carbon bridges is a novel effect which merits further investigation.

A few attempts were made to prepare (diphos)[$Mo(CO)_2(COR)(C_5H_5)]_2$ derivatives with other types of R groups. Reactions of $CF_3Mo(CO)_3C_5H_5$ and of $(CH_3)_3SnMo(CO)_3C_5H_5$ with the very reactive $(CH_3)_2PCH_2CH_2P(CH_3)_2$ in acetonitrile solution failed to give any precipitate or other evidence of forming a (diphos)[$Mo(CO)_2(COR)(C_5H_5)]_2$ derivative. This is consistent with all previous data which repeatedly indicate the inability for both trifluoromethyl and trialkyltin derivatives of transition metals to undergo carbon monoxide insertion reactions. The reaction between $CH_3CO_2CH_2Mo(CO)_3C_5H_5$ and $(CH_3)_2PCH_2CH_2P(CH_3)_2$ in acetonitrile solution gave a small quantity of a yellow precipitate indicated by its infrared spectrum to be a $C_5H_5Mo(CO)_2LR$ derivative (ν(CO): 1966 and 1882 cm^{-1}) but exhibiting no acyl or ketonic ν(CO) frequency and giving analyses not corresponding to a likely $CH_3CO_2CH_2$ derivative.

In an attempt to prepare a tungsten derivative analogous to the molybdenum derivatives reported in Table I, the reaction between $CH_3W(CO)_3C_5H_5$ and $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ in acetonitrile solution was investigated. After 4 days at room temperature, the infrared spectrum in the ν(CO) region indicated the presence of unchanged $CH_3W(CO)_3C_5H_5$. This is a further example of the lower reactivity of a tungsten derivative relative to the analogous molybdenum derivative. When the mixture of $CH_3W(CO)_3C_5H_5$ and $(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2$ in acetonitrile was boiled under reflux for 14 days, a mixture was obtained which deposited a yellow precipitate. The low oxygen analysis and the absence of an acyl ν(CO) infrared frequency around 1600 cm^{-1} indicated this yellow compound to be the methyl derivative (Pf≡Pf)[$W(CO)_2(CH_3)(C_5H_5)]_2$ rather than an acetyl derivative.

The reaction between the $RMo(CO)_3C_5H_5$ derivatives (R = methyl or benzyl) and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (cPf═Pf) failed to give a (cPf═Pf)[$Mo(CO)_2(COR)(C_5H_5)]_2$ derivative. The same yellow crystalline substance was obtained from either the methylmolybdenum or the benzylmolybdenum derivative and was shown by analyses to be (cPf═Pf)$_2Mo(CO)_2$. The presence of two infrared ν(CO) frequencies of approximately equal relative intensities (1878 and 1810 cm^{-1}) in this complex indicates the two carbonyl groups to be in relative *cis* positions as expected. The reactions between $RMo(CO)_3C_5H_5$ and the excellent chelating agent cPf═Pf thus result in the removal of not only the R group but also the π-cyclopentadienyl ring from the molybdenum atom by the chelating ditertiary phosphine. A related example of the cleavage of the π-cyclopentadienyl ring from the halides $C_5H_5Mo(CO)_3X$ upon reactions with phosphines has been reported.[19] The compound *cis*-(cPf═Pf)$_2Mo(CO)_2$ is a new one not prepared in the previous study of metal carbonyl complexes of cPf═Pf.[20] An alternate preparation of *cis*-(cPf═Pf)$_2Mo(CO)_2$ utilizes the displacement of the two 1,3-cyclohexadiene ligand in (1,3-$C_6H_8)_2Mo(CO)_2$ with two molecules of the chelating ditertiary phosphine. Abel, Bennett, and Wilkinson[21] first reported a similar synthesis of *cis*-$(R_3P)_3Mo(CO)_3$ derivatives by the displacement of the cycloheptatriene ligand in $C_7H_8Mo(CO)_3$ with the three R_3P ligands; the present work appears to represent the first application of this synthetic technique to a (diene)$_2M(CO)_2$ complex.

