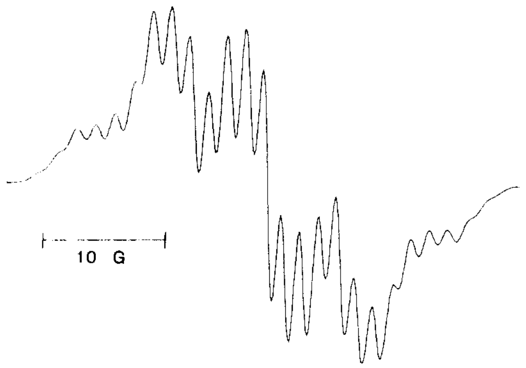

Figure 3. Room temperature, X-band EPR spectrum of the ZnTPP-*meso*-$^{13}C_4$ cation **6**.

Although the pentyl substituent has a greater influence on the spin density distribution than does the aryl group, this disparity is not manifested in the half-wave potentials ($E_{1/2}$) for the six different meso-substituted porphyrins. These potentials are summarized in Table I. As can be seen, the $E_{1/2}$ values of **3a** and **3b** are equal and approximately midway between those of **1** and **5**. In addition, the replacement of each pentyl group by an aryl group results in an approximately linear shift of the $E_{1/2}$ to a more anodic potential (~60 mV/group). It seems reasonable that this disparity in the behavior of the redox potentials versus the ^{14}N hyperfine splittings is due to the fact that the $E_{1/2}$ is a property of the entire macrocycle whereas the hyperfine splittings reflect the electronic properties at specific sites on the ring.

In view of the asymmetry in the ^{14}N hyperfine splittings of the binary hybrid porphyrin cations, it would be of interest to examine the spin density on the *meso*-carbon atoms. The spin density at this position is calculated to be considerably greater than at the pyrrole nitrogen atoms. To our knowledge, however, ^{13}C hyperfine splittings have not been previously reported even for a symmetrically substituted porphyrin cation. As a consequence, we examined the EPR spectrum of the ZnTPP-*meso*-$^{13}C_4$ cation radical **6**. This EPR spectrum is shown in Figure 3, and the hyperfine splittings that were obtained via computer simulation of the spectrum are given in Table I. The ^{13}C hyperfine splitting is 5.72 ± 0.02 G (~0.06 MHz). This value can be compared with that which is estimated from the modified McConnell relation[24]

$$a_i = 30.5\rho_i - 13.9\sum_j \rho_j$$

where a_i is the hyperfine splitting in gauss and ρ_i and ρ_j are the spin densities at the *meso*- and α-carbon atoms, respectively. The values of ρ_i and ρ_j, which are calculated with (without) configuration interaction, are 0.193 (0.158) and −0.0094 (0.0066).[18] These calculated spin densities result in a predicted *meso*-^{13}C hyperfine splitting of 6.15 G (4.64 G), which is in reasonable agreement with the experimentally observed splitting.

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Registry No. **1**, 106469-09-4; **1**$^+$, 113451-71-1; **2**, 113451-68-6; **2**$^+$, 113451-72-2; **3a**, 113451-76-6; **3a**$^+$, 113451-75-5; **3b**, 113451-69-7; **3b**$^+$, 113451-73-3; **4**, 113451-70-0; **4**$^+$, 113451-74-4; **5**, 64466-25-7; **5**$^+$, 113474-61-6.

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[24] Karplus, M.; Fraenkel, G. K. *J. Chem. Phys.* **1961**, *35*, 1312.

Additions and Corrections

1987, Volume 26

Steven G. Rosenfield, Hilde P. Berends, Lucio Gelmini, Douglas W. Stephan, and Pradip K. Mascharak*: New Octahedral Thiolato Complexes of Divalent Nickel: Syntheses, Structures, and Properties of $(Et_4N)[Ni(SC_5H_4N)_3]$ and $(Ph_4P)[Ni(SC_4H_3N_2)_3]\cdot CH_3CN$.

Page 2793. In Table I, the values of *a* and *c* for compound **3** are interchanged; the correct values are *a* = 15.090 (4) Å and *c* = 18.958 (5) Å.—Pradip K. Mascharak