0.083	0.099	0.085	0.061
Al p–F	0.201 ($\pi = 0.076$)	0.274 ($\pi = 0.066$)	0.241	0.190 ($\pi = 0.101$)
Al d–F	0.101 ($\pi = 0.063$)	0.212 ($\pi = 0.073$)	0.163	0.133 ($\pi = 0.061$)
Total	0.218	0.585	0.499	0.384

the Al–F, bond amounts to about one-quarter of the total, while for BF$_3$[13] there is a 30% π component of the B–F bonds. This is an illuminating example of the diminishing importance of the π bonding, especially the p_π–p_π component, upon the replacement of a first-row atom by a second-row element in a bond. The aluminium 3d-bonding component is quite significant and this is also manifest in the calculated total energy of the system, which is destabilised by 212.82 kJ mol^{-1} by exclusion of the 3d orbitals.

The electronic populations of AlF are also presented in Table I. Comparison of these values between the two aluminium fluorides is enlightening. The aluminium in AlF possesses a relatively smaller positive charge (+0.55) which is approximately one-third of the charge on aluminium in AlF$_3$. A similar observation was obtained in boron–fluorine systems[1] where the charge on boron bore a linear relation to the number of fluorines present. The 3s orbital of the aluminium is substantially filled and, coupled with the information that the overlap population for the Al$_s$–F is negative, indicates that the Al 3s electrons in AlF are non-bonding. This is confirmed by inspection of the eigenvectors, where it is revealed that the highest bonding orbital is largely composed of the Al 3s orbital. Moreover, the energy of this orbital is −0.335, which indicates comparatively labile electrons. We expect the reactivity of AlF to be dominated by this non-bonding orbital. The lowest vacant orbitals are π^* in nature and are localised about the aluminium p orbitals.

An interesting property of the Group IIIb elements is the increased stability of compounds of the elements with a formal oxidation state of one as the Group is descended. It was thought that the electronic structures of the monofluorides of the elements from boron to indium might reveal some reasons for this tendency. A single-zeta basis was used in this particular series of calculations although each Slater orbital was represented by a linear combination of five gaussian functions. The orbital exponents of boron and aluminium were obtained from Clement and Raimondi[13] while a procedure due to Burns[14] was used to calculate the orbital exponents of gallium and indium. The interatomic distances were taken from reference 15. The resulting electronic information concerning these four diatomics are presented in Table II. The transfer of charge to the fluoride increases as we progress from BF to InF. However the valence s-electronic population of the Group IIIb element is enlarged as we progress from BF to InF. It is the valence p electrons which are increasingly displaced as the atomic number of the Group IIIb elements is augmented. These figures seem to lend credence to the so-called inert pair effect which refers to the resistance of the pair of valence s-electrons to be lost or to be involved in bond formation. In contrast the energy of the highest filled molecular orbitals of these diatomic fluorides increases from BF to InF. This would seem to indicate that the fluorides of the heavier Group III elements would be more reactive and hence less able to consolidate the univalent state. The critical factor, however, could be the bond strengths which are related to the bond populations presented in Table II. It can be seen that the overlap bond populations decrease rapidly from AlF to InF. Inspection of the relevant components of these bonds reveals that it is the M$_p$–F$_p$ and to a lesser extent the M$_d$–F$_p$ portions which show a corresponding diminution. The most drastic reduction occurs for the M$_p\sigma$–F$_p\sigma$ population which amounts to 0.237 for BF but only 0.004 for InF. This gives support to the idea that the

TABLE II. The Valence Electronic Population, Charge Overlap Population and the Energy of the Highest Filled Molecular Orbital of BF, AlF, GaF and InF.

M–F	Charge Transfer	Valence Population							Overlap Population	Energy of Highest Filled Molecular Orbital (a.u.)
		M				F				
		s	p_σ	p_π	*d*	*s*	p_σ	p_π	M–F	
B–F	0.132	1.711	0.627	0.266	–	1.936	1.728	1.734	0.574	–0.374
Al–F	0.184	1.806	0.500	0.194	0.233	1.929	1.732	1.762	0.614	–0.274
Ga–F	0.261	1.827	0.589	0.184	0.076	1.954	1.687	1.810	0.388	–0.274
In–F	0.425	1.890	0.185	0.246	0.010	1.959	1.965	1.750	0.118	–0.271

trivalent state becomes unstable as the group III is descended because of the decrease in bond strength and the increase in the ionic character of the M–F bond.

