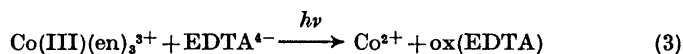
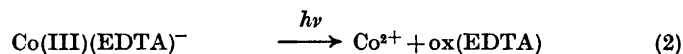
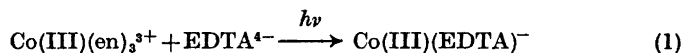


The Diminished Inertness of the Tris(ethylenediamine)-cobalt(III) Ion when Irradiated with Ultraviolet Light in Presence of Ethylenediaminetetraacetate

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In an investigation of the possibilities of obtaining a photolytical resolution of enantiomers of transition metal complexes with possibility of dissymmetry,^{1,19} it was discovered that the tris(ethylenediamine)cobalt(III) ion, $\text{Co}(\text{en})_3^{3+}$, which is normally inert to substitution reacted in the presence of ethylenediaminetetraacetic acid EDTA, when irradiated with ultraviolet light according to one of the following alternatives:



[ox(EDTA) represents an oxidation product from EDTA].

Reaction (1) occurs on irradiation with light of wavelength longer than 300 nm and very probably proceeds *via* formation of $\text{Co}(\text{en})_2(\text{EDTA})^-$. Reaction (2) is strongly favoured by a high concentration of free EDTA and by more energetic irradiation ($\lambda=250-300$ nm). Reaction (3) predominates when light of short wavelength ($\lambda=250$ nm) is used. All reactions (and especially the photoreductions) are found to proceed more readily with increasing pH.

It is shown that the photolytical labilization which results in substitution [reaction(1)] is caused by light absorption in the $d \rightarrow d$ bands of $\text{Co}(\text{en})_3^{3+}$ (D_3 -symmetry) which have ${}^1A_{1g} \rightarrow {}^1T_{2g}$ parentage in the O_h -symmetry. In other words, the promotion of an electron to an antibonding orbital in the CoN_6 moiety causes a decrease in the Co-N bond strength.

The inertness of the $\text{Co}(\text{en})_3^{3+}$ ion to substitution is wellknown (*cf. e.g.*, Ref. 2). Even during the racemization of an enantiomeric form, which can actually be effected under forcing conditions (high temperature and strongly

basic solutions of amines), no internal ligand reorganisation or S_N1 substitution takes place, but rather the change in configuration proceeds *via* an S_N2 collision mechanism.³ It was thus not surprising to find that a (+)Co(en)₃(ClO₄)₃ solution was not racemized when irradiated with ultraviolet light.

In preliminary experiments it was discovered, however, that a (+)Co(en)₃(ClO₄)₃ solution containing EDTA, which had been irradiated with ultra-violet light over night, had changed colour from yellow to violet. The absorption spectrum showed that Co(III)(EDTA)⁻ had been formed (see Experiment 1 below, the results of which are quite similar to those obtained in the original experiment in which the effect was first noticed). It was also found that a photoreduction had occurred simultaneously: about 3/4 of the original Co(III) had been reduced to Co(II) (*i.e.*, Co(EDTA)²⁻). The decrease of the circular dichroism (CD) was paralleled by a corresponding decrease of the absorbance. This implied that no racemisation had occurred, but neither had the configuration been retained on the substitution.

Plan of investigation. When it was found that Co(en)₃³⁺ reacted in the presence of EDTA on irradiation with ultra-violet light, a series of experiments was performed in order to try to ascertain the mechanism of the labilization.

Several possible "trivial" causes for the reaction were investigated (Expt. 6). The possibility of heterogeneous catalysis by traces of active carbon from the synthesis of the tris(ethylenediamine)cobalt(III) salt was not unthinkable.⁴ Furthermore, it is known that certain complexing reagents can, on heating with Co(en)₃³⁺ enter into inner coordination with cobalt.²

The dependence of the photolysis reaction on the wavelength of the light, pH, and the EDTA concentration was investigated. It was found that less Co(EDTA)⁻ was formed at higher EDTA concentrations (Expt. 3). This suggested that Co(EDTA)⁻ was sensitive to photolysis, especially if the EDTA concentration was high. To test this hypothesis, a separate experiment on K[Co(EDTA)] was performed (Exp. 4). Finally the changes in absorption spectrum of Co(en)₃³⁺ on irradiation with light of shorter wavelength were observed, and the resistance of a pure EDTA solution to photolysis was studied.

