A STUDY OF THE BONDING PROPERTIES OF SULPHUR IN BORNITE

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ABSTRACT

The bonding properties of the (seemingly) 5- and 7-coordinate S atoms in bornite (Cu₄FeSe) have been studied in relation to the availability of the 3d orbitals for bonding. Three bonding schemes have been considered, (i) some of the M-S bonds are non-coordinate (ionic), (ii) the high coordination numbers are due to covalent-ionic resonance and (iii) the S atoms are, in actuality, 5- and 7-coordinate.

It is shown that bornite can be likened qualitatively to a sphalerite skeleton containing layers of ionically-bound interstitial metal atoms. Hence, the S atoms are tetrahedrally coordinated.

INTRODUCTION

The 3d orbitals of free sulphur atoms are too weakly bound and diffuse to partake prominently in covalent chemical bonding. Craig & Magnusson (1956) have shown, however, that highly electronegative ligands can polarize the diffuse 3d orbitals, thus contracting the d orbital and bringing the electrons closer to the neighbouring bonding atoms. The covalent bonding and d²sp³ hybridization of S orbitals in SF₆ is an example of 3d orbital contraction. The bonding in SF₆ has been classed as highly covalent (Dwyer & Mellor, 1964).

Because metals are, in general, of relatively low electronegativity (compared with F), it is conceivable that the S 3d orbitals will be unavailable in the M-S bonding scheme, and S will either use its 3s and 3p orbitals in forming 4 sp³ orbitals (tetrahedral bonding) or will “spread” the bonding power of the 3s and 3p orbitals over a larger number of weaker bonds. The tetrahedral (sp³) bonding scheme in ZnS suggests that the former is energetically the more favourable, because the Zn²⁺:S⁻ radius ratio favours octahedral bonding. Coulson (1952) has pointed out that directional (covalent) forces play an important part in tetrahedral structures, which suggests that the Zn-S bonds possess some covalent character. It would seem, however, that the bonding in ZnS is mainly ionic (Berlincourt, Joffe & Shiozawa (1963); Title (1969)).

In some metal sulphides, the M-S bond would seem to possess appreciable covalency, e.g. pyrite. Pappalardo & Dietz (1961) and Manning (1966) demonstrated that the S ligand field is slightly weaker than that of O. However, for high-spin Fe(OH₄)₆²⁺, the splitting (Δ) of the Fe t₂g and

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\( e_g \) orbitals is \( \sim 10,000 \text{ cm}^{-1} \), while for diamagnetic pyrite \( \Delta > 15,000 \text{ cm}^{-1} \). This large \( \Delta \) value is indicative of a high degree of covalency. Also, the S coordination number is greater than 4 in FeS. In any analysis of \( M-S \) bonding schemes, therefore, the utilization of the S 3d orbitals must be considered.

The structure of the metastable rhombohedral form of bornite, \( \text{Cu}_3\text{FeS}_4 \), has recently been determined by Morimoto (1964), and the crystal structure is portrayed in Fig. 1. Bornite is of great interest from the bonding point of view because the S atoms are seemingly 5- and 7-coordinate, while the metals are tetrahedrally bound. However, the metal atoms in bornite do not appear to lie at the centre of a S tetrahedron, but are displaced and lie at the corner of another tetrahedron whose centre coincides with the centre of the S tetrahedron (Fig. 1). The displacement is small compared with the \( M-S \) bond lengths, and, because the \( R \) factor for the structure is \( \sim 15 \) per cent, we feel we are justified in considering the grosser aspects of the structure. Our study of the bonding in bornite will be based on the average positions of the metals.

**Discussion**

It is customary when estimating the coordination number of an atom in a crystal to ascribe a coordinate bond to each of the atom’s closest neighbours provided the cation-anion distance is within reasonable limits, say \( \sim 2.5 \) Å. In this way, the S atoms in the rhombohedral form of bornite are 5- and 7-coordinate (\( S_{11} \) and \( S_1 \) atoms in Fig. 2a and 2b). Six of the 7 \( S_{1-M} \) bond lengths are equal, and although this suggests that these 6 bonds are of similar character, it in no way proves that they are. The 7 \( S_{1-M} \) bonds are not oriented in the lowest energy configuration, and it would seem that directional (covalent) forces are operative. If some of the \( S_{1-M} \) bonds are of the “purely” ionic or van der Waal’s type, the effective coordination number of the \( S_1 \) atoms is less than 7. In view of the low electronegativity of cations, it would be gratifying if the S coordination numbers (as defined by the number of electron pair bonds) could be explained in terms of hybridization schemes involving the S 3s and 3p orbitals. In discussing the bonding properties of S in bornite, therefore, the following possibilities will be considered:

