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An ESR study of the reaction of silver atoms with B_2F_4 under matrix isolation conditions

Lynda J. Hayton, Brynmor Mile, Peter L. Timms * and Jeremy N. Harvey

School of Chemistry, University of Bristol, Bristol, UK BS8 1TS.
E-mail: Peter.Timms@bristol.ac.uk

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Diboron tetrafluoride has been found by ESR to complex with silver atoms when the species are deposited together in hydrocarbon matrices at 77 K in a rotating cryostat. The major feature in the ESR spectra of the deposit in adamantane and cyclohexane matrices (Ag : B_2F_4 : matrix ratio of ~1 : 5 : 500) was an almost isotropic set of two doublets of 13 (or possibly 15)-line multiplets. The two sets of doublets arise from the almost equally abundant ^{107}Ag and ^{109}Ag isotopes with $I = 1/2$. The multiplets on each silver line indicate hyperfine interaction with either four equivalent ^{11}B nuclei ($I = 3/2$) or two equivalent ^{11}B nuclei and four equivalent ^{19}F nuclei. Multiplets from the less abundant ^{10}B isotope (19.8%, $I = 3$) were not resolvable. The almost isotropic multiplets are best simulated as axial spectra with $|A_\parallel|(^{11}B) = 17.5$ MHz and $|A_\perp|(^{11}B) = 14.1$ MHz and $A_{iso}(^{107}Ag) = 1371.0$ MHz. The complex is either $[Ag(B_2F_4)_2]$ or $[Ag(B_2F_4)]$. Assuming that $A_\parallel$ and $A_\perp$ are both positive, the total spin density is calculated to be 0.85 in $[Ag(B_2F_4)_2]$ and 0.80 in $[Ag(B_2F_4)]$. The most likely structures together with density function calculations on these two possibilities are discussed.

Introduction

In an attempt to prepare gaseous BF to study its properties as a ligand toward metal atoms by matrix isolation ESR spectroscopy, the vapour of diboron tetrafluoride was passed over a heated tungsten filament under vacuum and the off-gases were condensed with silver atoms in hydrocarbon matrices at 77 K. A complex ESR spectrum was obtained reproducibly but it was found to be largely independent of the filament temperature and due, not to the reaction of BF with silver atoms, but to the reaction of B_2F_4 with silver atoms. Although there are many examples of matrix isolated π bonded complexes of transition metals with alkenes and alkynes[1–4] the B–B single bond clearly differs from C–C multiple bonds in that B_2F_4 does not have electron-rich π orbitals which, together with close lying empty π* orbitals are the *modus operandi* of the synergistic bonding in unsaturated hydrocarbon complexes. A different bonding mechanism must exist for the boron fluoride silver complexes. Because of this unexpected result further investigations were conducted to try to determine the composition and to measure the stability of the $Ag(B_2F_4)_n$ complex.

Experimental

The rotating cryostat technique and furnaces used have been described in detail elsewhere.[5] From different ports in the outer housing, silver atoms, adamantane (or perdeuterocyclohexane) vapour and B_2F_4 vapour containing natural boron (^{11}B: 80.2%, $I = 3/2$, and ^{10}B: 19.8%, $I = 3$) were condensed onto the rotating drum at 77 K. Silver atoms were formed from natural silver (^{107}Ag: 51.35%, $I = 1/2$ and ^{109}Ag: 48.65%, $I = 1/2$) evaporated from resistively heated tungsten furnaces at 1200–1300 K. After some 10 min the deposit was several mm thick and consisting of ~10^4 interleaving spirals of each constituent (Ag : B_2F_4 : matrix ratio ~ 1 : 5 : 500) and was transferred from the drum, still at 77 K and $<10^{-6}$ Pa, into quartz ESR tubes. The ESR spectra were recorded at temperatures from 77 to 160 K on a Bruker ESP300E spectrometer. The computer programs ‘SimFonia’ and ‘Belford’ were used to simulate the experimental spectra.[6]

Preparation of the B_2F_4 was by established methods[7] and the adamantane and cyclohexane were commercial samples (Aldrich, >99.0% purity). All reagents were thoroughly degassed immediately before use.

