which enhances the stability of the fluoride complexes. Thus if Sc^{+3} has a highly strained, coördinated layer of eight water molecules around it, replacement of a water by the slightly smaller fluoride ion would relieve this strain and lead to an unusually stable complex. It would be necessary that additional strain be relieved as each of the next three replacements of water by fluoride ion occur because the first four complexes are known to be exceptionally stable. This explanation, however, is contrary to the fact that scandium shows only a coördination number of six in its solids[2] and that the radius ratio[2] fits a coördination number of six with oxygen.

It is possible that it is the aluminum complex which has unusually low stability relative to the stability expected from an ionic model. Such a decrease in stability could arise from steric repulsion. Aluminum ion is on the borderline between fourfold and sixfold coördination by fluoride ion[2];

consequently, there should be strong steric repulsion for sixfold coördinated aluminum ion. Since the water molecules on the hydrated ion are held considerably less tightly than the fluoride ions, the net effect of steric repulsion would be to decrease the binding of the fluorides and lower the values of the complexing constants. It is not apparent, however, how such an effect would lead to equilibrium constants for the aluminum complexes which are actually smaller than for scandium.

Although some of the above suggestions offer possible, partial explanations of the apparent unusual stability of the scandium fluoride complexes, none of them is really satisfying. The reason for this degree of failure of the simple ionic model is not clear.

Berkeley, California

The Stereochemistry of Complex Inorganic Compounds. XXIII. Double Optical Isomerism and Optical-Geometric Isomerism in Cobalt(III) Complexes[1]

By William E. Cooley, Chui Fan Liu and John C. Bailar, Jr.

Double optical isomerism, in which both the whole complex and one of its ligands are asymmetric, exists in the cis-dinitro-ethylenediamine-2,3-butylenediamine-cobalt(III) ion. This kind of isomerism exerts a stereospecific effect, and some of the four optically active isomers are less stable against racemization in solution than the others. Optical-geometric isomerism, in which the whole complex is asymmetric and a symmetric ligand is so constituted that it may be oriented in either of two ways, exists in the cis-dinitroethylenediamine-isobutylenediamine-cobalt(III) ion. The geometric isomerism modifies the optical isomerism so that this ion also has four optically active isomers, but there is no evidence of preferential stability. The crystals of two of the optical-geometric isomers appear different from those of the other two, but all the double optical isomers have like crystals. The absorption spectra of these cis complexes are different from those of the corresponding trans complexes in a way analogous to the behavior of other dinitro complexes of cobalt(III). A study of the preparation of the optically active complexes led to an improved method of preparing the non-electrolyte trinitrotriammine-cobalt(III).

In the preparation of complex compounds containing optically active ligands, stereospecific effects often appear, with the result that some of the possible isomers of such compounds occur as small fractions of the total yield, or they do not occur at all. For example, Hürlimann[2] prepared the dinitro-bis-(propylenediamine)-cobalt(III) ion, $[Co\ pn_2(NO_2)_2]^+$. There are twelve possible isomers of the cis form of this ion, corresponding to the two optical isomers of propylenediamine, three geometric orientations of the two propylenediamine molecules, and two optical forms of the whole complex. The trans form has four possible isomers, corresponding to the two isomers of propylenediamine and two geometric orientations. More isomers of both cis and trans form are theoretically possible, of course, if the two propylenediamine molecules in each complex ion are permitted to have either the same or opposite optical configuration. Concluding that he had prepared

the cis form, Hürlimann found that only two isomers, Dll and Ldd,[3] could be isolated instead of twelve. Rotatory dispersion studies by O'Brien, McReynolds and Bailar[4] have shown that Hürlimann probably worked with the trans form but, even so, the theoretically possible number of isomers was not realized.

Similarly, Smirnoff[5] was able to isolate only the Dlll and Lddd isomers of the tris-(propylenediamine)-platinum(IV) ion, $[Pt\ pn_3]^{4+}$. Smirnoff also showed that the analogous cobalt(III) complex, $[Co\ pn_3]^{3+}$, is stable only when all three of the propylenediamine molecules have the same optical configuration. Bailar, Stiegman, Balthis and Huffman[6] concluded that "mixed" isomers containing both configurations of propylenediamine may form but that they rearrange to form the two products

(1) This article is based on portions of dissertations submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois.

(2) Hürlimann, Thesis, University of Zurich, 1918. Reviewed in F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw–Hill Book Co., Inc., New York, N. Y., 1930, pp. 157–168.

(3) The optically active complexes of this type are designated here and later by such symbols as Dll and Dlll, where the capital letter symbolizes the direction of rotation of the complex as a whole, while the small letters symbolize the number and rotation of the optically active ligands.

(4) T. D. O'Brien, J. P. McReynolds and J. C. Bailar, Jr., This Journal, 70, 749 (1948).