(i) some of the \( M-S_1 \) bonds are ionic (non-coordinate),

(ii) the \( S_1 \) coordination number is a manifestation of covalent-ionic resonance,

(iii) the \( S_1 \) atoms are 7-coordinated, implying the ready availability of the 3d orbitals for bonding.
Fig. 1. Structure of the rhombohedral form of bornite (Morimoto, 1964).
Scheme (\(i\)):

In considering this scheme, we are, in essence, attempting to explain the S bonding in terms of 3s and 3p hybridization, i.e., 3- or 4-coordinated S atoms. To consider a 6-coordinated S atom does not seem worthwhile, as energetically the system would be little different from that of a 7-coordinate S (from the point of view of the availability of the \(d\)-orbitals for bonding). Also, for a 5-coordinate \(S_1\) (two non-coordinate bonds), it is difficult to choose two bonds that are in any way exceptional; and such a scheme would seem artificial. This leaves us with two possibilities, either the \(S_1\) atoms are 3-coordinate with four non-coordinate bonds or the \(S_1\) atoms are 4-coordinate with three non-coordinate bonds. The latter is energetically the more favourable scheme, and, moreover, it is not possible to choose uniquely three coordinate bonds that correspond to any simple 3-coordinate structure (Figs. 1 and 2). It is apparent, therefore, that Scheme (\(i\)) demands a 4-coordinate (tetrahedral) S atom.

These thoughts transcribe into practice well, because the \(M_\text{I} - S_1\) and the three \(S_1 - M_{\text{III}}\) bonds are oriented tetrahedrally. According to Morimoto (1964), the \(M\) atoms lie at the apices of small tetrahedra, and the \(M_\text{I} - S_1 - M_{\text{III}}\) angles range between 100° and 113°, with an average value of 110°. These angles are close to the classical tetrahedral angle of 109°28′, and it seems reasonable to suppose that the \(S_1\) are bonded tetrahedrally to an \(M_\text{I}\) and three \(M_{\text{III}}\) atoms. The small displacement of the metal atoms from the centres of the S tetrahedra (Fig. 1) could be due to the admixing of e.g. \(sp^3\) hybrid orbitals or the balancing of electrostatic forces over many cell distances. However, the small displacement

![Figure 2. S environments in bornite. (a) "5-coordinate" \(S_{\text{II}}\), (b) "7-coordinate" \(S_1\).](image-url)
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would seem to be of secondary importance in an understanding of the basic structure of the crystal.

According to Scheme (1), the $M_{II}$ atoms are bound through electrostatic forces. There is a strong argument in favour of the scheme—the "5-coordinate" $S_{II}$ atoms are also tetrahedrally coordinated (to one $M_{II}$ and three $M_{I}$ atoms). Hence, this one bonding theory can account for the high coordination number of both the $S_{I}$ and $S_{II}$ atoms, and more importantly, the theory proposes tetrahedral coordination for $S_{I}$ and $S_{II}$.

The bornite structure on this model may be likened qualitatively to a sphalerite-type skeleton containing layers of ionically bound interstitial atoms. The different bulk appearance of sphalerite and bornite should not invalidate this comparison, because the lustre of bornite is a manifestation of the low band gap. Thus chalcopyrite has a sphalerite-type structure and a metallic lustre. Of great relevance is the recent demonstration that Cu as Cu(II), occupies the interstitial octahedral sites in doped ultra-high-purity sphalerite (Manning, 1966). A similar spectrophotometric investigation has detected Fe(III) in octahedral sites in natural Fe-containing sphalerites (Manning, 1967), and the ratios of substitutional:interstitial Fe is $\sim$10:1. The crystals contained 16 per cent Fe. It would seem, therefore, that the interstitial sites in sphalerite are stable with respect to metal occupation.

