Free Radical Reactions with Dimeric Cobalt(II) Sulphophthalocyanine. A Pulse Radiolytic Study

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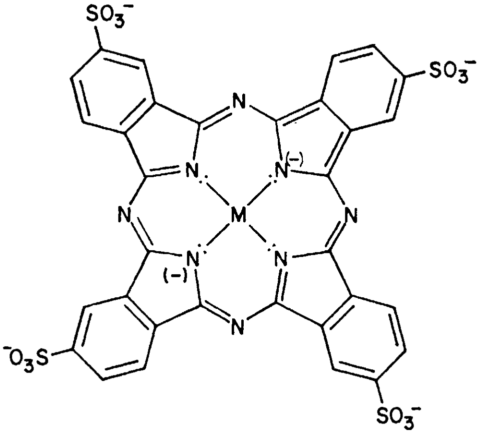
Reactions of cobalt(II) sulphophthalocyanine dimers with the free radicals e⁻(aq), $\dot{O}H$, $\dot{C}H_2OH$, $Me_2C(OH)\dot{C}H_2$, and $Me_2\dot{C}OH$ have been investigated by optical pulse-radiolysis methods. Rate constants have been determined to be *ca.* 3×10^9 dm^3 mol^{-1} s^{-1} for $\dot{O}H$ and e⁻(aq), but an order of magnitude less for the alcohol radicals. Similarity has been observed in the spectra produced by $\dot{O}H$ and $Me_2C(OH)\dot{C}H_2$ although the kinetics are markedly different. It is proposed that, following ligand-radical formation by $\dot{O}H$, oxidation of the metal centre and subsequent dimer splitting occurs. In the case of $Me_2C(OH)\dot{C}H_2$ the formation of a metal–alkyl bond appears likely, followed by splitting of the dimeric intermediate. The transient spectra produced by e⁻(aq), $\dot{C}H_2OH$, and $Me_2\dot{C}OH$ are also very similar to one another. In these cases spectral behaviour suggests reduction of the metal centre by a ligand radical, followed by dimer dissociation ($t_{\frac{1}{2}}$ *ca.* 2 ms).

THE chemical properties of phthalocyanine complexes with transition-metal ions have been extensively investigated.[1] Studies of the redox properties of the sulphophthalocyanines have demonstrated that one-electron redox processes can change the oxidation state of either the metal centre in the compounds of Co^{II} and Fe^{II}, or of the ligand in compounds of Cu^{II}, Ni^{II}, and Zn^{II}.[2-5] Moreover, the photoredox behaviour of the dimeric complex has been found to exhibit some of the features of the electrochemistry of the monomeric species.[2] Photodissociation produces either ligand-radical species [equation (1), M = Co^{III} or Cu^{II}] or sulphophthalocyanines with oxidized and reduced metal centres [equation (2), M = Co^{II} or Fe^{II}],[6] where (pts) is the sulphophthalocyanine ligand.† Secondary reactions of the metastable products of the photodissociation, equations (3) and (4), return the system to its original condition.



M = Cu^{II}, Co^{II}, Co^{III}, Fe^{II}, or Ru^{II}

$$[\{M^z(pts)\}_2]^{(8-2z)-} + h\nu \longrightarrow [M^z(pts)]^{(3-z)-} + [M^z(pts)]^{(5-z)-} \quad (1)$$

$$[\{M^z(pts)\}_2]^{(8-2z)-} + h\nu \longrightarrow [M^{z+1}(pts)]^{(3-z)-} + [M^{z-1}(pts)]^{(5-z)-} \quad (2)$$

$$[M^z(pts)]^{(3-z)-} + [M^z(pts)]^{(5-z)-} \longrightarrow [\{M^z(pts)\}_2]^{(8-2z)-} \quad (3)$$

$$[M^{z+1}(pts)]^{(3-z)-} + [M^{z-1}(pts)]^{(5-z)-} \longrightarrow [\{M^z(pts)\}_2]^{(8-2z)-} \quad (4)$$

Previous workers have shown that reactions of oxidizing and reducing radicals with co-ordination complexes can be conveniently investigated by pulse radiolysis.[7-9] In the present work reactions of cobalt(II) sulphophthalocyanine with reducing radicals [e⁻(aq), $\dot{C}H_2OH$, or $Me_2\dot{C}OH$] and oxidizing radicals [$Me_2C(OH)\dot{C}H_2$ and $\dot{O}H$] have been investigated to characterize electron transfer as well as possible metal–carbon bonding within the cobalt(II)–ligand system.