Results and discussion

Fig. 1 shows the X-band 100 K ESR spectrum of the products from reacting B_2F_4 with Ag atoms in adamantane. The resonances marked A are readily assigned to trapped ^{109}Ag atoms;[8,9] the corresponding ^{107}Ag atom lines are obscured by multiplet signals of features labelled B. The intense sharp doublet B and B′ multiplet signals are only seen in the presence of diboron tetrafluoride and can therefore be assigned to complexes containing single ^{109}Ag and ^{107}Ag atoms associated with one or more B_2F_4 molecules, the ratio of magnetic field separation of the two sets of multiplets being that expected from the ratio of the magnetic moments of the two silver isotopes ($\gamma\ ^{109}Ag : \gamma\ ^{107}Ag = 1.15$). The broad signals C, D and E are due to one or more unidentified species, most likely small Ag clusters with associated B_2F_4 ligands.

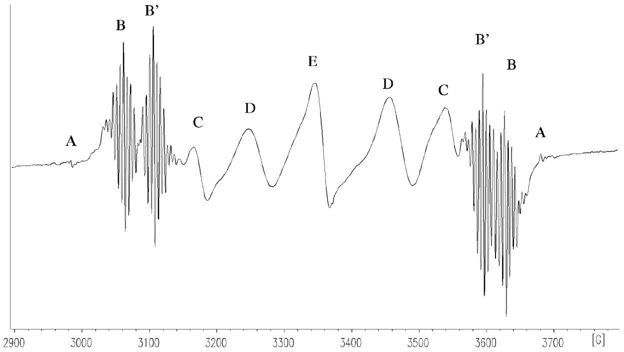

Fig. 1 The ESR spectrum of Ag atoms with B_2F_4 in an adamantane matrix at 100 K.

The multiplet features of B and B′ in expanded scale (Fig. 2)

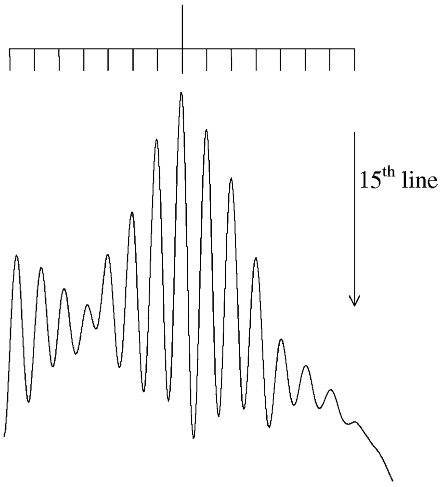

Fig. 2 The low field multiplet assigned to the complex [$^{107}Ag(B_2F_4)_n$] recorded at 106 K. The position of the possible 15th spectral line is indicated.

appear to be isotropic (but see below). Thirteen lines of each multiplet with 5 G (~15 MHz) separation can be seen clearly but there is a possibility that there are fifteen rather than thirteen lines with the outer two lines of the pentadecate being incompletely resolved and/or partially obscured by noise. The position of these possible flanking lines is indicated in Fig. 2. In most of our experiments these lines were not observed, but were discernible in particularly strong spectra of samples with higher concentrations of the complex. However, these very weak outer lines could be associated with another unidentified species. Multiple scanning (500 scans) of the outer reaches of the multiplet features and recording the spectra over the temperature range of 10 K to 215 K and applying microwave powers from 0.1 mW to 60 mW did not enable us to delineate these two possibilities. Disappointingly the ENDOR spectra of the deposits over a range of temperatures showed only single lines at the frequencies of boron and fluorine in both adamantane and deuterocyclohexane. The singlet signals arise from boron and fluorine nuclei in B_2F_4 molecules isolated in the matrix; presumably the relaxation rates of energy levels associated with ESR resonances of the [$Ag(B_2F_4)_n$] complex do not allow us to observe its ENDOR spectrum in these matrices. Hence we are unable to use ENDOR to determine whether the multiplets arise from hyperfine interactions with only boron nuclei or with both boron and fluorine nuclei.