EXPERIMENTAL

Chemicals. Tris(ethylenediamine)cobalt(III) chloride, [Co(en)₃]Cl₃, was prepared according to the method of Work and McReynolds.⁵ The perchlorate was obtained from the chloride by precipitation with concentrated perchloric acid and recrystallization in water (precipitation with ethanol). (+)Tris(ethylenediamine)cobalt(III) perchlorate, (+)[Co(en)₃](ClO₄)₃, was prepared from the (+)tris(ethylenediamine)cobalt(III)chloride (+)tartrate in an analogous way. The latter salt was prepared according to the method of Busch.⁶ Potassium(ethylenediaminetetraacetate)cobalt(III), K[Co(EDTA)]·2H₂O was prepared according to the method of Dwyer, Gyarfás and Mellor.⁷ All other reagents used were of *p.a.* quality and the water was doubly distilled. If deionized water was used large variations in the rate of photolysis were observed in replicate experiments. This is probably due to the presence of UV-absorbing contaminants leached from the ion-exchange resin.

Light sources. One of the following lamps was used for the irradiations: Original Hanau, Q 81, highpressure mercury lamp, which provides high intensities in the short wavelength ultra-violet bands (254, 313 and 366 nm); Philips, SP 500, super highpressure mercury lamp with watercooling, which provides high intensities in the near ultra-violet

to visible range. (The relative emission spectra of the lamps are given schematically in Fig. 1.)

The sample solutions, contained in either glass or quartz cells, were placed 20–30 cm in front of the lamp. Due to the rapid decrease in the intensity of the lamps with time

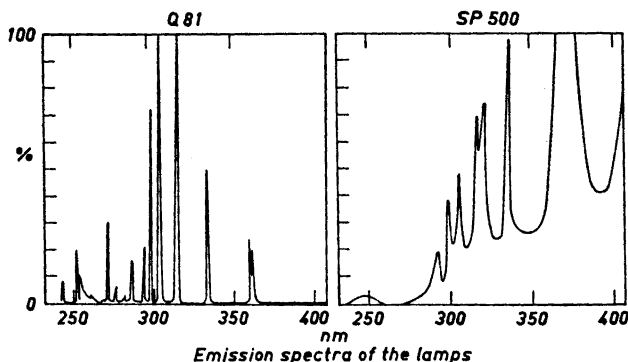


Fig. 1. Emission spectra of the lamps.

(especially that of SP 500), the reaction yields (per unit time) in the experiments described below cannot directly be compared.

When filters (Zeiss coloured glass filters) were used, they were placed immediately in front of the sample. No convergent lens or mirror was used.

Spectroscopic measurements. Absorption spectra (340–700 nm) were recorded before and after irradiation with a Hitachi EPS-3T spectrophotometer. Circular dichroism (CD) was measured with a Roussel Jouan Dichrographe, Model B.

The spectroscopic measurements were performed at 25°C and the photolyses were performed at 20–30°C (air cooling).

EXPERIMENTS AND RESULTS

Experiment 1: A solution, 9.1 mM (+)Co(en)₃(ClO₄)₃ and 9.1 mM EDTA (pH = 5), was irradiated in a glass test-tube with filtered light (BG 31, cf. Expt. 2) from SP 500 for 15 h. Fig. 2 shows CD and absorption spectra before and after irradiation.