EXPERIMENTAL

Radiolytic Procedures.—Optical pulse-radiolysis measurements were carried out with a computerized system similar to that described earlier.[10] However, some modifications in data treatment have been made to utilize a Hewlett-Packard 9830A calculator offline.[11] The apparatus now makes use of the Notre Dame 10 MeV ‡ linear accelerator which is capable of providing up to 5 ns pulses at a current of 7 A. A 500-mm Bausch and Lomb monochromator was used in these studies. Thiocyanate dosimetry was carried out at each experimental session to calibrate the output signal of a secondary emission monitor (DOSE) against radical concentration produced in the radiolysis cell by the LINAC electron pulse. Absorbance data are given in terms of the absorption coefficient ε from the expression $\varepsilon = AK/G$ (Dose), where A is the absorbance for a particular pulse and K is chosen such that ε for $[(CNS)_2]^-$ in N_2O-saturated solutions is 7 600 dm^3 mol^{-1} cm^{-1} and its G value is taken as 6.0. The G value in the denominator is that for the absorbing species. This means that ε represents absorbance data normalized against the dose delivered to the system for each pulse. A flow system was used to ensure that the solution was always fresh. Where processes in a time interval >200 ms were investigated, the solution was not flowing during the time of measurement but was replenished after each irradiation. All measurements

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† Ligand abbreviations: $[pts]^{6-}$ = phthalocyanine-3,10,17,24-tetrasulphonate hexa-anion; $[p\dot{t}s]^{5-}$ = one-electron oxidized species; $[pts]^{7-}$ — one-electron reduced species.

‡ Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

were carried out in aqueous solutions adjusted to pH = 9, and were deaerated with N_2O or N_2.

Materials and Methods.—Cobalt(II) sulphophthalocyanine sodium salt was obtained and purified using procedures reported by Weber and Busch.[12] Other materials were of reagent grade and were used without further purification. Water for the radiolysis experiments was obtained from a Milli-R015 Millipore filtering system. Neither hydrated-electron nor $\dot{\mathrm{O}}\mathrm{H}$ lifetime measurements gave evidence of impurities which could interfere with the studies carried out here.

Radiolysis of aqueous solution generates several primary species as indicated in reaction (5).[13] The G value is

$$\begin{array}{l} \mathrm{H_2O} \rightsquigarrow \underset{G\,=\,2.65}{\mathrm{e^-(aq)}} + \underset{2.65}{\dot{\mathrm{O}}\mathrm{H}} + \\ \qquad \underset{0.60}{\mathrm{H}} + \underset{[\mathrm{e^-(aq)} + \mathrm{OH^-}]}{\mathrm{H_3O^+}} + \underset{0.75}{\mathrm{H_2O_2}} + \underset{0.45}{\mathrm{H_2}} \end{array} \quad (5)$$

the number of molecules or radicals generated per 100 eV of radiation. Here the first two agents, $e^-(aq)$ and OH, would be expected to exhibit the most pronounced reactivity toward $[\{Co(pts)\}_2]^{8-}$. In N_2O-saturated solution, $e^-(aq)$ may be converted quantitatively into $\dot{\mathrm{O}}\mathrm{H}$ *via* reaction (6) providing essentially a single radical system (the

$$\mathrm{e^-(aq) + N_2O + H_2O} \xrightarrow{k_6=5.6\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}} \mathrm{N_2 + OH^- + \dot{O}H} \quad (6)$$

