Inorg. Chem. **1983**, *22*, 479–484

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

Comparisons of the Electronic Structures of B_8S_{16}, the Porphine Dianion, and Their Complexes with Copper(2+)

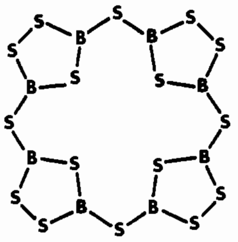
BENJAMIN M. GIMARC* and JI-KANG ZHU[1]

Received May 18, 1982

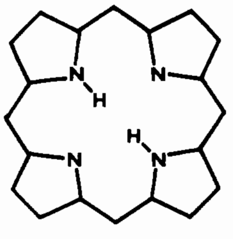
The B_8S_{16} macrocycle and porphine are isostructural but not isoelectronic. No complexes have been reported for B_8S_{16}, which has only recently been synthesized, but porphyrins are known to form a wide variety of complexes with both transition metals and simple metal ions. We have performed extended Hückel calculations to compare the valence electronic structures of B_8S_{16} and porphine and of the Cu^{2+} complexes of these two macrocycles. We have also made comparisons to the ligands 14-ane-S_4 and 14-ane-N_4 and their Cu^{2+} complexes. Our results indicate that the B_8S_{16} complex might have a stability (relative to free ligand and metal ion) that is comparable to that of the porphine complex. This conclusion is strongly dependent on the inclusion of sulfur 3d AOs in the basis set. Unfortunately, the results also depend on the choice of semiempirical parameters for the sulfur 3d AOs. Results are interpreted with use of qualitative MO arguments.

Introduction

The macrocycles B_8S_{16} (**1**) and porphine (**2**) are isostructural



1



2

but not isoelectronic. In a recent article the π-electronic structures of these two molecules were compared at the simple Hückel level.[2a] In this paper we use the results of extended Hückel calculations[2b] to compare their full valence electronic structures and to discuss the differences in metal–ligand bonding between the Cu^{2+} complex of porphine and the complex that Cu^{2+} might form with B_8S_{16}. No complexes of B_8S_{16} have been reported. Although extended Hückel results can be expected to be quantitatively poor, we hope that they show the correct qualitative comparisons and they provide a particularly simple and convenient basis for qualitative interpretations of chemical bonding.[3] This work is part of a larger study of the electronic structures of planar inorganic rings.[4]

Figure 1 shows the central metal atom d AOS and the coordinate system and symmetry elements for the ligands and complexes. Symbols a and b represent oribtals that are either symmetric or antisymmetric with respect to a 90° rotation about the 4-fold rotation axis z, subscripts 1 and 2 denote symmetry or antisymmetry with respect to the 2-fold axis x, and subscripts g and u indicate symmetry or antisymmetry with respect to the center of inversion i. Note that the central atom d AOs have g symmetry only. We refer to the MOs that are antisymmetric with respect to reflection in the molecular plane as π orbitals and to those that are symmetric in the plane as σ orbitals. Simple electron-counting rules[2a] allocate 26 electrons to π orbitals of porphine while B_8S_{16} is *electron rich*[5] with 32 π electrons. Each macrocycle contains 88 σ electrons. This distribution of electrons into σ and π orbitals is supported by the results of the extended Hückel calculations which automatically apportion electrons to energy levels on the basis of low energy only.

Details of the Calculations

For the molecules mentioned in this paper we performed extended Hückel calculations using the program ICON8 written by Howell, Rossi, Wallace, Haraki, and Hoffmann and available as Program No. 344 from the Quantum Chemistry Program Exchange, Indiana University. We used the set of Coulomb integrals and orbital exponents built into the program for all atoms except Cu for which we adopted the parameters of Zerner and Gouterman.[6] The resonance intergrals were calculated with the assumption of their simple proportionality to the average of the Coulomb integrals times the overlap. We did not use the charge iteration feature of the ICON8 program. It turns out that even the qualitative conclusions based on our results strongly depend on the choice of the Coulomb integral for the sulfur 3d AOs. The value of this integral in the data block of ICON8 is −8 eV, and unless it is otherwise noted, this is the value we used to calculate all energy levels and other quantities mentioned in the text and depicted in the figures. Other values suggested in the literature are −4[7] and −2 eV.[8] There is evidence that a value around −5 eV might be a more appropriate choice. Cruickshank, Webster, and Mayers[9] have reported the energy difference between the $3s^23p^33d^1$ and $3s^23p^4$ configurations of sulfur as being around 8 eV. If the energy of the 3p AO is −13.3 eV (the ICON8 value of the Coulomb integral) then the 3d AO must have an energy of $-13.3 + 8 = -5.3$ eV. If a value of −4.4 eV is assumed and the energies of 3s and 3p AOs are taken as −20 and −13.3 eV, respectively (programmed data), then the energy difference between the configurations $3s^13p^33d^2$ and $3s^23p^4$ turns out to be consistent with the estimate of 24.5 eV ($=20 - 4.4 + 13.3 - 4.4$) based on other calculations.[9]

For the geometry of the porphine dianion we took the "best" set of structural parameters for the porphyrin skeleton recommended by Fleischer.[10] For B_8S_{16} we used the experimental structure reported by Krebs and Hürter.[11] We assumed the same structures for the complexes as we did for the free ligands. Although in some porphyrin complexes the metal ion is known to be displaced from the plane of the four nitrogens,[12] we did not investigate the possibility of noncoplanarity of Cu in the case of the B_8S_{16} complex.

