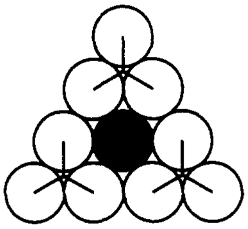

Figure 4. Structure of the complex $UO_2(CO_3)_3^{4-}$: filled circle, UO_2 moiety; open circles, carbonate oxygens.

In order to evaluate the rate law for the exchange reaction, the dependence of the line width of the coordinated carbonate signal on the pH was measured (Figure 2). The experimental findings show clearly that for pH > 8.7 line widths are independent of the pH. The line widths of the coordinated carbonate signal are also independent of the free-ligand concentration at constant $[UO_2(CO_3)_3^{4-}]$ and of the total uranyl concentration at constant $c_{CO_3}^{free}$. Therefore, the rate equation is

$$\text{rate} = -d[UO_2(CO_3)_3^{4-}]/dt = k_1[UO_2(CO_3)_3^{4-}] \quad (2)$$

with k_1 = 13 (±3) s^{-1}, calculated from the line width of $UO_2(CO_3)_3^{4-}$ signal. ($\Delta\nu_c^0$, the nonexchange line width of the $UO_2(CO_3)_3^{4-}$ signal, was measured to be 1.0 (±0.3) Hz at −1 °C and assumed not to be much different at 25 °C. This assumption was based on the fact that the nonexchange line width of the free-carbonate signal, $\Delta\nu_{free}^0$, which could be measured directly in solutions not containing uranium, was not significantly changed within this temperature range.) Thus, the mechanistic consideration is quite straightforward: the mechanism is dissociative according to the following reaction

$$UO_2(CO_3)_3^{4-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} UO_2(CO_3)_2^{2-} + CO_3^{2-} \quad (3)$$

The Arrhenius plot (Figure 3) gives $\Delta H^\ddagger$ = 82 (±11) kJ mol^{-1} and $\Delta S^\ddagger$ = 50 (±30) J mol^{-1} K^{-1}. The positive value of the activation entropy is in agreement with our proposal that the dissociation of the carbonate ligand from the $UO_2(CO_3)_3^{4-}$ complex is the rate-determining step (eq 3). This proposal seems reasonable, since the complex is coordinatively saturated (three carbonate ligands are bidentately bound to the UO_2^{2+} ion in the equatorial plane with uranyl oxygens perpendicular to the plane[17]) (cf. Figure 4). There is no water in the inner coordination sphere of $UO_2(CO_3)_3^{4-}$ in the solid state.[17] Neither does there seem to be any water coordinated to uranyl in the structurally related complex $(UO_2)_3(CO_3)_6^{6-}$ in aqueous solution.[6] Hence, it seems less probable that the complex $UO_2(CO_3)_3^{4-}$ is aquated in solution. Thus, a second-order reaction is less probable. Obviously, water molecules can take part in the exchange reaction (3). However, water exchange for $UO_2(H_2O)_5^{2+}$ is relatively fast, $k = 7.6 \times 10^5$ s^{-1}.[18] In addition, coordination of negative ions to the metal ion weakens and labilizes the metal–water bond(s).[18,19] Concluding, even if coordination of water to a uranyl complex, $UO_2(CO_3)_3^{4-}$ or $UO_2(CO_3)_2^{2-}$, occurs, an association or a dissociation of water will not be the rate-determining step for reaction 3.

Tomiyasu and Fukutomi[20] reviewed some ligand-exchange reactions involving uranium. For these reactions, mostly D or I_d mechanisms were proposed for monodentate ligands, but no conclusion was reached for more complicated systems of bidentate or mixed-ligand complexes.