yield of H is only 10% by comparison). Due to N_2O scavenging effects, the G value of $\dot{\mathrm{O}}\mathrm{H}$ *via* equation (6) will slightly exceed 2.8. From reaction with $\dot{\mathrm{O}}\mathrm{H}$ various alcohol radicals have been produced for this study. Rate constants

$$\mathrm{CH_3OH + {\cdot}OH} \xrightarrow{k_7=1.0\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}} \mathrm{{\cdot}CH_2OH} \quad (7)$$

$$\mathrm{(CH_3)_2CHOH + {\cdot}OH} \xrightarrow{k_8=2.1\times10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}} \mathrm{(CH_3)_2\dot{C}OH} \quad (8)$$

$$\mathrm{(CH_3)_3COH + {\cdot}OH} \xrightarrow{k_9=4.5\times10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}} \mathrm{(CH_3)_2C(OH)\dot{C}H_2} \quad (9)$$

reported for reactions (6)—(9) have been taken from standard sources.[14]

As will be seen below, the rate constants of reactions (7)—(9) indicate that the radicals under study are produced from $\dot{\mathrm{O}}\mathrm{H}$, without interference from direct reaction between $\dot{\mathrm{O}}\mathrm{H}$ and the complex. Alcohol concentrations were maintained at 0.1—0.2 mol dm^{-3} in each case. The spectra were recorded at [Co(pts)] concentrations of 4×10^{-5} mol dm^{-3}, and the rate constants measured by varying the complex concentration up to 3×10^{-4} mol dm^{-3}.

RESULTS

Redox reactions of various radiolytically generated radicals with dimeric cobalt(II) sulphophthalocyanine form stable products which have been identified as sulphophthalocyanine complexes with either oxidized or reduced metal centres. In the case of the $Me_2C(OH)\dot{C}H_2$ radical, carbon–metal bonding may be involved (see below). Generation of these products involves intermediates whose spectra and kinetic behaviour may be used to determine the various mechanisms.

Reaction with $\dot{\mathrm{O}}\mathrm{H}$.—Hydroxyl radical interaction with the sulphophthalocyanine dimer $[\{Co(pts)\}_2]^{8-}$ is accompanied by bleaching of the parent compound. This feature was used to monitor rates of $\dot{\mathrm{O}}\mathrm{H}$ attack by measuring time-resolved loss of absorbance at 580 nm. Good pseudo-first-order behaviour was observed with a rate constant $k = 4.0 \times 10^9$ dm^3 mol^{-1} s^{-1}. This value is in the middle of the range of reported constants for reactions of $\dot{\mathrm{O}}\mathrm{H}$ with inorganic complexes (10^9—10^{10} dm^3 mol^{-1} s^{-1}).

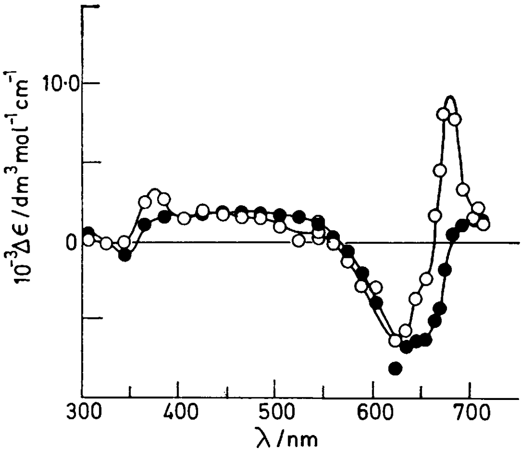

FIGURE 1 Transient spectra following pulse radiolysis of $[\{Co(pts)\}_2]^{8-}$ (2×10^{-5} mol dm^{-3}) in N_2O-saturated solutions: (●), immediately after pulse; (○), 200 ms after the pulse

