

Detection of Chlorothioborine, $\text{ClB}=\text{S}$, a New Unstable Triatomic Molecule, by Photoelectron and Microwave Spectroscopy

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Abstract: When disulfur dichloride, S_2Cl_2 , is passed over crystalline boron at 800–1000 °C, the new unstable triatomic molecule chlorothioborine, $\text{ClB}=\text{S}$, can be detected in the reaction products. The identity of the species has been confirmed by joint photoelectron and microwave spectroscopic experiments. The photoelectron spectrum between 6 and 20 eV consists of three bands, one of which appears to be composite, and the pattern is consistent with that expected for such a species. The first band is split by spin-orbit coupling and yields energies associated with the adiabatic ionization to the ground $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states of ClBS^+ of 10.51 and 10.55 eV, respectively. Many lines associated with the $J = 4, 5,$ and 6 rotational transitions of this species have been detected by microwave spectroscopy. The observed rotational constants for the two most abundant isotopic variants $^{35}\text{Cl}^{11}\text{B}^{32}\text{S}$ and $^{37}\text{Cl}^{11}\text{B}^{32}\text{S}$ are $B_0 = 2796.7793 \pm 0.0004$ and $B_0 = 2722.9996 \pm 0.0001$ MHz, respectively. The mechanism of formation is discussed.

Introduction

The interesting unstable species thioborine has now been well characterized by several techniques such as mass spectrometry¹ as well as microwave,² infrared,³ and photoelectron spectroscopy.^{4,5} Little, if anything, however, is known about related substituted monomeric species of the type XBS where X is a halogen or other group such as CH_3 , though the trimers are quite well known.⁶ Nor is much known in the case of the analogous monomeric oxygen-containing species XBO , the borines, though some work has shown that monomers are formed from the trimers at high temperatures.^{7–9} The lifetime of HBO certainly appears to be much shorter than that of HBS , which is several seconds.⁴

Photoelectron and/or microwave techniques have recently proven very successful in the study of a wide range of similarly unstable and reactive species in addition to HBS . These include $\text{H}_2\text{C}=\text{C}=\text{S}$,¹⁰ CH_3CHSe ,¹¹ $\text{CH}_2=\text{PCl}$,¹² $\text{CH}_3\text{C}\equiv\text{P}$,¹³ and $\text{FC}\equiv\text{P}$.¹⁴ The last two species are phosphalkynes which contain the group $-\text{C}\equiv\text{P}$ which is isoelectronic with the thioborine group $-\text{B}=\text{S}$. These techniques have now been extended to explore methods of producing new monomeric thioborines (other than $\text{HB}=\text{S}$) and characterizing their molecular properties. We report here on the development of a useful method of producing these species which involves a high-temperature reaction between solid boron and a gaseous disulfide. In this case we have been able to observe the microwave spectrum of chlorothioborine, $\text{ClB}=\text{S}$, produced by passing Cl_2S_2 over crystalline boron at 800 °C. The identity of the species has been further confirmed by photoelectron measurements.

That this process has more general applicability is witnessed by recent work which indicates that the methyl analogue, CH_3BS , is formed when dimethyl disulfide, CH_3SSCH_3 , is used.¹⁵ HBS itself was made originally by the passage of H_2S over boron at 1100 °C. The more facile scission of the disulfur bond on which the present studies are based implies that HBS should be more readily produced if H_2S_2 is used. The possible reasons for this are considered in the Discussion.

Experimental Section

In these experiments the high-temperature reaction was carried out by passing gaseous S_2Cl_2 (B. D. H.) via a needle valve over solid crystalline boron chips (Koch-Light) heated to ca. 800–1000 °C. The reactor consisted of a quartz tube (i.d. 8 mm) lined internally with a 0.125-mm thick molybdenum sheet. It was packed for ca. 20 cm of its length with boron and heated by a small furnace over this length. The new species is readily detected when the pyrolysis products are passed directly into the cell of a microwave spectrometer or the ionization chamber of a photoelectron spectrometer. The photoelectron experiments indicated that between 400 and 800 °C the main product is BCl_3 and at ca. 1000 °C several so far unidentified species are produced. At slow flow rates the main product is ClBS and the features belonging to BCl_3 are much diminished. In both the microwave and photoelectron experiments significant quantities of HBS are detected.