The isolation of a (diphos)$_2Mo(CO)_2$ derivative rather than the usual (diphos)[$Mo(CO)_2(COR)(C_5H_5)]_2$ from the reactions of $RMo(CO)_3C_5H_5$ derivatives with *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ suggests that this ditertiary phosphine cannot act as a bridging ligand although it is now well established[20,22] to be an excellent chelating ligand. The inability for *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ to act as a bridging ligand may be attributed to the rigidity of the carbon–carbon double bond forcing the phosphorus atoms to remain so close together in *cis* positions that serious steric interference would occur between other ligands on the two metal atoms being bridged. By contrast, the free rotation around the carbon–carbon single bond in the link between the two phosphorus atoms in the likewise chelating ditertiary phosphines $R_2PCH_2CH_2PR_2$ permits the phosphorus atoms to assume transoid positions in bridging complexes thereby eliminating steric interference between other ligands on the two metal atoms being bridged.

Acknowledgment.—We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1435-68. We are also indebted to the Alfred P. Sloan Foundation for support of P. N. K. during the period of his contribution to the project.

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Mixed-Ligand Complexes of Triethylenetetramine and Ethylenediamine with Cobalt(III)

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Received February 3, 1969

Octahedral complexes containing a linear tetramine ligand can exist in nine different geometrical and optical isomers (Figure 1). In the case of triethylenetetramine disubstituted complexes of cobalt(III), most of these possibilities have been realized. Sargeson and Searle[1]

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(1) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965); **6**, 787 (1967).

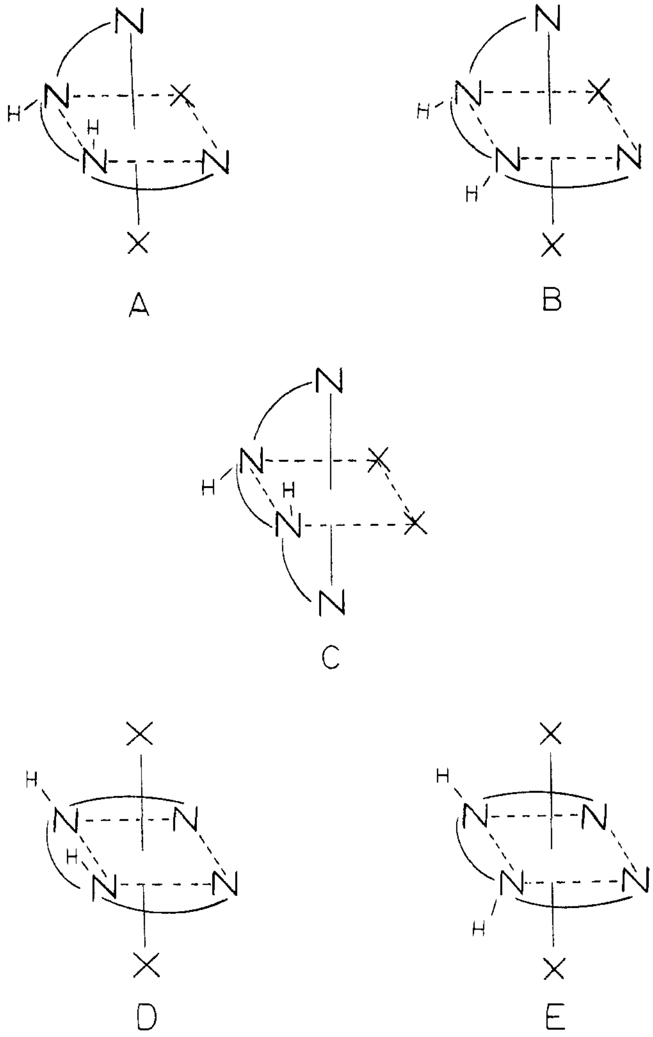

Figure 1.—Isomers of octahedral complexes containing triethylenetetramine: (A) Δ-β-(*RR*); (B) Δ-β-(*RS*); (C) Λ-α-(*RR*); (D) *trans*-(SR); (E) *trans*-(SS). A, B, C, and E are optically active.