The transient spectrum, obtained by pulse radiolysis, is given in Figure 1 both immediately following the pulse and again after an interval of 200 ms. Between the intense absorption bands of the parent compound, in the 350—550 nm region, is a broad transient absorption with ε *ca.* 2 000 dm^3 mol^{-1} cm^{-1}. It is apparent that the true maximum for this absorption is slightly obscured by the spectrum of the parent compound. In the region 400—530 nm, very little change is observed in the transient absorption over the period of monitoring. However, it can be seen that in both regions where bleaching takes place a second transient eventually grows in. This growth follows a first-order rate law in the initial step and exhibits a half-life of *ca.* 7 ms both in the u.v. and the red bands. There follows a second complex dose-dependent growth in the same region. The time course of the absorption change is shown in Figure 2(*a*) at 675 nm. The apparent absorption coefficient, Δε, equal to the difference between the absorptions of the parent and transient species, is 1×10^4 dm^3 mol^{-1} cm^{-1}. The absorption coefficient of the $[\{Co(pts)\}_2]^{8-}$ at the same wavelength was found to be 3.9×10^4 dm^3 mol^{-1} cm^{-1}.

Reactions with $Me_2C(OH)\dot{C}H_2$.—Tertiary butanol is most often used as an $\dot{\mathrm{O}}\mathrm{H}$ scavenger in studies of $e^-(aq)$ reaction

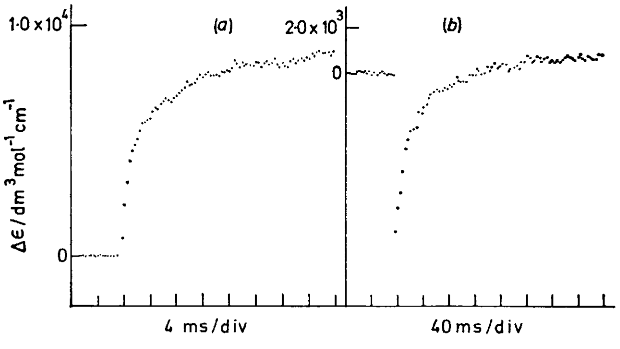

FIGURE 2 Time-resolved transient absorption at 675 nm following pulse radiolysis of $[\{Co(pts)\}_2]^{8-}$ (2×10^{-5} mol dm^{-3}): (*a*) N_2O-saturated solution; (*b*) N_2O-saturated solution containing 0.1 mol dm^{-3} methanol. Initial radical concentrations were 6×10^{-6} mol dm^{-3}

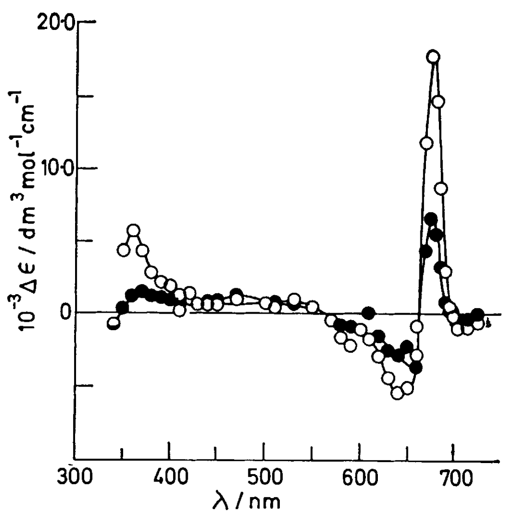

FIGURE 3 Transient spectra resulting from $Me_2C(OH)\dot{C}H_2$ attack on [Co^{II}(pts)]: (●), immediately following radical attack; (○), after an interval of 10 ns

