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 (Cu_5FeS_4) have been studied in relation to the availability of the 3*d* 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 3*d* 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 3*d* orbitals, thus contracting the *d* orbital and bringing the electrons closer to the neighbouring bonding atoms. The covalent bonding and d^2sp^3 hybridization of S orbitals in SF_6 is an example of 3*d* orbital contraction. The bonding in SF_6 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 3*d* orbitals will be unavailable in the *M*-S bonding scheme, and S will either use its 3*s* and 3*p* orbitals in forming 4 sp^3 orbitals (tetrahedral bonding) or will "spread" the bonding power of the 3*s* and 3*p* orbitals over a larger number of weaker bonds. The tetrahedral (sp^3) bonding scheme in ZnS suggests that the former is energetically the more favourable, because the Zn^{2+}:S^{2-} 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 (1963)).

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 $Fe(OH_2)_6^{2+}$, the splitting (Δ) of the Fe t_{2g} and

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e_g orbitals is ~10,000 cm^{-1}, while for diamagnetic pyrite $\Delta > 15{,}000$ cm^{-1}. This large Δ 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 3*d* orbitals must be considered.

The structure of the metastable rhombohedral form of bornite, Cu_5FeS_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 ~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 ~2.5 Å. In this way, the S atoms in the rhombohedral form of bornite are 5- and 7-coordinate (S_{II} and S_I atoms in Fig. 2a and 2b). Six of the 7 S_I-*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_I-*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_I-*M* bonds are of the "purely" ionic or van der Waal's type, the effective coordination number of the S_I 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 3*s* and 3*p* orbitals. In discussing the bonding properties of S in bornite, therefore, the following possibilities will be considered:

(i) some of the *M*-S_I bonds are ionic (non-coordinate),

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

(iii) the S_I atoms are 7-coordinated, implying the ready availability of the 3*d* orbitals for bonding.

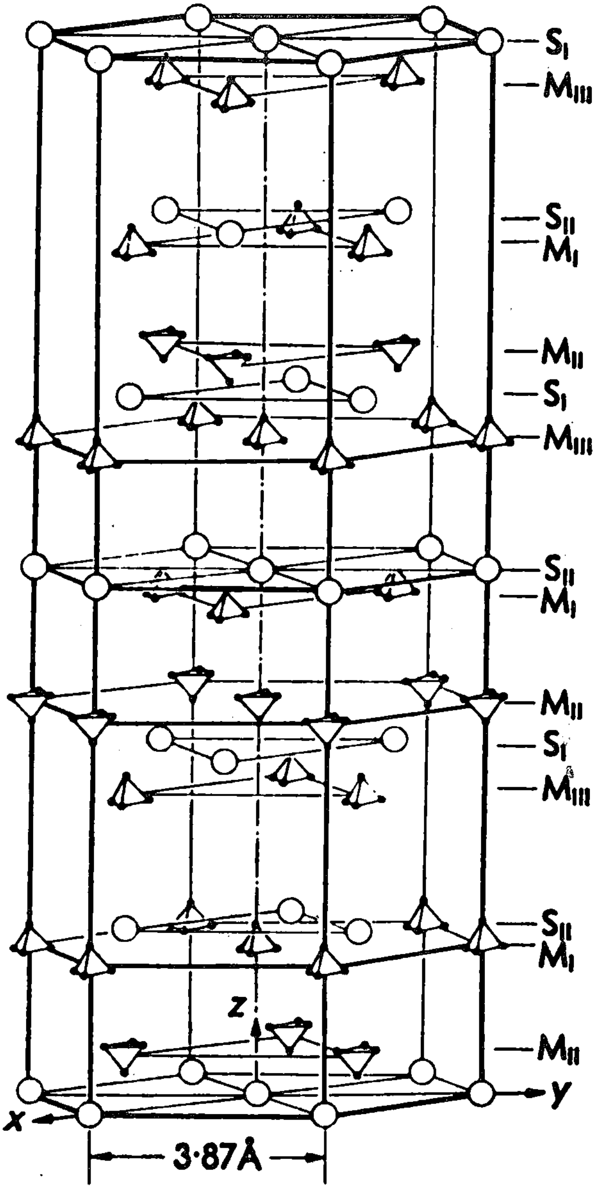

FIG. 1. Structure of the rhombohedral form of bornite (Morimoto, (1964)).

