rigorously in a crystal field model which parametrizes the crystal field splitting in terms of three parameters: Δ, the total cubic field splitting of the b_1 and b_2 orbitals, and δ_1 and δ_2, the tetragonal splitting of the t_{2g} and e_g orbitals.[18] The isotropic proton shifts can then be calculated within this model in a manner as described by Gregson.[20] By the use of the free-ion values of Racah and spin–orbit coupling parameters the data in Figure 3 can be best fitted for $\Delta = 33\,100\ \text{cm}^{-1}$, $\delta_1 = 1250\ \text{cm}^{-1}$, and $\delta_2 = 12\,500\ \text{cm}^{-1}$. This gives an energy-level scheme as shown in Figure 4. While the exact values of the energies would be dependent on the choice of the Racah and spin–orbit coupling parameters, their relative values are realistic, giving credence to the relative ordering of the energy levels. The low-lying $^4A_2$ state mixes very substantially into the ^6A state, producing a spin-mixed ground state with 68% $^6A_1$ ($\pm^1/_2$) and ca. 31% $^4A_2$ ($\pm^3/_2$), the contribution of all other states being not more than 1%. The features of the electronic structure are interesting. First, several ferric heme proteins and porphyrins show spin-state mixing and are known to have a $^6A_1$ and $^4A_2$ spin-mixed ground state.[14,21-26] In some cases[21,24] the ground state is predominantly $^6A_1$; in others, the latter.[22,26] Second, ^2E, not ^4E, lies immediately above $^4A_2$. ^4E in fact lies very high in energy, which appears to be a common feature in iron(III) porphyrins.[8d,19]

For the phenyl protons, the isotropic shifts are very small and the contact terms are only about 10% of the IPS. Since the spin-state mixing will affect predominantly only the contact term, its effect is not apparent in the temperature dependence of the phenyl protons, hence the linear variation in Figure 3.

Conclusion

The present work has shown that when weak axial ligands such as Me_2SO or alcohols coordinate to iron(III) porphyrins, forming six-coordinated iron(III) porphyrins, these six-coordinated porphyrins are not always high spin. A careful temperature-dependent NMR study is important to establish the nature of the ground electronic state of the metal ion.

Registry No. $Fe(PP)(Me_2SO\text{-}d_6)_2Cl$, 89936-20-9; $Fe(TPP)(CD_3OD)_2ClO_4$, 89922-45-2.

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Electronic Spectrum of the Planar $S_4N_3^+$ Cation

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The planar ring structure of the $S_4N_3^+$ cation has been known for almost 2 decades,[1] and early studies were directed to the interpretation of its electronic spectrum and structure.[2-5] In a recent work Waluk and Michl[6] reported its magnetic circular dichroism (MCD) spectrum. The MCD results indicate that each of the two electronic bands, at 340 and 263 nm, respectively, consists of two pairs of nearly degenerate transitions.

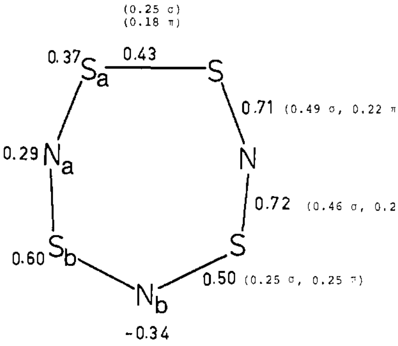

Figure 1.

We have employed the Hartree–Fock–Slater (HFS) method, which is well documented in the literature[7] and widely used for sulfur nitrides[8] in order to elucidate the nature of these transitions. The calculation was performed in terms of a double-ζ basis augmented with a 3d polarization function on sulfur. The experimental geometry[1] was suitably averaged to C_{2v} symmetry.