because of the well established inert nature of the $Me_2C(OH)\dot{C}H_2$ radical toward many substrates. In this investigation, however, it was found that $Me_2C(OH)\dot{C}H_2$ exhibits considerable reactivity toward the cobalt(II) complex. To characterize the mechanisms involved, t-butanol was added to N_2O-saturated solution and $Me_2C(OH)\dot{C}H_2$ was generated *via* reactions (6) and (9). The pseudo-first-order rate constant for attack on $[\{Co(pts)\}_2]^{8-}$ was obtained from the transient growth of the absorbance at 440 nm ($k = 2.2 \times 10^8$ dm^3 mol^{-1} s^{-1}). Transient spectra due to reaction with $[\{Co(pts)\}_2]^{8-}$ are given in Figure 3. The growth of a second transient with very distinct bands at 675 and 360 nm may be seen in the spectrum which is obtained 10 ms after the pulse ($\Delta\varepsilon_{675}$ *ca.* 2×10^4 dm^3 mol^{-1} cm^{-1}). The rate of appearance of the second transient is very much faster than that observed following $\dot{O}H$ reaction ($t_{\frac{1}{2}} = 0.3$ ms). Such behaviour suggests that different reaction pathways are initiated by $\dot{O}H$ and by $Me_2C(OH)\dot{C}H_2$ which, in the end, produce species with similar spectral properties.

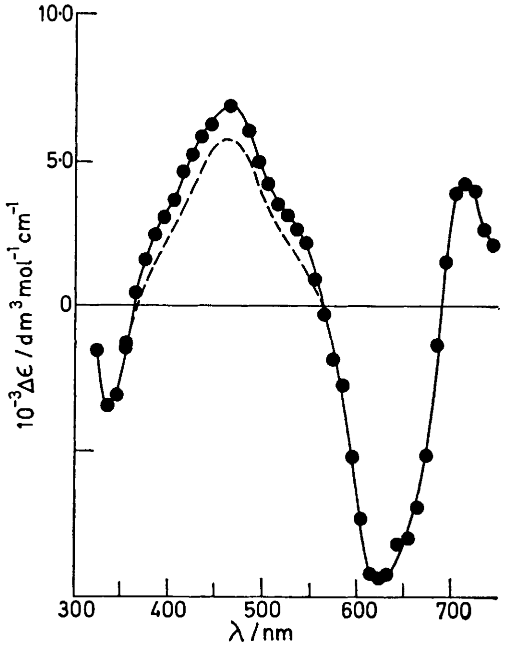

FIGURE 4 Pulse-radiolysis spectrum of N_2-saturated $[\{Co(pts)\}_2]^{8-}$ after reaction by $\dot{O}H$ and e$^-$(aq). The spectrum corrected for contributions from $\dot{O}H$ reaction is indicated by the broken line

Reactions with e$^-$(aq).—Initial reaction of $[\{Co(pts)\}_2]^{8-}$ with e$^-$(aq) results in a reduced species *via* electron attachment. However, it is not possible, under the experimental conditions used here, to measure e$^-$(aq) reactions in isolation from other radicals. In this work we have monitored time-resolved processes in both N_2-saturated solutions, where e$^-$(aq) and $\dot{O}H$ coexist, and in t-butanol-containing solutions where both e$^-$(aq) and $Me_2C(OH)\dot{C}H_2$ are present. As the spectral contributions from both $\dot{O}H$ and $Me_2C(OH)\dot{C}H_2$ have been characterized above, we have introduced corrections for the contributions from either of these radicals. The transient spectrum obtained from pulse radiolysis of N_2-saturated solutions of the complex is presented in Figure 4 and indicates a moderately intense band with a maximum in the 460 nm region. The spectrum corrected for $\dot{O}H$-related contributions between 350 and 550 nm is included. In this case, there also appears to be long-term growth of a second transient, again with pronounced absorption between 650 and 700 nm. The measured $t_{\frac{1}{2}}$ for the overall growth was 2 ms, which may reflect a composite from both $\dot{O}H$ and e$^-$(aq) related transients or indicate some cross reaction between them.

