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EPR Detection of Heterodimer Species between Copper(II), Silver(II) and Oxovanadium(IV) Porphyrins

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Abstract

The EPR spectra of glassy solutions in tetrachloroethane containing equimolar amounts of two metalloporphyrins were measured at 77 K. The metalloporphyrins are CuP, AgP and VOP, where P is mesoporphyrinIX dimethyl ester. The spectra show evidence of heterodimer formation: in the case of CuP–AgP the EPR spectrum of the heterodimer was obtained through computer manipulation and the EPR parameters determined. The spectra of CuP–VOP and AgP–VOP are consistent with the presence of two heterodimeric species.

Introduction

Association of porphyrin molecules in solution is well known [1–5] and has been subject to increasing investigation because of their biological interest and of their use as catalysts. However, the effect on the type and the extent of aggregation of factors such as the nature of the metal atom and the geometry of the complex is not yet fully understood. Furthermore, many studies on aggregation deal on water-soluble metalloporphyrins [6–10], and much less is known about the naturally-occurring porphyrins in organic solvents. Formation of heterodimers between porphyrins differing in the metal ion has also been reported [11, 12]; in particular the EPR spectrum of frozen solutions containing copper(II) and silver(II) mesoporphyrinIX dimethyl ester provided evidence of heterodimer formation [11] and the decrease in intensity of the EPR signal of CuP, VOP or AgP in the presence of FePCl (where P is again mesoporphyrinIX dimethyl ester) at room temperature was also taken as evidence of heterodimer formation [12]. In the latter case the dimer formation constants were measured and found on a purely statistical basis to be larger than expected.

A further insight into the problem of heterodimer porphyrins can be achieved by subtracting from the EPR spectrum of a glass containing two different metal complexes the spectra of the parent species, in order to obtain the spectrum of the pure heterodimer. We report here some features of the EPR spectra of heterodimers present in frozen solutions of CuP–AgP, CuP–VOP, and AgP–VOP in tetrachloroethane.

Experimental

Metal-free mesoporphyrinIX dimethyl ester was provided by the Sigma Chemical Co. and was used without further purification. Its Cu(II), Ag(II), and V(IV)O complexes were prepared according to the literature [13, 14] and purified by thin layer chromatography [12]. All the solvents were of analytical grade and were used without further purification.

The EPR spectra were recorded at X-band frequency with 100 kHz modulation on a BRUKER ER 200 spectrometer interfaced with an ASPECT 2000 computer. The spectra at liquid nitrogen temperature of concentrated (containing both monomeric and dimeric species) and dilute (containing only monomeric species) solutions were recorded as glasses in 1,1,2,2-tetrachloroethane. Care was taken to record all the spectra at the same frequency and to keep the signal-to-noise ratio comparable in all the spectra.

Results and Discussion

The EPR spectrum of a frozen solution containing $\sim 10^{-2}$ M CuP and AgP is shown in Fig. 1, together with the spectra of the solutions of the pure parent complexes. The latter spectra show evidence of monomeric and dimeric species, as discussed elsewhere [11, 12]. Such spectra are the same as previously reported [11]. Three features, at 0.270 T, 0.280 T and at 0.365 T (indicated by arrows in Fig. 1), are evidence of heterodimer formation. The spectrum of the solution containing both CuP and AgP is due to five species: CuP, $(CuP)_2$, AgP, $(AgP)_2$, AgPCuP; the spectra of the four former species were subtracted from the spectrum of the mixture, in order to obtain the spectrum of the heterodimeric species.

