[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CONNECTICUT]

The Photochemical Decomposition of the Halides of Tris-(ethylenediamine)-cobalt(III) in the Solid State[1]

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The halides of tris-(ethylenediamine)-cobalt(III) undergo photochemical decomposition upon exposure of the solids to 2537 Å. radiation. The order of the photosensitivity is F > Cl > Br > I. The decomposition of the chloride appears to involve the loss of two NH_3 molecules for each atom of cobalt. Under 2537 Å. radiation solid *cis*-dichlorotriethylenetetraminecobalt(III) chloride yields a similar product. The photolysis reactions in aqueous solution differ from that of solid tris-(ethylenediamine)-cobalt(III) chloride.

The photochemical decomposition of coördination complexes in water solution was first observed by Burger[2] in the case of nitrosopentamminecobalt(III) nitrate solution from which, by the action of light, a precipitate of cobaltous hydroxide was obtained. The later investigations of Schwartz and Weiss[3] on cobalt(III) nitrito ammines and of Schwartz and Tede[4] on tetramminecobalt(III) complexes containing anion ligands pointed to some correlation between the sensitivity and the acidic character and orientation of the ligands. They regarded the hexamminecobalt(III) complex as essentially insensitive. The more recent studies of Linhard and others[5] on the photolysis of solutions of various ammine complexes of cobalt(III) of the type $[Co(NH_3)_{6-n}X_n]^{(3-n)+}$ where $X = N_3^-$, halide and NO_2^-, have led them to the general conclusion that the cobalt is reduced to Co(II) by transfer of an electron from the negative ligand. The *cis*-isomer of the dinitrito complex was found to be more sensitive than the *trans*-isomer.

So far as the photolysis of solid compounds is concerned, the literature contains only casual observations that some solid complex compounds, *e.g.*, the trioxalato complexes of trivalent manganese, iron and cobalt, decompose on exposure to light. Beacom[6] showed that the solid compounds $[Co(NH_3)_6]_2(SO_4)_2S_2O_8$, $[Co\ en_3]_2(S_2O_8)_3$ and $[Cr\ en_3]_2(S_2O_8)_3$ were photosensitive inasmuch as after exposure to ultraviolet radiation, they could be thermally decomposed at temperatures between 80 and 100° while the unexposed compounds were stable in this temperature range. The products obtained in this way from the cobalt compounds contained Co(II), and it was thought that the mechanism of activation involved an electron transfer from the peroxydisulfate ion to the Co(III) complex. The thermal decomposition following exposure to ultraviolet radiation occurred rapidly and resulted in the oxidation of the ligand. Nitrogen, carbon dioxide and water were the principal products identified in the mass spectrometer.

The present paper stems from the observation that the orange solid tris-(ethylenediamine)-cobalt(III) chloride upon prolonged exposure to 2537 Å. radiation gave a bright green product, while no change was observed upon irradiation with 3650 Å. or longer wave length. It was found that by the use of circular paper chromatography, the rate of formation of the decomposition product could be determined quantitatively. Since this procedure appeared to offer a quantitative measure of photosensitivity, it was used to compare the relative behavior of the different halides of tris-(ethylenediamine)-cobalt(III). The products were examined by spectrophotometric studies, magnetic susceptibility measurements, polarographic analysis and infrared studies as well as by chemical analyses.

Experimental

Preparation of Compounds.—The procedure of Work[7] was used to prepare $[Co\ en_3]Cl_3$ and this compound was used to prepare the other halides.[8] The fluoride was prepared by treating the chloride with silver fluoride solution. After removing the silver chloride precipitate, the solution of $[Co\ en_3]F_3$ was evaporated to small volume and the salt precipitated by the addition of alcohol. The bromide and the iodide were obtained by the addition of solid sodium bromide and iodide, respectively, to a concentrated solution of the chloride and cooling the solution until crystals were obtained. The crude products were recrystallized from water solution. A check on the composition of the compounds was made by the determination of the nitrogen content using the standard micro-Kjeldahl method. After drying *in vacuo* at 100° for 15 hr. the results agreed closely with those expected for the anhydrous chloride, bromide and iodide, but the nitrogen value for the fluoride was low and total analysis indicated the formula to be $[Co\ en_3]F_3 \cdot 6HF \cdot 2H_2O$.