B_8S_{16}

Figure 2 compares those energy levels on either side of the HOMO–LUMO gap in B_8S_{16} as calculated by the simple Hückel method and by the extended Hückel method, first with the assumption of no d AOs on the sulfurs and then with the inclusion of sulfur d AOs in the basis set. The most prominent feature of the simple Hückel energy levels is the large HOMO–LUMO gap: 2.23β. This qualitatively agrees with the extended Hückel results (without sulfur d AOs), for which

---

(1) Permanent address: Anhui Institute of Optics and Fine Mechanics, Academia Sinica, Hofei, Anhui, China.

(2) (a) B. M. Gimarc and N. Trinajstić, *Inorg. Chem.*, **21**, 21 (1982). (b) R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).

(3) B. M. Gimarc, "Molecular Structure and Bonding", Academic Press, New York, 1979.

(4) B. M. Gimarc and N. Trinajstić, *Pure Appl. Chem.*, **52**, 1443 (1980).

(5) A. J. Banister, *Nature* (*London*), *Phys. Sci.*, **237**, 92 (1972).

(6) M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **4**, 44 (1966).

(7) R. Gleiter, *J. Chem. Soc. A*, 3174 (1970).

(8) L. C. Cusachs, D. J. Miller, and C. W. McCurdy, Jr., *Spectrosc. Lett.*, **2**, 141 (1969).

(9) D. W. J. Cruickshank, B. C. Webster, and D. F. Mayers, *J. Chem. Phys.*, **40**, 3733 (1964).

(10) E. B. Fleischer, *Acc. Chem. Res.*, **3**, 105 (1970).

(11) B. Krebs and H.-U. Hürter, *Angew. Chem., Int. Ed. Engl.*, **19**, 481 (1980).

(12) M. D. Glick, G. H. Cohen, and J. L. Hoard, *J. Am. Chem. Soc.*, **89**, 1996 (1967).

0020-1669/83/1322-0479$01.50/0

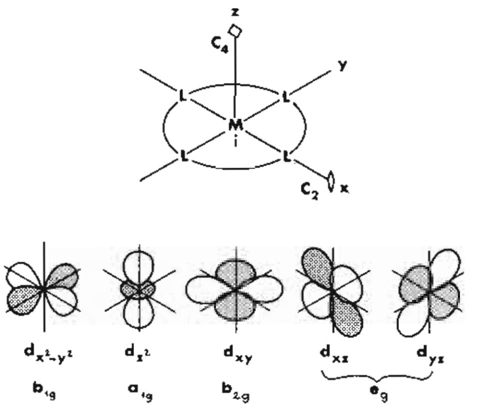


Figure 1. Central-metal d AOs and the coordinate system and symmetry operations for the planar, 4-fold macrocyclic ligands B_8S_{16} and the porphine dianion. L represents the internal nitrogen or sulfur atoms that form bonds to the central metal M.

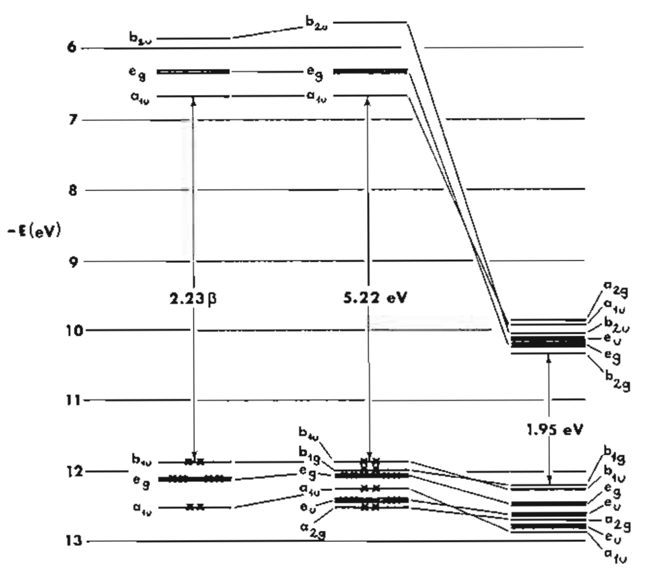
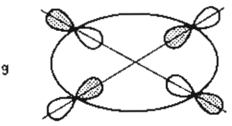


Figure 2. Energy levels of B_8S_{16} around the HOMO–LUMO gap and a comparison of Hückel levels with those of the extended Hückel method without and with d AOs on the sulfurs. The Hückel levels were located on the eV scale by matching the HOMO and LUMO with those of the extended Hückel results without d AOs.

the gap is 5.22 eV. Equating 2.23β and 5.22 eV gives β = 2.34 eV, a reasonable value for a spectroscopic β value for aromatic hydrocarbons.[13] In the preparation of Figure 2 the Hückel HOMO and LUMO were matched to those of the extended Hückel results (without d AOs) and the value β = 2.34 eV was used to position the remaining Hückel levels on the eV scale with the extended Hückel results.