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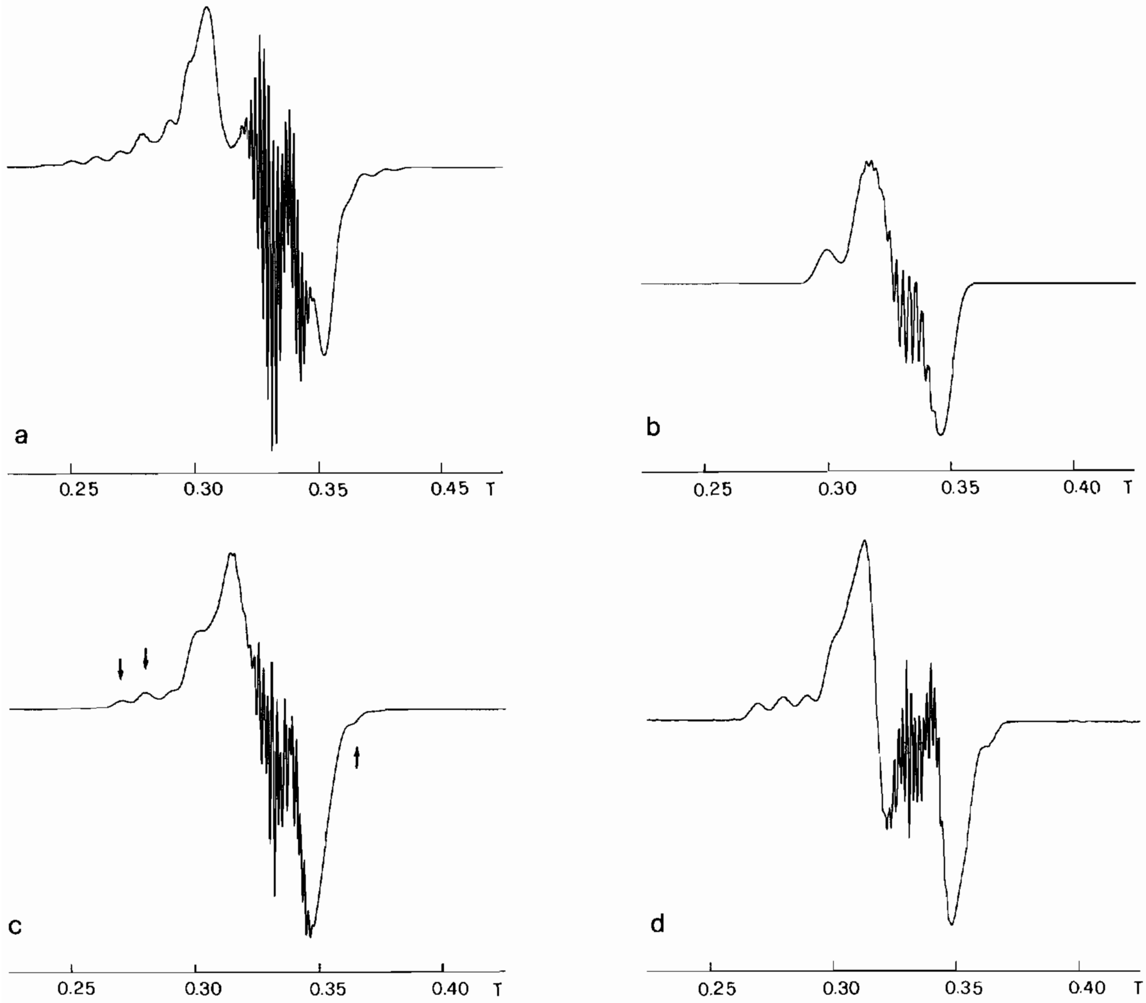

Fig. 1. EPR spectra at 77 K of tetrachloroethane glasses of: A) CuP, 3×10^{-2} M; B) AgP, 2×10^{-2} M; C) equimolar mixture of CuP, 1×10^{-2} M and AgP, 1×10^{-2} M solutions; D) spectrum obtained by subtraction of the CuP, $(CuP)_2$, AgP, $(AgP)_2$ spectra from spectrum C as discussed in the text.

