Inorganica Chimica Acta, 44 (1980) L211–L212
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Charge Transfer Spectra of Tetrabenzporphyrin Complexes of Iron(II)

A. VOGLER* and H. KUNKELY

Universität Regensburg, Institut für Chemie, D-8400 Regensburg, F.R.G.

Received December 11, 1979

The optical absorption spectra of metalloporphyrins are generally dominated by the intense intraligand bands of the porphyrin ligand [1]. These spectra provide direct information about the electronic structure of the porphyrin. The perturbation of the porphyrin spectrum by the central metal can then be related to the electron distribution at the metal. To gain more insight into the electronic structure of the metal it is desirable to identify electronic transitions without direct participation of the porphyrin ligand. This would be of particular value for hexacoordinated low spin Fe(II) porphyrins [2] with regard to the influence of extraplanar ligands on redox potentials (cytochromes) and the ability of Fe(II) to bind small molecules as O_2 and CO (hemo- and myoglobins). Ligand field bands would be very useful. They are difficult to observe [1–4], however, due to their low intensity compared to the porphyrin bands which cover most of the visible region.

For hexacoordinated low spin Fe(II) porphyrins, a suitable choice of extraplanar ligands can lead to the occurrence of charge transfer bands (CT Fe to axial ligand) which may be intense enough to be easily identified. In the spectra of Fe(II) porphyrins with pyridine in both axial positions, a shoulder near 470 nm has been assigned to such a CT transition [5–7]. However, this assignment is not unambiguous [8].

We report clear evidence for the occurrence of CT (Fe to L) bands in the spectra of tetrabenzporphyrin (TBP) complexes of Fe(II) with pyrazine and N-methylpyrazinium cation as axial ligands L. The choice of ligands was guided by two considerations. TBP has very narrow Soret (B) and α (Q) bands which are separated by a large energy gap [9]. Any additional absorptions should be more readily observed than with other porphyrins. The ligands L were selected because in the spectra of $[Fe(II)(CN)_5L]^{n-}$ the most prominent absorptions are CT (Fe to L) bands which show large shifts to longer wavelengths and an increase of intensity on going from L = pyridine (362 nm, ϵ = 3715) to pyrazine (452 nm, ϵ = 5012) and N-methylpyrazinium (655 nm, ϵ = 12022) [10].

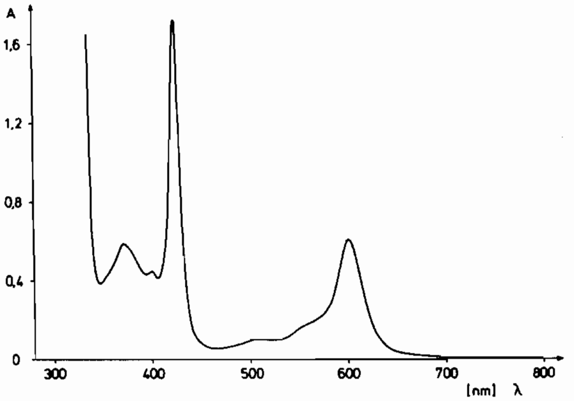

Fig. 1. Absorption spectrum of 1.07 × 10^{-5} *M* FeTBP(pyridine)$_2$ in $CHCl_3$ in the presence of pyrazine; 1 cm cell.

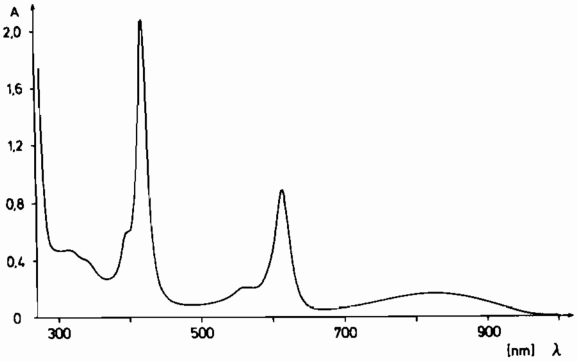

Fig. 2. Absorption spectrum of 1.34 × 10^{-5} *M* FeTBP(pyridine)$_2$ in $CHCl_3$ in the presence of N-methylpyrazinium iodide; 1 cm cell.