If after some period (1–2 h) the S_2Cl_2 flow is shut off, the temperature maintained, and the reacted boron sample pumped, it was found that the ClBS spectrum persists for several hours.

A Perkin-Elmer PS16 photoelectron spectrometer and a Hewlett-Packard A8460 microwave spectrometer were used in these experiments. The theoretical calculations were carried out using the GAUSSIAN 70 program¹⁶ with an STO-4-31G basis.

Observed Microwave and Photoelectron Spectra. During the microwave experiments on the flowing system, three $\Delta J = 1$ rotational transitions of a small linear molecule were readily identified. The spectra showed Stark patterns and vibrational satellite structure typical of a linear molecule. Each transition had a partner of the order of one-third its intensity to lower frequency and a second partner of the order of one-fourth its intensity just to high frequency. This is just the right isotopic satellite pattern to be expected for a system involving both chlorine and boron where the natural abundancies are ^{35}Cl : ^{37}Cl (75.5:24.5) and ^{10}B : ^{11}B (19.6:80.4). There are many other weaker lines. In addition, each ground-state line showed a simple quadrupole pattern of the right order of magnitude for a molecule containing chlorine. Finally, we note that using the bond lengths $r(\text{B}-\text{Cl}) = 1.728$ Å from BClF_2 ¹⁷ and $r(\text{B}=\text{S}) = 1.600$ Å from HBS ² the predicted B value for $^{35}\text{Cl}^{11}\text{B}^{32}\text{S}$ is 2729.36 MHz whereas that observed is 2796.779 MHz (Table 1). All these results are consistent and leave no doubt that the identity of the species is indeed chlorothioborine, ClBS .

The microwave spectrum is in fact quite rich in lines showing many isotopic and vibrational satellites. The stronger ground-state lines are listed in Table 1 together with the derived rotational parameters. A detailed study of the spectrum is in progress and will be published when completed.

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Table I. Rotational Frequencies (MHz) and Derived Parameters^a

	F'	F''	$^{35}\text{C}^{11}\text{B}^{32}\text{S}$	o-c^b	$^{37}\text{C}^{11}\text{B}^{32}\text{S}$	o-c^b
$J = 5 \leftarrow 4$	13/2	11/2	27 967.849	0.000	27 230.012	-0.001
	11/2	9/2				
	9/2	7/2	27 967.111	-0.004	27 229.442	0.001
7/2	5/2					
$J = 6 \leftarrow 5$	15/2	13/2	33 561.227	0.001	32 675.852	0.001
	13/2	11/2				
	11/2	9/2	33 560.742	0.005	32 675.469	-0.001
9/2	7/2					
$J = 7 \leftarrow 6$	17/2	15/2	39 154.572	-0.003	38 121.659	0.000
	15/2	13/2				
	13/2	11/2	39 154.225	0.001	38 121.386	0.000
11/2	9/2					
B_0 , MHz			2796.7793 \pm 0.0004			2722.9996 \pm 0.0001
D , Hz			336 \pm 5			316 \pm 2
eQq , MHz			-42.8 \pm 0.2			-33.33 \pm 0.05

^a All errors are one standard deviation. ^b o-c means observed - calculated frequency.