have isolated dichloro complexes for Λ-α-(*RR*), Δ-α-(*SS*), Λ-β-(*SS*), and Δ-β-(*RR*) isomers. Sargeson, *et al.*,[2] later reported isolation of the *trans*-(*SS*) and *trans*-(*RR*) dichloro complexes as well as detection of Λ-β-(*SR*) and Δ-β-(*RS*) diaquo complexes. Basolo[3] prepared a complex Co(trien)(en)$^{3+}$ (trien = triethylenetetramine, en = ethylenediamine) but did not determine its geometry. We now report the preparation of α- and β-Co(trien)(en)$^{3+}$ and the resolution of the compounds into their optical isomers.

Experimental Section

The absorption spectra were measured on a Beckman Model DBG recording spectrophotometer using matched 1-cm cells. ORD curves were recorded with a Cary Model 60 spectropolarimeter using approximately 0.07% solutions in a 0.5-dm cell. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany.

Preparation of α- and β-[Co(trien)Cl$_2$]Cl.—These were prepared according to the directions of Sargeson and Searle.[1]

Preparation of α-[Co(trien)(en)]I$_3$.—Finely powered α-[Co(trien)Cl$_2$]Cl (14 g, 0.045 mol) was suspended in 100 ml of absolute ethanol containing 3.3 g (0.055 mol) of ethylenediamine and refluxed with mechanical stirring until the suspension turned orange (approximately 3 hr). After cooling, crude α-[Co(trien)(en)]Cl$_3$ was removed by filtration, washed with ethanol, and then quickly dissolved in a small volume of warm water and filtered to remove unreacted α-[Co(trien)Cl$_2$]Cl. The filtrate was diluted to 70 ml and warmed on a steam bath. To this solution was added 21 g (0.135 mol) of NaI in 40 ml of warm water. After cooling overnight α-[Co(trien)(en)]I$_3$ was removed by filtration, washed with ice-cold water, ethanol, and ether, and recrystallized once from hot water. *Anal.* Calcd for $CoC_8N_6H_{26}I_3$: C, 14.86; H, 4.02; N, 13.00. Found: C, 14.81; H, 4.19; N, 12.87.

Preparation of β-[Co(trien)(en)]I$_3$.—This compound was prepared as was α-[Co(trien)(en)]I$_3$ using β-[Co(trien)Cl$_2$]Cl in place of α-[Co(trien)Cl$_2$]Cl. *Anal.* Calcd for $CoC_8N_6H_{26}I_3$: C, 14.86; H, 4.02; N, 13.00. Found: C, 15.09; H, 4.16; N, 13.19.

The perchlorate salts of each of the above compounds can be prepared by stirring a solution of the iodide salt with an equivalent quantity of $AgClO_4$, removing the AgI, adding concentrated $HClO_4$ and an equal volume of ethanol to the solution, and cooling.

Preparation of β-[Co(trien)(en)]I$_3$ in Aqueous Solution.—To a solution of α- or β-[Co(trien)Cl$_2$]Cl (3.1 g, 0.01 mol) in 20 ml of water on a steam bath was added ethylenediamine (0.6 g, 0.01 mol). Heating was continued for 30 min after which excess NaI was added. After cooling, the yellow-orange product was filtered, washed with ethanol and ether, and recrystallized from hot water. The product was spectrophotometrically identical with β-[Co(trien)(en)]I$_3$.

Resolution of α-[Co(trien)(en)]I$_3$.—α-[Co(trien)(en)]I$_3$ (8.0 g, 0.0123 mol) was dissolved in 150 ml of hot water. Five grams (0.0123 mol) of Ag(+)SbO(tart) was added slowly to the solution and stirring and heating were continued for 15 min. Silver iodide was then removed by filtration. The filtrate was cooled in the refrigerator for 24 hr after which the diastereoisomer (+)-α-[Co(trien)(en)]I(SbO(+)$C_4H_4O_6$)$_2$ which crystallized was filtered off, washed with a little ice-cold water, ethanol, and acetone, and recrystallized from hot water; $[\alpha]_{546}$ 295° and $[M]_{546}$ 2840°. *Anal.* Calcd for $CoC_{16}H_{34}IN_6O_{14}Sb_2$: C, 19.93; H, 3.53; N, 8.72. Found: C, 20.00; H, 3.78; N, 8.34.