Anal. Calcd. for $[Co\ en_3]Cl_3$: N, 24.32. Found: N, 24.44. Calcd. for $[Co\ en_3]Br_3$: N, 17.55. Found: N, 17.40. Calcd. for $[Co\ en_3]I_3$: N, 13.55. Found: N, 13.62. Calcd. for $[Co\ en_3]F_3 \cdot 6HF \cdot 2H_2O$: Co, 13.00; C, 15.99; H, 7.52; N, 18.58; F, 37.80; O, 7.08. Found: Co, 12.87; C, 16.01; H, 6.14[9]; N, 18.49; F, 37.70.

The synthesis of the *cis*-dichlorotriethylenetetraminecobalt(III) chloride was according to the method of Basolo.[10] The blue-purple crystals were recrystallized from 6 *N* HCl.

Anal. Calcd. for $[Co\ trien\ Cl_2]Cl$: Cl to Co ratio, 3.00. Found: Cl to Co ratio, 2.95.

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[2] O. K. H. Burger, *Proc. Chem. Soc.*, **27**, 160 (1911).

[3] R. Schwartz and H. Weiss, *Ber.*, **58B**, 746 (1925).

[4] R. Schwartz and K. Tede, *ibid.*, **60B**, 63 (1927).

[5] (a) M. Linhard and H. Flygare, *Z. anorg. allgem. Chem.*, **262**, 328 (1950); (b) M. Linhard, M. Wiegel and H. Flygare, *ibid.*, **263**, 233 (1950); (c) M. Linhard, M. Wiegel, *ibid.*, **263**, 245 (1950); **264**, 321, 327 (1951); **266**, 73 (1952); **267**, 113, 121 (1952).

[6] S. Beacom, Doctoral Thesis, University of Connecticut, 1954.

[7] J. B. Work, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 221.

[8] The following abbreviations will be used: en = ethylenediamine; pn = propylenediamine; trien = triethylenetetramine; dien = diethylenetriamine.

[9] The hydrogen associated with the compound as HF is unavailable for the formation of H_2O. The theoretical value for the "available" hydrogen is 6.20.

[10] F. Basolo, THIS JOURNAL, **70**, 2634 (1948).

Basolo also attempted the preparation of *trans*-dichlorotriethylenetetraminecobalt(III) chloride but decided that the green product obtained was not the desired product since it became orange in water solution and precipitated more than one chloride ion per atom of cobalt. The procedure of Basolo[10] was repeated and the green solid obtained was recrystallized from water and HCl.

The binuclear complex [Co$_2$ trien$_3$]Cl$_6$ was prepared by the method of Basolo.[10]

The hexamminecobalt(III) chloride was prepared according to the directions of Bjerrum and McReynolds.[11]

Anal. Calcd. for [Co(NH$_3$)$_6$]Cl$_3$: N, 31.42. Found: N, 31.47.

The tris-(propylenediamine)-cobalt(III) chloride was prepared by a procedure analogous to that used for the tris-(ethylenediamine) compound.

Anal. Calcd. for [Co pn$_3$]Cl$_3$: N, 21.73. Found: N, 21.52.

Spectrophotometric Studies.—The reflectance spectra of the solids were determined using a Beckman Model DU Spectrophotometer with a diffuse reflectance attachment. Powdered MgO was used as the standard. The reproducibility of the surfaces was 1 to 2% according to the agreement between reflectance spectra of duplicate samples. The samples were exposed to the unfiltered radiation from a 140 watt high pressure mercury source at a distance of 7.5 cm. for 20 hr., and the reflectance spectra were again determined. Before irradiation broad absorption peaks were found at 325 mμ and at 450 mμ for [Co en$_3$]X$_3$, where X represents F, Cl, Br or I. After the specified period of irradiation, new absorption peaks appeared at higher wave lengths. Thus for [Co en$_3$]Cl$_3$ a broad absorption was found between 650 to 700 mμ with a shoulder at about 625 mμ.