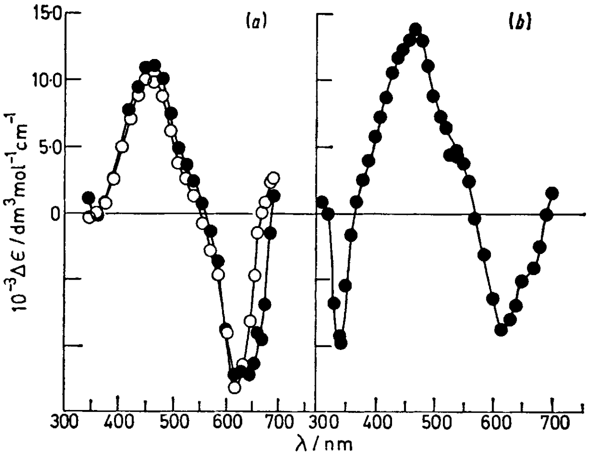

FIGURE 5 Transient spectra following pulse radiolysis of $[\{Co(pts)\}_2]^{8-}$ (2×10^{-5} mol dm^{-3}) in N_2O-saturated systems: (*a*) in methanol-containing solution, (●) following $\dot{C}H_2OH$ attack, (○) after an interval of 300 ms; (*b*) in propan-2-ol-containing solution, (●) following $Me_2\dot{C}OH$ reaction

The rate of the reaction between e$^-$(aq) and $[\{Co(pts)\}_2]^{8-}$ was obtained by measurement in two separate systems. With N_2-saturated solution, rates of bleaching and transient growth closely coincide. However, both e$^-$(aq) and OH can be expected to make similar contributions to bleaching while the absorption at 460 nm is predominately related to e$^-$(aq) reaction. Hence determination of the pseudo-first-order rate constant was made at that wavelength and found to be 3.3×10^9 dm^3 mol^{-1} s^{-1}. Conversely, in t-butanol-containing solutions, the rate of disappearance of e$^-$(aq) absorbance at 570 nm, where both bleaching and transient absorption compensate, was monitored as a function of cobalt(II) complex concentration. A rate constant of 3.0×10^9 dm^3 mol^{-1} s^{-1} was obtained for e^-(aq) attachment in good agreement with the above value.

Reactions with $Me_2\dot{C}OH$ *and* $\dot{C}H_2OH$.—Both $Me_2\dot{C}OH$ and $\dot{C}H_2OH$ may be readily obtained in N_2O-saturated solutions *via* reactions (6)—(8). Each of these radicals reacts readily to give a transient spectrum similar in absorption coefficient and shape to that observed following e^-(aq) reduction. These spectra are shown in Figure 5. Rates of $\dot{C}H_2OH$ and $Me_2\dot{C}OH$ attack on $[\{Co(pts)\}_2]^{8-}$ were determined by monitoring bleaching of the parent compound following the pulse. Rate constants of $k = 2.2 \times 10^8$ for $\dot{C}H_2OH$ and $k = 1.5 \times 10^9$ dm^3 mol^{-1} s^{-1} for $Me_2\dot{C}OH$ were obtained from these measurements. The appearance of the second transient in the 650—700 nm region [see Figure 2(*b*)] was characterized by a complex growth pattern which appears to involve two overlapping processes: one fast first-order step ($t_{\frac{1}{2}}$ *ca.* 20 ms) and one shown to be dose-dependent, by measurements in which electron-beam intensity was varied.