The relative intensities of the spectra of the different species were set in such a way to have, upon subtraction, the disappearance of the features surely due to the monomeric and homodimeric species. In particular in the C spectrum of Fig. 1, superimposed to the spectrum of the heterodimer, there is a line at 0.280 T due to a parallel component of the copper nucleus hyperfine coupling, split by the superhyperfine coupling with nitrogen: this is due to the copper monomeric complex which has narrow lines and which is independently measured in a dilute solution [12, 15]. Furthermore there are seven lines at low field that are due to the hyperfine coupling of a $\delta = 1$ state with two magnetically equivalent $I = 3/2$ copper nuclei; then they belong to the copper dimer. The pure spectrum of the latter species was obtained from concentrated frozen solutions upon subtraction of the spectrum of the monomeric species. In the silver spectrum the superhyperfine splitted lines are due to the monomer complex whereas the feature at 0.30 T is due to the silver homodimer.

The final subtraction spectrum D of Fig. 1 is obtained from spectrum C by subtracting the spectra of all the species; each subtraction was performed to such an extent that no evident trace of the subtracting spectra remained in the resulting spectrum. The subtraction was successful; only traces of the superhyperfine lines of the monomers remain because such lines have somewhat different linewidths in the dilute and the concentrated solutions. The spectrum so obtained is typical of a triplet state and is assigned to the heterodimer CuP–AgP complex. The spin hamiltonian parameters obtained from the analysis of the spectrum are: $g_{\parallel} = 2.150$, $g_{\perp} = 2.035$, $A_{\parallel} = 100 \times 10^{-4}\ \text{cm}^{-1}$, $D = 300 \times 10^{-4}\ \text{cm}^{-1}$. The four transitions at low field are due to the hyperfine coupling of an $S = 1$ state with the copper nucleus, whereas the splitting due to the silver nucleus is not