The absorption spectra indicate that Co(en)_3^{3+} was decomposed and cobalt(III)EDTA was formed: Literature reports^{8,9} show, as was confirmed in the Experiment 4 (below), that Co(EDTA)^- has two absorption bands, one at 380 nm and one at 535 nm, and that the ratio of their respective absorbances is about 1:1.5. It is not possible to explain the effects shown in Fig. 2 by the formation of species of the type $[\text{Co(III)(en)}_2\text{XY}]$, (XY = H₂O, OH⁻). Although such complexes have been produced by photolyses of basic Co(en)_3^{3+} -solutions containing high iodide concentrations,¹ they give spectra consisting of one band at 350–370 nm and another of about half the absorbance of the first, at 490–510 nm.¹⁰ Cobalt(II)EDTA, on the other hand, has a spectrum composed of only one broad maximum at 490 nm with an absorptivity about 10 times less than that of Co(en)_3^{3+} at 470 nm.¹⁰

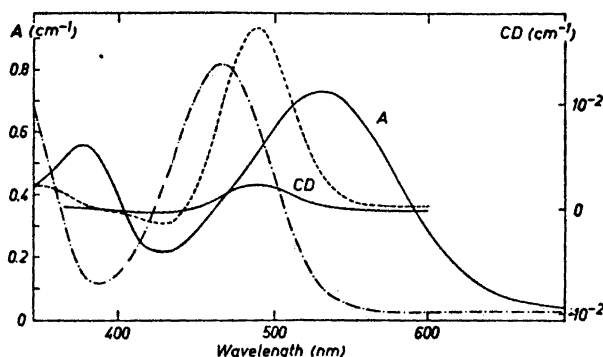


Fig. 2. Expt. 1. Absorption spectra before (---) and after (—A) irradiation. Circular dichroism spectra before (---) and after (—CD) photolysis.

The change in circular dichroism implies that the transition $\text{Co(en)}_3^{3+} \rightarrow \text{Co(EDTA)}^-$ proceeds without retention of configuration. The ORD spectrum of $(+)\text{Co(EDTA)}^-$ ¹¹ shows a weak positive Cotton effect at 380 nm and two superimposed Cotton effects at 560 nm, one positive at shorter and one negative at longer wavelength. In Fig. 2 there actually appears a feeble indication of a negative CD band at 550–600 nm. This suggests the same absolute configuration for $(+)\text{Co(EDTA)}^-$ as for $(+)\text{Co(en)}_3^{3+}$, provided, of course that no inversion of configuration has occurred. This is very probable since it has been reported^{7,12} that the reaction $(+)\text{Co(EDTA)}^- + 3 \text{ en} \rightarrow \text{Co(en)}_3^{3+} + \text{EDTA}^{4-}$ gives mainly $(+)\text{Co(en)}_3^{3+}$. After irradiation a CD decrease of 86 % was recorded. The corresponding absorbance at 470 nm decreased by approximately 90 % which proves that no appreciable racemization of $(+)\text{Co(en)}_3^{3+}$ has occurred.

Experiment 2: From preliminary experiments it was evident that “photo-substitution” could only be induced if short wavelength light ($\lambda > 300 \text{ nm}$) was

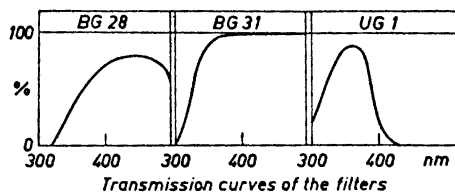


Fig. 3. Transmission spectra of the filters.

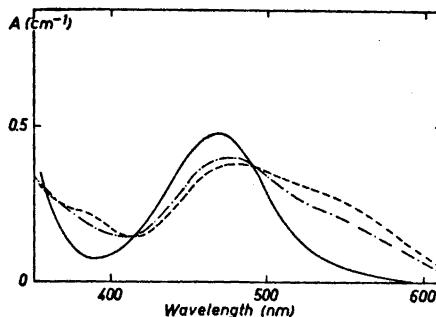


Fig. 4. Expt. 2. Absorption spectra before (—) and after irradiation (— BG 28, --- BG 31, - · - UG 1).

excluded, for example by using a glass cell. In order to examine this wavelength dependence, three samples of 5.55 mM $(\text{Co(en)}_3(\text{ClO}_4)_3)$ with 5.55 mM EDTA (pH = 5) were irradiated (SP 500, 5 h) through the filters BG 28, BG 31, and UG 1 (Zeiss). The transmission curves of the filters¹⁸ are reproduced in Fig. 3.