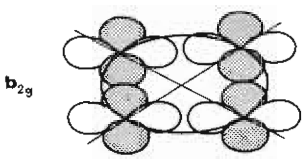
For both the simple Hückel calculations and the extended Hückel results (without d AOs) the same two sets of four π levels border the HOMO–LUMO gap above and below. The σ level b_{1g} enters the set of filled extended Hückel levels just below the HOMO. The principal components of this b_{1g} orbital (3) are the internal sulfur p AOs that lie in the plane of the macrocycle and point toward the center. This is the ligand orbital that interacts with the $d_{x^2-y^2}$ (b_{1g}) AO of the central transition-metal ion and is mainly responsible for the chemical bonding in the metal–ligand complex.



3

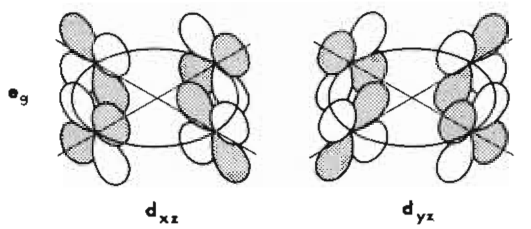
The nodal properties of the HOMO (b_{1u}) and the LUMO (a_{1u}) eliminate any AO contributions from the internal sulfurs in the Hückel MOs and in the extended Hückel MOs calculated without sulfur d AOs. Furthermore, because of their *ungerade* symmetry neither of these π MOs can interact with d AOs of a central metal atom.

When d AOs of sulfur are included in the basis set for the extended Hückel calculations, dramatic changes occur among the lower vacant orbitals: the HOMO–LUMO separation is decreased to less than half of that for calculations without sulfur d AOs, and new MOs now appear among the low-lying empty orbitals. The HOMO and LUMO are now both σ orbitals, a result that is probably not significant since there is always great uncertainty in the ordering of closely spaced energy levels. Among the higher occupied MOs the inclusion of sulfur d AOs results mainly in the shuffling or rearrangement of order of orbitals that were already very close in energy. In particular, the b_{1g} (3) orbital, which lay just below the HOMO in the minimal basis set results, becomes the HOMO when sulfur d AOs are added. On the other hand, among the lower energy vacant MOs (including the sulfur d AOs) a number of MOs appear that were not low in energy in the results without d AOs. One of these is the new LUMO itself, b_{2g} (4), which is composed mainly of the internal sulfur d_{xy} AOs that lie in the plane of the macrocycle.



4

Above b_{2g} lie the degenerate pair of e_g orbitals (5). These orbitals are principally the d_{xz} and d_{yz} AOs on the internal sulfurs.



5

The lowest empty e_g MOs from the calculations without sulfur d AOs are composed mainly of $2p_z$ AOs on the boron atoms.

The lower energy vacant orbitals of B_8S_{16} have high symmetry and nodal characteristics such that 3p AOs on the internal sulfurs of this macrocycle are either completely excluded by symmetry or are present with small coefficients only. In contrast, the 3d AOs of sulfur have just the right symmetry and nodal character to enter these MOs as major contributors at the sites of the internal sulfurs. Therefore, the MO energies of the lower vacant orbitals are strongly influenced by the choice of sulfur 3d AO Coulomb integrals. Using values of these Coulomb integrals smaller than −8.0 eV produces a smaller lowering of the vacant energy levels.

Porphine Dianion

Figure 3 compares energy levels of the porphine dianion as calculated by the simple Hückel and extended Hückel methods.

---

(13) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961, p 208.

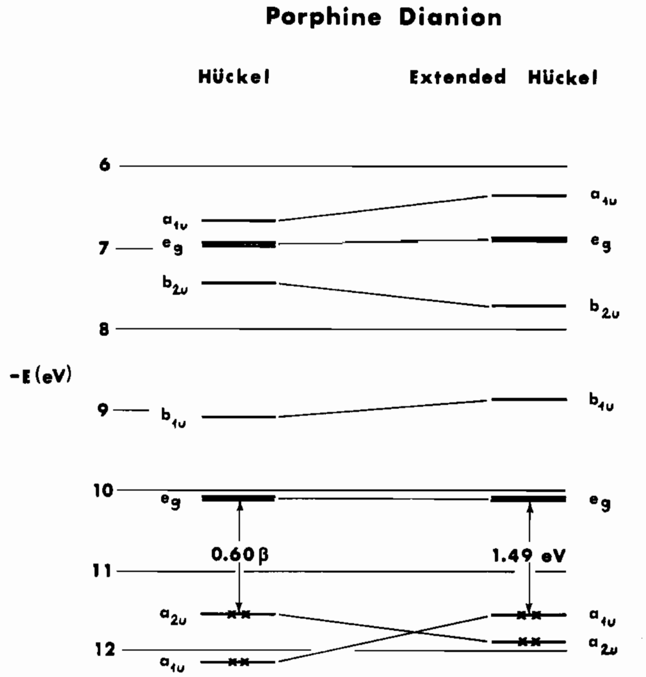


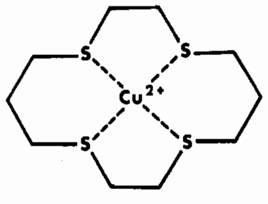
Figure 3. Energy levels of the porphine dianion around the HOMO–LUMO gap and a comparison of Hückel energy levels with those of the extended Hückel method. The Hückel levels were plotted on the eV scale with the assumption that the HOMO and LUMO match those of the extended Hückel results.