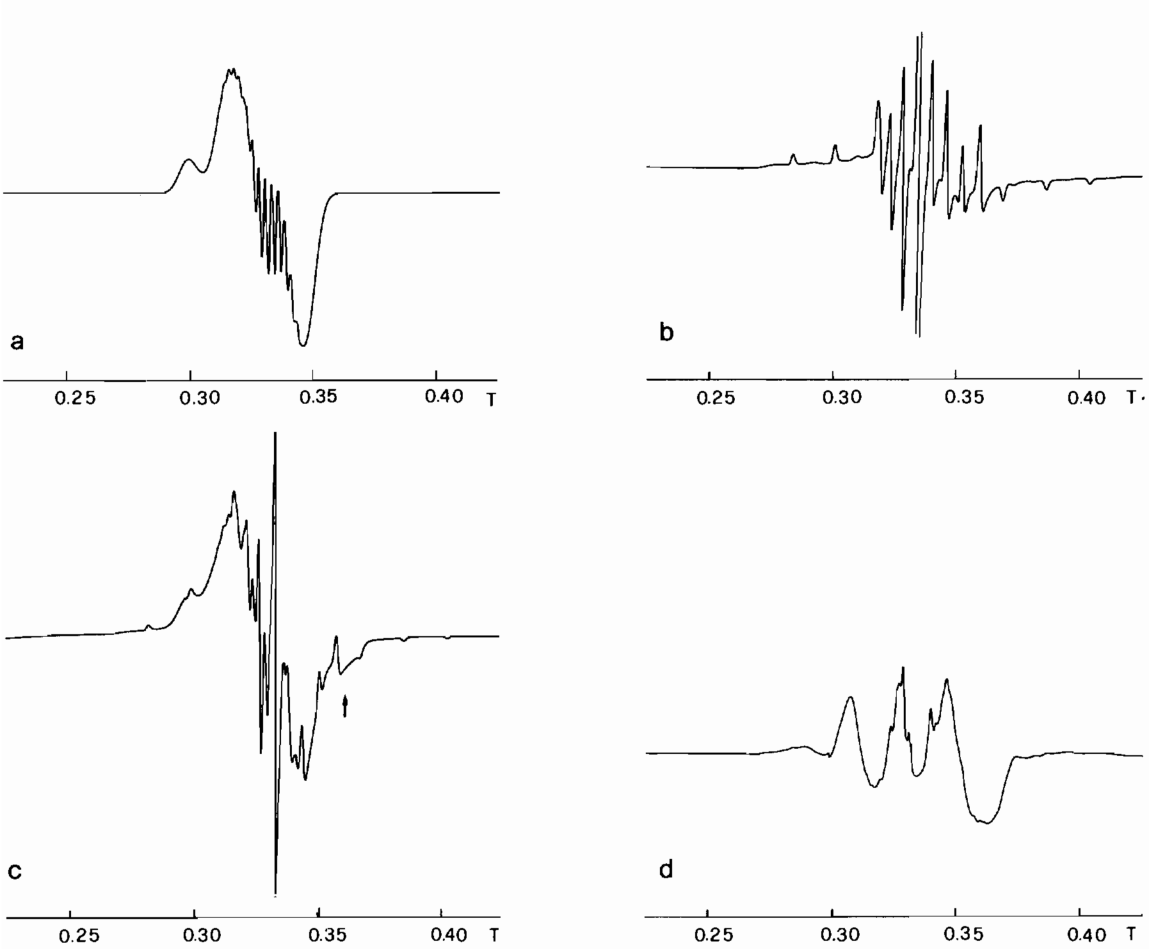

Fig. 2. EPR spectra at 77 K of tetrachloroethane glasses of: A) AgP, 2×10^{-2} M; B) VOP, 5×10^{-2} M; C) equimolar mixture of AgP, 1×10^{-2} M and VOP, 1×10^{-2} M solutions; D) spectrum obtained by subtraction of the AgP, $(AgP)_2$, and VOP concentrated solution spectra from spectrum C as discussed in text.

observed. The $A_{\parallel}$ value is almost half of that found in the copper monomer complex, consistent with heterodimer formation [16]. The g values are in the range expected for two weakly coupled $S = 1/2$ ions ($g_i = 1/2\, g_{1i} + 1/2\, g_{2i}$, where i is x, y, or z) [16, 17]; also the value of D is intermediate between those of the parent dimeric complexes. This D value is consistent with a face-to-face dimer structure with a distance between the metal ions of 4.5 Å [11]. The values of some of the above parameters were determined in a previous research [11] without any subtraction, and they agree with the present data.

The spectra of the AgP–VOP and CuP–VOP systems are less instructive because the parallel transitions of the heterodimeric species are not identified and the interpretation of the signals in the perpendicular region is not straightforward. The hyperfine splitting could provide eight lines in the parallel region in the case of the AgP–VOP dimer and thirty-two in the case of the CuP–VOP dimer, owing to the vanadium nucleus ($I = 7/2$). The spectrum of a concentrated solution of VOP was interpreted as being due to two different dimeric species, besides the monomeric species [12]. Finally, the formation constants for the above heterodimers at room temperature are expected to be small since one parent complex is square pyramidal [12] and has little tendency to aggregate.

Despite the above limitations, evidence of the AgP–VOP heterodimer formation in the spectrum of the solution containing both complexes is provided by a new transition, indicated by an arrow in Fig. 2C. The spectrum of the heterodimer is obtained with a procedure analogous to that used for the CuP–AgP system. The concentration of the dimeric species in concentrated VOP solutions is low owing to the low formation constant (1.7 M^{-1}) [12]; therefore the spectrum of such a solution was subtracted directly from the spectrum of the AgP–VOP system. From the result of this first subtraction the spectra of both the monomeric AgP and homodimeric $(AgP)_2$ species were subtracted, ensuring complete disappearance in the same way as discussed for the CuP–AgP system. The spectrum shown in Fig. 2D is attributed to the