(In order to further confirm the dissociative character of the ligand-exchange reaction, one could follow a ligand substitution reaction:

$$UO_2(CO_3)_3^{4-} + L^{n-} \rightleftharpoons \{UO_2(CO_3)_2L\}^{(n+2)-} + CO_3^{2-}$$

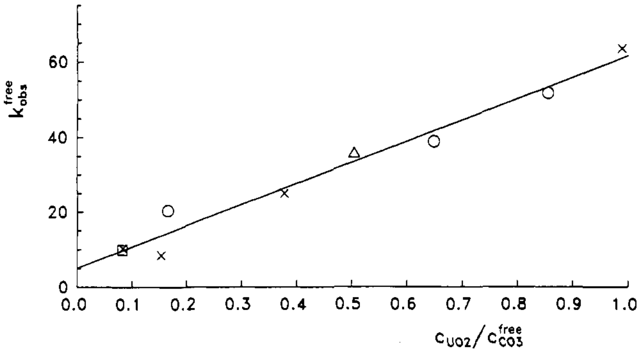

Figure 5. k_{obs}^{free} versus $c_{UO_2}/c_{CO_3}^{free}$. pH = 9.0 ± 0.1; c_{UO_2} = 0.0045 (□), 0.010 (○), 0.020 (×) and 0.027 M (△) (±0.001 M).

in which the rate-determining step could be the dissociation of the carbonate ion. Unfortunately, according to our knowledge there is no mono- or bidentate ligand L for which the forward reaction mentioned above is thermodynamically favorable.)

Since the rates of the formation and of the dissociation of $UO_2(CO_3)_3^{4-}$ have to be equal, one can calculate the value of k_{-1} for the back-reaction (cf. eq 3) using the stability constant $K_3 = [UO_2(CO_3)_3^{4-}]/\{[UO_2(CO_3)_2^{2-}][CO_3^{2-}]\} = 2.24 \times 10^6$ M^{-1}.[5] Thus, $k_{-1} = k_1K_3 = 2.9 \times 10^7$ M^{-1} s^{-1}.

From the line width of the free-carbonate signal a value of k'_{-1} ($k_{-1} = k'_{-1}/3$; cf. eq 3) can also be calculated:

$$\text{rate} = -dc_{CO_3}^{free}/dt = k_{CO_3}^{free} = k'_{-1}[UO_2(CO_3)_2^{2-}][CO_3^{2-}] \quad (4)$$

where $c_{CO_3}^{free} = c_{CO_3} - 3c_{UO_2}$. Substituting $[UO_2(CO_3)_2^{2-}] = [UO_2(CO_3)_3^{4-}]/\{K_3[CO_3^{2-}]\}$ and $c_{UO_2} = [UO_2(CO_3)_3^{4-}]$ into eq 4 and rearranging give

$$k_{obs}^{free} = (k'_{-1}/K_3)(c_{UO_2}/c_{CO_3}^{free}) \quad (5)$$

Figure 5 shows that the plot of k_{obs}^{free} versus ($c_{UO_2}/c_{CO_3}^{free}$) gives a straight line with a slope of k'_{-1}/K_3 = 57 (±4) s^{-1}. Thus, this slope yields $k'_{-1} = 1.3 \times 10^8$ M^{-1} s^{-1}. In order to compare this value to the value calculated above from the coordinated carbonate signal, one has to divide k'_{-1} by the stoichiometric factor equal to 3. The result is 4.3×10^7 M^{-1} s^{-1}, which is in reasonable agreement with the value of 2.9×10^{-7} M^{-1} s^{-1} calculated from $k_{-1} = k_1K_3$ (see above). This means that the simple two-site-exchange model is applicable to this system. The intercept of Figure 5 is $\pi(\Delta\nu_f^0)$ = 5 (±2) Hz. Hence, the nonexchange line width of the free-carbonate signal, $\Delta\nu_f^0$, is equal to 1.6 (±0.6) Hz, which is not significantly different from the measured value, $\Delta\nu_{free}^0$ = 0.5 (±0.2) Hz. The latter was obtained for solution not containing uranyl at 25 °C and was independent of pH in the range 7.5 < pH < 11.5.

At pH values lower than 8.6 the exchange rate is considerably higher and a different exchange mechanism seems to dominate.[7]

Acknowledgment. Useful discussions with Dr. I. Banyai are gratefully acknowledged. The financial support was provided by the Swedish Natural Science Research Council (NFR).