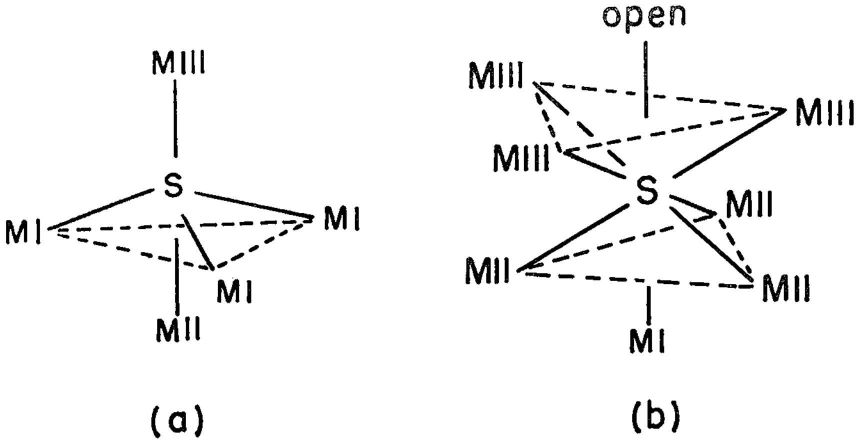

FIG. 2. S environments in bornite. (a) "5-coordinate" S_{II}, (b) "7-coordinate" S_I.

Scheme (i):

In considering this scheme, we are, in essence, attempting to explain the S bonding in terms of 3*s* and 3*p* 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_I (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_I atoms are 3-coordinate with four non-coordinate bonds or the S_I 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_I-S_I and the three S_I-M_{III} bonds are oriented tetrahedrally. According to Morimoto (1964), the M atoms lie at the apices of small tetrahedra, and the M_I-S_I-M_{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_I are bonded tetrahedrally to an M_I and three M_{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^2 hybrid orbitals or the balancing of electrostatic forces over many cell distances. However, the small displacement would seem to be of secondary importance in an understanding of the basic structure of the crystal.

According to Scheme (*i*), 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_{III} 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 ~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 seen 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_{III} sites, and it has been suggested by Morimoto (1964) that Fe is an M_I atom. We can now write the bornite structure as:

$$[Cu_3FeS_4]^{2-}.2Cu^+$$

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 $3s^23p^4$, 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^5 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^5 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_I and S_{II} atoms are 4-coordinate,

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

(c) the bornite-sphalerite analogy seems reasonable, especially in view of the detection of interstitial cations in sphalerite and the correlation 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_I and three M_{III} atoms are tetrahedrally oriented about the S_I atom. Similar calculations show that the M_{II}-S_I-M_{II} angles are also close to the tetrahedral, and the 7 S_I-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_I are shown in Fig. 4. The eighth direction of an S_I cube has a dangling electron pair.

There is one serious objection to this theory. The S_{II} atoms resonate in synchronism with S_I, 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 predominate. Scheme (*ii*) therefore leads us to the same conclusion as Scheme (*i*)—that the M_{II} atoms are bound ionically.