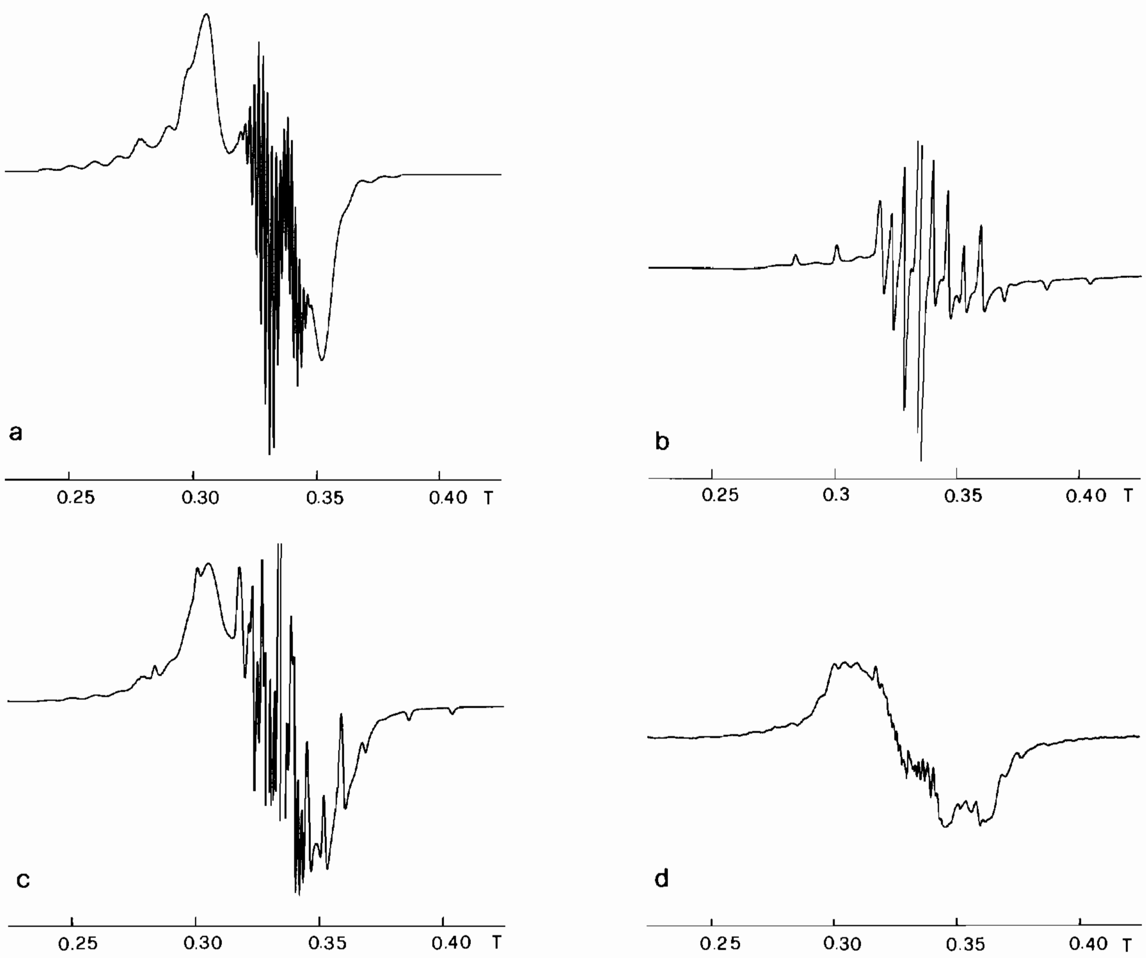

Fig. 3. EPR spectra at 77 K of tetrachloroethane glasses of: A) CuP, 3×10^{-2} M; B) VOP, 5×10^{-2} M; C) equimolar mixture of CuP, 1.5×10^{-2} M and VOP, 1.5×10^{-2} M solutions; D) spectrum obtained by subtraction of the CuP, $(CuP)_2$, and VOP concentrated solutions spectra from spectrum C as discussed in the text.

heterodimeric AgP–VOP species; the signal at 0.329 T and the different intensities of the external signals are not an artifact of computer manipulation. The spectrum shows three features that cannot be assigned to only one dimeric species. It is possible therefore that the observed spectrum is due to four perpendicular transitions, the two at high field overlapping to give one feature. In this case two different heterodimeric species would be present; some weak transitions present in the spectrum D of Fig. 2 can be due to favourable summation of the expected sixteen lines. The two heterodimers should differ substantially in their D value since two features at 0.307 T and at 0.329 T would each be assigned to a different dimeric species.

