Table I. Dissociation Constants of Porphyrin Ion Pairs[a]

pair	$K \times 10^8$, M
$(P^+)(P^-)$[b]	1.1
$(P^+)(ZnP^-)$[c]	5.8
$(P^+)(CuP^-)$	1.0
$(ZnP^+)(P^-)$	1.2
$(CuP^+)(CuP^-)$	0.65
$(ZnP^+)(CuP^-)$	2.5
$(CuP^+)(ZnP^-)$	7.3

[a] In 1:1 water/acetone; room temperature. [b] P^+ = TTAP; P^- = TPPS. [c] With 5% pyridine.

cofacial structures formed by multiply linked cyclophanes,[10-12] metal–oxo bridges[13] or association at low temperatures or in films.[14] The effects described here correspond to those seen in cofacial diporphyrins,[10] as expected from the charge distribution of the cationic and anionic monomers. The magnitude of the interactions may of course be limited by steric constraints imposed by noncoplanarity of the phenyl rings.

These systems are evidently well adapted, through their ease of preparation and controllable equilibria, to study phenomena in mixed metalloporphyrin pairs. More detailed reports on ion-paired porphyrins and reduced porphyrins will appear shortly, including studies on magnetic, photophysical, and photochemical behavior.

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Triplet ESR Study of Dimerization of Cationic and Anionic Water-Soluble Porphyrins

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A new class of electrostatically linked porphyrins well suited for spectroscopic study is reported above by Ojadi, Selzer, and Linschitz.[1] These authors show that combination of cationic and anionic water-soluble porphyrins [*meso*-tetrakis(4-(trimethyl-ammonio)phenyl)porphyrin (TTAP) and *meso*-tetrakis(4-sulfonatophenyl)porphyrin (TPPS)] leads to the formation of a stable 1:1 complex (TTAP/TPPS). As part of a systematic study of the spectroscopic properties of these compounds, we report here

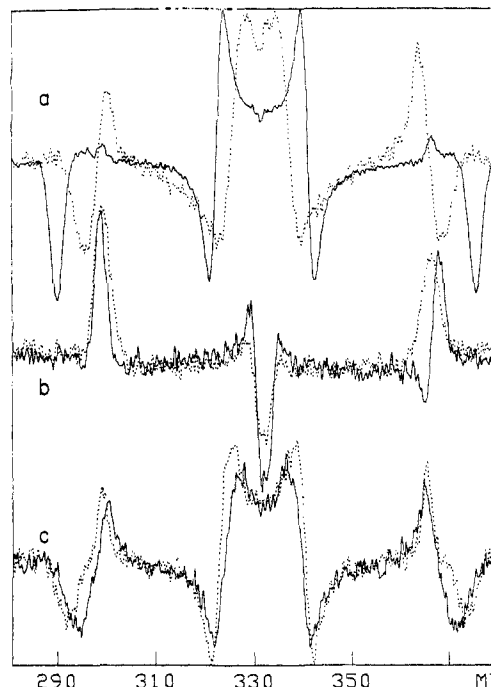(1) Ojadi, E.; Selzer, R.; Linschitz, H. *J. Am. Chem. Soc.*, preceding paper in this issue.

Figure 1. ESR spectra of photoexcited triplets of porphyrins in frozen 1:1 H_2O–glycerol recorded at 10 K. For experimental details see ref 2–4. (a) Solid line TTAP, dotted line TTAP/TPPS; (b) solid line ZnTTAP, dotted line ZnTTAP/ZnTPPS; (c) solid line ZnTTAP/TPPS, dotted line ZnTPPS/TTAP.

Table I. Triplet Zfs Values[a] and Decay Rates

system	D, 10^{-4} cm^{-1}	E, 10^{-4} cm^{-1}	k, s^{-1}
TTAP (TPPS)[b]	400	75	110
TTAP/TPPS[c]	343	80	260
ZnTTAP (ZnTPPS)[b]	323	95	
ZnTTAP/ZnTPPS[c]	316	91	
ZnTTAP/TPPS[c]	361	75	150
ZnTPPS/TTAP[c]	380	75	
[TPPS]$_2$[d]	334	80	
TCP[e]	377	79	200
[TCP]$_2$[e]	332	73	200
ZnTCP[e]	298	99	
[ZnTCP]$_2$[e]	291	69	

[a] Estimated uncertainty $\pm(5 \times 10^{-4})$ cm^{-1}. [b] Monomers. [c] Dimers. [d] TPPS dimerization induced by K^+-18-crown-6 addition.[2] [e] TCP = *meso*-tetrakis(benzo-15-crown-5)porphyrin, dimerization is induced by K^+ addition.[4]

results of ESR measurements on photoexcited triplets of dimers and monomer precursors. Comparisons are made with data on other porphyrin dimers,[2-4] and a tentative interpretation of dimerization effects is presented.