The diastereoisomer was stirred in the dark at room temperature for 1 hr with an equivalent quantity of $AgNO_3$. Silver iodide and AgSbO(tart) were removed and the solution was checked for excess Ag$^+$ ions by the addition of NaI. Excess NaI was added and the solution was cooled. The crystals of (+)-α-[Co(trien)(en)]I$_3$[4] were filtered, washed with ethanol and ether, and air dried; $[\alpha]_{546}$ 293° and $[M]_{546}$ 1890°. *Anal.* Calcd for $CoC_8N_6H_{26}I_3$: C, 14.86; H, 4.02; N, 13.00. Found: C, 14.70; H, 4.14; N, 13.21.

The filtrate from the formation of (+)-α-[Co(trien)(en)]I-[SbO(tart)]$_2$ was evaporated to 15 ml. Impure solid racemate was removed and discarded. The solution was then treated with enough $AgClO_4$ to precipitate all of the AgI and AgSbO(tart) which was removed. After evaporation of the solution to 5 ml, concentrated perchloric acid (5 ml) and ethanol (10 ml) were added. Upon cooling, (−)-α-[Co(trien)(en)](ClO$_4$)$_3$ crystallized, was filtered, washed with ethanol and ether, and air dried; $[\alpha]_{546}$ −307° and $[M]_{546}$ −1820°. *Anal.* Calcd for $CoC_8N_6H_{26}Cl_3O_{12}$: C, 17.03; H, 4.61; N, 14.90. Found: C, 16.89; H, 4.70; N, 14.84.

Resolution of β-[Co(trien)(en)]I$_3$.—β-[Co(trien)(en)]I$_3$ (4.7 g, 0.0073 mol) was dissolved in 60 ml of warm water and Ag(+)-SbO(tart) (5.8 g, 0.0156 mol) was added. Heating and stirring were continued for 15 min after which AgI was removed. Crystallization of the diastereoisomer (+)-β-[Co(trien)(en)]I(SbO-(+)$C_4H_4O_6$)$_2$ was initiated by scratching the sides of the beaker. The solution was then allowed to stand at room temperature for 24 hr. The diastereoisomer was filtered, washed with a

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[2] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967).

[3] F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).

[4] (+) or (−) refers to the sign of the dominant Cotton effect derived from the octahedral $^1A_{1g} \rightarrow {}^1T_g$ transition.