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A Planar Binuclear Tetrabenzoporphyrin and Its Dicopper Derivative

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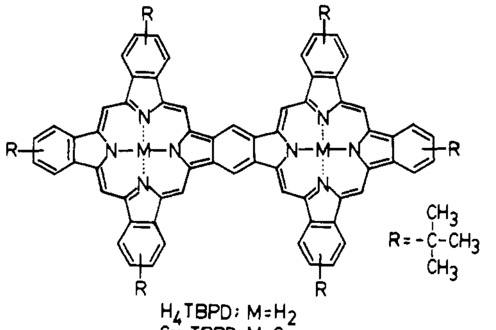
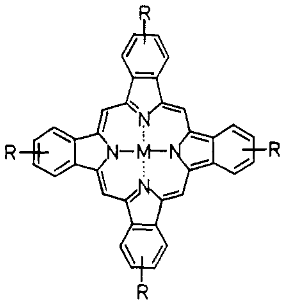
Received November 16, 1990

Several porphyrin dimers with relatively rigid structures have received increasing attention mainly to elucidate intramolecular interactions. Two porphyrins have been connected, for example, through two positions of either benzene,[1] naphthalene,[2a] anthracene,[2b] biphenylene,[2c] spirobiindan,[2d] or phenanthroline.[2e] Except for a few examples, however, the porphyrin units in these molecules have freedom to rotate about each other, since they are linked to the above aromatics by single bonds. The porphyrins we report here are planar binuclear tetrabenzoporphyrins (BPs) in which two BP rings share a common benzene ring. They have, accordingly, a very rigid structure with an intramolecular center-to-center distance of 10.8 Å (CPK molecular model). The synthesis of a planar binuclear porphyrin sharing a pyrazine ring was once reported briefly,[3] but very little is known about the spectroscopic properties of such rigid planar binuclear compounds. In this paper, we describe the synthesis and spectroscopic and electrochemical properties of *tert*-butylated planar binuclear BP (H_4TBPD) and its dicopper derivative (Cu_2TBPD) in comparison with those of the corresponding mononuclear control molecules (H_2TBP and CuTBP).[4] Also, since similar planar binuclear phthalocyanine (Pc) analogues have been known,[5] we compare the results with those of these Pc derivatives.



H_4TBPD; M=H_2
Cu_2TBPD; M=Cu



H_2TBP; M=H_2
CuTBP; M=Cu

Experimental Section

Measurements. Electronic spectra were recorded with a Shimadzu UV-250 spectrophotometer, and magnetic circular dichroism (MCD) measurements were made with a JASCO J-400X spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields up to 1.17 T (T = tesla) with parallel and then antiparallel fields. Its magnitude was expressed in terms of molar ellipticity per tesla, $[\Theta]_M/10^4$ deg mol^{-1} dm^3 cm^{-1} T^{-1}. Fluorescence and excitation spectra were recorded with Shimadzu RF-500 spectrofluorimeters with appropriate filters to eliminate scattered light. Fluorescence quantum yields were determined by the use of quinine bisulfate in 1 N H_2SO_4 ($\Phi_F = 0.55$ at 296 K)[6] and free-base tetraphenylporphyrin in air-saturated benzene ($\Phi_F = 0.11$).[7] Data were obtained by a comparative calibration method with use of the same excitation wavelength and absorbance for H_4TBPD and H_2TBP and the calibrants and the same emission energies. Fluorescence decay curves were obtained at 20 °C by a Horiba NAES-550 series, using combinations of glass filters and solution filters (saturated $CuSO_4{\cdot}5H_2O$ aqueous solution and K_2CrO_4 0.27 g/1000 mL of H_2O) and a monochromator for monitoring the emission. The lifetimes were determined from the decay curves by use of the least-squares method. All sample solutions for fluorescence measurements were purged with argon before measurement.

Cyclic potential sweeps were generatred by an NF circuit design block FG-100AD function generator in conjunction with a potentiostat that was built according to the literature.[8] Differential pulse voltammetry was conducted on a Yanaco Model P-1000 electric analyzer.

