abundant evidence that the heats of donor acceptor type interactions are generally small in value and do not vary widely with changes in component structure.[3]

Further work on the heats of formation of these complexes is under way. The authors are indebted to the National Science Foundation for a grant in support of this research.

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RECEIVED AUGUST 29, 1955

RESOLUTION AND MUTAROTATION OF *cis*-NITRITO-NITRO-BIS-(ETHYLENEDIAMINE)-COBALT(III)

Sir:

It previously has been demonstrated[1] that the nitrite ion can attach itself to the inner coördination sphere of a cobalt ion in two ways: through an oxygen (Nitrito) or through the nitrogen (Nitro). The conversion of the nitrito form to the nitro takes place rapidly and completely in solution or in the solid state with little or no *cis–trans* interconversion. The mechanism of this reaction is of especial interest since it may provide valuable information on the mode of substitution in coordination compounds.

In connection with a study of the mechanism of the formation of nitrito compounds and of the nitrito-nitro conversion, we have recently succeeded in resolving *cis*-$[Co(en)_2(NO_2)(ONO)]^+$ by the use of ammonium *d*-α-bromocamphor-π-sulfonate, (*d*-NH_4BCS), and a partial resolution has been achieved with active powdered quartz. This is believed to be the first reported isolation of a nitrito complex in optically active form.

The resolution was achieved by the addition of a slight excess of solid *d*-NH_4BCS to a saturated solution of *cis*-$[Co(en)_2(NO_2)(ONO)]ClO_4$ at 0°. Reddish-yellow needles were deposited, which were dissolved in water at 0° and recrystallized by the addition of solid *d*-NH_4BCS. The crystals were washed with ice-cold acetone and dried under vacuum: (I) *d-cis*-$[Co(en)_2(NO_2)(ONO)]$*d*-BCS, $[\alpha]^{18}D$ $+81°$.[2] The resolving agent was removed by triturating the diastereomer with a saturated solution of sodium perchlorate at 0° and washing the precipitated powder with ice-cold ethanol. Recrystallization was accomplished by solution in cold water and addition of solid sodium perchlorate. The orange crystals were freed of sodium perchlorate by washing with ice-cold ethanol and dried under vacuum: (II) *d-cis*-$[Co(en)_2(NO_2)(ONO)]ClO_4$, $[\alpha]^{18}D$ $+ 62.3°$[2]. *Anal.* Calculated for $CoC_4H_{16}N_6O_8Cl$; Co, 15.92; C, 13.02; H, 4.33; N, 22.76. Found: Co, 15.61; C, 13.13; H, 4.42; N, 22.58. Since conversion to the nitro form takes place rapidly, the resolved compounds were used immediately.

Absorption spectra and molecular rotation were used to demonstrate that the resolved products were the nitrito form. The molecular extinction coefficients (extrapolated) of compounds I and II are exactly the same as for the known inactive compounds and quite different from the dinitro compounds. The compounds *d-cis*-$[Co(en)_2(NO_2)(ONO)]$*d*-BCS[2], *d-cis*-$[Co(en)_2(NO_2)(ONO)]ClO_4$[2] and *dl-cis*-$[Co(en)_2(NO_2)(ONO)]ClO_4$[2] had values of $\epsilon_{408\ m\mu} = 82$, $\epsilon_{434} = 106$, $\epsilon_{439} = 113$, $\epsilon_{461} = 130 \pm 2$ while the extinction coefficients for *d-cis*-$[Co(en)_2(NO_2)_2]$*d*-BCS[3], *d-cis*-$[Co(en)_2(NO_2)_2]ClO_4$ and *dl-cis*-$[Co(en)_2(NO_2)_2]ClO_4$[4] were $\epsilon_{408} = 120$, $\epsilon_{434} = 180$, $\epsilon_{439} = 181$, $\epsilon_{461} = 129 \pm 2$.

Either I or II mutarotates rapidly at room temperature reaching a constant value after several hours owing to the formation of the optically stable *d-cis*-$[Co(en)_2(N_2O)_2]^+$ ion. On warming this with dilute sodium hydroxide solution overnight, only the activity of the resolving agent remains. Table I compares the observed changes in rotation with those calculated. Preliminary kinetic studies indicate that the rate of mutarotation and the rate of conversion to the nitro form are equal, and have a half-time of about 70 minutes (19°). Thus the reaction

TABLE I

MOLECULAR ROTATIONS

	Compound I		Compound II	
	Obs.	Calcd.	Obs.	Calcd.
Initial[2]	+469	+470	+228	+230
After 24 hours	+394	+384	+146	+144
After heating in dilute NaOH	+240	+241	+ 0	+ 0

$$d\text{-}cis\text{-}[Co(en)_2(NO_2)(ONO)]^+ \longrightarrow d\text{-}cis\text{-}[Co(en)_2(NO_2)_2]^+$$

proceeds with no appreciable racemization and since the *d*-form of the starting material and the product is the least soluble diastereomer with *d*-BCS^-, the generic configuration is probably retained.[5] Tracer experiments now in progress indicate that this reaction proceeds completely by an intramolecular process.

In the near future a more detailed account of this work as well as new results on the kinetics of these reactions will be communicated.

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[1] M. Linhard, H. Seibert and M. Weigel, *Z. anorg. Chem.*, **278**, 287 (1955).

[2] Since the rate of reaction is much more rapid in solution, all absorption spectra and optical rotations have been extrapolated to the time of addition to water.

[3] Prepared by allowing *d-cis*-$[Co(en)_2(NO_2)(ONO)]$*d*-BCS to stand in water overnight.

[4] A. Werner, *Ber.*, **44**, 2452 (1911).

[5] A. Werner, *Bull. soc. chim.*, [4] **11**, xix (1912); J. P. Mathiew, *Compt. rend.*, **199**, 278 (1934); **201**, 1183 (1935).

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RECEIVED AUGUST 22, 1955

THE REQUIREMENT OF TRIPHOSPHOPYRIDINE NUCLEOTIDE IN FATTY ACID SYNTHESIS[1]

Sir:

The enzymatic reactions involved in the biological oxidation of fatty acids have been investigated extensively. It has been postulated[2] that fatty acids are synthesized from acetyl Coenzyme A (CoA) by a reversal of the oxidative pathway.

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[1] This work was supported in part by a grant from the National Heart Institute, U. S. Public Health Service.

[2] F. Lynen and S. Ochoa, *Biochim. et Biophys. Acta*, **12**, 299 (1953).