Spectral assignment and analysis

A thirteen line multiplet is readily explained by equal isotropic hyperfine interaction (hfi) with four boron nuclei as given by the formula $2nI + 1$ (where n = no. of equivalent interacting nuclei and I = nuclear spin quantum number). This would require two B_2F_4 molecules to be associated with one silver atom *i.e.* the complex is the dimer [$Ag(B_2F_4)_2$]. A fifteen line isotropic multiplet with hfi to both boron and fluorine can only result if the hfi to the four magnetically equivalent fluorine nuclei is accidentally twice that with two boron nuclei in a mono ligand complex, [$Ag(B_2F_4)$]. Both thirteen and fifteen line possibilities can be reasonably well simulated by using the following isotropic parameters: [$Ag(B_2F_4)$] $^{107}Ag(1)$ = 1371.0 MHz, $^{11}B(2)$ = 14.3 MHz, $^{19}F(4)$ = 29.1 MHz, g = 2.0010 and for [$Ag(B_2F_4)_2$] $^{107}Ag(1)$ = 1371.0 MHz, $^{11}B(4)$ = 14.3 MHz, g = 2.0010. A hfi of 4.8 MHz with the less abundant ^{10}B isotope was included in the computations of the simulated spectra. However the relative intensities of the lines across the multiplets in the experimental spectrum are not correctly simulated, *i.e.* when the peak heights of the central lines of the simulation are normalised to those of the experimental spectrum, the outer 3 lines of the simulated multiplet are too intense. This discrepancy is removed by the inclusion of a small degree of anisotropy in the boron hyperfine interaction. The equal interaction with two boron nuclei dictates that the silver is located centrally to the B–B bond in a 'side on' configuration. Treating the multiplets as slightly axial, rather than isotropic, was found to improve the simulated line intensities whilst maintaining the line positions as shown in Fig. 3. The axial parameters are listed in Table 1.

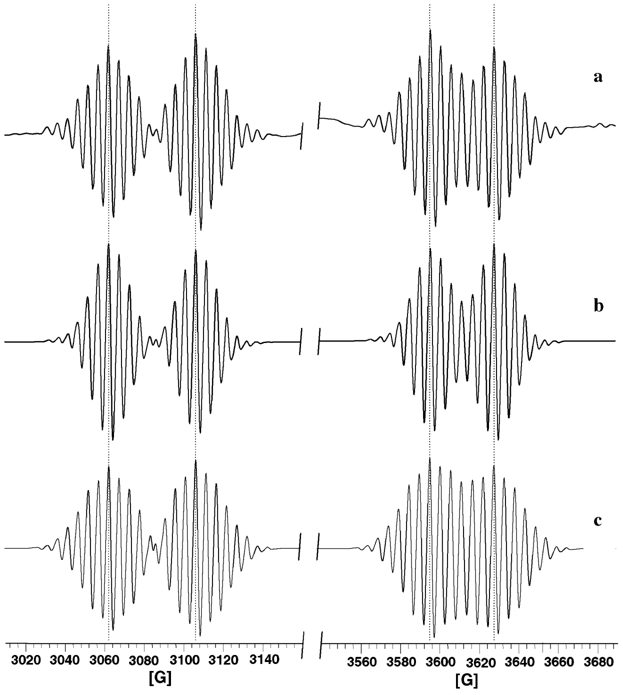

Fig. 3 Experimental and simulated spectra of [$Ag(B_2F_4)_2$] and [$Ag(B_2F_4)$] (central region of the spectra is omitted for clarity): (a) experimental spectrum; (b) simulation for [$Ag(B_2F_4)_2$]; (c) simulation for [$Ag(B_2F_4)$]. Simulation parameters are given in Table 1.

Only small differences (~3 MHz) between $A_{\parallel}$ and $A_{\perp}$ are needed to achieve these better simulations. The slight anisotropy arises from incomplete averaging by fluxional and/or tumbling motions of the complex. The inclusion of even a small anisotropic Ag component (~3 MHz) resulted in poor fits of the experimental line intensities.

The two possible structures are considered in turn.