Spectra were obtained from solutions of FeTBP(pyridine)$_2$ [11] in $CHCl_3$ in the presence of a large excess of L. The CT bands (Figs. 1 and 2) are readily observed for L = pyrazine (508 nm, ϵ = 9300) and N-methylpyrazinium (826 nm, ϵ = 8950). For the former complex the CT band changes the usual green color of solutions of TBP complexes to a distinct blue. The intensities and the energy dependence on L are comparable to those of the CT bands of the corresponding $[Fe(CN)_5L]^{n-}$ complexes. However, the absolute energies are considerably smaller for the TBP complexes.

In the spectrum of FeTBP(pyridine)$_2$ (Fig. 3) a small inflection is observed at 460 nm (ϵ = 10500). This is nearly at the same wavelength as the shoulder of other Fe(porphyrin)(pyridine)$_2$ complexes (see above). Assuming the same energy dependence on L for the CT bands of TBP and pentacyano complexes, as it has been verified for L = pyrazine and N-methyl-

---

*Author to whom correspondence should be addressed.

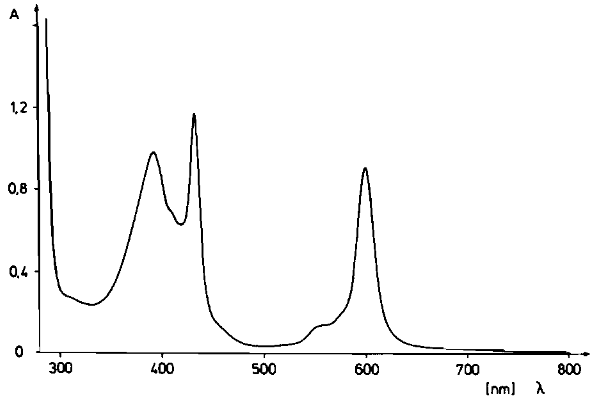

Fig. 3. Absorption spectrum of 1.07 × 10^{-5} *M* FeTBP(pyridine)$_2$ in CHCl$_3$; 1 cm cell.

pyrazinium, the CT band of FeTBP(pyridine)$_2$ should appear around 400 nm where it would be covered by TBP bands. This suggests that the inflection at 460 nm is not the Fe–pyridin CT band [8].

Acknowledgements

Financial support for this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

1 M. Gouterman, in 'Porphyrins', Vol. III, D. Dolphin, Ed., Academic Press, New York, 1978, chapter 1.
2 F. Adar, in ref. 1. chapter 2.
3 W. A. Eaton and E. Charney, *J. Chem. Phys., 51*, 4502 (1969).
4 W. A. Eaton J. Hofrichter, L. K. Hanson and M. W. Makinen, *Proc. Taniguchi Int. Sympo. Biophys.*, Lake Birva, Japan, 1974.
5 H. Kobayashi and Y. Yanagawa, *Bull. Chem. Soc. Jpn., 45*, 450 (1972).
6 T. G. Spiro and J. M. Burke, *J. Am. Chem. Soc., 98*, 5482 (1976).
7 P. G. Wright, P. Stein, J. M. Burke and T. G. Spiro, *J. Am. Chem. Soc., 101*, 3531 (1979).
8 A. Antipas, J. W. Buchler, M. Gouterman and P. D. Smith, *J. Am. Chem. Soc., 100*, 3015 (1978).
9 L. Edwards, M. Gouterman, and C. B. Rose, *J. Am. Chem. Soc., 98*, 7638 (1976).
10 H. E. Toma and J. M. Malin, *Inorg. Chem., 12*, 1039 (1973).
11 A. Vogler, H. Kunkely and B. Rethwisch, unpublished results.