Figure 1a shows the ESR spectra of photoexcited TTAP (identical with that of TPPS[2]) and a 1:1 mixture of TTAP and TPPS. Figure 1b gives the spectra of triplet ZnTTAP (identical with that of ZnTPPS[3]) and ZnTTAP/ZnTPPS. Finally, in Figure 1c the spectra of ZnTTAP/TPPS and ZnTPPS/TTAP are presented. Values of zero field splitting (zfs) parameters D and E[5] are given in Table I.

There is a striking similarity between dimerization effects observed for systems that contain a free base moiety. This includes dimers studied earlier.[2-4] The value of D is reduced by 10–20% with respect to the monomer free base value, the E values remains unaffected. The effect on D and E of the formation of [TPPS]$_2$

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and [ZnTPPS]$_2$ (cf. Table I) was attributed[2,3] to a combination of excitation transfer and charge transfer. Here it is shown that formation of free base–Zn porphyrin dimers and of free base–free base dimers has similar effects on zfs parameters. For reasons that will be outlined below, this suggests that we are probably dealing with localized triplet states.

In TPP systems the phenyl rings make an angle of 60–70° with the tetrapyrrole plane.[6] Hence, for steric reasons, the macrocycles in TPP dimers must be rotated with respect to each other. As a consequence, excitation transfer should cause a reduction in E.[7] This has been found for a Zn crown porphyrin[4] (ZnTCP, cf. Table I). Charge transfer will reduce D.[7] Formation of ZnTTAP/ZnTPPS does not affect D and E (cf. Table I). This indicates that the excitation energy is localized. It must be localized as well in ZnTTAP/TPPS and ZnTPPS/TTAP because the triplet state of the free base lies well below that of Zn porphyrins.[8] The ZnTTAP/TPPS triplet lifetime is similar to that of TPPS and TTAP. This supports the localized triplet interpretation.[7] The triplet ESR spectra of ZnTTAP/TPPS and ZnTPPS/TTAP are strikingly similar to those of TTAP/TPPS, [TPPS]$_2$,[2] and [TCP]$_2$.[4] The logical conclusion is that in the free base dimers the excitation energy is localized as well. In free base TPP two of the pyrrole rings are turned out of the least-squares plane defined by the porphyrin core.[6] The D-value reduction is attributed tentatively to a change in the degree of nonplanarity induced by dimerization. In Zn porphyrins the metal ion imparts a greater rigidity to the porphyrin core. For this reason dimerization is less likely to affect the structure.

The effect of TTAP/TPPS formation on triplet lifetime (cf. Table I) may be reconciled with the above interpretations by considering the great sensitivity of radiationless transitions to small changes in structure of the porphyrin core.[9]

The triplet energies of TTAP and TPPS (ZnTTAP and ZnTPPS) may differ enough to account for localized excitation in the dimers. In [TCP]$_2$ and [TPPS]$_2$ the energy levels of dimer constituents are degenerate, consequently one expects the triplet excitation to be shared. The finding that this is apparently not the case is puzzling and deserves further study.

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Models for the Triply Bridging Site in Chemisorption: The First Complex Containing the Pt3(μ3-H) Group and Evidence for Inversion of the Pt3(μ3-H) Unit and for Reversible Coordination of CO

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Dissociative chemisorption of hydrogen on a Pt(111) surface leads to PtH, Pt$_2$(μ-H), and Pt$_3$(μ_3-H) linkages,[1–4] but the Pt$_3$-(μ_3-H) group has not been reported in platinum–hydride clusters which may be used as models for chemisorption.[5–7] Following observations that the cation [Pd$_3$(μ_3-CO)(μ-dppm)$_3$]$^{2+}$, dppm = Ph$_2$PCH$_2$PPh$_2$, could bind halide ions at the triply bridging site