As with the B_8S_{16} macrocycle we have matched the energies of HOMOs and LUMOs. (In this case the HOMOs generated by the two methods are not the same, the two highest occupied levels being interchanged between the two sets.) Equating the 1.49-eV HOMO–LUMO separation of the extended Hückel results with the 0.60β value of the simple Hückel calculations gives $\beta = 2.48$ eV, in reasonable agreement with the value obtained from the B_8S_{16} calculations (2.34 eV).

Now compare the energy levels of B_8S_{16} with those of the porphine dianion. Keep in mind that the two macrocycles differ in numbers of electrons and that even the nature and pattern of their energy levels are different. Their HOMO–LUMO gaps represent different transitions. In the simple Hückel study it was found that the HOMO–LUMO gap in B_8S_{16} is much larger than that in porphine, a result in agreement with "eyeball" spectroscopy: porphyrins are colored compounds while crystals of B_8S_{16} are white.[11] This conclusion is supported by a comparison of extended Hückel results, at least for those without sulfur d AOs. When sulfur d AOs are included, the HOMO–LUMO separation narrows, but even with use of the heaviest sulfur 3d Coulomb integral the separation is still 30% larger than that in the porphine dianion.

Complex Formation

We chose to compare complexes of Cu^{2+} with the porphine dianion and B_8S_{16} because porphine is known to form a complex with Cu^{2+} [14] and the diameter of the hole in B_8S_{16} is very close to the S–Cu–S distance in the complex of Cu^{2+} with tetrathiacyclotetradecane (14-ane-S_4, **6**).[15] The four sulfurs in **6** form a square plane with Cu^{2+} at its center. Presumably the aliphatic chains are flexible enough to allow an optimum Cu–S distance. Compare the transannular S- - -S distances of 4.606 Å in **6** with 4.667 Å in free B_8S_{16} (**1**). The nitrogen analogue of **6** is known: 14-ane-N_4. In its copper complex, Cu(14-ane-N_4)$(ClO_4)_2$, the Cu–N distance is 2.02 Å.[16] The Cu–N distance in the complex with tetraphenylporphine is 1.981 Å. The M–N distance in the "best" porphyrin structure suggested by Fleischer[10] is 2.03 Å. The Cu–N distances in the complexes of 14-ane-N_4 and of porphine are not strictly comparable; the nitrogens must be sp^3 hydridized in the former and sp^2 hybridized in the latter. The same applies to Cu–S bonds in the 14-ane-S_4 and B_8S_{16} complexes.



6

In the Cu^{2+} complexes of 14-ane-S_4 and 14-ane-N_4 and in the porphyrin complexes of some metals, additional ligands occupy the octahedral sites above and below the plane of the macrocycle. We did not include such ligands in our work although negatively charged ligands would probably play an important part in the stabilization of the copper–B_8S_{16} complex.

Our extended Hückel results show that B_8S_{16} (including sulfur d AOs) and the porphine dianion are stabilized to almost exactly the same extent by complexing with Cu^{2+}. The calculated energy differences between the complex and free ligands plus free metal ion are 7.92 eV for the B_8S_{16} system and 7.99 eV for the porphine system. These values give bond energies of 45.7 kcal/mol for each Cu–S bond and 46.1 kcal/mol for each Cu–N bond. We make no claim for the quantitative significance of these numbers; the results tell us that we might expect Cu–S and Cu–N bond energies to be qualitatively comparable. Experimental values for these bond energies are unknown, but estimates can be calculated from Pauling's formula relating bond energies E(A–B) and electronegativity differences $X_A - X_B$:[17]

$$E(\mathrm{A{-}B}) = \tfrac{1}{2}[E(\mathrm{A{-}A}) + E(\mathrm{B{-}B})] + 23.9(X_A - X_B)^2 - 1.55(X_A - X_B)^4 \text{ kcal/mol}$$

Using values of 63.58, 38.0,[17] and 47.0[18] kcal/mol for E(S–S), E(N–N), and E(Cu–Cu), respectively, and 3.0, 2.5, and 1.9 for X_N, X_S, and X_{Cu}, respectively, we get 63.7 kcal/mol for the Cu–S bond energy and 69.2 kcal/mol for the Cu–N bond, qualitatively equal energies.

When smaller sulfur 3d Coulomb integrals are used in the calculations, the Cu^{2+} complex with B_8S_{16} is much less stable. For example, with use of –4 eV for this integral, the Cu–S bond energy drops to 22.6 kcal/mol compared to 18.6 kcal/mol with sulfur d AOs omitted from the basis set. Thus the calculated stability of the complex depends not only on the participation of sulfur 3d AOs but also on a rather deep value for the Coulomb integral.

Figures 4 and 5 correlate free-ligand and free-metal energy levels with those of the complex for the porphine dianion and B_8S_{16}, respectively. As in Figures 2 and 3, only a few levels on either side of the HOMO–LUMO gap are shown. The interaction mainly responsible for bonding in both complexes is that between b_{1g} (**3**) of the ligand and the $d_{x^2-y^2}$ AO of the metal atom to form b_{1g} (**7**). Of the low-lying vacant orbitals in the porphine dianion, only e_g has the proper symmetry to interact with the copper d AOs, but this interaction is negligible. The major components of the porphine dianion LUMO, e_g, are $2p_z$ orbitals on the α-carbons of the pyrrole

---

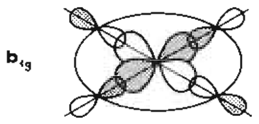
(14) E. B. Fleischer, C. K. Miller, and L. E. Webb, *J. Am. Chem. Soc.*, **86**, 2342 (1964).