(5) O. P. Smirnoff, Helv. Chim. Acta, 3, 177 (1920).

(6) J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman, This Journal, 61, 2402 (1939).

that Smirnoff found. The same restriction on the isomers of tris-(1,2-*trans*-diaminocyclopentane)-cobalt(III) was observed by Jaeger and Blumendal.[7] Jaeger summarized the effects of optically active ligands by saying that two or more such ligands in the same complex usually have the same configuration, and the complex exists in only one configuration. The sign of rotation of the whole complex is sometimes the same as that of the ligands, sometimes opposite.

A few examples are known of less restrictive effects of optically active ligands. Lifschitz[8] prepared tris-(*d*-alaninato)-cobalt(III) and noted that it yields α- and β-geometric isomers; he resolved one of these into optical isomers with D*ddd* and L*ddd* configurations. This complex is an exception to Jaeger's generalization. Sister Mary Martinette, McReynolds and Bailar[9] have found that the carbonato-bis-(*l*-propylenediamine)-cobalt (III) ion exists in both D and L forms and that the configuration of its salts depends on the method of crystallization. Bailar, Jonassen and Gott[10] have demonstrated the existence of both *d*-tartrato-bis-(*l*-propylenediamine)-cobalt(III) ion and *l*-tartrato-bis-(*l*-propylenediamine)-cobalt(III) ion. In these complexes, however, the two isomers are not equally stable; the *l*-tartrate group is the less tightly bound.

The isolation of the eight theoretically possible isomers of the *cis*-dinitro-ethylenediamine-propylenediamine-cobalt(III) ion was accomplished by Werner and Smirnoff and reported by Werner.[11] This achievement prompted our own work; it is especially interesting because it combines geometric (α–β) isomerism with a kind of optical isomerism in which preferential stability is not sufficient to repress completely the formation of any of the isomers. The optical isomerism of propylenediamine and of the whole complex gives rise to the four forms D*d*, D*l*, L*d* and L*l*. Each of these is capable of existing in either of two geometric forms, depending on the position of the methyl group of propylenediamine
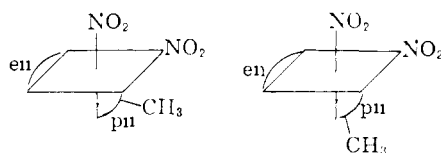
Werner and Smirnoff separated the eight isomers by fractional crystallization of the *d*-α-bromocamphor-π-sulfonates. Since the α- and β-forms are geometric isomers, their crystalline forms and solubilities need not be the same. Actually, one series (α) crystallizes as prisms and the other (β) as needles. The solubilities are similar enough so that the separation of all four isomers corresponding to one form of propylenediamine was made by the
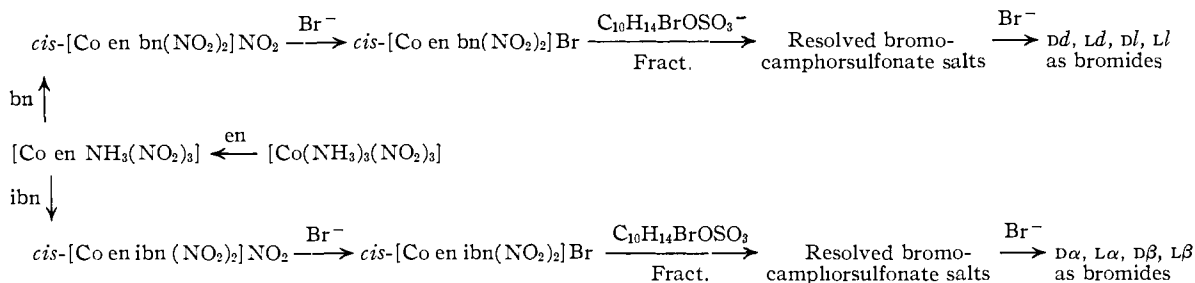
bromocamphorsulfonate method. Separate preparations with each of the isomers of propylenediamine made it possible to avoid the presence of all eight isomers in a single batch. The eight separated bromocamphorsulfonates were converted to the bromides, whose four positive optical rotations and four negative rotations matched in four pairs. The many steps of crystallization, with their inevitable losses of material, prevented an estimate of the relative quantities of the isomers. Thus, Werner and Smirnoff left unanswered the question of whether some degree of preferential stability operates to produce some of the isomers more abundantly than others. If it does, it would be interesting to discover whether the effect can be attributed to the optical isomerism, or to the geometric isomerism, or both.

For these reasons we have studied complex ions in which one source of isomerism is asymmetry of the whole complex and the other is either optical isomerism of the ligand or geometric isomerism caused by the position of an optically inactive ligand. The sources of isomerism due to the nature of the ligand have been considered separately, instead of together, as in Werner and Smirnoff's work.