Fig. 4 shows that the Co(en)_3^{3+} absorption spectrum of the sample irradiated through filter BG 28 was practically unchanged and that in the two other samples, only one absorbing product had been formed. If the photolysis is driven further, however, the isobestic point disappears, probably due to the rapid decrease in Co(en)_3^{3+} concentration caused by the parallel photoreduction. The experiment shows that the highest yield is obtained with light in the wavelength range 300–350 nm, which corresponds to the excitation ${}^1A_{1g} \rightarrow {}^1T_{2g}$.

Experiment 3: In a preliminary experiment the total photolytical yield was found to decrease with increasing concentration of disodiummethylenediaminetetraacetate. However, as the pH of the solution decreased with increasing EDTA-concentration it was suspected, that the reaction rate difference was caused by the pH-difference. This was shown to be the case. The photolytical substitution rate decreases with decreasing pH. In this experiment the EDTA-concentration was varied but pH was kept constant (7.2). Samples of the composition given in Table 1 were irradiated with SP 500 (filter BG 31).

Table 1. Expt. 3

Sample No.	Concentrations in mM before irradiation	
	$\text{Co(en)}_3(\text{ClO}_4)_3$	EDTA
0	5.55	0
1	5.55	5.55
2	5.55	11.11
3	5.55	22.2
4	5.55	27.8
5	5.55	33.3
6	5.55	38.9
7	5.55	44.4

Fig. 5 shows the absorption spectra after the irradiation. Spectra of all of the samples before irradiation were identical to each other and to the spectrum of sample No. 0 after irradiation. In sample 1 about 1/4 of the total cobalt is present as Co(EDTA)^- .^{8,9} This yield, which is of about the same magnitude as in Expt. 1, obviously decreases as the original concentration of EDTA is increased.

Experiment 4: In order to explain the results from Expt. 3, the photosensitivity of K[Co(EDTA)] and its dependence on EDTA concentration were investigated.

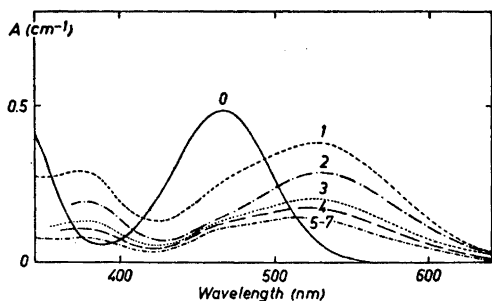


Fig. 5. Expt. 3. Absorption spectra after irradiation of solutions with increasing concentrations of EDTA (0-7).

The following solutions were exposed for one hour to unfiltered ultraviolet light (Q 81) in 1 cm quartz cell.

Sample	[Co(EDTA) ⁻] (mM)	[EDTA] (mM)	pH
1	2.00	0	5.0
2	2.00	50	5.0

From the result (Fig. 6) it appears that Co(EDTA)⁻ in sample 2 decomposed remarkably faster than it did in sample 1.

Note: When two 1 mM Co(EDTA)⁻ solutions, one with pH=5, the other with pH=6.5, were irradiated (Q 81), the rate of decrease in absorbance at 535 nm in the solution with the higher pH was about twice that in the solution with the lower pH.

Experiment 5: On irradiation of a sample closely corresponding to sample 2 in Expt. 3 (for composition see Fig. 7) with short wavelength ultra-violet light (Q 81), it was found from the absorption spectrum (Fig. 7) that the amount Co(en)₃³⁺ present decreased rapidly and simultaneously only Co(II)-EDTA²⁻ was formed.