Sphalerite also has tetrahedral interstitial sites, but octahedrally bound Cu(II) is favoured because of the greater ligand field stabilization energy (LFSE). Both octahedrally and tetrahedrally bound Fe(III) complexes are known, but in the Fe-containing sphalerites the octahedral sites are favoured (Manning, 1967). If we take the sphalerite-bornite analogy one step further, the "interstitial" ionic $M_{II}$ atoms in bornite would seem to be Cu(I) because the preferred coordination of Cu(I) is tetrahedral. The remaining Fe and Cu atoms are, therefore, distributed among the $M_{I}$ and $M_{II}$ sites, and it has been suggested by Morimoto (1964) that Fe is an $M_{I}$ atom. We can now write the bornite structure as:

$$[\text{Cu}_{3}\text{FeS}_{4}]^{3-}.2\text{Cu}^{+}$$

Electrical measurements in these laboratories have shown that bornite has the properties of a semiconductor. Therefore, the electrons of the "interstitial" Cu$^{+}$ must partake in the tetrahedral coordination of the sphalerite-type skeleton. The electronic configuration of the free S atom is 3$s^23p^4$, so that an additional two electrons can make up the four tetrahedrally oriented electron pairs. The sphalerite-type skeleton of bornite is therefore one of Cu(I) and Fe(III).

For transition metals of the $d^0$ and $d^{10}$ configuration, the LFSE = 0. In view of the unavailability of the S 3$d$ orbitals, it would seem that
tetrahedral structures are favoured. Thus some sulphide minerals with
tetrahedral structures are: zinc sulphide \((d^{10}\) cation\), CdS\((d^{10})\), red
MnS\((d^{5}\) (Wyckoff, 1948) and chalcopyrite \((d^{6}\) and \(d^{10}\) \,(Donnay, Corliss,
Donnay, Elliott & Hastings, 1958). It seems reasonable, at this point, to
suggest that the metal excess in chalcopyrite could be due to interstitial
cations.

In summarizing, therefore, it can be said that Scheme (\(i\)) has a number
of attractive features. These are:

(a) The \(S_1\) and \(S_{II}\) atoms are 4-coordinate,

(b) a single theory can explain the coordination properties of \(S_1\) and
\(S_{II}\),

(c) the bornite-sphalerite analogy seems reasonable, especially in view
of the detection of interstitial cations in sphalerite and the correla-
tion of tetrahedral structures with \(d^{5}\) and \(d^{10}\) cations.

Scheme (\(ii\)):

The logical scheme to consider here is one that stems directly from
Scheme (\(i\)). The \(M_1\) and three \(M_{III}\) atoms are tetrahedrally oriented
about the \(S_1\) atom. Similar calculations show that the \(M_{III}S_1-M_{III}\) angles are also close to the tetrahedral, and the 7 \(S_1-M\) directions radiate
to 7 corners of a cube. The spatial relationship between a cube and a
tetrahedron is shown in Fig. 3, and it is evident that the cube is the ideal
arrangement for two superimposed (resonating) tetrahedra. In our scheme,
the extreme resonance structures of \(S_1\) are shown in Fig. 4. The eighth
direction of an \(S_1\) cube has a dangling electron pair.

There is one serious objection to this theory. The \(S_{II}\) atoms resonate
in synchronism with \(S_1\), and the valence structures of the resonating \(S_{II}\)
atoms are shown in Fig. 5. It is apparent that these two structures must
be of markedly different energy, and it is extremely unlikely that the
R.H.S. structure can partake significantly in the resonance. The R.H.S.
structure has three dangling bonds—a quite unrealistic situation.

Although these considerations do not rule out resonance completely,
it would seem that the L.H.S. structures in Figs. 4 and 5 would predomi-
nate. Scheme (\(ii\)) therefore leads us to the same conclusion as Scheme (\(i\)—
that the \(M_{III}\) atoms are bound ionically.

Scheme (\(iii\)):

The 7 \(S_1-M\) bonds are directed towards 7 corners of a cube. If the
eighth direction is open \(i.e.\) no lone electron pair\), it would be expected
that the 7 bonding electron pairs would "spread" in order to adopt the
Fig. 3. Relationship between a cube and tetrahedral array of ligands.