For quantitative study, the following procedure was followed with each of the halides. From a micropipet 0.02 ml. of an aqueous solution of the halide was deposited at the center of a Whatman No. 1 filter paper of 11 cm. diameter. The spot was dried and then exposed to the light from a 140-watt high-pressure mercury lamp at 7.5 cm. for a fixed time. The sample was next eluted using circular paper chromatographic techniques employing an acetone-hydrochloric acid–water mixture (87:8:5 parts by volume). The tris-(ethylenediamine) compounds were, except for the iodide, quite unaffected by the solvent, but the decomposition product was carried out of the central spot and developed a blue ring just behind the solvent front. In the case of [Co en$_3$]I$_3$ some migration was noted, but the blue band was distinctly separated from the unchanged iodide. The band of eluted product was cut out and extracted several times with small amounts of a solution made by dissolving 75 g. of ammonium thiocyanate in 100 ml. of water and adding acetone to a total volume of 250 ml. The cobalt was then determined spectrophotometrically using a wave length of 625 mμ. The accuracy of the chromatographic method was checked in two ways. First, there were deposited on filter paper 0.1-ml. samples of a standard Co(II) solution containing 1 mg./ml. of solution. After drying, the deposits were chromatographed as described above, and the blue Co(II) ring was extracted from the paper and determined spectrophotometrically. The average of five determinations yielded a value of 98.8 ± 1.8 μg. of Co(II) compared to the actual value of 100.0 μg.

Also, test sheets of [Co en$_3$]Cl$_3$ were prepared by depositing 0.02 ml. of 0.466 *M* solution of the complex on filter paper. Two sets of four sample sheets were irradiated, one set for 25 minutes and the other set for 45 minutes. After irradiation the amount of Co(II) formed was determined to be 41.0 ± 1.5 μg. for 25 minutes and 54.5 ± 1.0 μg. for 45 minutes of exposure.

An aqueous solution of solid irradiated [Co en$_3$]Cl$_3$ was found to yield a positive Co(II) test when treated with NH$_4$SCN in the presence of a large excess of acetone. The absorption spectrum of this solution was found to be the same as that of a standard CoCl$_2$ test solution also treated with the thiocyanate reagent.

The completely photolyzed product dissolved readily in water to give an orange-brown solution which upon evaporation gave a green crystalline residue. The addition of HCl to the orange-brown solution produced a green colored solution. The absorption spectrum of the photolysis product in water was still increasing at 220 mμ and tapered off at about 600 mμ. The molar extinction coefficient was 390 at 300 mμ. In 12 *N* HCl solution the absorption in the ultraviolet was unchanged, but three peaks appeared in the visible at 625, 665 and 690 mμ. The molar extinction coefficients were 175, 277 and 295, respectively. Peaks were found at the same wave lengths for CoCl$_2$ in 12 *N* HCl with molar extinction coefficients of 345, 525 and 565.

Mass Spectrometer Studies.—A sample of [Co en$_3$]Cl$_3$ was placed in a Vycor tube which was then attached to the mass spectrometer. The sample was further dried by placing the Vycor tube in boiling water while the system was under high vacuum. After exposure to 2537 Å. radiation for 20 hr. the liberated gas was found to give the spectrum of ammonia with peaks corresponding to mass numbers 17, 16 and 15.

Magnetic Susceptibility Measurements.—The magnetic susceptibility of the completely photolyzed solid product of [Co en$_3$]Cl$_3$ was measured by means of a conventional Gouy balance. In contrast to the diamagnetic starting material, the substance was paramagnetic with a gram susceptibility of 11.3 × 10^{-6} c.g.s. units. After making suitable corrections for the diamagnetism of the atoms, this corresponds to a moment of 2.94 Bohr magnetons per cobalt atom. Another solid sample which was only 30% photolyzed according to magnetic measurements was extracted with water and recrystallized five times from HCl solution to isolate the pure green compound. The magnetic moment of this solid sample was 2.96 Bohr magnetons.