The electronic structures of the fluoro-anions are outlined in Table I. Comparison of the atomic charges of the anions with those of AlF_3 discloses that the addition of one or three fluoride ions results in the extra charge being smeared over all the atoms. The positive charge of aluminium becomes smaller as we add fluoride ions but this decrease is quite small, with a difference of only 0.27 between the charge of aluminium in AlF_3 and in AlF_6^{3-}. The *d*-orbital population of aluminium is marginally increased by the additional fluoride ions, while the overlap population of the Al–F bond is decreased by increased coordination.

The energies of formation of the anionic species were calculated with respect to the fluoride ion and AlF_3 according to:

$$AlF_{3(g)} + F^-{}_{(g)} \rightarrow AlF_4^-{}_{(g)} \quad (1)$$

$$AlF_{3(g)} + 3F^-{}_{(g)} \rightarrow AlF_6^{3-}{}_{(g)} \quad (2)$$

It was found that for reaction 1 there was a considerable stabilisation of energy (640.6 kJ mol^{-1}) upon formation of the tetrafluoride, while for reaction 2 the hexafluoride ion was unstable with respect to the trifluoride and the three fluoride ions by 83.2 kJ mol^{-1}. These calculations indicate that in the gas phase, the aluminium hexafluoride ion would decompose to the aluminium tetrafluoride anion and two fluoride ions, with a gain in energy of 723.5 kJ mol^{-1}. There is always a danger in assuming that conclusions of gas phase calculations will be true of other phases. However, the energy differences involved are so large that it is doubtful whether the different conditions in a melt will drastically alter the conclusions. Hence, we can say, with the above reservation, that these calculations seem to indicate that in a melt the aluminium hexafluoride will decompose to aluminium tetrafluoride and two fluoride ions.

Reaction (1) is also a direct measure of the fluorine affinity of AlF_3. This is in reasonable agreement with a previously proposed value of 548.1 kJ mol^{-1} obtained by Holm[16] using thermochemical data. Comparison with the corresponding reaction involving boron reveals that the fluoride affinity of BF_3[3] (555.7 kJ mol^{-1}) is smaller than that of AlF_3. It is generally accepted[17,18] that the two main energy terms involved in the formation of donor–acceptor complexes of Group III halides are, (i) the energy required to reorganise the planar acceptor into a pyramidal configuration and (ii) the energy gained by the formation of the donor–acceptor bond. The reorganisation energy of planar AlF_3 is calculated to be 164.0 kJ mol^{-1} which is very similar to the quantity required to transform BF_3[3]. The stabilisation energy gained by the formation of a fourth fluoride bond is 804.6 kJ mol^{-1} and 720 kJ mol^{-1} for AlF_3 and BF_3[3], respectively. Now, it is found that the order of acceptor power for the Group III acceptors is Al>B>Ga>In[19]. We can therefore propose that the relative positions of Al and B arise because aluminium forms stronger bonds than boron with donor species, while they both possess the same reorganisation energy. The reorganisation process causes minor changes in the electronic population of aluminium with a more positive charge (+1.63) on the aluminium due to a lower *d*-orbital occupancy, and a smaller Al–F bond population in pyramidal AlF_3.

In a crystal lattice, AlF_6^{3-} is a stable ion. We attempted to obtain a description of AlF_6^{3-} in this environment by surrounding the AlF_6^{3-} unit by an array of positive charges so positioned to simulate the influence of the nearest neighbouring sodium cations in cryolite. It was found that the energy of the system was substantially lowered (2111.4 kJ mol^{-1}). AlF_6^{3-} is clearly stabilised by an envelope of the positive charges. This stabilisation energy is related to the lattice energy, although most certainly is not equal to it, since our model only simulates the immediate environment of AlF_6^{3-} and does not attempt to describe an infinite lattice. Nevertheless, it clearly illustrates the order of energy gain by AlF_6^{3-} due to the introduction of positive charges and provides a rationale for its existence in a crystalline environment. The Mulliken population analysis of the anion surrounded by positive charges reveals that, surprisingly, there are only small changes in the atomic populations of AlF_6^{3-}. The enclosing array of positive charges produces only a very limited movement of electrons to the fluorine atoms. The existing positive charge on the aluminium prevents a large donation of electrons to the fluorines.

We can conjecture from these calculations that in the crystalline state, AlF_6^{3-} will be a stable species but in a melt where the influence of the cations will be less, then it will disproportionate to AlF_4^- and two F^- ions.

