Inorganica Chimica Acta, *99* (1985) L9–L11

Electron Spin Resonance Studies of Two Copper(II) N-alkylporphyrins

W. V. SWEENEY, DEBASISH KUILA and DAVID K. LAVALLEE

Department of Chemistry, Hunter College of the City University of New York, 695 Park Avenue, New York, N.Y. 10021, U.S.A.

Received November 23, 1984

Numerous studies of the EPR properties of Cu(II) porphyrins have been reported [1–13]. This, however, is the first report of an EPR spectrum of an N-substituted metalloporphyrin. The EPR spectra of copper porphyrins generally exhibit approximate axial symmetry, with $A_{\parallel}^{Cu} \gg A_{\perp}^{Cu}$, and a well resolved superhyperfine splitting from the porphyrin nitrogens. We report here the X-band frozen solution EPR spectra of two N-alkyl Cu porphyrin complexes: N-methyl-5,10,15,20-tetraphenylporphinatocopper(II) trifluoromethanesulfonate, $[Cu(N\text{-}CH_3TPP)]CF_3SO_3$, and N-p-nitrobenzyl-5,10,15,20-tetraphenylporphinatocopper(II) trifluoromethanesulfonate, $[Cu(N\text{-}CH_2C_6H_4NO_2TPP)]CF_3SO_3^-$.

Experimental

Materials and Methods

Acetonitrile was kept over molecular sieves for several days, then stored with calcium hydride, and finally distilled from P_2O_5. Spectrograde chloroform (Aldrich) was used as such without further purification. The preparation and purification of $Cu(CF_3SO_3)_2 \cdot 6H_2O$ has been described [14]. The $Zn(ClO_4)_2 \cdot 6H_2O$ and 2,2,6,6-tetramethylpiperidine (Aldrich) were used without purification.

The $[Cu(N\text{-}CH_3TPP)]CF_3SO_3$ and $[Cu(N\text{-}CH_2C_6H_4NO_2HTPP)]CF_3SO_3$ were prepared according to previously described procedures [15, 16]. The Zn complex, $[Zn(N\text{-}CH_3TPP)]ClO_4$, was prepared by mixing $Zn(ClO_4)_2 \cdot 6H_2O$ and $N\text{-}CH_3HTPP$ (40 and 16 mg respectively) in CH_3CN with the addition of an excess of the non-coordinating base, 2,2,6,6-tetramethylpiperidine. The mixture was then evaporated to dryness (UV–visible maxima (CH_3CN) were similar to those previously reported in CH_2Cl_2 for $[Zn(N\text{-}CH_3TPP)Cl]$ [17]: 434, 446, 559, 606 and 655 nm). The Zn complex was then mixed with $[Cu(N\text{-}CH_3TPP)]CF_3SO_3$ (3 mg) in 0.5–0.7 ml of CH_3CN. The mixture was filtered through glass wool and transferred to the EPR tube. The ratio of Zn:Cu was 4:1. The sample of N-p-nitrobenzyl-5,10,15,20-tetraphenylporphinatocopper(II) was prepared by mixing an excess of $Cu(CF_3SO_3)_2 \cdot 6H_2O$ with $N\text{-}CH_2C_6H_4NO_2HTPP$ in the presence of 2,2,6,6-tetramethylpiperidine in acetonitrile and the formation of the complex was confirmed by visible absorption spectroscopy. Excess free ligand was added when the spectrum was recorded in the presence of free base. In all cases the mixtures were filtered.

EPR spectra were recorded using an X-band Varian V-4500 series spectrometer. Samples were observed while immersed in a dewar containing liquid nitrogen.*

Results and Discussion

While the N-alkyl complexes are very closely related to CuTPP structurally, differing only in the presence of an alkyl group on one ring nitrogen, the presence of the alkyl group alters the symmetry, covalency and the charge of the metalloporphyrin complex. In metal N-alkylporphyrin complexes, the metal sits out of the plane of the ring, with the metal–alkylnitrogen bond considerably lengthened [19–21]. Thus the symmetry is decreased from square planar to distorted square pyramidal, and there is diminished metal–nitrogen interaction. Further, the alkylated nitrogen is formally neutral, resulting in a net +1 charge for the complex. These changes alter not only the reactivity of the complex [15, 16], but also the nature of the EPR spectrum and the behavior of the complex in solution.