Table II. Ionization Potential Data (eV)

Obsd	IP ^a	Calcd IP	Assignment
10.51	(10.68) ^{b,c}	10.83	$^2\Pi_{3/2}$
10.55	(10.73) ^{b,c}		$^2\Pi_{1/2}$
13.63	(13.63) ^{b,d}	14.26	$^2\Sigma^+$
~13.7		14.86	$^2\Pi$
	(16.77) ^b	17.90	$^2\Sigma^+$

^a Adiabatic IP, vertical IP in parentheses. ^b Ionization potential to ± 0.1 eV. ^c Spin-orbit splitting 370 ± 30 cm⁻¹. Vibration frequency 1375 ± 30 cm⁻¹. ^d Vibrational frequency 1400 ± 30 cm⁻¹.

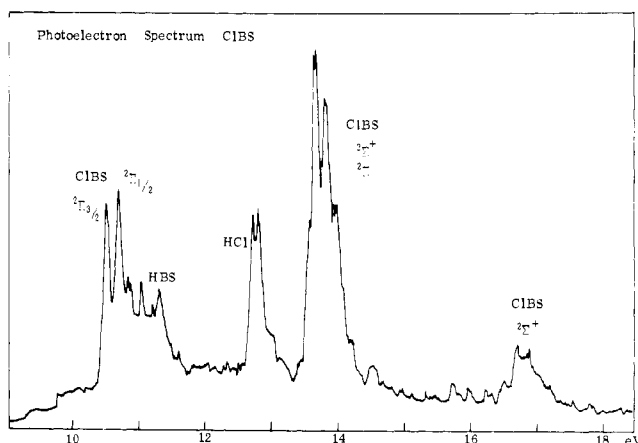


Figure 1. Photoelectron spectrum of the products of the high-temperature (850 °C) reaction between Cl_2S_2 and B. The strongest features belong to CIBS and weaker ones to HBS and HCl.

The photoelectron spectrum in Figure 1 shows four distinct features. The first band is clearly composite and the weaker component at 11.1 eV can be assigned to an IP of HBS as can the weak shoulder at 13.54 eV on the third feature. This is shown more clearly in Figure 2b. These two bands vary together in intensity and their ionization energies are consistent with those of HBS.⁴ The band at 12.75 eV can be assigned to HCl and some further weaker features to H_2 . The origin of the hydrogen is not clear and so far it has proven impossible to eliminate it completely during these particular experiments.

After these known bands have been assigned, three strong ones remain; these are listed in Table II. The relative intensities of these bands remained constant throughout the course of our experiments and have been assigned to the new species CIBS. The assignment is discussed in the next section.

Analysis of Photoelectron Spectrum. The CIBS molecule is a 38-electron system which is expected to have the ground-state electron

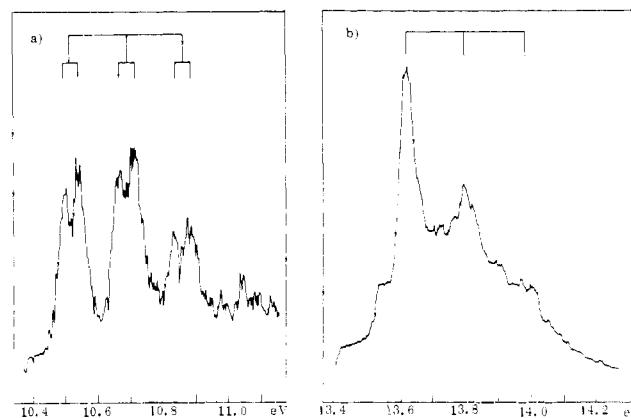


Figure 2. (a) Higher resolution expansion of the first band of CIBS. (b) Higher resolution expansion of the second composite band of CIBS.