The spectra of the system CuP–VOP are shown in Fig. 3. It is hard to detect in the spectrum C of Fig. 3 any particular feature which may be attributed to heterodimeric species; however, the overall shape of the spectrum is suggestive of an underlying broad signal which is not present in the spectra of the two parent glasses. This feature is shown in the spectrum of the heterodimer obtained by subtracting the monomeric CuP and homodimeric $(CuP)_2$ spectra, as well as the spectrum of a concentrated VOP solution. The spectrum shows a broad absorption between 0.300 T and 0.360 T; two weaker transitions could be present in spectrum D of Fig. 3 around 0.296 T and 0.360 T, which would account for the extreme broadness of the spectra. If this is true, these spectra would also indicate the presence of two heterodimeric species.

Conclusions

The present research has provided evidence of the general occurrence of heterodimers in porphyrin complexes and has shown that deconvolution of the EPR spectra may provide spectra of species that cannot be studied as a pure species. A meaningful example is provided by the CuP–AgP system where the full spectrum of the pure heterodimeric species is obtained and analyzed.

In the case of VOP-containing heterodimers only the perpendicular transitions have been observed, which has been interpreted as being due to two different dimers. The non-detection of signals in the parallel region is attributed to: (*i*) the large multiplicity of the parallel hyperfine-splitted lines; (*ii*) the formation of two dimeric species; and (*iii*), the low formation constants of such species. Since the EPR spectra of concentrated frozen solutions of VOP also showed evidence of two $(VOP)_2$ dimers [12], the formation of two different dimers appears to be general when the VOP moiety is involved. It appears reasonable to suggest that VOP can form dimers by interaction with both sides of the porphyrin plane. Involvement of oxygen in VOP dimer formation has already been suggested [18].

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References

1 W. I. White, in D. Dolphin (ed.), 'The Porphyrins', Vol. V, Academic Press, New York, 1978, p. 303.
2 H. Scheer and J. J. Katz, in K. M. Smith (ed.), 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1975, chap. 10.
3 P. D. W. Boyd, T. D. Smith, J. H. Price and J. R. Pilbrow, *J. Chem. Phys., 56,* 1253 (1972).
4 K. Migita and G. N. La Mar, *J. Phys. Chem., 84,* 2953 (1980).
5 J. F. Boas, J. R. Pilbrow and T. D. Smith, *J. Chem. Soc. A:,* 721 (1969).
6 W. I. White and R. A. Plane, *Bioinorg. Chem., 4,* 21 (1974).
7 J. A. De Bolfo, T. D. Smith, J. F. Boas and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans.,* 1523 (1975).
8 R. F. Pasternack, L. Francesconi, D. Raff and E. Spiro, *Inorg. Chem., 12,* 2606 (1973).
9 R. R. Das and R. A. Plane, *J. Inorg. Nucl. Chem., 37,* 147 (1975).
10 M. Krishnamurthy, J. R. Sutter and P. Hambright, *J. Chem. Soc., Chem. Commun.,* 13 (1975).
11 S. Konishi, M. Hoshino and M. Imamura, *J. Phys. Chem., 86,* 4888 (1982).
12 L. Banci, *Inorg. Chem.,* in press.
13 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem., 32,* 1992 (1970).
14 J. W. Buchler, G. Eikelmann, L. Puppe, K. Rohbock, H. H. Schneehage and D. D. Weck, *Justus Liebigs Ann. Chem., 745,* 135 (1971).
15 H. Yokoi and M. Iwaizumi, *Bull. Chem. Soc. Jpn., 53,* 1489 (1980).
16 C. C. Chao, *J. Magn. Reson., 10,* 1 (1973).
17 J. Scaringe, D. J. Hodgson and W. E. Hatfield, *Mol. Phys., 35,* 701 (1978).
18 F. E. Dickson and L. Petrakis, *J. Phys. Chem., 74,* 2850 (1970).