DISCUSSION

A comparison of transient spectra produced by reaction between dimeric cobalt(II) sulphophthalocyanine and the reducing radicals, e^-(aq), $\dot{C}H_2OH$, and $Me_2\dot{C}OH$ indicates that the same intermediate is produced in each case although at different rates. These spectra bear a strong resemblance to the spectrum recorded earlier for a cobalt(II)-ligand radical, $[Co^{II}(p\dot{t}s)]^{5-}$.[2,6] Equations (10)—(12) give probable mechanisms for formation of the primary dimeric radical $[Co_2(pts)(p\dot{t}s)]^{9-}$ by reactions of the parent complex with e^-(aq), $Me_2\dot{C}OH$, or $\dot{C}H_2OH$. Transformation of the cobalt(II) ligand radical, $[Co_2(p\dot{t}s)(pts)]^{9-}$, yields a stable product with visible and near-i.r. spectral features comparable to those reported for monomeric cobalt(I) sulphophthalocyanine.[4,6] This transformation, observed as a modification of the transient spectrum at extended reaction times, does not obey a simple first-order rate law. Overall, it is considerably slower than that for the intramolecular electron process by which the $[Co^{II}(p\dot{t}s)]^{5-}$ monomer is converted into $[Co^{I}(pts)]^{5-}$, $k = 1.7 \times 10^3$ s^{-1} (see ref. 6). The relative rates of these two processes in monomeric and dimeric species suggest that the dissociation of dimeric cobalt(II) ligand radical, equation (13), could be the rate-determining step in conversion of the intermediate into the stable cobalt(I) complex *via* equations (13) and (14). However, a conversion into cobalt(I) sulphophthalocyanine by means of a slow, intramolecular electron transfer in the dimeric form, followed by dimer dissociation, equations (15) and (16), is also in good agreement with our experimental observations. With either pathway, the data on dimer dissociation suggest that a significant amount of the binding energy, present initially in $[\{Co^{II}(pts)\}_2]^{8-}$, remains in the dimeric cobalt(II) ligand radical after the initial reduction.

$$e^-(aq) + [\{Co(pts)\}_2]^{8-} \longrightarrow [Co_2(pts)(p\dot{t}s)]^{9-} \quad (10)$$

$$Me_2\dot{C}OH + [\{Co(pts)\}_2]^{8-} \longrightarrow Me_2CO + H^+ + [Co_2(pts)(p\dot{t}s)]^{9-} \quad (11)$$

$$\dot{C}H_2OH + [\{Co(pts)\}_2]^{8-} \longrightarrow CH_2O + H^+ + [Co_2(pts)(p\dot{t}s)]^{9-} \quad (12)$$

$$[Co^{II}{}_2(pts)(p\dot{t}s)]^{9-} \longrightarrow [Co^{II}(pts)]^{4-} + [Co^{II}(p\dot{t}s)]^{5-} \quad (13)$$

$$[Co^{II}(p\dot{t}s)]^{5-} \longrightarrow [Co^{I}(pts)]^{5-} \quad (14)$$

$$[Co^{II}{}_2(pts)(p\dot{t}s)]^{9-} \longrightarrow [Co^{I}(pts)Co^{II}(pts)]^{9-} \quad (15)$$

$$[Co^{I}(pts)Co^{II}(pts)]^{9-} \longrightarrow [Co^{I}(pts)]^{5-} + [Co^{II}(pts)]^{4-} \quad (16)$$

The spectral characteristics of the intermediate generated by $\dot{O}H$ attack suggest it may be a dimeric oxidized ligand radical. Moreover, the stable product formed in the slow second step can be characterized as monomeric cobalt(III) sulphophthalocyanine when compared by spectral means with photolysis data in the literature.[1,6b,15] The transformation of the primary intermediate into the suggested cobalt(III) product initially obeys a first-order rate law, although this is followed by a secondary process of complex nature (see below). The rate constant for transformation of the ligand radical to $[Co^{III}(pts)]$, even in the first step, is somewhat slower than that reported for monomeric $[Co^{II}(p\dot{t}s)]^{3-}$ ($k = 3 \times 10^2$ s^{-1}).[6b] These results are consistent with processes which can be explained using either of two mechanistic schemes outlined for the overall oxidation process following formation of the oxidized dimeric ligand radical [see equation (17)]. Subsequent to this initial step, conversion into $[Co^{III}(pts)]^{3-}$ may involve dissociation followed by electron transfer, equations (18) and (19). Alternatively electron transfer may occur in the dimer prior to dissociation, equations (20) and (21). Either way one should assume that the growth of the second transient is a consequence of electron transfer.

