alcohol, involving spontaneous dimerisation of the initially formed spiroepoxy-2,4-cyclohexadienone.[8] In order to examine whether or not the configurational characteristics of the dimeric *o*-quinol *9* differed from those established for the bis(bromohydrin) *17*, both compounds were reduced with Raney nickel in boiling ethanol. They were found to give the same tetrahydroxy compound *19*. Hence, the dimeric *o*-quinol *9* is sterically analogous to *17* and *18*, *i.e.*, it has *endo* configuration and steric arrangements at C-3 and C-5 analogous to those found for compounds *17* and *18*.

The following experimental results indicate that the structural and steric orientation thus established for dimer *9* is also true for its homologues *10*–*13*.

(a) The NMR spectrum (60 Mc, $CDCl_3$ + D_2O) of dimer *13* clearly shows the vicinal hydrogen atoms at positions 4a and 4 (H-4a, δ 2.84, d; H-4, δ 3.15, t; $J_{4,4a}$ and $J_{4,10}$ 2.0 cps), indicating that the structural orientation of the diene and the dienophile moieties in *13* is the same as in *9* and *18*.

(b) Similar to the diacetate of dimer *9*, the diacetates of *10* and *11* on treatment with ethanolic KOH eliminate acetic acid from the unbridged ring (C-4a, C-5) with concomitant aromatisation of this ring.[2c,10] This elimination reaction indicates that the configuration at C-5 of dimers *10* and *11* is the same as that of dimer *9*.

(c) Whereas dimers *9*–*11* were found to consume 1 mol of $NaIO_4$ with cleavage of the 2,3-ketol bridge, dimers *12* and *13* proved to be stable towards this oxidant. This striking difference can be understood by assuming that dimers *10*–*13* have the same configuration at C-3 as established for dimer *9*, and that the bulky methyl group present at C-8a in *12* and *13* hinders the formation of the cyclic periodic ester – involving the hydroxyl group at C-3 and the (hydrated) keto group in position 2 – which precedes the cleavage reaction (*cf.* Ref. 11).

The diacetate *14* obtained by acetylation of dimer *9* is identical with that obtained by thermal dimerisation of the *o*-quinol acetate *6*;[1] likewise, the diacetate of *10* is identical with the dimerisation product of the acetate of *o*-quinol *2*.[2c] Thus, the dimerisation of *o*-quinol acetates seems to follow the same rules as that of the free *o*-quinols.

Experimental details will be given in a forthcoming publication.

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Photoreaction Between Trisethylenediamine Cobalt(III) ($Co(en)_3^{3+}$) and Ethylenediaminetetraacetate (H_2Y^{2-})

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Only few *photoanations* have been reported with coordination compounds.[1,2] The common photosubstitution is the photosolvation and generally any photosubstitution is accompanied by a dark (thermal) reaction.[1] Therefore, the reaction

$$Co(en)_3^{3+} + H_2Y^{2-} \rightarrow CoY^- + 2H^+ + 3en \quad (1)$$

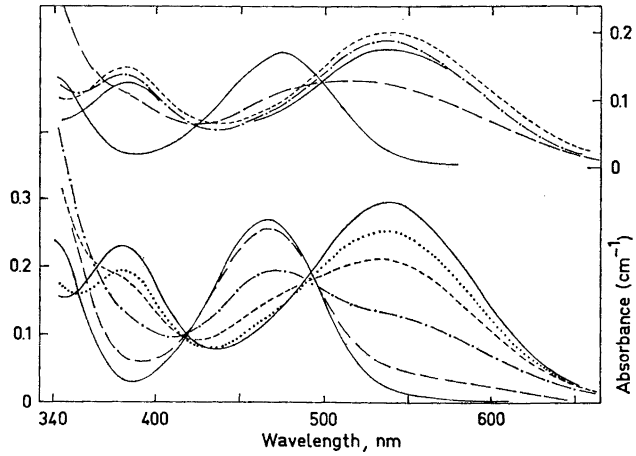

Fig. 1. Below: 3.00 mM(+)$Co(en)_3(ClO_4)_3$, 4.00 mM Na_2H_2Y after 0 (—), 1 (– –) 2 (–.–),3 (---) 4 (....), and 5 or 6 (———) hours of irradiation with (corrected) constant intensity. *Above:* 3.00 mM $Co(NH_3)_6(ClO_4)_3$, 4.00 mM Na_2H_2Y after 0 (———), 1 (– –), 2 (–.–), 3 (---), and 5 (———) hours of irradiation with the same intensity as in the experiment below.

appears especially interesting as it could be only photolytically induced. Even at comparatively high temperatures (90°C) no reaction could be observed. In an earlier report [3] we have suggested that the outer sphere complex, $[Co(en)_3]H_2Y^+$, should be the active component (reactant). The aim of the present study has been to determine the quantum yield of the reaction (1) and to see if this formal quantum yield (Φ_1) might directly reflect the concentration of the outer sphere complex.

The quantitative estimates were based on absorption measurements (*cf.* Fig. 1). The table presents the formal quantum yields, Φ_1 and Φ_2, for the reactions (1) and $Co(en)_3^{3+} \rightarrow Co(II)$ (2),[3] respectively, at different ionic strengths ($NaClO_4$) and different total concentrations of H_2Y^{2-}. Obviously, both Φ_1 and Φ_2 decrease rapidly with increasing ionic strength and also with increasing original H_2Y^{2-} concentration. We have also found that a solution of (+)$Co(en)_3^{3+}$(3 mM)+H_4Y (4 mM) was completely unaffected judging both from visible absorption spectrum and from circular dichroism (CD) spectrum. From earlier experiences [4,5] we know that these effects should indeed be expected if the equilibrium $Co(en)_3^{3+} + H_2Y^{2-} \rightleftharpoons Co(en)_3H_2Y^+$ was a link in the photoreaction. Considering the outer-sphere complex [5] as the reactant, a quantum yield of about 6×10^{-4} mol einstein^{-1} is thus obtained for $Co(en)_3H_2Y^+ + h\nu$ (300 – 400 nm)$\rightarrow CoY^-$.