The magnetic susceptibility of the green solid dissolved in water was determined and corresponded to a moment of 3.2 Bohr magnetons per cobalt atom. In concentrated HCl the moment was again 3.2 Bohr magnetons. These values were calculated by assuming the Wiedemann additivity law was valid and based on a molecular weight of 311.5.

Infrared Spectra.—The infrared spectra of *cis*-[Co trien Cl$_2$]Cl and [Co en$_3$]Cl$_3$ before and after irradiation were compared using a Perkin–Elmer double beam, recording spectrometer. The samples were prepared for examination by pressing the solids into KBr discs. The results are indicated in Table II.

Polarographic Analysis.—A Leeds and Northrup "Electro-Chemograph" was used for the polarographic determination of the oxidation state of the cobalt in the green product obtained by irradiation of [Co en$_3$]Cl$_3$. A conventional cell, consisting of a dropping mercury electrode and a mercury pool anode, was employed. The supporting electrolyte was 1.0 *M* Na$_2$SO$_4$ and no maximum suppressant was used.

The green product showed two reduction waves, at approximately −0.47 v. and −1.22 v., *vs.* Hg, corresponding to the reduction of Co(III) → Co(II) and Co(II) → Co, respectively. The diffusion current ratio of the second to the first wave was found to be 2.10. This is close to the expected value of 2.00 for the reduction of a Co(III) complex if equal diffusion coefficients for both reduced species are assumed. The Co(II) reduction wave exhibits no maximum in contrast to that observed for [Co en$_3$]Cl$_3$. For the latter, $E_{1/2}$ values equal −0.534 and −1.37 v. *vs.* Hg. This maximum appears to be characteristic for ethylenediamine complexes and is not affected by the common suppressants.[12] *cis*-[Co trien Cl$_2$]Cl has reduction waves at −0.15 and −1.38 v. *vs.* Hg. Addition of Co(II) to the *cis* compound caused no change in the ratio of the two wave heights until more than 100% Co(II) was added. Similar results were reported previously for [Co (NH$_3$)$_6$]Cl$_3$.[13]

Chemical Analyses.—A sample of the [Co en$_3$]Cl$_3$ was spread over the bottom of a 10 cm. petri dish and exposed to the unfiltered radiation from the high pressure mercury lamp. The sample was removed frequently for grinding to expose a fresh surface. The complete analysis of the photolysis product gave Co = 1.0, C = 5.72, N = 3.98, H = 18.1, Cl = 2.92; these values correspond closely to the formula CoC$_6$N$_4$H$_{18}$Cl$_3$. It may be noted that all of the chloride ions could be precipitated readily from the brown solution in water.

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(11) N. Bjerrum and J. P. McReynolds, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 217.

(12) J. B. Willis, J. A. Friend and D. P. Mellor, THIS JOURNAL, **67**, 1680 (1945).

(13) H. A. Laitinen, A. J. Frank and P. Kivalo, *ibid.*, **75**, 2865 (1953).

Discussion

Hexammine Cobalt(III) Halides.—When solid samples of the halide salts of [Co $en_3]^{+3}$ were exposed for 20 hr. to radiation from a mercury lamp, visible color changes occurred. These are summarized together with similar compounds in Table I.

TABLE I

COBALTAMMINES FOUND PHOTOSENSITIVE TO 2537 Å. IN THE SOLID STATE

Compound	Color change
[Co $en_3]F_3 \cdot 6HF \cdot 2H_2O$[a]	Yellow to red-brown
[Co $en_3]Cl_3$	Orange to green
[Co $en_3]Br_3$	Orange to brown-green
[Co $en_3]I_3$	Orange to brown
[Co $pn_3]Cl_3$	Orange to green
$[Co(NH_3)_6]Cl_3$	Orange to brown-green
[Co_2 $trien_3]Cl_6$	Orange to green
cis-[Co trien Cl_2]Cl	Violet to green

[a] The red product obtained by 2537 Å. radiation upon irradiation with shorter wave lengths (hydrogen discharge lamp) changes to green.