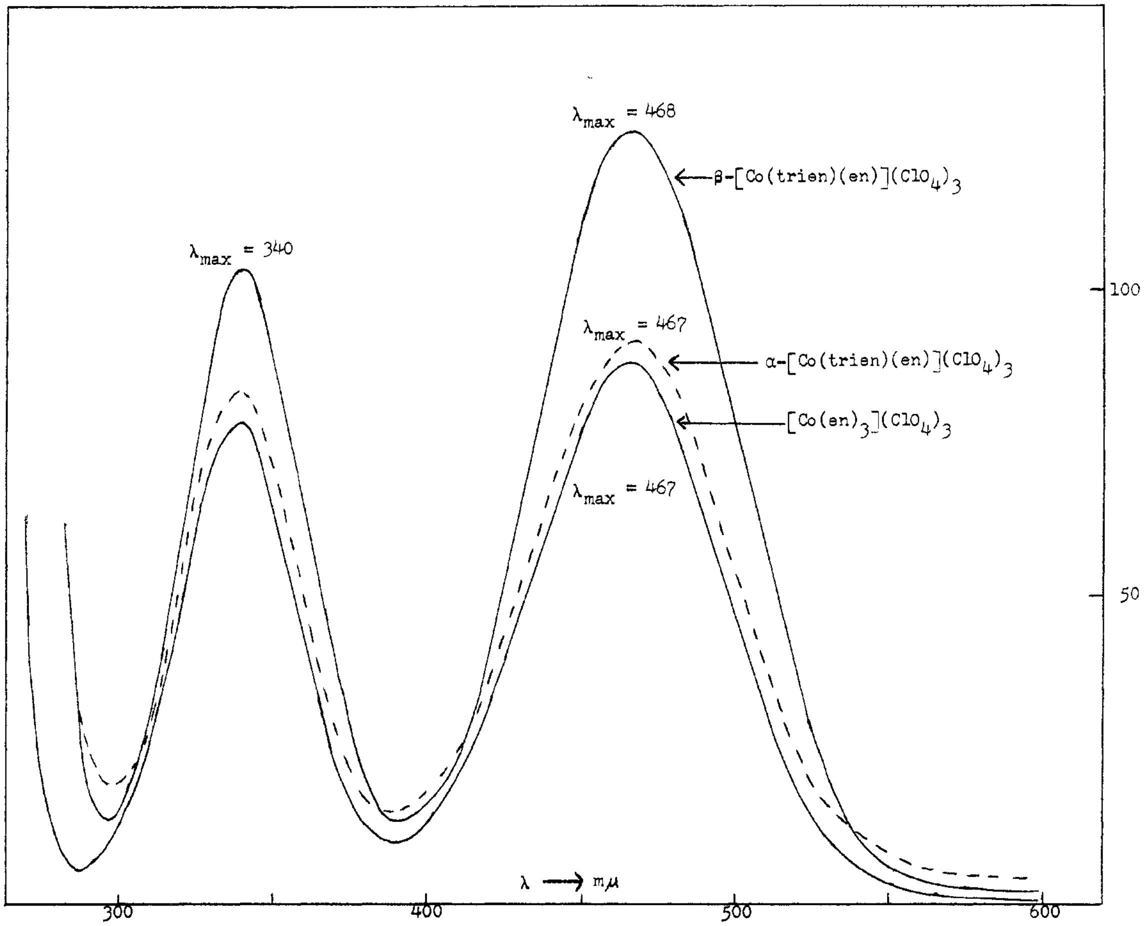

Figure 2.—Absorption spectra for $[Co(en)_3](ClO_4)_3$, α-$[Co(trien)(en)](ClO_4)_3$, and β-$[Co(trien)(en)](ClO_4)_3$.

little cold water, and recrystallized by dissolving it in a large volume of warm water and slowly evaporating the solution under a stream of air at room temperature. The other antimer (−)-β-$Co(trien)(en)^{3+}$ was not obtained in pure form since on evaporation of the filtrate from formation of the disasteroisomer an oil formed; $[\alpha]_{546}$ 250° and $[M]_{546}$ 2410°. *Anal.* Calcd for $CoC_{16}H_{34}IN_6O_{14}Sb_2$: C, 19.93; H, 3.53; N, 8.72. Found: C, 20.21; H, 3.71; N, 8.85.

(−)-β-(*SS*)-$[Co(trien)(en)]I_3$ was prepared in analogous fashion to the conversion of the α diastereoisomer to its idodide salt; $[\alpha]_{546}$ 220° and $[M]_{546}$ 1420°. *Anal.* Calcd for $CoC_8H_{26}N_6I_3$: C, 14.86; H, 4.02; N, 13.00. Found: C, 15.09; H, 4.12; N, 12.97.

Discussion

The complex $Co(trien)(en)^{3+}$ was prepared by Basolo[3] by refluxing $[Co(trien)Cl_2]Cl$ and ethylenediamine in ethanol. Basolo's attempted resolution of the compound through the bromide *d*-tartrate and through the α-bromo-π-camphorsulfonate failed because of the great solubility of the complex. The same preparative route was used in this work starting with pure α- or β-$[Co(trien)Cl_2]Cl$ to obtain pure α- or β-$Co(trien)(en)^{3+}$, respectively. If the same reactions are carried out in aqueous solution, the only product formed is the β isomer. Exclusive formation of the β isomer in aqueous solution is probably a consequence of the isomerization of the reacting cobalt species to the β form before coordination of ethylenediamine takes place. Similar results have been noted in amino acid complexes where only the β isomers of $Co(trien)(aa)^{2+}$ (aa = amino acid) have been prepared in aqueous solution.[5] Assignment of α and β configurations to the respective $Co(trien)(en)^{3+}$ compounds was made on the basis of the known configurations of the starting dichloro complexes and the greater molar absorption in the visible absorption spectrum (Figure 2) and lower molar rotation in the visible region (Figure 3) for the lower symmetry β isomer, consistent with previous work.[1]