Scheme I
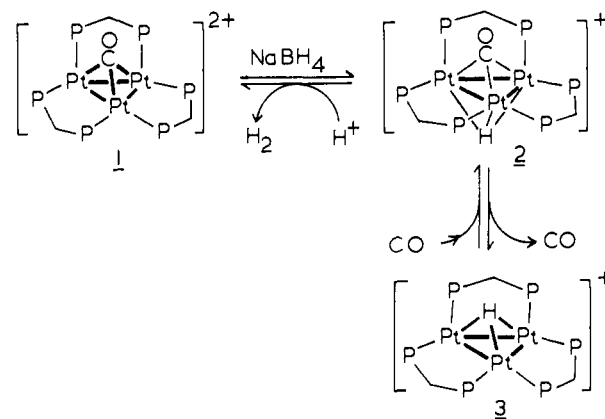
below the Pd$_3$ triangle[8] and that the platinum analogue [Pt$_3$-(μ_3-CO)(μ-dppm)$_3$]$^{2+}$ (1) could be prepared,[9] attempts were made to synthesize a complex containing the desired Pt$_3$(μ_3-H) grouping.[10]

Reaction of 1 as the trifluoroacetate salt with NaBH$_4$ in methanol gave first [Pt$_3$(μ_3-H)(μ_3-CO)(μ-dppm)$_3$]$^+$ (2) and then [Pt$_3$(μ_3-H)(μ-dppm)$_3$]$^+$ (3) as monitored by ^{31}P NMR spectroscopy[11] and 3 as the trifluoroacetate salt could be isolated after 24 h reaction times (Scheme I). The hydride signal in the ^{1}H NMR spectrum of 3 was observed at δ 4.16[12] as a septet due to coupling to six equivalent phosphorus atoms, ^2J(PH) = 23 Hz, and with satellites due to coupling to ^{195}Pt [^1J(PtH) = 710 Hz] having the intensities expected for a Pt$_3$(μ_3-H) group.[12] The presence of a single hydride was confirmed by recording the ^{195}Pt and ^{195}Pt{^{1}H} NMR spectra of 3. An extra doublet splitting due to ^1J(PtH) ~ 710 Hz in the ^{1}H coupled spectrum was observed.[13]

The resonance due to the CH$_2$P$_2$ protons in the ^{1}H NMR spectrum of 3 at –60 °C appeared as an "AB" quartet [δ(CH^{a}H^b) 5.61, 5.02, ^2J(H^{a}H^b) = 14 Hz], as expected for a nonplanar Pt$_3$(μ_3-H) complex.[9,15] However, at room temperature a single resonance was observed, indicating a fluxional process in which an effective plane of symmetry containing the Pt$_3$P$_6$C$_3$ unit is introduced. Since the ^{31}P NMR and the Pt–H resonance in the

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(10) Attempts to prepare Pd$_3$(μ_3-H) groups by reaction of [Pd$_3$(μ_3-CO)(μ-dppm)$_3$]$^{2+}$ with NaBH$_4$ were unsuccessful.

(11) ^{31}P NMR data for 1, –15.1 [s, ^1J(PtP) = 3720, ^3J(PP) = 170 Hz, PtP]; 2, –17.3 [s, ^1J(PtP) = 3019, ^2J(PtP) = 200, ^3J(PP) = 200 Hz, PtP]; 3, –11.1 [s, ^1J(PtP) = 3250, ^2J(PtP) = 235, ^3J(PP) = 175 Hz, PtP].

(12) The natural abundance of ^{195}Pt(I = $^1/_2$) = 33.8%. Therefore, the abundances of isotopomers with 0, 1, 2, or 3 ^{195}Pt atoms is 29.0%, 44.4%, 22.7%, and 3.9% respectively. Superposition of spectra due to these species should give a 1:15:61:104:61:15:1 septet with lines separated by 0.5J(PtH). The outer lines were not observed, but the intensities of the inner lines were as expected. We cannot explain the unusual shift of the Pt$_3$(μ_3-H) proton but note that clusters with encapsulated hydride ligands may give low-field shifts, though other M$_3$(μ_3-H) groups give high-field shifts, and that there is a binuclear platinum hydride with δ 3. Forrow, N. J.; Knox, S. A. R.; Morris, M. J.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1983,** 234. Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983,** *12,* 415. Ciriano, M.; Green, M.; Howard, J. A. K.; Murray, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *Adv. Chem. Ser.* **1978,** *167,* 111.

(13) ^{195}Pt NMR data for 1, –2685 [m, ^1J(PtP) = 3740, ^1J(PtPt) ≃ 380 Hz, Pt]; 2, –2440 [m, ^1J(PtP) = 3018, ^2J(PtP) = 200, ^1J(PtPt) = 1800, ^1J(PtH) = 598 Hz, Pt]; 3, –2520 [m, ^1J(PtP) = 3250, ^2J(PtP) = 240, ^1J(PtH) ~ 2700, ^1J(PtH) = 710 Hz, Pt].