The green colors of the irradiated chlorides of [Co $en_3]^{+3}$ and [Co $pn_3]^{+3}$ were thought to indicate a mixture of blue $CoCl_2$ and the orange of the original complex; the Co(II) resulted from a photoreduction process. A comparison of the absorption spectra of the photolysis product in water and in HCl with those of $CoCl_2$, also in these solvents, does show the similarities one would expect if Co(II) were contained in the product. Further, the reflectance spectrum of the solid irradiated [Co $en_3]Cl_3$ exhibits the same absorption peaks in the region 600 to 700 mμ as does Co(II) in HCl.

Although the original compounds were unaffected by the chromatographic elution process, it was found that the photolysis products upon elution gave positive tests for Co(II). The amount of Co(II) carried by the eluent was increased with the time of irradiation. The rate of the photolysis reaction based on the amount of Co(II) determined chromatographically agrees quantitatively with that based on the change in the reflectance spectrum; the latter was measured at 675 mμ. The rate was rapid initially until about 5% of the product had formed. The reaction then continued at about one-third the initial rate.

Using the elution process to separate the photolysis product from the remaining starting material, it was possible to check the amount of product at successive reaction times for each of the hexamminecobalt(III) halides. Upon plotting the rates of the solid photolysis reactions for the various substances listed in Table I, it was found that the rates for the halides were in the order F > Cl > Br > I and for the ligands in the case of the chlorides $[Co(NH_3)_6]Cl_3 >$ [Co $en_3]Cl_3 >$ [Co $pn_3]Cl_3$.

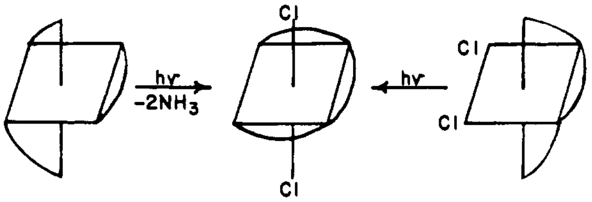
Tris-(ethylenediamine)-cobalt(III) Chloride.—The order of sensitivity of the various halides is just the reverse of that which would be predicted on the basis of electron transfer from the halide, but, if it is assumed that the rate is controlled by the mobility of the halide ion in the crystal, the smaller the halide the more rapid would be the reaction. Analyses with AgCl precipitation showed three chloride ions per cobalt atom after photolysis of [Co $en_3]Cl_3$. Further, the data obtained with the mass spectrometric analysis of the products from the photolysis reaction gave no evidence of mass numbers 35, 71 or 36, corresponding to Cl, Cl_2 or HCl, respectively. Ammonia was the only gaseous product identified, and chemical analysis indicated two molecules of NH_3 eliminated per atom of cobalt. Thus halide oxidation is not involved in the photolysis reaction.

The infrared absorption studies of photolyzed [Co $en_3]Cl_3$ indicate considerable decrease of the absorption peaks corresponding to primary amine, as shown in Table II. The spectrum of the photolysis product of *cis*-[Co trien Cl_2]Cl in the infrared, as well as in the visible and ultraviolet, was almost identical to that of the photolysis product of [Co $en_3]Cl_3$. For both products a new peak was observed at 6.11 μ which may be associated with carbon–nitrogen double bonding.[14]

These results were first interpreted to indicate the formation of triethylenetetramine by elimination of two moles of ammonia from three moles of ethylenediamine

$$3NH_2CH_2CH_2NH_2 \xrightarrow{h\nu} NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2 + 2NH$$

The possibility that this could occur in a single molecule of [Co $en_3]Cl_3$ to yield *trans*-[Co trien Cl_2]Cl received some support from the observation that the purple *cis*-[Co trien Cl_2]Cl gave on exposure to 2537 Å. radiation a similar green product. When this transformation was carried out in the mass spectrometer, no loss of ammonia was observed. The reflectance and absorption spectra of this green product were the same as that of the photolyzed [Co $en_3]Cl_3$. Thus the interpretation given by the following equation seemed to be reasonable.