Syntheses. H_4TBPD and H_2TBP. Well-dried pyromellitic dipotassium diimide,[9] potassium *tert*-butyl phthalimide, sodium acetate, and zinc acetate (molar ratio 1:20:50:2) were mixed well and heated at 320–360 °C under a nitrogen atmosphere for ca. 1.5 h.[10] After cooling, the residue was washed well with hot water and then refluxed in an acetic acid–concentrated hydrochloric acid mixture (5:1 to 3:1 v/v) for several hours (generally more than 2 h). After removal of the solvent, the residue was dried and placed on a silica gel column with toluene, methylene chloride (CH_2Cl_2), or tetrahydrofuran (THF) as eluent. The green fraction was collected, and the combined H_2TBP and H_4TBPD complexes were separated by gel permeation chromatography using a Bio-Beads SX-2 column and THF or CH_2Cl_2. The yields of H_4TBPD were ca. 6–8% depending on the trial. Anal. Calcd for $C_{90}H_{86}N_8$: C, 84.47; H, 6.77; N, 8.76. Found: C, 83.60; H, 6.98; N, 8.25. Mass spectrum (FAB): *m/z* 1279 (M^+, 100%), 1223 ($M^+ - C_4H_9$, 73). IR (KBr, cm^{-1}): 2950, 2870, 1720, 1705, 1610, 1602, 1465, 1360, 1252, 1095, 1015, 810, 738. ^{1}H NMR ($CDCl_3$): δ −3.17 (br s, 4 H), 1.88–1.92 (m, 54 H), 8.35 (m, 6 H), 9.42–9.54 (m, 14 H), 10.58 (br s, 4 H). The yields of H_2TBP were ca. 17–19% depending on the trial. Anal. Calcd for $C_{52}H_{54}N_4$: C, 84.97; H, 7.41; N, 7.62. Found: C, 84.39; H, 7.74; N, 7.46.

Cu_2TBPD and CuTBP. These were obtained by reacting H_4TBPD or H_2TBP with excess copper acetate in refluxing *N,N*-dimethylformamide (DMF).[11] After removal of DMF, these compounds were purified by using a basic alumina column and CH_2Cl_2 as eluent. Anal. Calcd for Cu_2TBPD, $C_{90}H_{82}N_8Cu_2$: C, 77.06; H, 5.89; N, 7.99. Found: C, 76.43; H, 6.21; N, 8.24. Mass spectrum (FAB): *m/z* 1401 (M^+, 100%). IR (KBr, cm^{-1}): 2950, 2860, 1610, 1465, 1362, 1260, 1195, 1100, 818, 694. The analysis was similar for CuTBP. Anal. Calcd for $C_{52}H_{52}N_4Cu$: C, 78.41: H, 6.58; N, 7.03. Found: C, 78.07; H, 6.80; N, 6.76.

Results and Discussion

Figures 1 shows UV–visible–near-IR absorption and MCD spectra for the compounds synthesized in this study. The absorption spectra of H_2TBP and CuTBP retain the characteristics of nonmetalated and metalated BP spectra:[12] i.e., H_2TBP has two intense Soret peaks and three small peaks in one of the Q bands, while the relative intensity of the Q band to the Soret band in CuTBP (ca. 0.5) is much larger than that in common porphyrins (ca. 0.05–0.1). Compared with these spectra, those of H_4TBPD and Cu_2TBPD are broader, have less structure, and are shifted to longer wavelength. A notable characteristic common to those planar binuclear dimers is the appearance of a new band in the region above >700 nm.[13] The red shift broadening of the spectra

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(4) Although not explicitly shown in the displayed structures, because of the position of the *tert*-butyl groups, CuTBP and Cu_2TBPD are present as mixtures of 4- and 20-positional isomers, respectively, while H_2TBP and H_4TBPD are mixtures of 5- and 72-positional isomers, respectively, due to the *tert*-butyl groups and pyrrole protons, assuming that two pyrrole protons bind to two pyrrole nitrogens at "opposite" sides.