Scheme (*iii*):

The 7 S_I-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

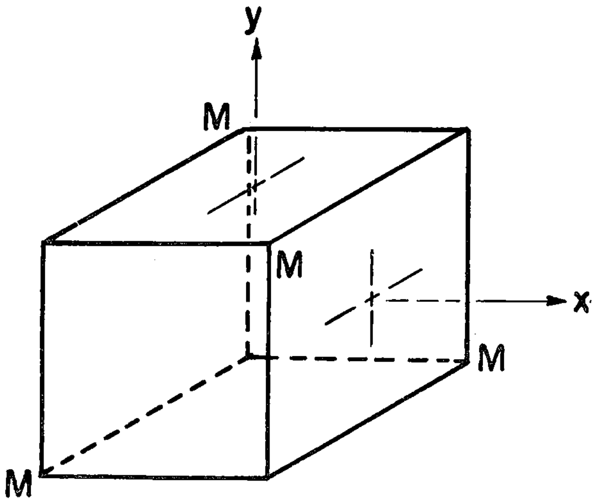

FIG. 3. Relationship between a cube and tetrahedral array of ligands.

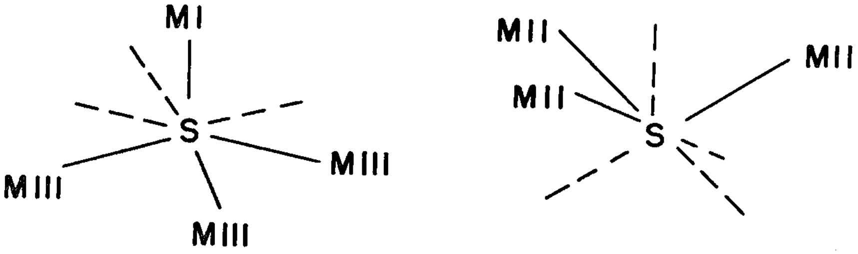

FIG. 4. Resonance structures for S I.

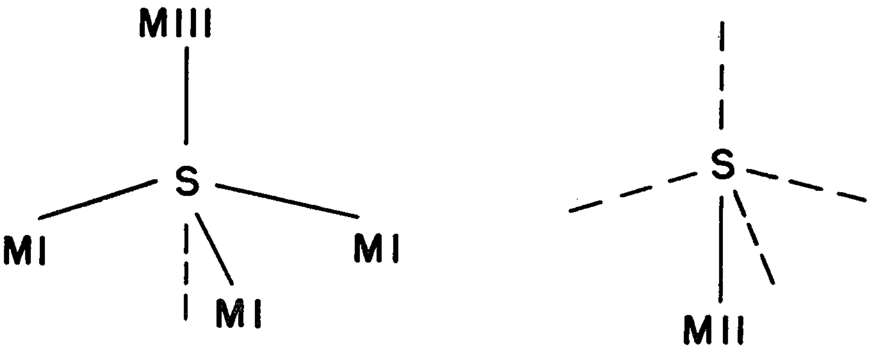

FIG. 5. Resonance structures for S II.

minimum energy configuration, *e.g.* the M_{I}-S_{I}-M_{III} bond angles would be $>109°28'$. 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 $s^1p^3d^3$ and f-type orbitals (Liehr, 1962). The tetrahedral bonding of the M_{I}-S_{I}-M_{III} system suggests that the electron density along the S_{I}-M_{II} axes is low, which leads us to the conclusion reached in Schemes (*i*) and (*ii*) that the M_{II} atoms are bound ionically. A 7-coordinate S atom would be $s^1p^3d^3$ hybridized which is an expensive proposition energywise. The (unusually 5-coordinate) S_{II} atoms require the hybridization of at least one $3d$ 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_{I} coordinate bonds) and one ionic (S_{II}-M_{II}) bond. These arguments do not, of course, rule out $s^1p^3d^3$ 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 π-bonding. Bornite has semiconductor properties which suggests that metal-metal bonding is weak.

Schemes (*i*)–(*iii*) have been discussed from the σ-bonding viewpoint only. However, because orbital overlap is usually greater in the σ-bond than in the π-bond, σ-bonds are stronger than π-bonds. It is reasonable to assume, therefore, that our approach is a valid one. Furthermore, π-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 σ-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 $3d$ 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.

ACKNOWLEDGMENTS

The author wishes to thank Drs. J. D. Keys and E. H. Nickel and Mr. T. Baleshta for their great assistance in this work.

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Manuscript received May 27, 1966, emended September 29, 1966