Two conformations of the triethylenetetramine ligand as determined by the secondary nitrogen atoms exist in the β isomer. The β-(*SS*) and β-(*RR*) isomers are thermodynamically more stable than the β-(*RS*) and β-(*SR*) isomers. Since configurational and conformational interchange require loss of the proton on the secondary nitrogen of the tetramine, the less stable isomers can be obtained in acid solution. The work performed here was carried out in neutral solution leading to the β isomer assumed to have the thermodynamically more stable β-(*SS*) and β-(*RR*) conformations.

Both α- and β-$Co(trien)(en)^{3+}$ were resolved by means of the iodide bis(antimonyl *d*-tartrate) salt. Though both α and β diastereoisomers have the same composition, the ratio of added AgSbO(tart) to [Co-

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(5) L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, **6**, 1042 (1967).

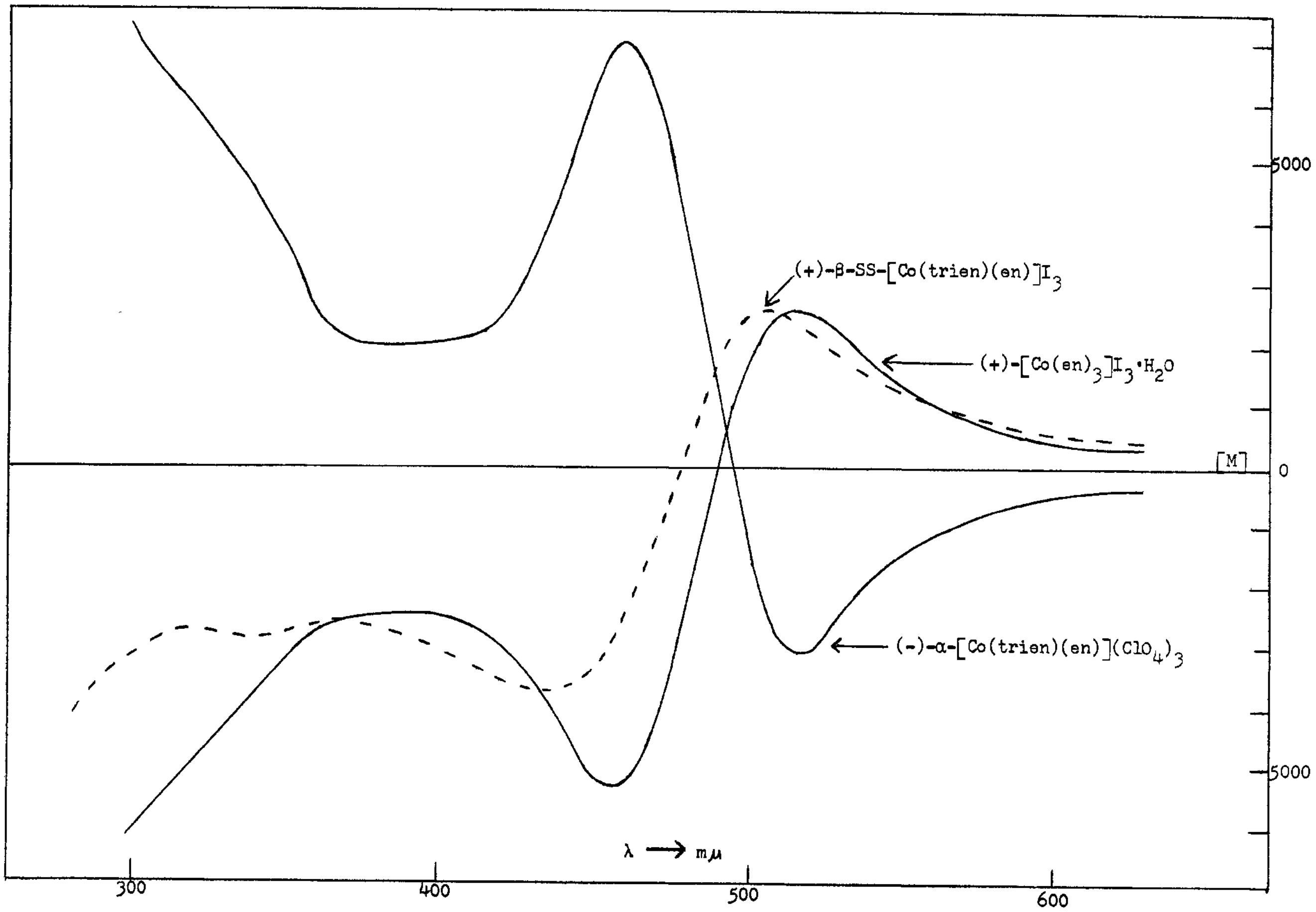

Figure 3.—Optical rotatory dispersion spectra for (+)-[Co(en)$_3$]I$_3$·H$_2$O, (−)-α-[Co(trien)(en)](ClO$_4$)$_3$, and (+)-β-(*SS*)-[Co(trien)(en)]I$_3$.

(trien)(en)]I$_3$ in the resolution procedure is different for the two isomers. If the experimental procedure is not carefully followed, one obtains only an oil.

Absolute configurations have been assigned as follows. Cobalt(III) in a regular octahedral site has two absorption bands ascribed to the transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. Under a trigonal field the first absorption band ($^1A_{1g} \rightarrow {}^1T_{1g}$) splits into two overlapping optically active bands which have been approximated to the transitions $^1A_{1g} \rightarrow {}^1E_a$ and $^1A_1 \rightarrow {}^1A_2$. The longer wavelength band for (+)-Co(en)$_3{}^{3+}$ has been shown by a polarized CD spectrum on an oriented single crystal to correspond to the transition $^1A_1 \rightarrow {}^1E_a$.