We have prepared and resolved the four isomers of the *cis*-dinitroethylenediamine-active-2,3-butyl-enediamine-cobalt(III) ion, *cis*-[Co en bn $(NO_2)_2$]$^+$. Here the asymmetry stems from the ligand isomerism and the asymmetry of the whole complex. The four isomers are D*d*, L*d*, D*l* and L*l*, and for purposes of reference and comparison we call this kind of isomerism *double optical isomerism*. There is evidence that the four isomers were formed in nearly equal amounts in the preparative reaction, but there were marked differences in rates of racemization, so that not all the isomers were obtained in an optically pure state. The restrictive influence of an optically active ligand is apparent, at least when geometric isomerism does not occur at the same time.

We also have prepared and resolved the four isomers of the *cis*-dinitroethylenediamine-iso-butylenediamine-cobalt(III) ion, *cis*-[Co en ibn $(NO_2)_2$]$^+$. The asymmetry of this ion depends on geometric isomerism and asymmetry of the whole complex. Geometric isomerism is introduced in the same way as it is in the propylenediamine complex diagrammed above, but the ligand is not optically active, because of the presence of two methyl groups on one carbon atom. The four isomers are D*α*, L*α*, D*β* and L*β*; we call this kind of isomerism *optical-geometric isomerism*. No differences in rates of racemization were observed, and the matching pairs of rotations of the resolved isomers indicates that they were optically pure. As in the preparation of the 2,3-butylenediamine complex, nearly equal amounts of the four isomers were formed. We conclude that optical-geometric isomerism does not produce a preferential stability effect. Its effect on crystal type was demonstrated by the appearance of the α- and β-isomers as crystals of different kinds.

The starting material for each of our preparations was trinitrotriammine-cobalt(III), [Co(NH₃)₃-

(7) F. M. Jaeger and H. B. Blumendal, *Z. anorg. allgem. Chem.*, **175**, 161 (1928).

(8) I. Lifschitz, *Z. physik. Chem.*, **114**, 493 (1925).

(9) Sister Mary Martinette and J. C. Bailar, Jr., THIS JOURNAL, **74**, 1054 (1952); J. C. Bailar, Jr., and J. P. McReynolds, *ibid.*, **61**, 3199 (1939).

(10) J. C. Bailar, Jr., H. B. Jonassen and A. D. Gott, *ibid.*, **74**, 3131 (1952).

(11) A. Werner, *Helv. Chim. Acta*, **1**, 5 (1918).

$$cis\text{-}[\text{Co en bn}(\text{NO}_2)_2]\text{NO}_2 \xrightarrow{\text{Br}^-} cis\text{-}[\text{Co en bn}(\text{NO}_2)_2]\text{Br} \xrightarrow[\text{Fract.}]{\text{C}_{10}\text{H}_{14}\text{BrOSO}_3{}^-} \begin{array}{c}\text{Resolved bromo-}\\\text{camphorsulfonate salts}\end{array} \xrightarrow{\text{Br}^-} \begin{array}{c}\text{D}d,\ \text{L}d,\ \text{D}l,\ \text{L}l\\\text{as bromides}\end{array}$$

bn ↑

$$[\text{Co en NH}_3(\text{NO}_2)_3] \xleftarrow{\text{en}} [\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$$

ibn ↓

$$cis\text{-}[\text{Co en ibn }(\text{NO}_2)_2]\text{NO}_2 \xrightarrow{\text{Br}^-} cis\text{-}[\text{Co en ibn}(\text{NO}_2)_2]\text{Br} \xrightarrow[\text{Fract.}]{\text{C}_{10}\text{H}_{14}\text{BrOSO}_3} \begin{array}{c}\text{Resolved bromo-}\\\text{camphorsulfonate salts}\end{array} \xrightarrow{\text{Br}^-} \begin{array}{c}\text{D}\alpha,\ \text{L}\alpha,\ \text{D}\beta,\ \text{L}\beta\\\text{as bromides}\end{array}$$

$(\text{NO}_2)_3]$. This non-electrolyte usually is prepared by the method of Jörgensen.[12] We found that seemingly inconsequential variations of technique and preparative conditions may introduce serious contamination. All the significant contaminants are electrolytes; by using a conductance criterion of purity we were able to modify Jörgensen's method so that it consistently yielded a product of acceptably high purity. The scheme shown summarizes the steps of preparation and resolution of the double optical and optical-geometric isomers. The *trans* isomers of $[\text{Co en bn}(\text{NO}_2)_2]^+$ and $[\text{Co en ibn}(\text{NO}_2)_2]^+$ were separated from the desired *cis* isomers by allowing the more soluble *trans* nitrites to remain in solution when the *cis* nitrites were crystallized after the reactions with the butylenediamine. Spectrophotometric absorption maxima of the *cis* and *trans* complexes are distinct, and they are similar to those found by Basolo[13] for analogous cobalt complexes.