The 38-electron single-determinant ground state that we obtained can be represented by $(1a_1)^2(1b_1)^2(2a_1)^2(2b_1)^2(3a_1)^2(3b_1)^2(4a_1)^2(5a_1)^2(1b_2)^2(4b_1)^2(1a_2)^2(6a_1)^2(2b_2)^2(5b_1)^2(7a_1)^2(6b_1)^2(3b_2)^2(2a_2)^2(8a_1)^2$ where the orbitals are arranged in ascending energy. The energy of the two highest occupied π orbitals $3b_2$ and $2a_2$ were respectively -0.432 and -0.429 au while the two lowest unoccupied orbitals $3a_2$ and $4b_2$ had energies of -0.310 and -0.282 au, respectively.

The calculated electronic transitions were obtained from the difference between one-electron HFS eigenvalues shifted by a constant 0.40 eV; this procedure has been shown to be quite adequate for other sulfur nitrides[9] and has been given theoretical justification recently.[10] The experimental electronic spectrum contains two bands, one at 340 nm and another at 263 nm. Our calculations show that the 340-nm band appears to be produced by the almost degenerate $2a_2 \rightarrow 3a_2$ and $3b_2 \rightarrow 3a_2$ transitions whereas the 263-nm band is a result of the $2a_2 \rightarrow 4b_2$ and $3b_2 \rightarrow 4b_2$ transitions. The values given by the MCD analysis of Waluk and Michl of 28 500 and 30 500 cm^{-1} or 351 and 328 nm correspond well with the calculated pair at 341 and 332 nm. Michl's values of 267 and 250 nm are also in reasonably good agreement with the calculated pair at 282 and 277 nm. All four orbitals involved in these transitions, i.e., $3b_2$ (the HOMO − 2), $2a_2$ (HOMO − 1), $3a_2$ (LUMO), and $4b_2$ (LUMO + 1), are of π symmetry, and this

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0020-1669/84/1323-1981$01.50/0

also agrees with the seven-center 10 π-electron perimeter model discussed by Waluk and Michl and predicted earlier by Banister.[6] The separation Δ(HOMO) between the two highest occupied π MO's $2a_2$ and $3b_2$ is much less than separation Δ(LUMO) between $3a_2$ and $4b_2$. This has some significance for the detailed nature of the MCD term and is indeed consistent with Waluk and Michl's results. It is worthwhile emphasizing however that this excellent agreement is accomplished within the constraints of a single-determinant HFS scheme—a result counter to the position of Waluk and Michl that configuration interaction was essential for an adequate MO description of such systems.[11]

In addition to the electronic spectrum there is more general interest in $S_4N_3^+$ as a 10 π-electron system (cf. $S_3N_3^-$, $S_4N_4^{2+}$). The characteristics of the π bonding and indeed the overall bonding are relevant to interpreting the stability and the reactions of this cation, e.g. in scission[12] etc. Consequently, in Figure 1 we have provided the total overlap populations and charges of the ground state.[13]

From Figure 1 it is clear that the charge associated with each center indicates the usual strongly polar SN bonds; there is, as a result, a deficiency of charge on the sulfide fragment relative to the rest of the cation. These charges are consistent with the NMR measurement on ^{15}N.[14] The overlap population for the sulfide link is depressed to only 0.43 compared to 0.64 or higher in the open-chain S_3N^-[15] or S_4N^-[16] species but is comparable to that for the SS linkage in S_4N_2.[8c] In comparison to the SN bonds the SS bond is certainly weaker than either the S_aN_a or S_bN_a bonds and somewhat weaker than the S_bN_b link. This should be compared to S_4N_2 where the SN bond linking the S_3 portion to N_2S has the lowest overlap population and is indeed the point of scission. The overlap population of 0.50 for the S_bN_b bond is similar to that found in other π-electron-rich species (e.g., in $S_3N_3^-$[8c] it is 0.52) but is considerably less than in the cyclic dication $S_4N_4^{2+}$[9b] where the SN population is 0.61. The other SN bonds S_aN_a and S_bN_a are certainly quite strong with noticably enhanced overlap population of 0.71 and 0.72, respectively. In summary then, the total charges and overlap populations describe $S_4N_3^+$ as having strongly polar SN bonds, a weak sulfide single bond, a strong bond (roughly 1.5) between the sulfide and the rest of the molecule, and a SN single bond holding the unique nitrogen to its neighbors.