Table 1. Variation in Φ_1 and Φ_2 with original concentration of H_2Y^{2-} (C_{HY}) and with the ionic strength (I). $C_{Co(en)_3^{3+}} = 3.00$ mM.

C_{HY} (mM)	I (M)	$\Phi_1 \times 10^3$	$\Phi_2 \times 10^3$
4.00[a]	1.03	0.00	0.00
4.00[a]	0.53	0.01	0.02
4.00[a]	0.23	0.08	0.06
4.00[a]	0.13	0.17	0.16
4.00[a]	0.08	0.27	0.47
4.00[a]	0.03	0.46	0.89
0		0.00	0.00
4.00		0.55	0.85
6.00		0.38	0.93
10.0		0.21	0.65
26.0		0.11	0.16
0 [a]	0.10	0.00	0.00
4.00[a]	0.10	0.20	0.42
6.00[a]	0.10	0.24	0.33
10.0[a]	0.10	0.17	0.17
26.0[a]	0.10	0.09	0.05

[a] Medium: $NaClO_4$.

Due to difficulties in estimating and comparing quantum yields at different concentrations of $Co(en)_3^{3+}$, it could only be stated that at high concentrations both Φ_1 and Φ_2 appeared to be independent of the original concentration of $Co(en)_3^{3+}$ (in the range 0.012 – 0.027 M with $I = 0.15$ M and with 0.004 M H_2Y^{2-}: $\Phi_1 = 2 \times 10^{-4} \pm 10\%$ $\Phi_2 = 3 \times 10^{-4} \pm 10\%$). As the absorbance in all samples was greater than 1, due to $Co(en)_3^{3+}$, such a zero-order rate law might indicate $Co(en)_3^{3+}$ as the photoreactant. The ionic strength effect and the pH effect mentioned above could then be explained by an equilibrium $Co(en)_3^{*3+} + H_2Y^{2-} \rightleftharpoons Co(en)_3{}^*H_2Y^+$, the outer-sphere complex still being an intermediate step at the formation of CoY^-. However, one might expect $Co(en)_3^{*3+}$ to be labile, *e.g.* to aquation, racemization. However, pure $Co(en)_3(ClO_4)_3$ was found completely resistant to light with not too short wavelength (> 300 nm),* the changes in CD spectra could in all cases only be attributed to the reactions (1) and (2), *i.e.* no racemization occurred.

In Fig. 1 the spectral variation during a photolysis is visualized together with a parallel experiment with $Co(NH_3)_6^{3+} + H_2Y^{2-}$. In the latter case, the formation of CoY^- as well as the photoreduction proceeds more rapidly than in the $Co(en)_3^{3+}$ case, though the photosubstitution is slower relatively, probably due to a parallel decomposition of CoY^-.** It should be noted that the isosbestic points (at 420 and 490 nm) in the $Co(en)_3^{3+}$ case only indicate a constant ratio $[CoY^-]/[Co(II)]$ (≈ 0.5) during the photolysis ($\varepsilon_{Co(II)} \approx 0$).

Experimental. Chemicals and spectroscopic instruments have been described elsewhere.[3-5] The difficulty of exact reproduction of light intensities at repeated photolyses led us construct a simple device for simultaneous irradiation of many samples (Fig. 2). The solutions in test-tubes (pyrex, glass stoppers) were carried around (10 rpm) in front of the light source (SP 500). In this way all tubes obtained

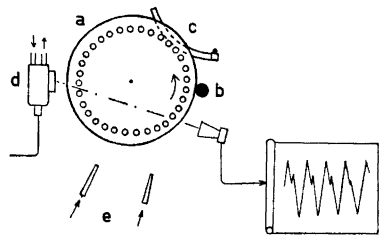

Fig. 2. a. Rotating disc with test-tubes, *b* motor, *c* rubber tubing for rotation of tubes. *d* light source (water cooling), *e* air cooling.

the same average intensity (± 2 %, an uncertainty probably due to varying glass thicknesses in the tubes). Air jets gave a constant temperature (27 ± 1°C). One of the tubes was used for actinometry (5 ml 0.02 M uranyl oxalate, 0.09 M oxalic acid diluted to give an absorption approximately equal to that of the sample, at 350 nm). The quantum yield for the oxalate decomposition was assumed to be 0.50 mol einstein^{-1} at 350 nm.[7,8] The oxalate concentration was determined before and after the irradiation by permanganate titration (Typical actinometer result: 8.3×10^{-4} einstein (350 nm)/10 min and 10 ml). The chemical actinometer was used with certain intervals (2 h) to calibrate a recording intensity meter (thermo-pile) the intensity spectrum of which (against time) gave the total light amount but also performed a rough picture of the transmittances of the individual tubes. The solutions were stirred by rotating the tubes.

* Recently a photoaquation, Φ between 10^{-4} and 10^{-5}, has been reported.[3,6] This result is incompatible with ours (less than 10^{-5}).

** Tests with CoY^- have revealed that neither Co^{2+}, $Co(NH_3)_6^{3+}$ nor Co(II)EDTA^{2-} has any catalytic effect on the decomposition.

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