Experimental

Preparation of Trinitrotriammine-cobalt(III) and Hexammine-cobalt(III) Hexanitrocobaltate(III).—Jörgensen's preparative method[12] for $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ involves air oxidation of a solution of cobalt(II) chloride, sodium nitrite, ammonium hydroxide and ammonium chloride. A batch of crude product prepared according to Jörgensen's directions contained a large amount of ammonium chloride, and water washing carried away much of the product without noticeable purification of the rest. Recrystallization from hot dilute acetic acid, used by Jörgensen, also failed to free the product from contamination. Grinding the crude crystals in a slurry with silver oxide, in an effort to precipitate the chloride, release ammonia from the ammonium ion, and then dissolve the pure complex, resulted in only slight purification.

An unsuccessful attempt was made to prepare trinitrotriammine-cobalt by charcoal-catalyzed rearrangement in the isomeric compound hexammine-cobalt(II) hexanitrocobaltate(III), $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$. This slightly soluble compound was prepared by adding a solution of 13.3 g. (0.05 mole) of hexammine-cobalt(III) chloride to a solution of 20.2 g. (0.05 mole) of sodium hexanitrocobaltate(III). Stirring was continuous during the addition. The thick, yellow-orange mixture was heated on the steam-cone for 5 hr. to digest the precipitate. The mixture then was filtered, and the fine yellow precipitate was washed with 95% ethanol, absolute ethanol and ether. The product, after drying in the oven at 65°, weighed 22.3 g. (90% yield).

Anal. Calcd. for $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$: Co, 23.76; N, 33.88; H, 3.66. Found: Co, 24.05; N, 33.80; H, 3.68.

A satisfactory preparation of $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ was achieved by modifying Jörgensen's method. A solution of 90 g. of cobalt(II) chloride 6-hydrate in 250 ml. of water was added to a solution containing 100 g. of ammonium chloride, 135 g. of sodium nitrite and 345 ml. of 29% ammonium

hydroxide in 900 ml. of water. A rapid stream of air was bubbled through the mixture for 4 hr. The solution was then evaporated under an air jet. When the solution had reached half the original volume, the crystalline product was washed with water, ethanol and ether, and air was drawn through for drying. The crude material was thoroughly ground in a mortar and again placed on the filter. Twelve 25-ml. portions of cold water were successively poured on and filtered off to remove ammonium chloride. Recrystallization was carried out by pouring successive 200-ml. portions of 1.5 M acetic acid at 60° onto the product, stirring and filtering off the liquid. This treatment was continued until 5 g. of solid remained on the filter. From five to seven liters of acid was required. The solid on the filter, consisting mostly of $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$, was discarded. The combined filtrates were evaporated to half their original volume under an air stream. The recrystallized complex was filtered, dried and ground, then washed with water, ethanol and ether. Air was drawn through the filter for final drying. The highest yield obtained by this method was 45 g. (48%, based on the cobalt(II) chloride). Some crude preparations required many more than twelve water washings to remove ammonium chloride, and the final yields were lower. The lowest yield was 21 g. (22%). The specific conductance is discussed below.

Preparation of *rac*-2,3-Butylenediamine.—Several methods given in the literature,[14–17] or adaptations of them, were too slow or gave small yields.

The method of Chappell[18] worked well. In a typical preparation, 29 g. of dimethylglyoxime (0.25 mole) was suspended in 250 ml. of absolute ethanol with 2 g. of platinum (IV) oxide.[19] Hydrogenation was carried out in a Parr low-pressure apparatus. Whenever absorption of hydrogen seemed to become sluggish, 1 ml. of concentrated hydrochloric acid was added to the mixture. The reduction required approximately 30 hr., and 5 hr. before the end, when the total absorbed hydrogen was about 0.9 mole, 20 ml. of concentrated hydrochloric acid was added in one portion. At the end of the reaction, the mixture was filtered, and the residue was washed with 100 ml. of hot ethanol. The combined filtrate and washings were evaporated to dryness, leaving the crude racemic dihydrochloride. Separation from possible small amounts of *meso*-dihydrochloride was accomplished by one recrystallization from 95% ethanol. The purified racemic salt melted with decomposition at 252° (lit. value[20] 250–254°). The average yield of *meso* and racemic dihydrochloride obtained in six preparations was 80%.

Anal. Calcd. for $\text{C}_4\text{H}_{14}\text{N}_2\text{Cl}_2$: C, 29.8; H, 8.69; N, 17.4; Cl, 44.1. Found: C, 29.94; H, 8.64; N, 16.44; Cl, 44.3, 44.0, 43.9.