(15) M. D. Glick, D. P. Gavel, L. L. Diaddario, and D. B. Rorabacher, *Inorg. Chem.*, **15**, 1190 (1976).

(16) P. A. Tasker and L. Sklar, *J. Cryst. Mol. Struct.*, **5**, 329 (1975).

(17) L. Pauling, "General Chemistry", W. H. Freeman, San Francisco, 1970, p 182.

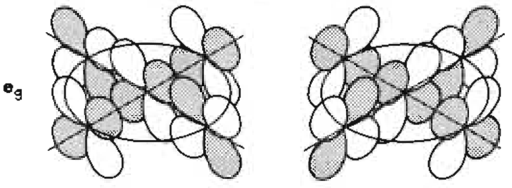
(18) T. L. Cottrell, "The Strengths of Chemical Bonds", 2nd ed., Butterworths, London, 1958, p 287.



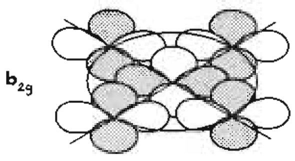
7

rings. Coefficients of $2p_z$ AOs on the internal nitrogens are much smaller. Other free-porphine vacant orbitals that are low in energy are of ungerade symmetry and therefore unable to interact with the central metal d AOs. The cluster of occupied a_{1g}, b_{2g}, and e_g orbitals of the porphine complex (Figure 4) consists of essentially pure metal d AOs.

In contrast, Figure 5 shows stabilizing interactions between the low-energy, vacant e_g and b_{2g} orbitals of the free ligand B_8S_{16} and the d AOs of copper. The interactions result from the presence of d AOs on the internal sulfurs of B_8S_{16} and generate rather weakly bonding MOs (**8**, **9**) of the complex.



8



9

We see the effect of these interactions in the net atomic charges. Although the numerical values of these charges are exaggerated and quantitatively unrealistic, we expect that the trends are real. Comparing net atomic charges for the Cu^{2+} complex of B_8S_{16} calculated first without and then with sulfur d AOs, we found that the addition of d AOs to the sulfur atoms shifts electron density away from the metal and onto the ligand.

Sulfur d AOs increase the stability of the complex by more than a factor of 2. This added stabilization comes mainly from the interposition of additional molecular orbitals among the higher occupied group. Consider the e_u orbitals, which are the HOMOs of the $Cu(B_8S_{16})^{2+}$ complex in the results including sulfur d AOs (see Figure 5). The corresponding e_u orbitals of the free ligand have the wrong symmetry (ungerade) to interact with the central metal atom, and therefore the e_u MOs of the complex do not directly contribute to Cu–S bonding. The primary components of these e_u MOs are the d AOs of the peripheral disulfide sulfurs. It is the sulfur d AOs that put these e_u MOs among the lower vacant MOs of the free ligand and among the higher occupied MOs of the complex. Comparable MOs in the results without sulfur d AOs are much higher in energy. The e_u orbitals of the complex stabilize the complex by holding an electron that would otherwise go into the higher energy b_{1g} MO that is the antibonding version of **7**.

Role of d Orbitals

There has been considerable controversy in the literature concerning the importance of vacant d orbitals in determining molecular properties in general and chemical bonding in particular. Coulson[19] observed that if vacant d, f, g, ··· orbitals are added to a minimal basis set they will surely improve the calculated energies through the normal variational procedure. These higher angular momentum orbitals are necessary to constitute a complete basis set, but in most cases, Coulson predicted, their addition will produce only a small numerical effect. Such orbitals would act as polarization functions that might make small improvements in bond distances and angles and help get the dipole moment right but usually the higher angular momentum orbitals are chemically insignificant.

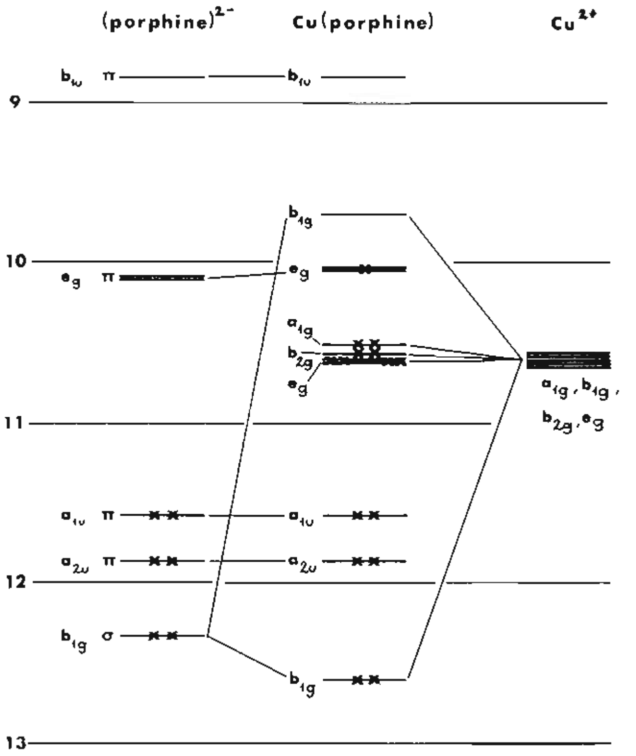


Figure 4. Correlation of extended Hückel energy levels between the free ligand porphine dianion, the free metal, and the Cu^{2+} complex.