[$Ag(B_2F_4)_2$]. An almost isotropic spectrum would be observed if the two B_2F_4 ligands were orientated perpendicularly to each other in a tetrahedral arrangement about a central silver atom. Alternatively, an isotropic spectrum would result if anisotropic interactions were averaged out to zero either by the two B_2F_4 ligands librating around the silver atom in a fluxional molecule at frequencies higher than the hfi or by the whole molecule tumbling rapidly in its matrix site. As discussed above the spectrum is in fact slightly anisotropic because the averaging is incomplete. $A_{\mathrm{iso}}(\mathrm{B})$ and $A_{\mathrm{dip}}(\mathrm{B})$ are calculated from $A_{\parallel}(\mathrm{B})$ and $A_{\perp}(\mathrm{B})$ by eqns. 1 and 2.

$$A_{\mathrm{iso}}(\mathrm{B}) = 1/3(A_{\parallel} + 2A_{\perp}) \qquad (1)$$

$$A_{\mathrm{dip}}(\mathrm{B}) = 1/3(A_{\parallel} - A_{\perp}) \qquad (2)$$

Since the signs of the hyperfine interactions are not determinable from ESR spectra, two alternative sign assignments have been examined.

If $A_{\parallel}(\mathrm{B})$ and $A_{\perp}(\mathrm{B})$ are both positive, $A_{\mathrm{iso}}(\mathrm{B})$ = 15.25 MHz and $A_{\mathrm{dip}}(\mathrm{B})$ = 1.13 MHz. Dividing by the atomic parameters for unit spin density in the s and p boron orbitals (^{11}B = 2547 MHz and 63.64 MHz, respectively) gives, for each single boron: $\rho s(\mathrm{B})$ = 15.25/2547 = 0.006 and $\rho p(\mathrm{B})$ = 1.13/63.64 = 0.018.

Table 1 The simulation parameters for the two interpretations of the [$Ag(B_2F_4)_n$] complex

	No. of interacting nuclei	A/MHz (G)	g	Linewidth/MHz (G)
$Ag(B_2F_4)_2$				
^{109}Ag	1	1585.0 (565.3)	2.0009	
^{107}Ag	1	1371.0 (488.9)	2.0008	
$^{11}B_{\parallel}$	4	17.5 (6.2)		8.4 (3.0)
$^{11}B_{\perp}$	4	14.1 (5.0)		5.6 (2.0)
$Ag(B_2F_4)$				
^{109}Ag	1	1585.0 (565.3)	2.0010	
^{107}Ag	1	1371.8 (488.9)	2.0010	
$^{11}B_{\parallel}$	2	17.5 (6.2)		8.4 (3.0)
$^{11}B_{\perp}$	2	13.9 (5.0)		5.6 (2.0)
^{19}F	4	29.1 (10.4)		

Division of the silver hyperfine of 1371 MHz by the atomic value (^{107}Ag 5s parameter +1837.4 MHz) gives $\rho Ag = 0.75$. Therefore for the dimer with four borons, $\Sigma\rho = 0.75 + 4(0.006 + 0.018) \approx 0.85$.

If $A_{\parallel}(B)$ is positive and $A_{\perp}(B)$ is negative, $A_{iso}(B) = -3.57$ MHz and $A_{dip}(B) = 10.53$ MHz, $\rho s(B) = -3.57/2547 = -0.0014$ and $\rho p(B) = 10.53/63.64 = 0.165$ giving a total spin density for the dimer of $\Sigma\rho = 0.75 + 4(-0.0014 + 0.166) \approx 1.4$.

A more reasonable total spin density results from positive values of both $A_{\parallel}$ and $A_{\perp}$.

[$Ag(B_2F_4)$]. An almost isotropic spectrum for the mono-ligand complex requires either a fluxional or a rapidly tumbling molecule. Treating the spectrum as axial allows similar calculations of the total spin density in the silver 5s and boron 2s and 2p orbitals to be made.

The values of $A_{iso}(B)$ and $A_{dip}(B)$ are those already calculated for the dimer but the spin is now on two boron and four fluorine nuclei.

If $A_{\parallel}(B)$ and $A_{\perp}(B)$ are both positive the total spin density is $\Sigma\rho = 0.75 + 2(0.006 + 0.018) \approx 0.8$. If $A_{\parallel}(B)$ is positive and $A_{\perp}(B)$ negative, the total spin density is calculated to be 1.08. The possible spin contribution from the four fluorine nuclei is only ~0.002. In the monomeric case the latter alternative gives a spin density closer to unity but considering the approximations made in using atomic parameters to determine orbital spin densities from ESR hyperfine interactions the value of 0.8 is sufficiently close to unity to make it difficult to differentiate between the two alternative structures. Therefore we are reluctant to delineate between the monomer [$Ag(B_2F_4)$] and the dimer [$Ag(B_2F_4)_2$] on the basis of total spin densities.