Some insight into these results can be gained by partitioning the overlap populations into π and σ contributions (by σ we denote those contributions that are symmetric to the molecular plane and include in this designation what are normally called σ bonds, "in-plane" p bonds, and lone pairs). In our calculations the π molecular orbitals belong to the a_2 and b_2 representations. As the entries in Figure 1 indicate, both the disulfide bond and the $S_bN_bS_b$ region have weak σ bonds (0.25 is roughly half a π bond) and also have only partial π-bond character (again 0.25 is roughly half a π bond). On the other hand, the large overlap populations of 0.71 and 0.72 for S_aN_a and S_bN_a bonds are a result of a full σ bond ($\sim$0.50) and a partial (half) π bond.

There is, of course, some variation in π-bond contribution around the ring (it is noticeably smaller in the disulfide bond), but it is clear that variations in bond strength in $S_4N_3^+$ can be attributed primarily to variations in the σ bond.

A more detailed analysis of calculated overlap populations reveals that is the orbitals $7a_1$ and $4b_1$ that are largely responsible for reducing the overlap in the S_bN_b and SS regions. They make antibonding overlap contributions of −0.055 and −0.074, respectively, to the S_bN_b and SS bonds. The "mechanism" of this destabilization can be illustrated by noting that in $4b_1$ there is a large self-atom population (or sulfur lone-pair character) of 0.44 that is carried in such a diffuse sulfur orbital that a strong antibonding interaction results with the neighboring nitrogen.

The 10 π electrons of $S_4N_3^+$ are distributed in orbitals that are essentially like those of a linear seven-center delocalized π system SNSNSNS, with the terminal sulfur folded back on one another. Thus, the first three π orbitals $1b_2$, $2b_2$, and $1a_2$ are clearly π bonding in the appropriate regions. However, the $3b_2$ and $2a_2$ π orbitals have both bonding and antibonding character depending on the region of the molecule. Indeed the π system is in some respects best interpreted as the strong interaction of four π electrons in a SS fragment (i.e., $\pi^2\pi^{*2}$) with six π electrons in a five-center NSNSN fragment (four π bonding and two nonbonding). This accounts for the depressed π-bonding character of the disulfide and the partial π bonds in the NS links.

The π orbitals $3b_2$, $2a_2$, $3a_2$, and $4b_2$ involved in the electronic transitions are of special interest. The overlap calculation indicates that the LUMO, $3a_2$, is primarily a disulfide orbital as are the HOMO − 1, $2a_2$, and HOMO − 2, $3b_2$. Consequently, the transitions $3b_2 \rightarrow 3a_2$ or $2a_2 \rightarrow 3a_2$ will weaken primarily the disulfide bond (especially in the case $3b_2 \rightarrow 3a_2$) but will have less effect on the remainder of the molecule. However, occupancy of the $4b_2$ orbital will weaken the $N_bS_bN_b$ region for both the $3b_2 \rightarrow 4b_2$ or $2a_2 \rightarrow 4b_2$ transitions and will weaken the disulfide only for the $3b_2 \rightarrow 4b_2$ transition.

In conclusion, the HFS calculation has allowed us to propose the identification of the molecular orbitals involved in the MCD spectrum. In addition, our results provide the basis for the analysis of both σ and π bonding in $S_4N_3^+$.

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Registry No. $S_4N_3^+$, 29631-23-0.

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[11] The remark on this point in ref 6 may have been induced by the fact that Waluk and Michl are commenting on PPP calculations, a long way from the present ab initio results.

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Optical Absorption and ESR Spectra of Monomeric Rhodium(II) Tetraphenylporphyrin in 2-Methyltetrahydrofuran Solution at 77 K

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Rhodium porphyrins have aroused much attention because of the wide variety of their chemical reactions.[1] For instance, rhodium porphyrins readily react with the simple diatomic molecules H_2, O_2, and NO to produce hydride, oxygen, and

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