The EPR spectrum of $[Cu(N\text{-}CH_3TPP)]CF_3SO_3$ in frozen $CHCl_3$ solution at 77 K is shown with a computer simulated spectrum in Fig. 1. The parameters used in fitting the observed spectrum were $g_{\parallel} = 2.213$, $g_{\perp} = 2.055$, and $A_{\parallel}^{Cu} = 149$ gauss. The poor resolution observed in the perpendicular region of the spectrum allowed only an approximate determination of $g_{\perp}$, and did not permit extraction of $A_{\perp}^{Cu}$. The spectrum of $[Cu(N\text{-}CH_2C_6H_4NO_2HTPP)]$ in CH_3CN appears similar (Fig. 1). Simulation of the spectrum yields $A_{\parallel}^{Cu} = 142$ gauss, $g_{\parallel} = 2.220$, and an estimate of $g_{\perp}$ as 2.065.

The EPR spectra of the N-alkyl complexes appear considerably different from those of CuTPP. They are distinguished by the absence of any observed nitrogen superhyperfine structure, as well as smaller $A_{\parallel}^{Cu}$ and larger $g_{\parallel}$ values. In addition, they also give

---

*Spectral simulations were performed using SIM14, a computer program written in Fortran IV by George P. Lozos, Brian M. Hoffman, and Charles G. Franz and obtained from the Quantum Chemistry Program Exchange (QCPE Program No. 265).

0020-1693/85/$3.30

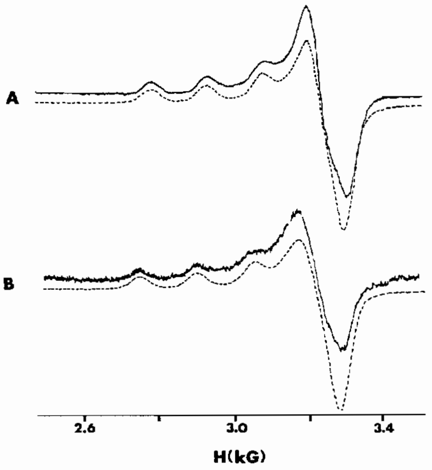

Fig. 1. Frozen chloroform solution X-band EPR spectra (77 K) of (A) $Cu(N\text{-}CH_3TPP)^+$ in the presence of excess $N\text{-}CH_3HTPP$, and (B) $Cu(N\text{-}p\text{-}CH_2C_6H_4NO_2TPP)^+$ in the presence of excess $N\text{-}p\text{-}CH_2C_6H_4NO_2HTPP$. Simulated spectra are shown below each spectrum, computed using fitting parameters as described in the text. A:Frequency, 9.295 GHz; power, 10 mW; gain, 100; field modulation, 2 gauss. B:Frequency, 9.291 GHz; power, 20 mW; gain, 400; field modulation, 8 gauss.

evidence of aggregation, in contrast to the spectra of CuTPP.

The loss of resolution of the nitrogen superhyperfine structure is a direct consequence of the structure. In CuTPP the four ring nitrogens are equivalent, leading to constructive overlap of the nitrogen superhyperfine splittings and resolution of the characteristic pattern of four sets of nine lines. However, in the case of the lower symmetry N-alkyl porphyrin complexes, a pattern of four sets of fortyfive lines is expected. This five-fold increase in spectral complexity leads to overlapping of lines with a consequent smoothing of the spectrum and a loss of resolution.

Variation in $A_{\parallel}^{Cu}$ and $g_{\parallel}$ between related compounds can result either from distortions of symmetry, or from differences in bonding or charge. $A_{\parallel}^{Cu}$ and $g_{\parallel}$ have been used as probes of geometry among closely related compounds [22, 23], partially because of the ease with which they can be determined. While the N-alkyl complexes do exhibit differences in bonding from CuTPP [18–21], the weakened ligand field which results from the N-alkyl copper bond would be expected to yield opposite trends in $A_{\parallel}^{Cu}$ and $g_{\parallel}$ from those observed. For this reason, the decrease in $A_{\parallel}^{Cu}$ and increase in $g_{\parallel}$ (relative to CuTPP) are attributed to geometric and charge differences.

Aggregation of copper porphyrins in solution is common [2, 4, 8, 11]. However, CuTPP does not aggregate, even to the extent of dimer formation, in $CHCl_3$, benzene, dioxan, or chloronaphthalene [13]. It has been suggested [12] that this is a consequence of the configuration of the phenyl rings. In contrast to this, the $[Cu(N\text{-alkylTPP}]^+$ complexes do exhibit evidence of aggregation. For example, the spectrum of $Cu(N\text{-}CH_3TPP)^+$ is considerably better resolved when diluted 1:5 with the corresponding Zn complex or in the presence of an excess of free ligand (Fig. 2). Thus, $Cu(N\text{-alkylTPP})^+$ complexes appear to aggregate even though CuTPP does not. These complexes differ from CuTPP in both geometry and charge. It is likely that the geometric difference by itself is not the origin of the aggregation. While the protrusion of the Cu out of the plane of the porphyrin in theory could promote dimer formation through direct metal–metal interaction, this mechanism of dimer formation is more likely for Cu(I) than Cu(II). A more attractive alternative is that aggregation arises from stacked $Cu(N\text{-alkylTPP})^+$ complexes bridged by intervening anions.