An aqueous solution of the racemic diamine was prepared by distilling a mixture of racemic dihydrochloride and 40%

(12) S. M. Jörgensen, *Z. anorg. Chem.*, **5**, 192 (1894); **7**, 302 (1894); **13**, 175 (1897); **17**, 475 (1898).

(13) F. Basolo, THIS JOURNAL, **72**, 4393 (1950).

(14) F. H. Dickey, W. Fickett and H. J. Lucas, *ibid.*, **74**, 944 (1952).

(15) M. Krajcinovic and D. Vranjican, *Bull. soc. chim.*, [4] **53**, 145 (1933).

(16) J. H. Balthis, Jr., and John C. Bailar, Jr., THIS JOURNAL, **58**, 1474 (1936).

(17) G. Darzens, *Compt. rend.*, **208**, 1503 (1939).

(18) C. H. Chappell, Thesis No. 333, Iowa State College (1935). Abstract, *Iowa State Coll. J. Sci.*, **11**, 45 (1936).

(19) R. Adams, V. Voorhees and R. L. Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 463.

(20) E. Strack and H. Schwaneberg, *Ber.*, **67**, 1006 (1934).

aqueous sodium hydroxide. Whenever the contents of the distilling flask became thick, water was added, and distillation was continued. A solution of diamine, boiling at about 110°, at one atmosphere, was collected and used as a stock solution for later preparation of the cobalt complex. The concentration of diamine was determined whenever necessary by titration to the methyl red end-point with 0.1 M hydrochloric acid.

Preparation of Trinitro-ammine-ethylenediamine-cobalt (III).—In a typical preparation, 19.1 g. of anhydrous ethylenediamine was added to a solution of 72 g. of [Co(NH₃)₃(NO₂)₃] (0.290 mole) in 250 ml. of water, and the mixture was heated with vigorous stirring. At about 80°, ammonia began to escape, and the solid dissolved slowly. The dark solution was boiled for three minutes, cooled and evaporated to dryness. The residue was washed with alcohol and ether, then ground to a fine powder. This crude product was recrystallized from hot 1.5 M acetic acid as described above for [Co(NH₃)₃(NO₂)₃]. About four liters of acid was required. The recrystallized product was washed several times with water, alcohol and ether. Yields were about 12% of the theoretical amount, and the purity, calculated from carbon content, averaged 95%.

Anal. Calcd. for [Co en (NH₃)(NO₂)₃]: Co, 21.5; C, 8.76; H, 4.05; N, 30.6. Found: Co, 21.4; C, 8.60; H, 3.93; N, 30.4. Specific conductances: crude product, 5.37 × 10⁻⁵ mhos/cm. cube; recrystallized product, 2.63 × 10⁻⁵ mhos/cm. cube; both values for 0.002 M solutions.

Preparation of cis-Dinitro-ethylenediamine-2,3-butylene-diamine-cobalt(III) Nitrite.—A suspension of 16.7 g. of [Co en (NH₃)(NO₂)₃] (0.069 mole) in 260 ml. of water was combined with 243.6 ml. of 0.250 M aqueous *rac*-2,3-butylenediamine solution. The mixture was heated on the steam-bath for 40 minutes, enough to cause complete solution. The dark solution was evaporated with an air stream. After an hour a small crop of crystals was filtered off. Continued evaporation finally left a mass of crystals and sirup, which repeated treatments with absolute ethanol rendered solid. Evaporation of the alcohol washings produced a mass which could be treated in the same way as the first one. The two crops of solids weighed 8.1 g. The ultraviolet absorption spectrum of this material (see below) showed that it was reasonable to identify it as the *cis* isomer.

Preparation of Dinitro-ethylenediamine-iso-butylenedia-minecobalt(III) Nitrite.—A mixture of 16.9 g. of [Co en (NH₃)(NO₂)₃] (0.0617 mole) in 500 ml. of water was combined with a solution of 5.45 g. of isobutylenediamine[21] in 25 ml. of water. Heating on the steam-bath for 45 minutes produced a dark solution. The filtered solution was evaporated to a thin sirup under the air stream. Ten times its volume of absolute ethanol was added, and the mixture was stirred thoroughly and set aside for an hour. The fine precipitate that had formed was filtered off and washed with ethanol and ether. The filtrate was evaporated to a pasty mass and worked with a small amount of ethanol. When the supernatant liquid had acquired a yellow opaque suspension of particles, an equal volume of *t*-butyl alcohol was stirred in. The upper suspension was decanted into a beaker. This extraction was repeated until all of the material had been reduced to a suspension and decanted into the beaker. The suspended material was filtered off, washed with ethanol and ether, and dried. It and the first crop together weighed 10 g. Evaporation of the final filtrate to a sirup at room temperature, then heating to dryness on the steam-bath, yielded 4.5 g. of solid product. Both solids were light yellow, but their ultraviolet absorption spectra identified the 10 g. of product as the *cis* salt and the 4.5 g. of product as the *trans* salt.