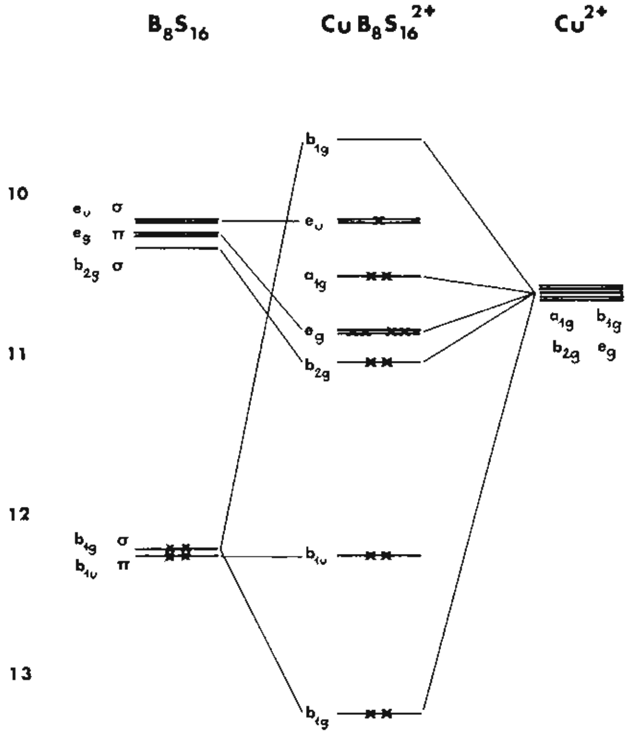


Figure 5. Correlation of extended Hückel energy levels between the free ligand B_8S_{16}, the free metal, and the Cu^{2+} B_8S_{16} complex. Sulfur d AOs were included in these calculations.

---

(19) C. A. Coulson, *Nature (London)*, **221**, 1106 (1969).

Coulson mentioned the rare-gas and interhalogen compounds as cases in which d-orbital participation should be negligible, but he held out hope that they might be significant in the phosphonitrilic halides, where molecular symmetry and electron filling levels are more favorable. Collins, Schleyer, Binkley, and Pople[20] have reported an extensive series of ab initio SCF MO calculations of molecular properties, comparing the results at the STO-3G level with those of an STO-3G set enhanced by the addition of five d-type functions. These comparisons showed that calculated bond angles and binding energies of "hypervalent" molecules (including SO_2 and SO_3) were significantly closer to experimental values when d orbitals of sulfur were included. However, for "normal" molecules (such as H_2S and H_3CSH) the changes made on the addition of sulfur 3d AOs were relatively minor and could reasonably be neglected. To prove that large improvements obtained in the hypervalent cases were due to the d orbitals, the Schleyer group also reported the results of calculations done with an extensive s and p basis set. Haddon and co-workers[21] have done ab initio SCF MO calculations on hypervalent sulfur–nitrogen rings, cages, and chains. They report that only after sulfur d orbitals are included is the correct isomer of S_2N_2 (ring with alternant S and N atoms) favored over the other possible cyclic isomer (adjacent S–S and N–N). They also note that sulfur d orbitals make a large contribution to the energy of conjugation of $(SN)_x$ polymers.

Ratner and Sabin[22] have proposed that vacant d orbitals should be included in MO calculations if they can add to MOs of symmetry classifications within the molecular point group where s and p functions cannot. Ratner and Sabin refer to the discussion of Santry and Segal,[23] who did CNDO calculations for SF_6. In the O_h point group of SF_6 the s and p AOs of sulfur cannot contribute to the e_g and t_{2g} MOs while d AOs can, making their presence in the basis set important for an understanding of chemical bonding in SF_6. On the other hand, the bonding in SF_6 can be explained qualitatively by the action of other orbitals such as the t_{1u} set, which are composed of s and p functions only.[19,24] Rösch, Smith, and Whangbo[25] have done SCF–Xα calculations on SF_6 that imply that sulfur 3d orbitals are not primarily responsible for the bonding in SF_6. Yet even these results show that inclusion of sulfur d AOs does produce an increase in stability, particularly through the highest occupied e_g MOs. Applying the symmetry criterion to the Schleyer group's results for SO_2 and SO_3, one can see that sulfur 3d orbitals will add to the a_2 MO of SO_2 and to the e'' orbitals of SO_3 while sulfur s and p AOs cannot. An a_2 orbital for H_2S would require p AOs on the hydrogens as well as a d orbital from sulfur. Consequently, a_2 is not among the set of valence MOs of H_2S. Similar limitations keep e'' out of the set of valence MOs of planar PH_3. Rodwell[26] has tested the symmetry criterion of Ratner and Sabin by carrying out ab initio SCF MO calculations for SO_2. Adding only that sulfur d AO required in the a_2 MO produced a lowering of the total energy that was only about 28% of the total energy lowering obtained by including by the full set of five d orbitals. The conclusion is that the d AO required by symmetry in a_2 can be only slightly more important than the other four that mix in where s and p AOs already appear. Thus, two criteria have been proposed to gauge the importance of vacant d orbitals: hypervalency and symmetry requirements. Undoubtedly the debate will continue over the applicability of these criteria and whether improvements from d orbitals are qualitative or merely numerical.