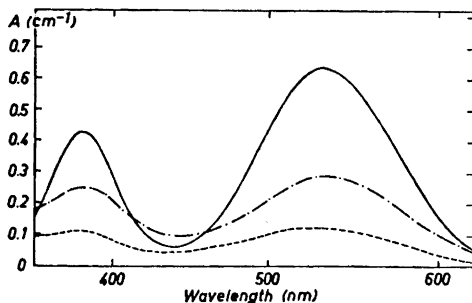


Fig. 6. Expt. 4. Absorption spectra of the solutions before (—) and after (1, - - - and 2, - - -) irradiation.

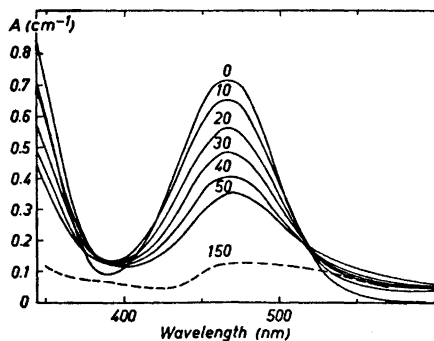


Fig. 7. Expt. 5. Absorption spectra of a solution, 8.33 mM Co(en)₃(ClO₄)₃, 17 mM EDTA, after 0, 10, 20, 30, 40, 50, and 150 min of irradiation.

In this case an EDTA solution (1 cm, 20 mM, pH=7) was used as a *filter* (its transmission is shown in Fig. 8). When the irradiation was performed with unfiltered light the decomposition rate was, however, more than double the rate shown in Fig. 7 (80 % decomp./30 min without filter compared with 30 % decomp./30 min with filter). It seems reasonable to believe, therefore, that the main photoreducing effect is restricted to wavelengths of about 260 nm, where the EDTA transmission is low but not zero. The transmission spectrum of the EDTA filter after the irradiation (Fig. 8) reveals a slight sensitivity of EDTA to photolysis. This suggests the possibility that the

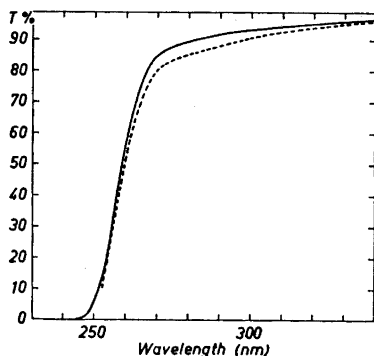


Fig. 8. Expt. 5. The transmission spectrum of the EDTA filter solution before (—) and after (---) irradiation.

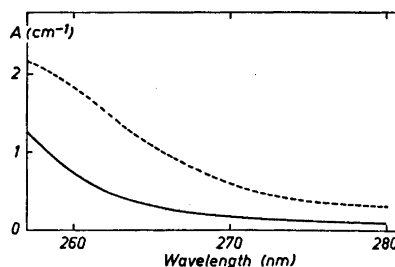


Fig. 9. Expt. 5. Differential charge transfer spectrum obtained from the measured absorbances given in Table 1.

decomposition of Co(en)_3^{3+} may be caused by some species photochemically derived from EDTA (*e.g.*, hydrogen atoms, solvated electrons).

The charge transfer (C.T.) band of the outer-sphere complex has been roughly calculated from recorded spectra of $\text{Co(en)}_3(\text{ClO}_4)_3$, EDTA, and a solution of $\text{Co(en)}_3(\text{ClO}_4)_3 + \text{EDTA}$ (Fig. 9). From Fig. 9 it is clear that the charge-transfer band is positioned at a wavelength slightly larger than that of the pure EDTA absorbance. Therefore the photoreduction can as well be explained by a charge transfer in the complex. If, in Experiment 4, the absorbance due to pure EDTA in the solutions with low EDTA-concentration had been very high (*e.g.* $A > 2$), the increasing photoreduction with increasing EDTA concentration could not be explained by the secondary effect of reducing species derived from EDTA but only by increasing outer-sphere complex formation. However, the absorptivity of EDTA is only about $14 \text{ M}^{-1}\text{cm}^{-1}$ at 260 nm (Table 2). Thus both explanations are satisfactory.