Conversion of the Nitrites to Bromides.—The nitrite salt containing either of the diamines could be converted to the less soluble bromide by agitating it with a highly soluble bromide in a minimum amount of water. The solubilities of the two complexes were different enough so that they were treated somewhat differently in this step. A solution of 8.1 g. of *cis*-[Co en bn(NO₂)₂]NO₂ in 50 ml. of water was ground in a mortar with 3 g. of solid ammonium bromide. The fine, yellow crystalline solid which separated was allowed to settle for 2 hr. The crystals were filtered, washed and dried with 95% ethanol, absolute ethanol and anhydrous ether. The filtrate was evaporated to a small

(21) Supplied by the Organic Preparation Laboratory of the University of Illinois.

volume on the steam-bath, and addition of 150 ml. of ethanol precipitated another crop. The total yield was 4.25 g.

Anal. Calcd. for [Co en bn(NO₂)₂]Br·H₂O: C, 18.13; H, 5.59; N, 21.16. Found: C, 18.40; H, 5.92; N, 21.17.

Conversion of *cis*-[Co en ibn (NO₂)₂]NO₂ to the bromide was accomplished by grinding 10 g. of the complex in 50 ml. of water with 5 g. of solid sodium bromide. The separation of two solid fractions was the same as for the 2,3-butylenediamine complex. The product weighed 5.12 g., and ultraviolet spectral analysis confirmed that it was still the *cis* isomer. This was the first point at which fair-sized crystals of this complex appeared. Microscopic examination revealed that two kinds of crystals were present, one prism-like and the other needle-like. Their presence helped to support the idea that geometric isomerism was involved.

Resolution of the Double Optical Isomers and the Optical-geometric Isomers.—Both complexes were resolved by fractional crystallization of their *d-α*-bromocamphor-π-sulfonates. For the 2,3-butylenediamine complex, 6.25 g. of the bromide salt was dissolved in 500 ml. of water, and 6.9 g. of solid silver bromocamphorsulfonate was stirred in in small portions. The mixture was digested on the steam-bath, and the precipitated silver bromide was filtered off and washed with warm water (40°). Evaporation of the combined filtrate and washings to dryness at room temperature yielded nine fractions of crystals, numbered S1 to S9 in order of increasing solubility. No effort was made to collect a particular number of fractions; rather, each one was filtered off as it reached what seemed to be a reasonable size. Further washing of the silver bromide precipitate with 1500 ml. of warm water produced a solution whose evaporation yielded five more fractions, SA to SE.

After later work showed that the dextrorotatory member of the more soluble pair of isomers had racemized extensively during fractionation, another solution was prepared so that this isomer could be recovered in a purer state. After combination of the complex bromide and silver bromocamphorsulfonate, the silver bromide was filtered off and extracted with 1000 ml. of hot water in 50-ml. portions. Filtrate and washings yielded fifteen fractions, R1-R15.

A similar procedure was followed with *cis*-[Co en ibn-(NO₂)₂]Br, 5.12 g. of the complex being allowed to react with 5.64 g. of silver bromocamphorsulfonate in 500 ml. of water. Here a smaller solubility range of the diastereoisomers made it unnecessary to wash or extract the silver bromide with the same thoroughness as before. Evaporation of the filtrate yielded eleven fractions. The first fraction was discarded. Further treatment of the others, numbered U1-U10, is described later.

The final four diastereoisomers of each complex were reconverted to the bromides. Enough concentrated hydrobromic acid was added to the solid complex to permit grinding it into a smooth paste. Grinding was continued for several minutes. When 50 ml. of absolute ethanol was added, a fine precipitate of the bromide complex began to form. The product was filtered off after 30 minutes, washed with ethanol and ether and dried under vacuum. One of the less soluble isomers of *cis*-[Co en bn(NO₂)₂]⁺ required warming on the steam-bath to bring about the conversion.

Instruments.—Optical rotations were measured with a Schmidt and Haensch polarimeter. Absorption spectra were determined with a Cary spectrophotometer. Conductance measurements were made in a thermostated cell fitted with platinized platinum electrodes, and the readings were taken from a Leeds and Northrup conductivity bridge.