$$\dot{O}H + [\{Co^{II}(pts)\}_2]^{8-} \longrightarrow OH^- + [Co^{II}{}_2(pts)(p\dot{t}s)]^{7-} \quad (17)$$

$$[Co^{II}{}_2(pts)(p\dot{t}s)]^{7-} \longrightarrow [Co^{II}(pts)]^{4-} + [Co^{II}(p\dot{t}s)]^{3-} \quad (18)$$

$$[Co^{II}(p\dot{t}s)]^{3-} \longrightarrow [Co^{III}(pts)]^{3-} \quad (19)$$

$$[Co^{II}{}_2(pts)(p\dot{t}s)]^{7-} \longrightarrow [Co^{II}(pts)Co^{III}(pts)]^{7-} \quad (20)$$

$$[Co^{II}(pts)Co^{III}(pts)]^{7-} \longrightarrow [Co^{II}(pts)]^{4-} + [Co^{III}(pts)]^{3-} \quad (21)$$

If the overall reaction proceeds *via* the first path then *no* transfer occurs in the dimer radical and the growth over 7 ms is due to an intramolecular electron transfer, equation (18). After the dissociation there is a relaxation process giving rise to the second very slow (*ca.* 100 ms) growth. By the second mechanism, equations (20) and (21), the intramolecular electron transfer in the dimeric radical must be slower than that reported in the monomeric species. The long second step may then be assigned to a slow dissociation accompanied by a small change in the $[\mathrm{Co^{III}(pts)}]^{3-}$ spectrum.[6] The latter has the advantage of exhibiting a dissociation step whose rate is in agreement with reported values. At least, the slower dissociation of the dimeric species can be attributed to the interaction of the metal centres. Such interaction may change the tendency for the metal-to-ligand electron transfer through some modification in the overlap of the electronic levels of the metal and the ligand. Also, part of this interaction might be seen as a perturbation of the electronic levels of the metal centres which will stabilize the cobalt(II) configuration in the dimeric radical. The different values for the rate constants of the intramolecular electron-transfer processes in dimeric and monomeric reduced ligand radicals may also be the result of the interactions discussed above for oxidized species.

The oxidation of the dimeric cobalt(II) sulphophthalocyanine by $\mathrm{Me_2C(OH)\dot{C}H_2}$ produces an intermediate which exhibits some spectral resemblance to cobalt(III) sulphophthalocyanine. Moreover, such species transform into the stable cobalt(III) sulphophthalocyanine by a reaction which is much faster than the transformation of the dimeric ligand radical, equation (18) and/or (20). These properties have suggested that the intermediate may well be an alkyl cobalt species formed in a reaction between the dimeric cobalt(II) sulphophthalocyanine and t-butanol radical, as is indicated in equation (22).* Further transformations, following attachment by the radical, have been related to dissociation of the dimeric species, equation (23).

$$\mathrm{Me_2C(OH)\dot{C}H_2} + [\{\mathrm{Co^{II}(pts)}\}_2]^{8-} \longrightarrow [\mathrm{Co^{II}(pts)Co(pts)\{CH_2C(OH)Me_2\}}]^{8-} \quad (22)$$

$$[\mathrm{Co^{II}(pts)Co(pts)\{CH_2C(OH)Me_2\}}]^{8-} \longrightarrow [\mathrm{Co^{II}(pts)}]^{4-} + [\mathrm{Co(pts)\{CH_2C(OH)Me_2\}}]^{4-} \quad (23)$$

Conclusion.—The reactivity of the t-butanol radicals towards dimeric cobalt(II) sulphophthalocyanine contrasts markedly with that of other carbon-centred radicals (see above). It seems feasible that attack on the sulphophthalocyanine and on the cobalt(II) centre are competitive reaction modes. In this case, there appears, not surprisingly, to be some relationship between the reducing potential of the carbon-centred radical and the tendency for attack at the ligand or the metal centre. This and other properties of the reaction are currently being studied at our laboratory.

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* This point of view gains some support in the light of the results obtained by Elroi and Meyerstein (see ref. 7) in reactions of carbon-centred radicals with cobalt(II) macrocyclic complexes.

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