

Photoelectron Spectrum of B_4Cl_4

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Summary The He(I) photoelectron spectrum of B_4Cl_4 is interpreted in terms of a simple molecular orbital scheme, and evidence for B-Cl π bonding is deduced.

THE boron subchloride B_4Cl_4 has the unique cage structure of a tetrahedron of boron atoms within a tetrahedron of chlorine atoms.¹ The bonding in this molecule has not been investigated in detail either experimentally or theoretically, though a SCFMO calculation has been published²

for the model compound B_4H_4 . We present here the He(I) photoelectron spectrum of B_4Cl_4 and attempt to relate the bonding to that in other tetrahedral molecules.

The spectrum is shown in the Figure, and contains six bands, of which the fifth is composite and the sixth is very weak. The first band has a convex shape to the leading edge, but no other fine structure has been detected. The sixth band is present in all the samples studied, including some which were recovered from the spectrometer cold trap

and were resublimed before use, so despite the weakness we consider this to be a real feature of the B_4Cl_4 spectrum. Vertical ionization potentials (I.P.) are: 10.60(1), 12.44(1), 13.00(1), 13.57(1), 15.36(1), 15.96(1), 19.51(2), where the figures in parentheses are standard deviations.

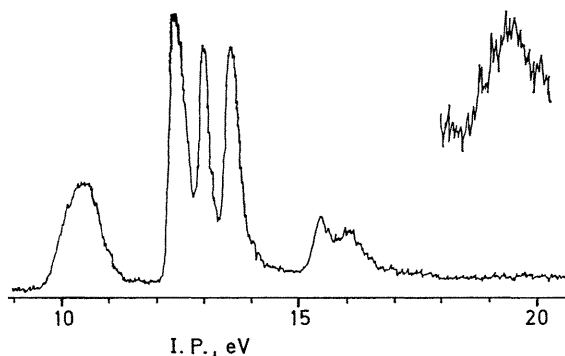


FIGURE 1. The photoelectron spectrum of B_4Cl_4 . The inset shows a portion of the spectrum with the vertical axis expanded by a factor of 10.

The molecule is expected to have T_d symmetry in the gas phase,¹ so resemblances to the Group IV_B tetrachlorides, whose spectra have been extensively studied,³⁻⁵ are expected. The set of three sharp bands, with an approximate intensity ratio 3:2:3, is very similar in appearance and in I.P. to the first three bands in the other tetrachloride spectra, except that these have intensities in the approximate ratio 3:3:2. We consider it most probable, therefore, that the second, third, and fourth bands result from ionization from π -type orbitals, mainly localised on the chlorine atoms.³⁻⁵

Because of the resemblance to the Group IV_B tetrachlorides, it is likely that the B_4 unit may be considered as a pseudo-atom, with a_1 and t_2 orbitals replacing the s and p valence orbitals of a single atom, but the orbitals holding the B_4 unit together also have to be considered. The usual basis set for a tetrahedron of atoms⁶ directs a p orbital of each atom towards the centre of the tetrahedron; these are p_σ orbitals and transform, like the s orbitals, as $a_1 + t_2$, and the remaining eight p_π orbitals transform as $e + t_1 + t_2$. Interaction between the two a_1 sets will give one orbital at low energy, mainly B₂s but directed in towards the centre of the tetrahedron and hence strongly bonding between all the B atoms, and another pointing outwards, less B-B bonding and mainly B₂p in character, which forms the "s-type" a_1 orbital of the pseudo-atom.

In a tetrahedron with a central atom the three t_2 sets (s , p_σ , p_π) interact independently, in a first approximation, with the central atom orbitals, so that the three sets are still recognisable in the final molecular orbitals. However, in an empty tetrahedron, the situation is different in that both $t_2(s)$ and $t_2(p_\sigma)$ are antibonding. Mixing a small amount of $t_2(p_\sigma)$ with $t_2(s)$ will decrease the B-B antibonding nature of $t_2(s)$ and direct this set outwards, forming the "p-type" orbitals of the B_4 pseudo-atom, but to obtain a t_2 set which binds the B_4 unit together it is necessary to combine p_σ and p_π in approximately equal amounts in-phase (the phases are those of ref. 6). This orbital set,

which may also include some $t_2(s)$ character, is such that each member of the set links an opposite pair of edges of the B_4 tetrahedron. The B₂p character will make this the highest-lying occupied orbital set, so we consider that the first photoelectron band arises from ionization of this set; the unusual shape of the band may be due to Jahn-Teller effects. The calculations² upon B_4H_4 , and our CNDO/2 calculations upon B_4F_4 , support these qualitative ideas.