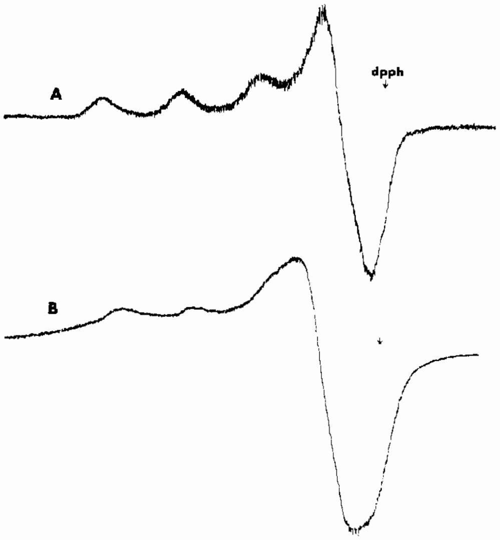

Fig. 2. Frozen chloroform solution X-band EPR spectra (77 K) of $Cu(N\text{-}CH_3TPP)^+$ recorded in the presence (A) and absence (B) of excess $N\text{-}CH_3HTPP$. A:Frequency, 9.296 GHz; power, 10 mW; gain, 200; field modulation, 2 gauss. B:Frequency, 9.299 GHz; power, 10 mW; gain, 100; field modulation, 0.8 gauss.

Acknowledgments

This work has been supported in part by grants CA25247 and RR08176 from the National Institutes of Health (DKL) and by grant 663144 from the Professional Staff Congress – Board of Higher Education Research Award Program (WVS).

References

1 W. C. Lin, in D. Dolphin (ed.), 'The Porphyrins, Vol. 7', 1979, p. 355.

2 A. MacCragh, C. B. Storm and W. S. Koski, *J. Am. Chem. Soc., 87,* 1470 (1965).

3 C. M. Guzy, J. B. Raynor and M. C. R. Symons, *J. Chem. Soc. A:,* 2299 (1969).

4 J. A. De Bolfo, T. D. Smith, J. F. Boas and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.,* 1523 (1975).

5 S. R. W. Loura and G. Bemski, *J. Magn. Reson., 28,* 427 (1977).

6 M. C. Findlay, L. C. Dickinson and J. C. W. Chien, *J. Am. Chem. Soc., 99,* 3108 (1977).

7 H. Yokoi and M. Iwaizumi, *Bull. Chem. Soc. Jpn., 53,* 1489 (1980).

8 S. Konishi, M. Hoshino and M. Imamura, *J. Phys. Chem., 86,* 4888 (1982).

9 J. Assour, *J. Chem. Phys., 43,* 2477 (1965).

10 P. T. Manoharan and M. T. Rogers, in T. F. Yen (ed.), 'Electron Spin Resonance of Metal Complexes', Plenum, New York, 1969.

11 P. A. W. Boyd, T. D. Smith, J. H. Price and J. R. Pilbrow, *J. Chem. Phys., 56,* 1253 (1972).

12 K. Alston and C. B. Storm, *Biochemistry, 18,* 4292 (1979).

13 J. M. Assour, *J. Chem. Phys., 40,* 365 (1964).

14 D. Kuila, *Dissertion,* City University of New York, 1983.

15 D. Kuila and D. K. Lavallee, *Inorg. Chem., 22,* 1095 (1983).

16 D. K. Lavallee and D. Kuila, *Inorg. Chem., 23,* in press.

17 D. K. Lavallee, *Bioinorg. Chem., 6,* 291, (1976).

18 O. P. Anderson and D. K. Lavallee, *Inorg. Chem., 16,* 1634 (1977).

19 O. P. Anderson and D. K. Lavallee, *J. Am. Chem. Soc., 99,* 1404 (1977).

20 D. K. Lavallee, A. B. Kopelove and O. P. Anderson, *J. Am. Chem. Soc.,* 100, 3025 (1978).

21 O. P. Anderson, A. B. Kopelove and D. K. Lavallee, *Inorg. Chem., 19,* 2101 (1980).

22 J. Peisach and W. E. Blumberg, *Arch. Biochem. Biophys., 165,* 691 (1974).

23 M. Yokoi and A. W. Addison, *Inorg. Chem., 16,* 1341 (1977).