Intermolecular Dimerisation of Copper Porphyrins and their Radical Cations. An Electron Spin Resonance Study

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The interactions and structural chemistry of neutral copper porphyrins, and their radical cations, with zinc and free-base porphyrins have been studied by e.s.r. spectroscopy. Mixed-dimer complexes exhibit characteristic e.s.r. spectra and redox properties.

Recent n.m.r. and e.s.r. studies of copper porphyrin radical cations have suggested the presence of distinct dimeric species in solution.[1] Concurrent studies in this laboratory led to similar conclusions and prompted the exploration of some of the solution structural chemistry of these complexes. In particular, it was of interest to define both the essential requirements, and the generality, of the aggregation reactions for both neutral and oxidised porphyrins.

Results and Discussion

Initial experiments on a cofacially-linked porphyrin dimer,[2] in which a copper metalloporphyrin was oriented parallel to a free-base porphyrin, demonstrated that there was no intermolecular interaction between distinct copper porphyrin faces. The e.s.r. spectrum of the molecule, shown in Figure 1(*a*) ($g_{\parallel} = 2.18$, $A = 0.021$ cm^{-1}),† was similar to that expected for a monomeric copper porphyrin. This suggested that any possible requirement for interchromophore interaction, in order to satisfy the π unsaturation of the copper-containing aromatic ring, was already met by the adjacent free-base porphyrin, and supports the idea of MacCragh *et al.*[3] that metal–metal interaction does not play an important role in the aggregation of porphyrin systems. Although this is likely to be dominated by π interaction, it does not exclude the possibility of coulombic interactions from regions of positive and negative electron density around the porphyrin ring.

The specificity of the interaction was tested by recording the e.s.r. spectra of equimolar mixtures of both copper and zinc porphyrins, and copper and free-base porphyrins (H_2P). A 'monomeric' [CuP]‡ to dimeric [CuP] signal ratio of *ca.* 4:1 and 3:2 respectively was determined in comparison with that for solutions of [CuP] alone, where the signal ratio is *ca.* 1:4 (Figure 2; Figure 1 shows representative monomeric and dimeric porphyrin spectra). Since both a [ZnP–CuP] or [H_2P–CuP] dimer would possess a monomeric [CuP] e.s.r. signature, these results are indicative of mixed-dimer formation, particularly in the case of [ZnP–CuP]. The distribution of π electron density over the free-base, copper, and zinc porphyrin rings is similar;[4] however, only the copper and zinc porphyrins have π orbitals of comparable energies,[4] hence the strength of CuP–CuP and ZnP–CuP interactions, in comparison to the H_2P–CuP system, can be readily understood in terms of the energetics of π orbital overlap. The reason for the apparent preference for ZnP–CuP interaction is not clear at this moment.

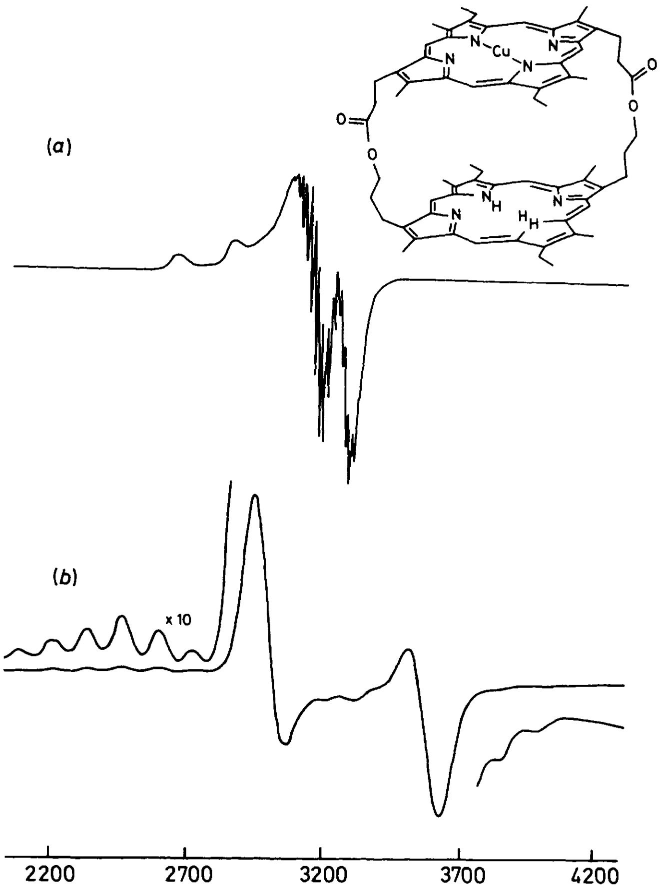

Figure 1. (*a*) 77 K e.s.r. spectrum of the cofacially-linked dimer indicated, corresponding to a single isolated copper porphyrin species, and (*b*) 4 K e.s.r. spectrum of the intermolecular dimer formed from [CuP]$^+$ (generated by bulk electrolysis). In each case [metalloporphyrin] = *ca.* 2 mmol dm^{-3}