Experiment 6: A number of tests were performed to rule out "trivial" reaction paths (see Plan of investigation).

a) No significant racemization could be detected in the following experiments.

Table 2. Measured absorbances (see text).

Wavelength (nm)	Absorbance (pathlength 0.100 cm)			
	5.00 mM Co(en) ₃ (ClO ₄) ₃ 50.00 mM EDTA	50.00 mM EDTA	5.00 mM Co(en) ₃ (ClO ₄) ₃	a - (b + c)
	a	b	c	
257	0.705	0.127	0.360	0.218
258	0.615	0.107	0.307	0.201
259	0.541	0.088	0.259	0.194
260	0.472	0.071	0.220	0.181
261	0.411	0.062	0.183	0.166
262	0.360	0.051	0.156	0.153
263	0.310	0.044	0.131	0.135
264	0.270	0.040	0.111	0.119
265	0.233	0.033	0.092	0.108
266	0.202	0.030	0.079	0.093
267	0.179	0.025	0.069	0.085
268	0.159	0.023	0.057	0.079
269	0.143	0.020	0.051	0.072
270	0.123	0.018	0.044	0.061
271	0.110	0.017	0.037	0.056
272	0.098	0.016	0.033	0.049
273	0.089	0.015	0.029	0.045
274	0.081	0.014	0.024	0.043
275	0.072	0.013	0.021	0.038
276	0.068	0.012	0.019	0.037
277	0.063	0.011	0.018	0.034
278	0.059	0.011	0.015	0.033
279	0.054	0.011	0.014	0.029
280	0.051	0.011	0.013	0.027

I. 24 h irradiation (SP 500) of a 10 mM (+)Co(en)₃(ClO₄)₃ solution in a glass test tube.

II. 1 month aging of a solution, 5.55 mM (+)Co(en)₃³⁺, 5.55 mM EDTA (pH = 6), 0.28 mM Co(ClO₄)₂.

III. 24 h irradiation of a solution, 10 mM (+)Co(en)₃(ClO₄)₃ and 1 mM Co(ClO₄)₂.

IV. 24 h aging at 60°C of a solution, 10 mM Co(en)₃(ClO₄)₃ and 10 mM EDTA.*

b) Irradiation of a solution, 5.00 mM (+)Co(en)₃(ClO₄)₃ and 50.0 mM EDTA (pH = 5), in a quartz cell with ultra-violet light (Q 81) was carried out to a reaction yield of about 50 % (estimated from the absorbance spectrum). A 57 % decrease in absorbance at 470 nm was measured, and a 71 % decrease

* In a corresponding experiment with active carbon present, a violet colour developed, indicating that substitution had occurred.

in CD at 490 nm. The CD spectrum decreased uniformly, so no active products were obtained, but 33 % of the total Co(en)_3^{3+} had photoracemized.

c) In tests paralleling the foregoing one, a number of solutions with varying amounts (0–1 mg/10 ml) of active carbon were irradiated. However, no indication of any significant increase in the rate of formation of Co(EDTA)^- was found.

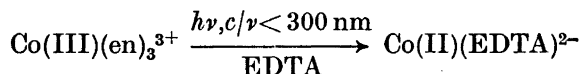
d) Mixing solutions of EDTA, which had been irradiated for 5 h, with solutions of Co(en)_3^{3+} did not affect the Co(en)_3^{3+} absorption spectrum. Thus, if photolysis products derived from EDTA are of importance in the photoreduction of Co(en)_3^{3+} , they must be short-lived.

e) The feeble CD-effect in Expt. 1, which was assigned to $(+)\text{Co(EDTA)}^-$, was shown not to be an induced effect caused by complex formation $((+)\text{Co(en)}_3:\text{Co(EDTA)}^{2+})^*$. The CD-spectrum of a solution, 10 mM $(+)\text{Co(en)}_3^{3+}$ and 2 mM Co(EDTA)^- , did not show any deviation from the pure $(+)\text{Co(en)}_3^{3+}$ spectrum.