Recent work on the spectra of hydrocarbons and fluorocarbons shows that the photoelectron bands from C₂s-type orbitals are considerably weaker than those from C₂p-type orbitals, and also that among the former, bands from bonding orbitals are very much weaker than those from antibonding or nonbonding orbitals.⁷ Since the orbital of mainly B₂s character in BCl₃ has an I.P.^{8,9} of 17.7 eV, and we have assigned a weak band in the B₂Cl₄ spectrum at 18.1 eV to a B₂s-B₂s bonding orbital,¹⁰ it is most reasonable to assign the very weak 19.5 eV band in B_4Cl_4 to the B₂s-B₂s bonding a_1 orbital. The remaining band in the B_4Cl_4 spectrum, with peaks at 15.4 eV and 16 eV, is then assigned to the bonding orbitals $a_1 + t_2$ formed from overlap of Clp orbitals with the B_4 pseudo-atom $a_1 + t_2$ orbitals. Since the B character of the t_2 set is mainly 2s while that of a_1 is mainly 2p, the similar intensities of the two peaks are compatible with this interpretation. In contrast, the corresponding two bands in the Group IV_B tetrachloride spectra have intensity ratios greater than 3:1, since the central atom character of t_2 is np , while that of a_1 is ns . Because of this, the B-Cl bonding is expected to have much more s character than p, in marked contrast to the "sp³ hybrid" description of Group IV_B tetrahalides.

The group of three sharp bands is due to the halogen p_π orbitals. Since the central band has the lowest intensity and the t_1 orbital is always at higher energy⁴ than the e orbital, the Cl p_π orbital energy sequence is $t_1 > e > t_2$. In the Group IV_B tetrachlorides the sequence is $t_1 > t_2 > e$ from interaction of $t_2(\pi)$ with the t_2 M-Cl bonding set,⁴ but in B_4Cl_4 the B-B bonding t_2 set at higher energy probably also interacts with $t_2(\pi)$ so that the final sequence is that predicted⁴ from Cl-Cl interactions alone. However, the t_1-e separation of 0.56 eV is comparable with that of 0.6 eV in SnCl₄, although the Cl-Cl distance in B_4Cl_4 is greater than that in SnCl₄. The only mechanism for increasing the t_1-e separation is a fairly strong interaction of $t_1 + e(Cl3p)$ with the unoccupied $t_1 + e(B2p)$ orbitals which have a large separation because of the small B-B distance. This implies a π -type back-donation of charge from Cl to B, and will be a factor contributing to the stability of this unusual molecule.

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Added in proof: Since this communication was submitted, Dr. D. S. Urch and Dr. A. G. Massey (Department of Chemistry, Queen Mary College, London, E.1) have drawn our attention to a paper (ref. 11) which anticipates the results reported here. They have provided the following comments:

The photoelectron spectrum of B_4Cl_4 reported in this communication is in good agreement with the prediction made by Massey and Urch¹¹ as to the ordering and nature

of the molecular orbitals in that molecule. No quantitative estimates of resonance integrals or ionisation energies were made then but it seems that the only correction that needs to be made to the original calculations is to reduce somewhat the estimated interaction between t_2 "sp" and t_2 "p" orbitals. The energy level diagram (Figure 4, ref. 11) can then be redrawn as shown in Figure 2. The ordering of the molecular orbitals in the B_4 unit is the same but the $e-t_2$ energy separation has been reduced. This in turn will mean that t_2 and t_2^0 molecular orbitals will have more ligand, and more B_4 character, respectively than was originally suggested for a molecule of type (b). e Type interaction will be unaffected and some donation from the ligands to the B_4 unit will be associated with these orbitals, thereby relieving the basic electron deficiency of central tetrahedron of boron atoms. It is this particular boron-chlorine π -bonding that is most important in stabilising B_4Cl_4 . It seems most reasonable to associate the peaks at 15.36 and 15.96 eV with B-Cl bonds by analogy with other compounds.

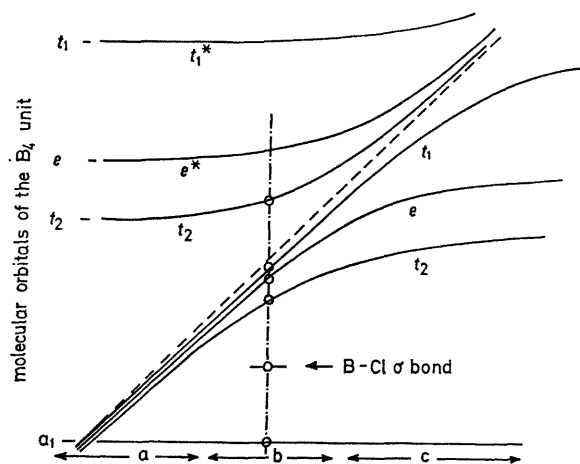


FIGURE 2. Revised molecular orbital energy level diagram for B_4X_4 . Ionisation energy of X orbital is indicated by the dashed line. B_4Cl_4 is roughly located by the line $-\cdot-\cdot-$ and relative orbital ionisation energies by the points \circ .

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