configuration and term

$$\dots (10\sigma)^2(3\pi)^4(11\sigma)^2(4\pi)^4 \quad ^1\Sigma^+$$

From this electron configuration we see that the first band should correspond to the excitation of a (4π) electron to yield a $^2\Pi$ state of the CIBS^+ ion. This state should be split into $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ substates and assuming an inverted configuration the $^2\Pi_{3/2}$ level would be the ground state. The first band, shown in more detail in Figure 2a, consists of a progression of doublets with three to four members. The doublet splitting of 370 ± 30 cm⁻¹ is close to that expected, comparing well with the values 443, 355, and 278 cm⁻¹ in CS_2 ,¹⁸ COS ,¹⁸ and CS ,¹⁹ respectively. The calculations confirm that, as expected, the first band results from the excitation of an electron localized mainly in the $\text{B}=\text{S}$ π system and thus the vibrational interval of 1375 ± 30 cm⁻¹ is assigned to the $\text{B}=\text{S}$ stretching frequency of the ion's electronic ground state. This band is quite analogous with the first band of HBS^4 which lies close by as an impurity in Figure 1. The photoelectron data are collected together in Table II and compared with the results of the theoretical calculation.

The second band assigned to CIBS^+ , which lies at ca. 13.6 eV, is quite strong (Figure 1), and is expected to arise from either the excitation of an electron from the (11σ) orbital or the degenerate (3π) chlorine lone-pair orbitals. These would be expected to lie in this region because the equivalent σ orbital of HBS lies at 13.54 eV⁴ and the equivalent chlorine excitation of CICN at 15.37 eV.²⁰ Calculation predicts a separation of only 0.6 eV (Table II). The observed relative intensity is much stronger than is consistent with a single band and it would thus appear that these two IPs are coincident. The vibrational structure is assigned to the σ excitation which might be expected to give rise to a short progression in the $\text{B}=\text{S}$ stretching frequency⁴ whereas the lone-pair π excitation is expected to be more symmetrical with less well-defined structure as in CICN ²⁰ and $\text{CIC}\equiv\text{CH}$.²¹ The

calculation procedure was tested on HBS and the results showed very satisfactory agreement with experiment and indicated that they are a reliable aid to the assignment of the CIBS spectrum.

The third band at 16.77 eV is assigned to the fourth IP and again experiment and theory are in close agreement (Table 11). The band is associated with the excitation of an electron in the B-Cl bonding (10σ) orbital and gives rise to a $2\Sigma^+$ state of the ion.

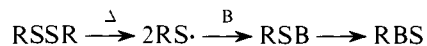
The calculation predicts no other band below 27.0 eV.

Discussion

The proximity with which the observed and predicted microwave and photoelectron spectra agree leaves no doubt as to the identity of the new species. The observed B value is somewhat larger than that predicted on the basis of bond lengths transferred from related molecules. This is almost certainly because the B-Cl bond is shorter in CIBS than in ClBF_2 ¹⁷ as might be anticipated as the hybridizations on boron differ in the two cases.

These joint photoelectron/microwave experiments show just how useful the two techniques are when combined. The species was originally readily identified by microwave spectroscopy because the technique is very sensitive to species such as these, i.e., small or linear or with a large dipole moment.^{22,23} The photoelectron measurements, on the other hand, yield data on all the fragments produced because photoionization cross sections are roughly comparable. Thus, for instance, the photoelectron study showed that BCl_3 and HCl were formed in significant amounts.

It is interesting to consider the possible mechanisms by which CIBS is formed. Although at first sight a solid-gas reaction of the type employed here might seem rather inefficient, our results indicate quite good yields of CIBS. It seems very likely that the initial process involves the scission of the S-S bond at the boron surface producing two highly reactive CIS-radicals. These may now react to form CIBS fragments which may isomerize to CIBS structures, i.e.,



Clearly more complex processes are going on as BCl_3 is formed. It also seems likely that the solid trimeric thioborane (CIBS)₃

is formed and this gives rise to the monomer which can be detected after the Cl_2S_2 supply is stopped. Further studies of these systems, to determine the reaction pathways, are in progress. The general applicability of this method has already been confirmed to some extent by the detection of $\text{CH}_3\text{B}=\text{S}$ when CH_3SSCH_3 is used instead of ClSSCl .¹⁵

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