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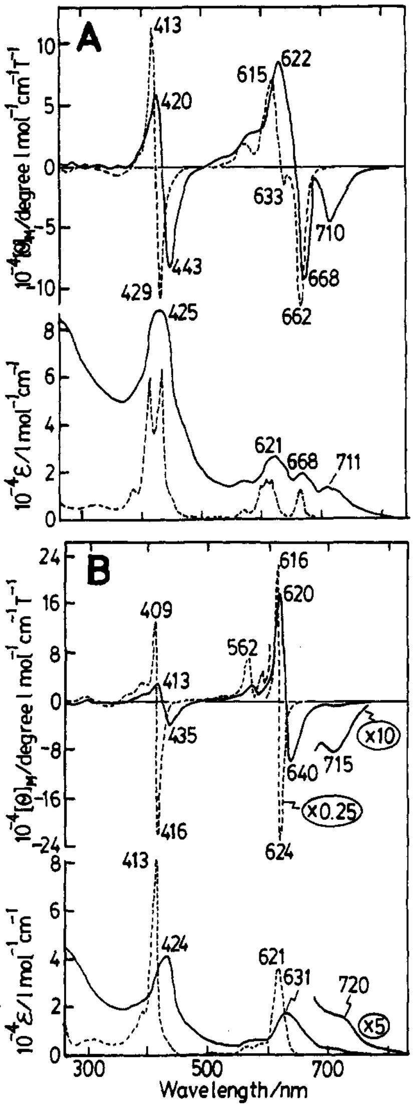

Figure 1. Absorption (bottom) and MCD spectra (top) of (A) H_2TBP (broken lines) and H_4TBPD (solid lines) and (B) CuTBP (broken lines) and Cu_2TBPD (solid lines) in chloroform. Pathlength/mm = 10; magnetic field/T = 1.09.

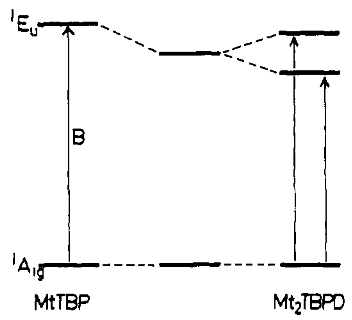

Figure 2. Qualitative orbital energy diagram for the B (Soret) band of the MtTBP and Mt_2TBPD system: column 1, a D_{4h} mononuclear MtTBP species; column 2, lowering of energy by enlargement of π-conjugated system; column 3, a D_{2h} binuclear Mt_2TBPD species. For details, see text.

can be explained by enlargement of the π-conjugated system plus the splitting due to intramolecular exciton coupling between two TBP units in the dimers and/or the effect of lowering of symmetry from approximate D_{4h} (of TBPs) to approximate D_{2h} (of TBPDs), as shown in Figure 2 for the B (Soret) band of metallo complexes. The Soret bands of H_2TBPD are obviously broader than that of Cu_2TBPD, since that of H_2TBP consists of the split x and y components.[14] If the broad dimer Soret bands are interpreted as caused by the intramolecular exciton coupling, this splitting seems very roughly ca. 10–13 nm in both H_4TBPD and Cu_2TBPD. A similar value, typically 14 nm, has been reported for an edge-on porphyrin dimer connected directly by a single C–C bond (center-to-center distance ca. 10 Å).[15] Compared with the spectra of the corresponding planar binuclear Pc analogues,[5] Q bands are weaker and lie at shorter wavelengths. Such Pc analogues also have a weaker band at a wavelength longer than that of the Q band (around 840–860 nm).[5] Thus, both these planar binuclear Pcs and TBPs may have similar conformations in solution, plausibly a slightly bent conformation about the common benzene ring, judging from the appearance of the near-IR band.[16] If H_4TBPD and Cu_2TBPD are perfectly flat, such near-IR bands do not appear theoretically.[16] It may be interesting to compare the absorption spectroscopic change on passing from CuTBP to Cu_2TBPD with that observed on cofacial dimer formation. In good contrast to the case of planar dimers, cofacial dimer bands generally appear at shorter wavelengths than monomer bands. If a cofacial dimer exhibits another weak band at a wavelength longer than that of a monomer band, this is generally an indication of departure from eclipsed conformation, although even perfectly eclipsed cofacial dimers sometimes show this band as a forbidden transition.[17]