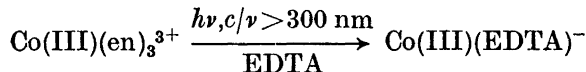
DISCUSSION

The results clearly show that Co(en)_3^{3+} is labilized by irradiation in the presence of EDTA^{n-} ($n=2, 3$, or 4) with ultra-violet light with a wavelength corresponding to the electronic transition ${}^1A_{1g} \rightarrow {}^1T_{2g}$ ($t_{2g}^6 \rightarrow t_{2g}^5 e_g$ breaks down, in an octahedral complex, into ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$). The photolysis causes a substitution reaction in which cobalt(III)EDTA is formed.

Light with shorter wavelengths ($\lambda < 300$ nm) promotes a reduction of the central cobalt atom by means of a charge transfer from EDTA co-ordinated in the outer sphere. Strongly reducing photolysis products derived from EDTA (e.g. hydrogen atoms, solvated electrons) probably contribute to the reduction of the cobalt. This latter mechanism has been proposed as an explanation of the photoreduction of $[\text{Co}(\text{NH}_3)_6]^{3+}$ in dilute solutions of potassium iodide: $\text{I}^- \rightarrow (\text{I} e^-)_{\text{aq}}$,¹³ whereas in more concentrated solutions, due to more extensive ion association, direct photoreduction *via* charge-transfer from the outer sphere ligand is the most important mechanism.^{1,14,15} Thus, while the reaction



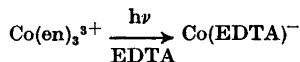
is neither unexpected nor difficult to explain, the reaction



is a more surprising one. A recent circular dichroism investigation in this laboratory on the perturbation of the $d \rightarrow d$ transitions ${}^1A_1 \rightarrow {}^1A_2$, ${}^1A_1 - {}^1E_g$ by the presence of EDTA gives evidence of a remarkable association between Co(en)_3^{3+} and EDTA^{n-} ($n > 0$).¹⁶ As an explanation for the substitution of

* This effect could be expected if, for example, in the complex $\text{Co(en)}_3:\text{Co(EDTA)}^{2+}$ a certain absolute configuration of Co(EDTA)^- is favoured (which is the case in the corresponding crystals⁷) and the free Co(EDTA)^- undergoes racemization.

ethylenediamine in Co(en)_3^{3+} with certain polarizable ions (diethyldithiocarbamate and Fe(CN)_6^{4-}), Larsson^{2,17} has suggested that the inert Co-N-bonding is labilized by an interaction between filled orbitals of the polarizable ions associated in the outer sphere of the cobalt complex and antibonding orbitals (e_g^*) of the central CoN_6 moiety. Accordingly, any suitable excitation of electrons to e_g^* should also produce increased lability in the CoN_6 moiety. Thus we have effected the substitution $[\text{Co(en)}_3]\text{EDTA}^- \rightarrow [\text{Co(EDTA)}]^- + 3 \text{ en}$ **by photo-excitation of the transition ${}^1A_{1g} - {}^1T_{2g}$.



Our results suggest a possible photochemical preparative method for obtaining substitution products from inert complexes in cases in which the heretofore common procedure of simply heating the reaction mixture has been unsuccessful. Furthermore, the technique should be useful in cases in which the oxidation state of the central metal is stabilized in the complex and must be preserved.

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** Larsson points out in his report¹⁷ that no Co(II) intermediate product is necessary for the substitution in Co(en)_3 (diethyldithiocarbamate)_n⁽³⁻ⁿ⁾⁺ or $\text{Co(en)}_3(\text{Fe(CN)}_6)^-$. Such a product is, however, considered necessary to explain the reactions catalyzed by active carbon (e.g., the racemization of (+)Co(en)₃³⁺). However, no evidence has been found (Expt. 6) for catalytic activity by either Co(II) or active carbon in the reaction.