

Journal of The Chemical Society, Chemical Communications

NUMBER 8/1981

The Detection of Unstable Monomeric Selenidoborons: Chloroselenidoboron, ClB=Se

By TERRY A. COOPER, MICHAEL A. KING, HAROLD W. KROTO,* and ROGER J. SUFFOLK
(School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ)

Summary High-temperature flow pyrolysis reactions carried out to detect unstable selenidoboron species, XB=Se (X = H or Hal) in the gas phase, have been successful in detecting the chloro-compound ClB=Se which is the first in this family to be identified; characterisation by microwave spectroscopy indicates that $r(\text{B}=\text{Se}) = 1.751 \pm 0.002 \text{ \AA}$.

MICROWAVE and photoelectron techniques are ideally suited to the study of small molecules which tend to polymerise. These techniques have been used extensively to characterise members of the sulphidoboron family XB=S with X = H,^{1,2} Cl,^{3,4} Br,⁵ and F⁵ which are produced in low-pressure (*ca.* 30 μmHg) flow pyrolysis reactions between crystalline boron and the appropriate sulphide or disulphide at *ca.* 1000 °C. In the condensed phase these species tend to exist as trimers (XBS)₃.⁶

The chemistry of the selenium analogues appears to be much less well known and no data on the trimers, let alone the monomers, have been reported. In a current series of experiments, similar to those carried out previously on the sulphur-containing molecules, we have attempted to detect both HB=Se and ClB=Se. The microwave spectrum of chloroselenidoboron, ClB=Se, has been obtained when Cl₂Se₂ is passed over B at 1000 °C. The observed spectrum is much weaker than that of ClB=S. Preliminary photoelectron measurements indicate that this is because ClB=Se is more unstable (the lifetime of ClB=Se was *ca.* 1.5 s) and also because the reaction which produces it is less efficient. Attempts to detect HB=Se by allowing H₂Se to react with B have been unsuccessful. The study indicates that hydrogen and elemental selenium are the major products and if HB=Se is formed at all it tends to poly-

merise rapidly, perhaps to the non-polar trimer (HBSe)₃ which cannot be detected by microwave spectroscopy.

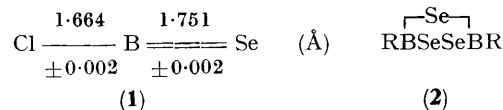
The microwave spectrum detected can be readily assigned to the $J = 7, 8, 9,$ and 10 transitions of the linear molecule ClB=Se. Each $\Delta J = +1$ transition consists of a group of lines due to the various isotopic species present in natural abundance. In addition to the ground state lines, vibrational satellites associated with the excitation of the ν_2 degenerate bending mode, in particular the l -doublet split $\nu_2 = 1$ transitions characteristic of a linear molecule, are detected.

TABLE. Rotational constants.

Isotopic variant	B_0/MHz^a
³⁵ Cl ¹⁰ B ⁸⁰ Se	1752.7261 ± 0.0016
³⁵ Cl ¹¹ B ⁷⁸ Se	1765.3568 ± 0.0062
³⁵ Cl ¹¹ B ⁸⁰ Se	1750.3202 ± 0.0011
³⁷ Cl ¹¹ B ⁷⁸ Se	1703.6283 ± 0.0013

^a Corrected for quadrupole interactions.

The derived rotational constants for four standard isotopic species, corrected for the quadrupole moment of the chlorine nucleus, are given in the Table. The observed B_0 values were within 0.5% of those calculated using the initially assumed structure: $r(\text{Cl}-\text{B}) = 1.66 \text{ \AA}$ and $r(\text{B}=\text{Se}) = 1.75 \text{ \AA}$ (from a comparison of the geometries of ClB=S,⁴ MeCH=S,⁷ and MeCH=Se⁸). Using the data of Table, r_s substitution co-ordinates^{9,10} can be derived which yield the r_s bond lengths shown in (1). The errors are derived



assuming the relation $\delta r_s = ca. 0.0012/r_s$ applies,¹¹ where r_s are the substitution co-ordinates and δr_s is the error.

The chemistry of selenidoboron compounds does not seem to have been investigated in any great detail. Whereas numerous cyclic polymers of the sulphidoborons such as $(XBS)_n$ with $n = 3$ or sometimes 2 and X = H, Hal, SH, and Ph are known, no analogous selenium species seem to have been reported though a speculative structure of the form (2) has been published.¹² Now that the first species of the form $XB=Se$ has been detected it seems very likely that the interesting chemistry of this system should become accessible. One problem may however be the strong

tendency for elemental Se to form in these systems. This certainly appears to be an important reason for the lack of detection of $HB=Se$. It may also be noted that although we were able to detect $MeCH=Se^8$ on the pyrolysis of $(MeCHSe)_3$, attempts to detect the microwave spectrum of $H_2C=Se$ by pyrolysing $(H_2CSe)_3$ have not so far been successful.

We thank the S.R.C. for the award of grants to T. A. C. and M. A. K.

(Received, 16th January 1981; Com. 048.)

¹ E. F. Pearson and R. U. McCormick, *J. Chem. Phys.*, 1973, **58**, 1619.

² H. W. Kroto, R. J. Suffolk, and N. P. C. Westwood, *Chem. Phys. Lett.*, 1973, **22**, 495.

³ C. Kirby, H. W. Kroto, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1978, **100**, 3766.

⁴ C. Kirby and H. W. Kroto, *J. Mol. Spectrosc.*, 1980, **83**, 130.

⁵ T. A. Cooper and H. W. Kroto, to be published.

⁶ W. Siebert, E. Gast, F. Riegel, and M. Schmidt, *J. Organomet. Chem.*, 1975, **90**, 13; E. L. Muetterties, 'The Chemistry of Boron and its Compounds,' Wiley, New York, 1967, p. 650.

⁷ H. W. Kroto and B. M. Landsberg, *J. Mol. Spectrosc.*, 1976, **62**, 346.

⁸ M. Hutchinson and H. W. Kroto, *J. Mol. Spectrosc.*, 1978, **70**, 347.

⁹ J. Kraitchman, *Am. J. Phys.*, 1953, **21**, 17.

¹⁰ C. C. Costain, *J. Chem. Phys.*, 1958, **29**, 864.

¹¹ C. C. Costain, *Trans. Am. Crystallogr. Assoc.*, 1966, **2**, 157.

¹² B. M. Mikhalov and T. A. Shchegoleva, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1959, **1**, 331.