MCD spectra of nonmetalated compounds are composed of Faraday *B* terms, since there is no degenerate excited state.[18] Thus, MCD peaks and troughs appeared corresponding roughly to the absorption maxima. In contrast, CuTBP, which has approximate D_{4h} symmetry, showed dispersion type MCD (Faraday *A* terms) corresponding to the main Soret and Q bands. The MCD spectrum of Cu_2TBPD should be, at least theoretically, composed of Faraday *B* terms, although Faraday *A* term like dispersion curves are seen corresponding to the main Q and Soret bands. However, as shown, the intensity of these two Faraday *A* term like curves is much smaller than that for CuTBP. This phenomenon may be interpreted as a superimposition of two closely located Faraday *A* terms produced plausibly by the exciton coupling due to the two CuTBP units in Cu_2TBPD. Broad bandwidth and small MCD intensity at both the Soret and Q bands can be produced by a cancellation of positive and negative signs of two closely lying dispersion curves (i.e. Faraday *A* terms). The apparent A/D (an MCD parameter) values at the Soret bands, estimated by the methods of Briat et al.,[19] were 3.00 and 2.96 for CuTBP and Cu_2TBPD, respectively. In the case of eclipsed cofacial dimers of MtPcs, Faraday *A* terms appeared associated with the main Q absorption bands, which lie at shorter wavelength than monomer Q bands. A/D values in eclipsed cofacial dimers do not differ greatly from those of monomers, as shown recently for crown ether substituted Pcs.[17]

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(13) The oscillator strength, f (absorption intensity, the area of absorption spectra), of H_4TBPD appears to be much larger than that of H_2TBP. Such a large f of the nonmetalated planar binuclear dimer compared to the nonmetalated monomer was also found in related Pc systems (Lever, A. B. P.; et al. Unpublished data), but the reason for this is presently unknown. Also, a reviewer asked why the Soret absorption of H_4TBPD is much larger than that of Cu_2TBPD. We do not know why, but such a phenomenon, i.e. that the Soret band of nonmetalated dimer species is much more intense than that of the corresponding copper species, was observed recently in imperfectly coplanar dimeric Pc systems, too (Kobayashi, N.; Opallo, M.; Osa, T. *Heterocycles* **1990**, *30*, 389). In addition to the above phenomenon regarding f, other phenomena in planar binuclear species seem difficult to explain on the basis of data for monomeric species.

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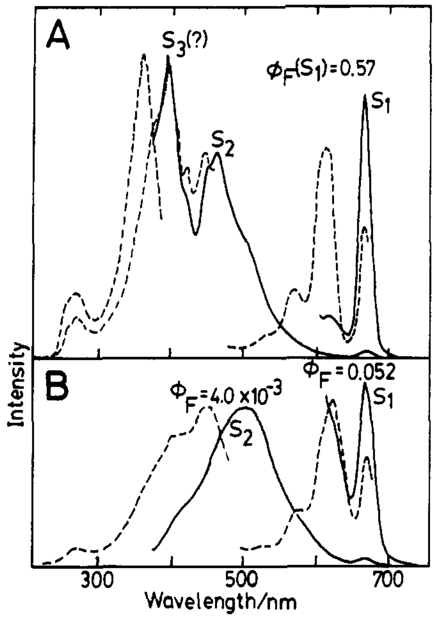

Figure 3. Emission (solid lines) and excitation spectra (broken lines) of (A) H_2TBP and (B) H_4TBPD in deaerated chloroform. Excitation was at 360 and 570 nm.

Figure 3 shows the emission and excitation spectra of H_2TBP and H_4TBPD. Both compounds show so-called S_1 and S_2 emissions, as has been detected in mononuclear ZnBP,[12b,c] and the quantum yield (Φ_F) of S_1 emission of H_4TBPD (0.052) is about 1 order smaller than that of H_2TBP (0.57). Such a weak emission in the dimer is an indication of intramolecular interaction of the two included units.[15a,20] In addition, the lifetime (τ) of the S_1 emission of the dimer in deaerated chloroform (9.80 ns) is shorter than that of the monomer (11.3 ns), as has been observed in porphyrin systems.[15a,20] Two S_2 emission τ values were obtained for both H_2TBP (τ_1 = 2.68 ns, 81.1%; τ_2 = 14.7 ns, 18.9%) and H_4TBPD (τ_1 = 3.17 ns, 71.6%; τ_2 = 11.6 ns, 28.4%). In addition, H_2TBP showed another emission at higher energy (S_3 emission?[12b]) (τ_1 = 1.87 ns, 94.7%; τ_2 = 7.14 ns, 5.3%). Since these fluorescence experiments were carried out at concentrations as low as 10^{-7} M, where aggregation phenomena may be neglected and all the excitation spectra were mirror images of the respective emission band, the presence of two components in the S_2 emission of H_2TBP and H_4TBPD suggests that the Soret region spectra of these porphyrins are not composed of a single pure transition.[21]