However, this mechanism does not account for the presence of Co(II). The appearance of paramagnetic susceptibility as photolysis proceeds indicates the conversion of diamagnetic Co(III) to Co(II), and the analytically determined ratio of three precipitatable chloride ions per cobalt atom suggests that some species other than halide is oxidized. The paramagnetic susceptibility might be due to a very unusual dsp^2 complex of Co(III) with two unpaired electrons.[15] However, the absorption spectrum in HCl and the qualitative tests for Co(II) indicate that this is not the case. The

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(14) D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **78**, 1139 (1956), and references listed therein.

(15) D. Klein, C. W. Moeller and R. Ward, Abstracts, 130th Meeting of the A. C. S., September, 1956, page 45-R.

TABLE II

INFRARED ABSORPTION PEAKS FOR [Co en_3]Cl_3 AND THE PHOTODECOMPOSITION PRODUCTS

Compound	Absorption peak wave length (μ)	Assignment
[Co en_3]Cl_3[a]	3.25	N–H stretching
	6.37	N–H bending
	11.17	Unassigned
	11.35	Unassigned
	12.33–12.70	N–H rocking
	14.15	Unassigned
Photolysis products of [Co en_3]Cl_3 and of *cis*-[Co trien Cl_2]Cl	3.25[b]	N–H stretching
	6.11[d]	C═N (?) or coördinated H_2O
	6.25[b,c]	N–H bending
	6.60[d]	Unassigned
	7.21[d]	Unassigned
	9.14[d]	Unassigned
	9.85[d]	Unassigned
	10.42[d]	Unassigned
	11.17[b]	Unassigned
	11.35[b]	Unassigned
	12.33[b]	Unassigned
	12.78[b,c]	N–H rocking
	14.15[b]	Unassigned

[a] Several other prominent peaks present were found also with ethylenediamine hydrochloride. [b] These peaks were all considerably lower than those of [Co en_3]Cl_3 [c] Indicates a shift of absorption peak. [d] Not found in [Co en_3]Cl_3.

absorption spectra, magnetic studies and polarographic analyses all indicate that Co(II) is not produced quantitatively. The results of the spectral and magnetic measurements can be explained if it is assumed that 50% of the Co is in the +2 state. The polarographic data are not in disagreement with this since Co(II) is not easily detected in these systems as discussed in the Experimental section and in reference 13. The reflectance spectrum indicates that the Co(II) is present as the tetra-coördinated anion, and this interacts with the hexacoördinated Co(III) cation to stabilize the system. When eluted, Co(II) is separated from Co(III), and the Co(III) then undergoes further photolysis when irradiated. That the mechanism is of this nature is indicated by some ion-exchange studies. A 9 *N* HCl solution of photolyzed [Co en_3]Cl_3, which had been irradiated in the solid state, was passed through a column of Dowex 1-X10 anion-exchange resin and the solution separated into a blue fraction containing Co(II) and a yellow fraction. The yellow fraction, when crystallized, was unstable thermally, converting to a green solid at 110°. In HCl solution the yellow fraction changed to a green solution on standing. Under these conditions [Co en_3]Cl_3 is stable;, also, the yellow product does not have the same absorption spectrum as that of [Co en_3]Cl_3. It would appear that two or more products result from the irradiation of [Co en_3]Cl_3 in the solid state.

In an attempt to prepare *trans*-[Co trien Cl_2]Cl Basolo[10] concluded that the green product obtained was probably a mixture of $CoCl_2$ and [Co_2 $trien_3$]-Cl_6. This decision was based on the change of color from green to orange upon addition of water and the high per cent. of ionizable chloride. Although these observations are just those found for the photolysis product of [Co en_3]Cl_3, the fact that [Co_2 $trien_3$]Cl_6 also is photolyzed readily excludes the possibility that the green product is the mixture proposed by Basolo. Following the method described by Basolo for the attempted preparation of *trans*-[Co trien Cl_2]Cl, a green material was isolated which yielded an absorption spectrum similar to that of photolyzed [Co en_3]Cl_3 and not similar to that of [Co_2 $trien_3$]Cl_6.