The stability of the Ag/B_2F_4 complex

Observations made regarding the behaviour of the ESR spectrum under temperature variation showed that the ESR signals of the complex decrease by ~10% over ~30 min at 175 K. This indicates a binding energy of at least 50 kJ mol^{-1}. The source of the bonding is most likely an overlap of the semi-filled Ag 5s orbital and possibly the filled 4d orbitals with the two empty B 2p orbitals perpendicular to the molecular plane. This could account for the observed 0.25 electron donation from the Ag atom to the B_2F_4 ligand or ligands.

There is a possibility of back donation from the boron p-orbitals which themselves are part-filled by back donation from the fluorine p-orbitals. The extent of this interaction for different conformations of B_2F_4 has been analysed by Mo and Lin.[10] For the planar conformation, where B_2F_4 is assumed to be coordinated to silver atoms, there is sufficient occupancy of the boron π-orbitals to allow some of this electron density to flow back to the silver to reduce the charge separation. The bonding cannot be as effective as that in metal atom/alkene complexes where electron donation is from the filled ligand π-orbitals to the metal with a counter flow of electrons from the silver to the ligand π*-orbitals. It seems unlikely that there could be electron donation from the fluorine lone pair orbitals since the distance between the Ag and F centres is estimated to be 3.5 Å.

Theoretical calculations on the binding in the Ag/B_2F_4 complexes

Preliminary density function calculations (DFT B3LYP/6-31+G*) on [$Ag(B_2F_4)$] indicate that the complex would have a C_{2v} symmetry with the Ag atom situated centrally above the B–B bond above the plane of the B_2F_4 molecule. Population analysis shows that 16% of unpaired electron density transfers from the Ag to B_2F_4 (mostly to the B atoms); the remaining 84% being in the 5s Ag orbital. [$Ag(B_2F_4)_2$] is predicted to have a fluxional character with respect to the relative orientation of the two B_2F_4 moieties but the structure is not yet fully characterised. There is a calculated 24% transfer of electron spin density from the Ag to the two B_2F_4 molecules and which is shared equally between the four boron atoms. The calculated binding energy of ~20 kJ mol^{-1} is less than half that required to explain the persistence of the complex at 175 K.

At present we are unable to decide from our experimental results whether the species giving the ESR spectrum is a monomeric or dimeric B_2F_4 silver complex. Preliminary experiments in which ^{107}Ag has been reacted with B_2F_4 in adamantane at 77 K have not given a clear indication of which structure to favour. We prefer the dimer because it does not require the accidental coincidence that the fluorine hfi is twice that of the boron and there is a precedent that the dimeric alkene metal complexes are the most abundant and stable when alkenes react with metal atoms.[11]

However, the work shows that B_2F_4 has an unexpected ability to complex with a metal atom.

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References

1 J. A. Howard, H. A. Joly and B. Mile, *J. Am. Chem. Soc.*, 1990, **94**, 6627.
2 J. H. B. Chenier, H. A. Joly, J. A. Howard and B. Mile, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3329.
3 P. H. Kasai, D. McLeod Jr. and T. Watanabe, *J. Am. Chem. Soc.*, 1980, **102**, 179.
4 P. H. Kasai, *J. Am. Chem. Soc.*, 1984, **106**, 3069.
5 J. E. Bennett, B. Mile, A. Thomas and B. Ward, *Adv. Phys. Org. Chem.*, 1970, **8**, 79.
6 WIN-SimFonia, Bruker; Belford, Prof. R. L. Belford.
7 P. L. Timms, *J. Am. Chem. Soc.*, 1967, **89**, 1629.
8 A. J. Buck, B. Mile and J. A. Howard, *J. Am. Chem. Soc.*, 1983, **105**, 3381.
9 P. H. Kasai and D. McLeod Jr., *J. Chem. Phys.*, 1971, **55**, 1566.
10 Y. Mo and Z. Lin, *J. Chem. Phys.*, 1996, **105**, 1046.
11 J. A. Howard and B. Mile, *Electron Spin Resonance, Specialist Periodical Report*, RSC, Cambridge, 1989, vol. 11B, p. 137.