The formation of intramolecular dimers for cation radicals of magnesium and zinc porphyrins has been documented for some time, however the geometry of these species has been uncertain. Both π-stacked dimers and *meso*-linked structures are possible.[5] It has been found that copper porphyrin radical cations also readily dimerise, both at ambient temperatures and at cryogenic temperatures in particular.[1,2,6] Studies in this laboratory have focussed on both the geometry and chemistry of these species.

In the dimer, the free electrons on the porphyrin rings are

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† The data were derived directly from the spectra and not by simulation.

‡ In the remainder of the paper, P will denote the dianions of both 2,3,7,8,12,13,17,18-octaethylporphyrin and mesoporphyrin II dimethyl ester. Similar results were obtained with both. 5,10,15,20-Tetraphenylporphyrins did not dimerise under the conditions used, presumably due to steric effects.

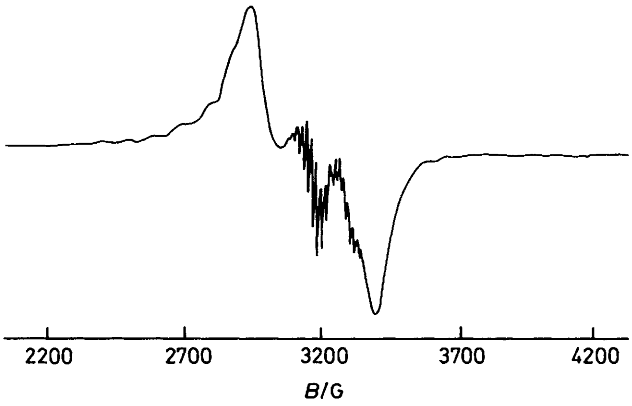

Figure 2. 77 K e.s.r. spectrum of [CuP] showing features due to both monomeric and dimeric character (see Figure 1); [metalloporphyrin] = *ca.* 2 mmol dm^{-3}

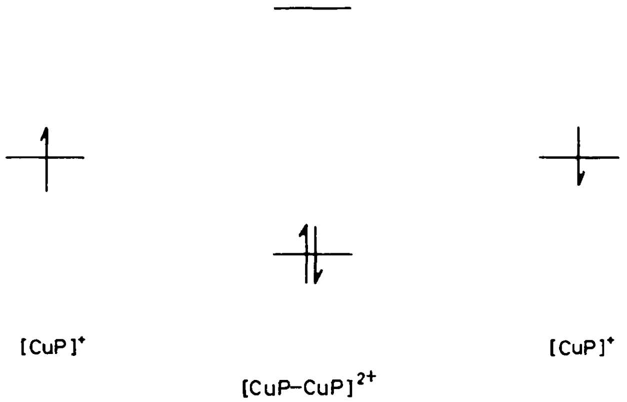

Figure 3. π-Electronic configuration interaction between ground-state $[CuP]^+$ radicals. In the dimer $[CuP–CuP]^+$ a net bonding configuration is obtained. See refs. 5 and 8

strongly coupled,[5] therefore only features due to dipole-coupled copper were observed in the 77 K e.s.r. spectrum in Figure 1(*b*) ($g_{\parallel} = 2.19$, $g_{\perp} = 2.03$, $A = 0.011$ cm^{-1}, $D = 0.045$ cm^{-1}),[7,*] from which an inter-copper distance of *ca.* 4.1 Å was determined.[7] This is too short to support a *meso*-linked dimer and implies that the radical must adopt a basically symmetric face-to-face geometry. The stability of such paired complexes has been explained in terms of orbital configuration interaction (Figure 3).[8] A ten-fold increase in intensity in the e.s.r. spectrum was observed upon lowering the temperature to 4 K due to an increased Boltzmann population of the lower triplet-state energy level.