The complex of Cu^{2+} with B_8S_{16} meets both criteria although the symmetry requirement is not rigorously met. The complex can be classified as hypervalent. But the symmetry requirement needs closer study. The MOs that form chemical bonds between metal and ligand are those such as b_{1g} (**7**) that involve overlap of AOs of the central metal and the internal sulfurs of the ligand. By combining the 16 s and p AOs in the internal sulfurs one can, by inspection, write down the 16 symmetry-adapted basis orbitals, which would then contribute to the MOs of the ligand and the complex. One of these, for example, is b_{1g} (**3**). In this set, orbitals of a_{1u} and b_{1u} symmetry are missing. Sulfur d_{xz} and d_{yz} AOs can form orbitals of these types, but clearly the a_{1u} and b_{1u} orbitals cannot contribute directly to bonding between ligand and metal because all the metal d orbitals are gerade while a_{1u} and b_{1u} are ungerade. An inspection of Figure 5 shows that a_{1u} and b_{1u} do not stabilize the complex indirectly as does e_u, for example, by holding electrons that would otherwise go into antibonding MOs. A practical effect of the high energy and nodal character of the lower vacant MOs of the ligand is to make s and p contributions from the internal sulfurs small, if not zero. When sulfur d orbitals are allowed to participate, these AOs become major components in the MOs b_{2g}, e_g, and e_u. Although b_{1g} (**7**) is mainly responsible for chemical bonding, our conclusions show that d-participating MOs such as b_{2g}, e_g, and e_u offer considerable additional stabilization to the complex. If the sulfur d AO Coulomb integral is as large as 8 eV, then the effect of the added d AOs is to make the B_8S_{16} complex about as stable as the corresponding porphyrin complex. If the d AOs are absence entirely, the calculated binding energy is much smaller.

Tetrathia Ether Complex

We did extended Hückel calculations for the complex of Cu^{2+} with the macrocyclic 14-ene-S_4 ligand **6**. Because we wanted to see how the ligand was set up to bond to the central metal, we used the same structure for both the complex and the free ligand although these are known to have different conformations.[15,27] The results show that the complex is more stable than the free ligand plus free metal ion by 13.75 eV, giving each Cu–S bond an energy of 79 kcal/mol. This energy is undoubtedly much too high because of the poor assumption of the conformation of the free ligand.

The 14-ane-S_4 complex **6** has much lower symmetry (C_i) than the complexes of B_8S_{16} and porphine (D_{4h}), making a qualitative interpretation of the nature of the ligand–metal binding less transparent. Nonetheless, the main bonding interaction between ligand and central metal ion is through a MO that involves sulfur p AOs that point directly toward the lobes of the $d_{x^2-y^2}$ AO of the metal ion as in **7**. As in the case of B_8S_{16} and its Cu^{2+} complex, exclusion of sulfur 3d AOs from the basis set drastically reduces the calculated stability of the complex between 14-ane-S_4 and Cu^{2+}.

Calculations by Others

The only other electronic structure studies on B_8S_{16} are the simple Hückel results reported previously.[2a] The number of calculations of porphine and metalloporphyrins, however, is legion. Tatsumi and Hoffmann have recently published an extensive bibliography.[28] The paper most closely related to ours is the one by Zerner and Gouterman,[6] who did the first extended Hückel calculations for porphine and its transition-

---

(20) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).

(21) R. C. Haddon, S. R. Wasserman, F. Wuld, and G. R. J. Williams, *J. Am. Chem. Soc.*, **102**, 6687 (1980).

(22) M. A. Ratner and J. R. Sabin, *J. Am. Chem. Soc.*, **93**, 3542 (1971); **99**, 3954 (1977).

(23) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

(24) Reference 3, p 71.

(25) N. Rösch, V. H. Smith, Jr., and M. H. Whangbo, *J. Am. Chem. Soc.*, **96**, 5984 (1974).

(26) W. R. Rodwell, *J. Am. Chem. Soc.*, **100**, 7209 (1978).

(27) R. E. DeSimone and M. D. Glick, *J. Am. Chem. Soc.*, **98**, 762 (1976).