Fig. 4. Resonance structures for $S_1$.

Fig. 5. Resonance structures for $S_{11}$. 
minimum energy configuration, e.g. the $M_{\Gamma}S_{\Gamma}-M_{III}$ bond angles would be $>109^\circ28'$. The repulsion effects of bonding and non-bonding electron pairs have been discussed by Gillespie (1963), and it was shown that electron pair repulsions were more important (in water, e.g.) than ligand repulsions. The possibility that a dangling electron pair occupies an orbital directed towards the eighth corner may be eliminated on the grounds that this potentially 8-coordinate S would require hybridization of $s^1p^6d^3$ and $f$-type orbitals (Liehr, 1962). The tetrahedral bonding of the $M_{\Gamma}S_{\Gamma}-M_{III}$ system suggests that the electron density along the $S_{\Gamma}-M_{III}$ axes is low, which leads us to the conclusion reached in Schemes (i) and (ii) that the $M_{III}$ atoms are bound ionically. A 7-coordinate S atom would be $s^1p^6d^3$ hybridized which is an expensive proposition energywise. The (unusually 5-coordinate) S$_{II}$ atoms require the hybridization of at least one 3$d$ orbital, but the S$_{II}$-$M$ bonds would seem to be more easily rationalized in terms of tetrahedral bonding ($M_{III}$-$S_{II}$ and three S$_{II}$-$M$ coordinate bonds) and one ionic (S$_{II}$-$M_{III}$) bond. These arguments do not, of course, rule out $s^1p^6d^3$ hybridization of S$_{I}$ atoms, but the 7-coordinate scheme does not have the attractive features of Scheme (i).

Other bonding schemes

We have neglected considering, hitherto, any metal-metal bonding and $\pi$-bonding. Bornite has semiconductor properties which suggests that metal-metal bonding is weak.

Schemes (i)–(iii) have been discussed from the $\sigma$-bonding viewpoint only. However, because orbital overlap is usually greater in the $\sigma$-bond than in the $\pi$-bond, $\sigma$-bonds are stronger than $\pi$-bonds. It is reasonable to assume, therefore, that our approach is a valid one. Furthermore, $\pi$-bonding increases the splitting of the $t_{2g}$ and $e_g$ orbitals in a ligand field, but the works of Pappalardo & Dietz (1961) show that the $d$ orbital splittings for transition metals in CdS and ZnS are of the expected order for $\sigma$-bonding only.

In this work, covalent models have been used to study the structure of bornite. An advantage in using covalent models lies in the spatial orientation of orbitals. Dickens (1965) has used the covalent bond approach to elucidate the structures of (the semiconductors) red and yellow PbO. We therefore feel there is some justification in employing our approach. The semiconducting bond approach of Mooser & Pearson (1956, 1960) has proved useful in predicting semiconductivity in solids. However, the concept of relating the structure of bornite to a sphalerite skeleton containing interstitial atoms is of interest, especially in view of the detection of interstitial Cu(II) and Fe(III) in sphalerite.
The present work would tie in with the Cu-sphalerite work in the following way. If we postulate that Cu(II) in tetrahedral S fields is a strong electron acceptor, the more stable Cu species in tetrahedral S fields will be Cu(I). For a Cu atom to substitute for a Zn atom in sphalerite, two electrons from each Cu must be used in the bonding. It is conceivable that two-thirds of the Cu dopant in the sphalerite is present as substitutional Cu(I) and that the extra electron is given by the ionically-bonded interstitial Cu(II). Similarly, in bornite, the $M_{II}$ Cu(I) ions give up electrons to the Cu atoms in the $M_I$ and $M_{III}$ positions.

**Conclusion**

An analysis of the bonding properties of the S atoms in bornite has shown that bornite has a sphalerite-type structure that contains layers of ionically-bound interstitial atoms (CuI). This scheme has the advantage that the S atoms are tetrahedrally coordinated, which agrees with the contention of Craig & Magnusson (*J. Chem. Soc.* 4895, 1956) that the S 3$d$ orbitals are unavailable for chemical bonding. The Cu atoms are Cu(I) and the Fe are Fe(III). It is also shown that ZnS structures are often observed for sulphides of $d^5$ and $d^{10}$ cations.

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**References**


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