Preliminary irradiation studies of solutions of some of those compounds studied in the solid state have been made. It has been found that irradiation of a solution of [Co en_3]Cl_3 gives a reddish-orange product which is diamagnetic both as a solid and in solution. A solution of this product in concentrated HCl is free of the characteristic Co(II) absorption spectrum. However, upon standing in the acid for 24 hr. the original substance is converted to a green product; [Co en_3]Cl_3 is stable under these conditions. The absorption spectrum of this material indicates the presence of Co(II). When *cis*-[Co trien Cl_2]Cl is irradiated in aqueous solution, the color of the solution changes from the original purple to reddish-orange. The solid product recovered by evaporation of such solutions is green in color. Apparently there is isolated in the solution irradiation of [Co en_3]Cl_3 an intermediate which is not obtained in the irradiation of solid [Co en_3]Cl_3, solid *cis*-[Co trien Cl_2]Cl or *cis*-[Co trien Cl_2]Cl in solution. The possibility of such a stepwise mechanism was indicated in the photolysis of [Co en_3]F_3·6HF·$2H_2O$ when a red intermediate was obtained initially with 2537 Å. radiation, and upon further irradiation with shorter wave lengths (from a hydrogen discharge lamp) this changed to green.

Further studies of the photolysis of the compounds reported here, as well as other related compounds, in the solid state and in aqueous solution are now underway. It is expected that this work will allow the identification of the irradiation products and thus make possible the elucidation of the photolysis mechanisms. From the present work it may be concluded that: (1) the order of photosensitivity of the halides of [Co en_3]$^{+3}$ in the solid state is F > Cl > Br > I. (2) The order of photosensitivity of the chloride salts of three Co(III) ammine complexes in the solid state is [Co-$(NH_3)_6$]$^{+3}$ > [Co en_3]$^{+3}$ > [Co pn_3]$^{+3}$. (3) The irradiation of [Co en_3]Cl_3 and *cis*-[Co trien Cl_2]Cl in the solid state leads to the same product. (4) For [Co en_3]Cl_3 the photolysis reactions differ in solution and in the solid state. (5) The photolysis product contains a 1:1 ratio of Co(III):Co(II), and it is stabilized either as a polynuclear complex or by cation-anion interaction. The Co(III) complex differs from [Co en_3]Cl_3 both in stability and absorption spectrum. (6) The oxidized species has not been identified. Analyses show that it is not halogen, and the presence of three ionizable halide ions per cobalt atom indicates the formation of an amine hydrochloride. (7) The data may be interpreted to indicate that there is formed a binuclear structure containing one atom each of Co(II) and Co(III) linked by the polyammine condensation product of ethylenediamine. One nitrogen atom is coördinated with HCl.

Acknowledgment.—The authors wish to thank Drs. J. C. Bailar, Jr., R. W. Parry, F. Basolo and L. J. Edwards for supplying a number of coördination compounds which were used in the initial stages of this study. They are also indebted to Mr. J. McNally for much of the analytical and infrared work included in this paper and to Mr. R. Strakna for the mass spectrometric data.[16]

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[16] Material supplementary to this article has been deposited as Document number 5343 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. This material includes figures showing the reflectance spectra of the solid halides before and after irradiation, the absorption spectra of the chloride in aqueous solution and in 12 *N* HCl solution and the decomposition rate curves. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

Storrs, Conn.