Oxidation to give a mixture of $[ZnP]^+$ and $[CuP]^+$ (electron loss from the porphyrin ring) gave an e.s.r. spectrum which was identical to that of the unoxidised copper monomer in Figure 1(*a*) (the hyperfine structures were similar because little radical spin density resides on the ligand nitrogen atoms, or is delocalised onto the metal centre).[9] There was no evidence for copper dimer formation, and so the results suggested a strong preferential interaction between $[ZnP]^+$ and $[CuP]^+$ radical cations (Figure 4). Further oxidation of the [ZnP] and [CuP] mixture, by electrolysis or the addition of bromine, produced $[CuP–CuP]^{2+}$ following the removal of a second electron from $[ZnP]^+$ and the elimination of the dication radical from the $[ZnP–CuP]^{3+}$ dimer due to cationic repulsion. Further oxidation led to the monomeric dication radical species (Figure 4). Cyclic voltammetry of a 1 : 1 solution of [ZnP] and [CuP] exhibited a two-electron oxidation at 0.81(1) V which encompassed the first oxidation of both [CuP] and [ZnP]. The individual $E_{ox}{}^1$ for both [CuP] and [ZnP] are 0.88(1) and 0.80(1) V respectively, hence the initial oxidation of [CuP] is more facile in the presence of [ZnP], supporting the stabilisation of the mixed bis-radical dimer, even at room temperature.*

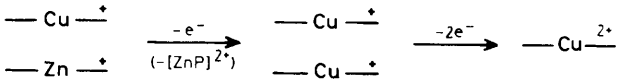

Figure 4. Structural chemistry of mixed radical copper–zinc porphyrins. Oxidation was carried out by either preparative electrolysis or the addition of bromine. In every case electrons were lost from the porphyrin rings

In contrast to the above, the 77 K e.s.r. spectrum of a 1 : 1 mixture of $[H_2P]^+$ and $[CuP]^+$ was typical of a copper dimer.[7] This indicated a preference, in this instance, for the self-interaction of $[CuP]^+$. In addition, the oxidation potentials for each porphyrin in the mixed solution were similar to those for the isolated porphyrins.

Clearly, these results for the cation radicals support the general trends found with the neutral species. However, the strong CuP–ZnP and weaker $CuP–H_2P$ interactions have now been taken to extremes. This is not unexpected since, according to the energy level diagram in Figure 3, a 'bonding' situation has been reached where the energetics of the π–π interactions will dominate.

In summary, much of the aggregation and interaction chemistry of neutral and oxidised copper, zinc, and free-base porphyrins can be explained in terms of the energetics of π-orbital overlap.

Acknowledgements

I wish to thank the S.E.R.C. and St. John's College, Cambridge, for financial support, Professor A. R. Battersby and Mr. C. Sporikou for a generous gift of mesoporphyrin II dimethyl ester, Dr. R. C. S. McQueen for advice with the electrochemical experiments, and Dr. J. K. M. Sanders for valuable advice and comments on this paper.

References

1 G. M. Godziela and H. M. Goff, *J. Am. Chem. Soc.*, 1986, **108**, 2237.
2 J. A. Cowan and J. K. M. Sanders, *J. Chem. Soc. Perkin Trans. 1*, 1987, 2395.
3 A. MacCragh, C. B. Storm, and W. S. Koski, *J. Am. Chem. Soc.*, 1965, **87**, 1470.
4 M. Zerner and M. Gouterman, *Theor. Chim. Acta*, 1966, **4**, 44.
5 J. H. Fuhrhop, P. Wasser, D. Reisner, and D. Mauzerall, *J. Am. Chem. Soc.*, 1972, **94**, 7996.
6 C. Mengersen, J. Subramanian, and J. H. Fuhrhop, *Mol. Phys.*, 1976, **32**, 893.
7 N. D. Chasteen and R. L. Bedford, *Inorg. Chem.*, 1970, **9**, 169.
8 K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, 1957, **27**, 500.
9 J. Fajer and M. S. Davis, in 'The Porphyrins,' ed. D. Dolphin, Academic Press, 1979, vol. 4, p. 197; J. H. Fuhrhop and D. Mauzerall, *J. Am. Chem. Soc.*, 1969, **91**, 4174.

Received 20*th January* 1988; *Paper* 8/00774H

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* Mixed-porphyrin dimer formation at ambient temperatures is supported by both e.s.r. spectral line shapes,[7] and by deviations from the Beer–Lambert law.