In contrast to aluminium, boron does not form a hexafluoride ion and as it is a related problem the electronic energy and structure of the BF_6^{3-} is reported. The B–F bond length was assumed to be the same as the boron–fluorine distance in BF_4^-[15] and the basis set consisted of the double zeta gaussian orbitals which had been employed in earlier calculations on BF_3 and BF_4^-.[3] The energies of formation of BF_6^{3-} and BF_4^- from BF_3 and the appropriate number of fluoride ions were obtained in a similar manner to the aforementioned energies of the related fluoroaluminium anions. It is found that the energy of BF_4^- ion is more stable than the component BF_3 and the F^- ion by 555 kJ mol^{-1} while the corresponding energy of BF_6^{3-} ion is less stable by 1579.7 kJ mol^{-1} than BF_3 and three F^- ions. Comparison with the AlF_6^{3-} system clearly demonstrates that it is this energy term which is responsible for the non-appearance of a stable BF_6^{3-} ion.

The electronic populations of BF_6^{3-} were examined in order to ascertain possible reasons for the instability of this ion. It is found that boron possesses a positive charge (+1.2) while the fluorine atoms have an extra 0.7 electrons. This atomic charge distribution is very similar to that found in AlF_6^{3-}. When we examine the overlap populations we observe that the value for the boron–fluorine bond (0.38) is much smaller than the corresponding quantity for BF_3 0.59 and BF_4^- 0.48. These values, however, bear a close resemblance to the bond orders of the related aluminium fluorides presented in Table I and hence do not account for the inherent instability of the BF_6^{3-} ion. Further scrutiny of the population data reveals that the neighbouring fluorine–fluorine interactions are antibonding (–0.183) which coupled to their abundance must be a major factor in the non-formation of BF_6^{3-}. This claim is further substantiated by comparison with the fluorine–fluorine interactions in AlF_6^{3-} (–0.023), AlF_4^- (–0.007), and BF_4^- (–0.076), as they are all considerably less destabilising and so the formation of these three ions is possible. Examination of the fluorine–fluorine interaction in BF_6^{3-} reveals that the largest negative overlap population component occurs between the *p* orbitals which lie along the B–F axis. There is also a substantial negative contribution from the interaction between the neighbouring fluorine *p* orbitals which are situated perpendicular to the B–F axis and are lying in the same plane.

References

1 D.R. Armstrong and P.G. Perkins, *Inorg. Chim. Acta, 10,* 77 (1974).
2 T.E.H. Walker and J.A. Horsley, *Mol. Phys., 21,* 939 (1971).
3 R.M. Archibald, D.R. Armstrong and P.G. Perkins, *J.C.S. Faraday II, 69,* 1793 (1973).
4 W.N. Lipscomb, *Accounts Chem. Res., 6,* 257 (1973).
5 J.H. Hall, I.R. Epstein and W.N. Lipscomb, *Inorg. Chem., 12,* 1915 (1973).
6 D.R. Armstrong, P.G. Perkins and K.S. Sorbie, *Rev. Roum. Chim., 19,* 747 (1974).
7 A. Stranden (ed.), *Kirk-Othmer Encyclopedia of Chemical Technology,* 2nd Edn., Vol. 9, Wiley, New York (1966).
8 J.L. Holm, *Inorg. Chem., 12,* 2062 (1973).
9 B. Gilbert, G. Mamantov and G.M. Begun, *J. Chem. Phys., 62,* 950 (1975).
10 R.F. Stewart, *J. Chem. Phys., 52,* 431 (1970).
11 JANAF *Thermochemical Tables, U.S. Department of Commerce, National Bureau of Standards* (1965), 3rd Addendum (1968).
12 E. Clementi, *J. Chem. Phys., 40,* 1944 (1964).
13 E. Clementi and D. L. Raimondi, *J. Chem. Phys., 38,* 2686 (1963).
14 G. Burns, *J. Chem. Phys., 41,* 1521 (1964).
15 *Interatomic Distances in Molecules and Ions, Chem. Soc. Special Publication,* London, No. 11 (1958).
16 J.L. Holm, *Acta Chem. Scand., 27,* 1410 (1973).
17 F.A. Cotton and J.R. Leto, *J. Chem. Phys., 30,* 993 (1959).
18 D.R. Armstrong and P.G. Perkins, *Theoret. Chim. Acta, 15,* 413 (1969).
19 J.W. Wilson and I.J. Worrall, *J. Chem. Soc. A,* 316 (1968).