[6] The absolute configuration of (+)-Co(en)$_3{}^{3+}$ is known by X-ray analysis to be Λ-(+)-Co(en)$_3{}^{3+}$ and for this ion the Cotton effect for the ^1E_a transition is positive and dominant. Under C$_2$ symmetry the E$_a$ level splits into two nondegenerate levels, A and B, both with the same sign for the Cotton effect as the parent E$_a$. This splitting is small enough in complexes of this type that it need not be used in relating absolute configurations from ORD and CD curves. On this basis the ions (+)-Co(en)$_2$X$_2{}^{n+}$ and (+)-α-Co(trien)X$_2{}^{n+}$, all of C$_2$ symmetry and all having dominant positive Cotton effects, have been assigned the Λ configuration.[1] Similarly, the ion (+)-α-Co(trien)(en)$^{3+}$ can be assigned the Λ configuration. This is borne out by the striking similarity in the ORD curves for (+)-α-Co(trien)(en)$^{3+}$ and Λ-(+)-Co(en)$_3{}^{3+}$ (Figure 3).

Both (+)-α-Co(trien)(en)$^{3+}$ and (+)-β-Co(trien)(en)$^{3+}$ crystallize as the least soluble diastereoisomers in the form [Co(trien)(en)]I[SbO(tart)]$_2$ indicating that they have the same configuration. The β isomer no longer has C$_2$ symmetry but from the form of the absorption and ORD curves can be assumed to approximate to it. The long-wavelength transition, ^1E_a, is positive for the (+)-β-Co(trien)(en)$^{3+}$ as well as the corresponding (+)-β-Co(trien)X$_2{}^{n+}$ compounds of Sargenson and Searle[1,2] and can be assigned the Λ-(+)-β configuration having the same configuration as Λ-(+)-α-Co(trien)(en)$^{3+}$.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research under Grant No. 1155G3. D. P. S. gratefully acknowledges support in the form of an NDEA Title IV fellowship.

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(6) R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc.*, 331 (1962).