[Contribution from the Departments of Chemistry of the Massachusetts Institute of Technology and Harvard University]

The Structure and Bonding of Cyclopentadienylthallium and Bis-cyclopentadienylmagnesium

By F. A. Cotton and L. T. Reynolds

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The infrared spectra of gaseous C_5H_5Tl and $(C_5H_5)_2Mg$ in the C–H stretching region are reported. They are in accord with C_{5v} molecular symmetry for C_5H_5Tl and a sandwich configuration for $(C_5H_5)_2Mg$. That the bonding in C_5H_5Tl is essentially ionic is suggested by chemical evidence, the magnitude of the overlap integrals involved in a molecular orbital treatment of the bonding and the ionization potentials. The concept of ionic bonding in sandwich molecules is discussed with special reference to $(C_5H_5)_2Mg$.

I. Cyclopentadienylthallium(I)

The compound C_5H_5Tl reported by E. O. Fischer[1] has properties so unusual that an inquiry into the structure of the molecule seemed of considerable interest. Its existence is in itself striking since no thallous alkyls are known except as postulated reaction intermediates.[2] It is in fact quite stable, as evidenced by the facts that it is prepared in an aqueous medium, that it can be sublimed *in vacuo* and that it darkens only slowly on standing in air or light. Although Fischer reported it to be insoluble in common organic solvents, we have found it to react with several. It is practically insoluble in tetrahydrofuran, but does not seem to react with it. Since the methyl derivative is quite reactive the stability of solid C_5H_5Tl may be in part due to a very stable lattice packing as has been suggested by Fischer. These facts suggested that the compound was unlikely to be an alkylthallous compound containing a Tl–C σ-bond; instead a half-sandwich configuration seemed possible. Furthermore it appeared that a clear decision could be made between these possibilities by a study of the infrared spectrum. Since the substance is insoluble in or reactive toward suitable solvents, the spectra were taken on the gaseous substance in a hot cell. In order to obtain a strong spectrum in the C–H stretching region, which in itself provides necessary and sufficient information, a cell having glass windows was used as described below. The spectrum is shown in Fig. 1.

A molecule of the alkyl type would have symmetry C_s, and a fairly complex spectrum in the C–H region would be expected. There would be five infrared active C–H stretching modes due to both H–C(saturated) and H–C(olefinic) bonds. The half-sandwich configuration on the other hand would have the relatively high symmetry C_{5v} and there would be three C–H stretching modes of symmetry types A_1, E_1 and E_2 of which only the first two could be infrared active. We might anticipate that they would be in the same general range as the C–H stretches for other sandwich molecules such as $(C_5H_5)_2Fe$ (3109 cm.$^{-1}$), $(C_5H_5)_2Ni$ (3107 cm.$^{-1}$), $(C_5H_5)_2Mn$ (3101 cm.$^{-1}$), $(C_5H_5)_2Mg$ (3095)[3] and for benzene (3099 cm.$^{-1}$). It is also unlikely that the two vibrations would be coincident. Actually as Fig. 1 shows only one sharp band at 3101 cm.$^{-1}$ is observed in the range 2700–3300 cm.$^{-1}$. This is not, however, inconsistent with the C_{5v} structure for the following reason.

The A_1 mode is a synchronized stretching of all 5 C–H coördinates which would absorb in the infrared only in proportion to the change in dipole moment produced in the *z*-direction (the C_5 axis and the *z*-axis are co-linear). In the free planar symmetrical C_5H_5 ring the symmetry would be D_{5h} and the corresponding totally symmetric C–H stretching mode (A_2) would be inactive in the infrared since no change in the *z*-component of dipole moment could be produced by such a motion. When bound to the Tl atom this mode becomes—in principle—infrared active because of the lower symmetry. If the bound ring remains perfectly planar the mode will still be inactive unless there is appreciable coupling of the C–H stretching with a change of some other coördinate so that the true normal vibration does result in a change of dipole moment in the *z*-direction. Such coupling is probably slight however because of the great disparity

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[1] E. O. Fischer, *Angew. Chem.*, **69**, 207 (1957).

[2] *Cf.* G. E. Coates, "Organo-Metallic Compounds," Methuen and Co. Ltd., London, 1956, pp. 95–102.

[3] Unpublished data of L. T. Reynolds, G. Wilkinson, and F. A. Cotton on the *gas phase* spectra of these molecules.