Results and Discussion

Trinitrotriammine-cobalt(III).—Several samples of [Co(NH₃)₃(NO₂)₃], prepared by students in laboratory courses, were found to badly contaminated with ammonium chloride. All these samples had been prepared from Jörgensen's original directions[12] or adaptations of them in laboratory manuals. We found that once the crude product is crystallized from solution, it is practically impossible to remove the ammonium chloride by methods suitable for batches of more than a few grams. It is better to avoid the inclusion of ammonium chloride by taking crops of [Co(NH₃)₃(NO₂)₃] only until the original reactant solution has

evaporated to half its original volume. Washing the pulverized crude product then readily removes the chloride. The chief contamination still remaining is $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$. This complex, although it is an electrolyte, is slightly less soluble in water or dilute acetic acid than is $[Co(NH_3)_3(NO_2)_3]$. The solubilities of both complexes increase as the concentration of acetic acid increases, but the solubility of the electrolyte complex increases more rapidly. Thus the conditions favoring a minimum quantity of recrystallizing solvent also favor greater contamination. For batches of 5–10 grams, 0.5 M acetic acid is a satisfactory recrystallizing solvent. For larger batches, like those we prepared, 1.5 M acetic acid is necessary to avoid unduly large volumes. Most of the electrolyte contaminant can be removed by stirring the chloride-free product with the hot acid until about 90% of the solid dissolves, then filtering and discarding the residue.

When $[Co(NH_3)_3(NO_2)_3]$ is to be recovered by evaporating a solution, the time of evaporation should be as short as possible. Aquation occurs more rapidly in hot solutions than at room temperature; a 0.002 M solution of the complex at 65° precipitates black cobalt(III) hydroxide in 1 hr. At 70° the black precipitate appears in five minutes.

The solubility of $[Co(NH_3)_3(NO_2)_3]$ in water at 25° is about 0.02 M (5 g./l.). Specific conductance values ranged from 1.14 × 10^{-5} to 2.08 × 10^{-5} mhos/cm. cube for 0.002 M solutions at 25°. Aquation of the complex is apparently rather fast during the first few minutes in solution, for the conductance of a typical sample after 10 minutes was 30% higher than the value after 5 minutes. The conductance increased very slowly after 10 minutes, and not until 80 minutes was it as much above the 10-minute value as it had been below it at 5 minutes. No sample could be completely dissolved in less than five minutes in preparation for the conductance tests. If the conductance increases from zero time as steeply as our observations imply, the compound may be close to a true non-electrolyte.

The Double Optical Isomers.—Samples of fractions S1 to S9 and SA to SE of the 2,3-butylenediamine complex were dissolved in water for immediate reading of their optical rotations. Figure 1 shows the distribution curve for fractions SA–SE. The length of each horizontal line represents the size of the corresponding fraction, and the ordinate of each line represents the specific rotation of the fraction. The distribution curve is fitted to the midpoints of the lines. If perfect fractionation had been reached during the first evaporation and if the four isomers had been prepared in equal amounts, there would have been four lines of equal length on the chart, each at a distinct ordinate. The total number of maxima and minima of the distribution curve, equal to the number of isomers in the mixture, would have been four, and the maxima and minima would have been equally spaced across the diagram. It is assumed that both diastereoisomers containing *levo*-diamine are either more soluble or less soluble
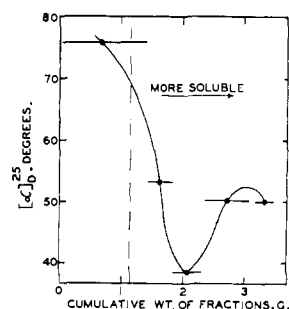

Fig. 1.—Distribution curve for fractions SA-SE.

than both containing *dextro*-diamine. The assumption is justified, as the rotations of the final fractions show.

Figure 2 is a distribution diagram for fractions S1–S9. Here, as in fractions SA–SE, there are only three isomers evident. The most soluble of all the fractions is in this group only, as the least soluble is in the first group only.
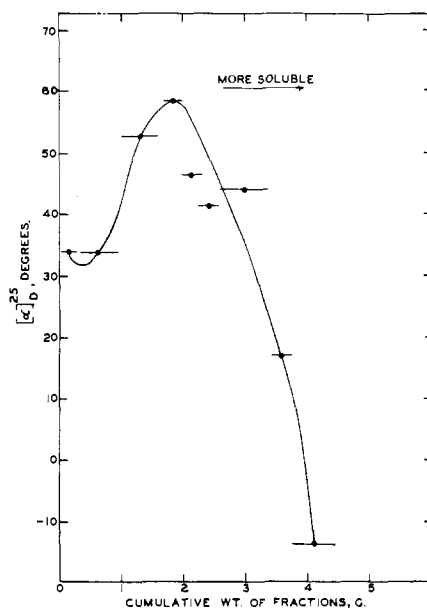

Fig. 2.—Distribution curve for fractions S1-S9.

For further fractionation we combined the fractions whose rotations were nearest the maxima and minima of the distribution curves. Some fractions, such as SA and S9, were large enough, with isolated rotation values, so that they were refractionated by themselves. The rotations of all subfractions were studied so that the same process of grouping maxima and minima could be continued and focused toward optical purity. In any fractionation scheme there are overlaps, discontinuities and irregularity of fraction sizes. The many fractions that were eventually discarded have little to do with the final results. Accordingly, only the steps leading to the four purest fractions are outlined here. These four fractions were converted to the optically active bromides. In Table I the fractionation results are summarized. The specific rotations are written below the fraction symbols.