Binuclear Cu_2TBPD shows voltammetry similar to that of mononuclear CuTBP, although the waves are generally broader and weaker. However, well-defined peaks were obtained by differential pulse voltammetry (Figure 4). Cu_2TBPD exhibited broad peaks, roughly corresponding in potential to two one-electron oxidations and one one-electron reduction of the porphyrin ring of CuTBP. Since the shapes of the response are not much different between the two compounds, the broadening of the peaks suggests that the oxidation and reduction in Cu_2TBPD occur stepwise at closely located potentials and accordingly that the two CuTBP units in Cu_2TBPD are interacting. If we deconvolute the first reduction wave of Cu_2TBPD into two components using the bandwidth of the first reduction wave of CuTBP, their splitting energy is approximately 110–120 mV. The potential difference between the first oxidation and reduction in Cu_2TBPD (1.63 V) is slightly smaller than that in CuTBP (1.75 V), consistent with the longer wavelength shift of the absorption and MCD spectra. The difference of their potential differences (0.12 V = ca. 970 cm^{-1}) is very close to that calculated for edge-on porphyrin dimers (ca. 1000 cm^{-1}),[15a] however somewhat larger than the values expected from the Soret band absorption (Figure 1B, ca. 630 cm^{-1}) and MCD spectra (ca. 660 cm^{-1}). Electrochemical data are often slightly at variance with the spectroscopic data.[22]

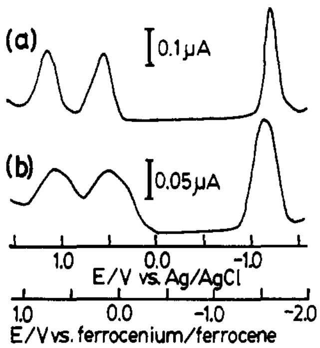

Figure 4. Differential pulse voltammograms of (a) CuTBP and (b) Cu_2TBPD in *o*-dichlorobenzene containing 0.3 M tetrabutylammonium perchlorate. Scan rate/(mV/s) = 5; [CuTBP] = [Cu_2TBPD]/mM = ca. 0.1; area of electrode/cm^2 = 0.07.

Thus, the above data consistently suggest that the two units rigidly constrained in a coplanar arrangement in H_4TBPD and Cu_2TBPD each retain independency and are interacting intramolecularly, as reported for several covalently linked relatively flexible binuclear porphyrin systems.[1,2,15,20] π-Conjugation of the two TBP units through the common benzene appears rather small.

Acknowledgment. We are indebted to the Uehara Memorial Foundation for the publishing costs of this paper.

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A Convenient Synthesis of the Manganese and Rhenium Alkoxides and Phenoxides *fac*-$(CO)_3$(dppe)MOR (R = CH_3, C_2H_5, C_6H_5; dppe = 1,2-Bis(diphenylphosphino)ethane). X-ray Structure of *fac*-$(CO)_3$(dppe)$ReOC_6H_5$

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Received November 13, 1990

Low-valent transition-metal alkoxides are reported to be likely intermediates in the carbalkoxylation of olefins[1] and in the catalytic hydrogenation of aldehydes and ketones,[2] and they continue to be the focus of much interest. However, relatively few of them have been fully characterized because not only are they frequently moisture and air sensitive but they are very labile as well, undergoing rapid spontaneous β-hydrogen elimination.[3] One of our interests in the synthesis and chemistry of transition-metal alkoxides stems from their presumed intermediacy in the conversion of acylmanganese complexes to the corresponding alkoxy carbonyl complexes when treated with synthesis gas (a formal insertion of formaldehyde).[4]

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