(28) K. Tatsumi and R. Hoffmann, *J. Am. Chem. Soc.*, **103**, 3328 (1981).

metal complexes including Cu. They used a self-consistent charge iteration procedure to refine Coulomb integrals. We omitted that procedure. While we employed the simplest assumption of direct proportionality of resonance integrals to an average of Coulomb integrals times overlap, Zerner and Gouterman used a more sophisticated relationship. Our extended Hückel energy levels for porphine (Figure 3) show a_{1u} as the HOMO with a_{2u} just below. Both are π orbitals. In the energy level scheme obtained by Zerner and Gouterman these levels are reversed. We agree on e_g as the porphine LUMO. Their HOMO–LUMO gap is about 2 eV compared to 1.49 eV from our results. More serious differences occur in comparisons of the energy level pattern for the Cu^{2+} complex of porphine. We found e_g (π) as the singly occupied HOMO of the complex with b_{1g} (σ) vacant above. Zerner and Gouterman show b_{1g} as the singly occupied HOMO with e_g as the LUMO. Both results are consistent with ESR data that has been interpreted as indicating that the odd electron resides primarily on the metal.[29]

Conclusions

On the basis of simple Hückel results it was previously concluded that B_8S_{16} would form much weaker complexes than would porphine and this conclusion is reinforced by extended Hückel calculations that do not include d AOs on the sulfur atoms. However, inclusion of sulfur d AOs changes the composition of the extended Hückel MOs and the pattern of the energy levels and leads to the prediction that the B_8S_{16} complex with Cu^{2+} might be about as stable as the porphine complex. Unfortunately, this conclusion depends on the magnitude of value chosen for the sulfur 3d AO Coulomb integral. Therefore, without a more specific basis for the selection of this parameter, reliable stability predictions for this system are not likely to result from further semiempirical calculations. We were surprised at the importance of the sulfur d AOs although their significance has been noted in other work.[20,21] Because of the consequences of sulfur d AO participation in the electronic structure of B_8S_{16}, this compound differs from the porphine dianion by more than a mere six π electrons. Ligand–metal bonding in both kinds of planar macrocyclic complexes **1** and **2**, as well as that in the tetrathia ether complex **6**, results mainly from a MO of b_{1g} symmetry in which the central-atom $d_{x^2-y^2}$ AO combines in phase with p AOs on the four ligand binding sites.

Registry No. **1**, 73825-17-9; $Cu^{2+}B_8S_{16}$, 83897-43-2; porphine dianion, 30882-36-1; porphine dianion, copper(2+) complex, 13007-96-0.

---

[29] E. M. Roberts and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 3006 (1960).

Contribution from the Department of Chemistry,
Wright State University, Dayton, Ohio 45435

EPR Studies of Cobalt–Dioxygen Complexes Containing Linear, Pentadentate Keto Iminato Ligands

MICHAEL D. BRAYDICH, JOHN J. FORTMAN, and SUE C. CUMMINGS*

Received March 23, 1982

The oxygen adducts of a series of pentacoordinate (keto iminato)cobalt(II) complexes, Co(acacDPT)·O_2, Co(benacDPT)·O_2, Co(tfacDPT)·O_2, Co(acacMeDPT)·O_2, Co(benacMeDPT)·O_2, Co(tfacMeDPT)·O_2, Co(benacPhDPT)·O_2, and Co(tfacPhDPT)·O_2, have been investigated by using EPR spectral techniques. EPR studies were conducted under four sets of conditions in order to provide insight into the interaction of cobalt with dioxygen and to learn if there were any substituent effects. The presence of eight hyperfine lines in both the solution and frozen-glass spectra confirms the formation of 1:1 adducts in all cases. Comparison of the anisotropic coupling constants suggests that the different central amine substituents modify electron density on the cobalt ion through σ effects, while the substituents derived from the β-diketone moiety change electron density via π interactions. Evidence obtained from variable-temperature isotropic spectra and overlapping anisotropic spectra for several of the adducts suggests the existence of two isomers. Time decay and reversibility experiments indicate that the adducts may decay through an oxy-bridged dimer intermediate. This work culminated with the isolation and characterization of the oxygen adduct of Co(benacMeDPT). The IR spectrum of the solid reveals an O–O stretching vibration at 1150 cm^{-1}, consistent with a monomeric adduct. Deoxygenation of the sample results in some irreversible oxidation.

Introduction

Recently we reported the synthesis and characterization of Ni(II), Cu(II), and Co(II) complexes with pentadentate keto iminato ligands formed from the condensation of various β-diketones and triamines.[1] The Co(II) derivatives are of special interest because of their ability to undergo reversible oxygenation.[2,3] Dioxygen adducts of cobalt(II) complexes containing tetradentate ligands have been studied and reviewed extensively.[4-7] In such systems, oxygen binding is generally accompanied by binding of a Lewis base in the coordination site trans to the dioxygen, which gives rise to six-coordinate adducts. The complexes can be viewed as Co(III)–O_2^- species, where the extent of electron transfer from cobalt to oxygen depends on the nature of the in-plane ring substituents and axial bases.

The oxygen adducts of cobalt(II) complexes containing pentadentate ligands have received much less study, even though these systems eliminate the need for addition of an external Lewis base in order to form a six-coordinate dioxygen adduct. Those reports that have appeared in the literature have

---

[1] Chen, Y.-Y.; Chu, D. E.; McKinney, B. D.; Willis, L. J.; Cummings, S. C. *Inorg. Chem.* **1981**, *20*, 1885, 3582.

[2] Braydich, M. D. M.S. Thesis, Wright State University, Dayton, OH, Dec 1978.

[3] Braydich, M. D.; Fortman, J. J.; Cummings, S. C. "Abstracts of Papers", 11th Central Regional Meeting of the American Chemical Society, Columbus, OH, May 1979.

[4] Wilkins, R. G. *Adv. Chem. Ser.* **1971**, *No. 100*, 111.

[5] McLendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1.

[6] Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

[7] Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1981**, *39*, 295.

0020-1669/83/1322-0484$01.50/0