Racemization and attendant change of rotation away from the maxima and minima were encountered during refractionation, particularly among the more soluble fractions. This evidence of unequal stabilities of the isomers is corroborated by the rotatory dispersion behavior of the bromides A, B, C and D (Fig. 3). The less soluble isomers,
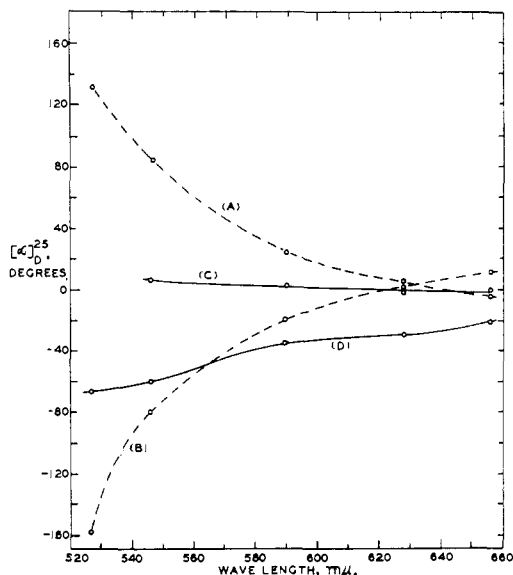

Fig. 3.—Rotary dispersion curves of the four isomers of cis-[Co en bn(NO₂)₂]Br.

A and B, have dispersion curves that are nearly symmetrical with respect to the line of zero rotation. The isomers are thus shown to be nearly optically pure. Although they could have racemized to almost exactly the same degree, it is unlikely that they did, since A arose through one refractionation, whereas B required two. The curves of the more soluble isomers, C and D, are not symmetrical. Isomer C evidently has undergone nearly complete racemization. Isomer D may have racemized or not; the dispersion curve does not settle the question.

Another fractionation process with a newly prepared solution of the mixed isomers of cis-[Co en bn (NO₂)₂]⁺ yielded fractions R1-R15 in increasing order of solubility. The specific rotations of fractions R12 and R13 were 52.8 and 53°, the highest values among the more soluble fractions. The bromide of fraction R13 showed a specific rotation slightly higher than that of isomer C in Fig. 4. The numerical values of these rotations were still not close to those of the opposite isomer, D. Even a single fractionation procedure obviously allowed extensive racemization, and isomer C is clearly the least stable of the four.

The configurational designations Dd and Dl are assigned to isomers A and C, and the designations Ld and Ll are assigned to B and D. It is not possible, of course, to determine by any of the means used here whether Dd, for example, belongs to A or C, so these assignments are made by pairs rather than individually.

The Optical-geometric Isomers.—A scheme of fractionation similar to that used on the double
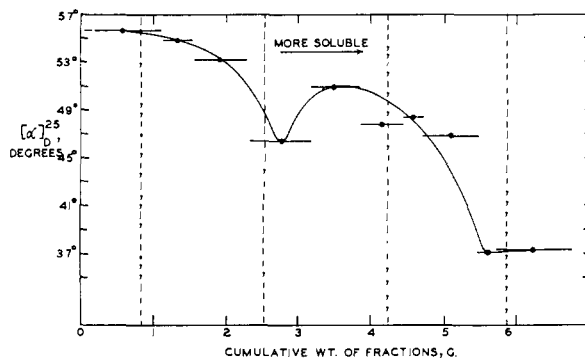

Fig. 4.—Distribution curve for fractions U1-U10.

optical isomers was successful for the optical-geometric isomers. The solubility range of the optical-geometric isomers was not as large as that of the others, and very little product remained to be washed from the original silver bromide precipitate. The first fraction was discarded, as described above, and the specific rotations of the others were measured.

TABLE I

FRACTIONATION LEADING TO THE FOUR ISOMERS OF
cis-[Co en bn(NO₂)₂]Br

Numerical values are $[\alpha]^{25}$D

$$\text{(Least soluble) S A} \xrightarrow{\text{refractionation}} \underset{43°}{\text{S}\alpha,} \ \underset{55°}{\text{S}\beta,} \ \underset{83°}{\text{S}\gamma,} \ \underset{65°}{\text{S}\delta,} \ \underset{45°}{\text{S}\epsilon}$$

$$\text{conversion to} \downarrow \text{bromide}$$

$$\underset{85°}{\text{A}}$$

$$\underset{34°}{\text{S1,}} \ \underset{34°}{\text{S2}} \xrightarrow{\text{refractionation}} \underset{31°}{\text{S}\zeta,} \ \underset{29°}{\text{S}\eta,} \ \underset{38°}{\text{S}\epsilon,} \ \underset{39°}{\text{S}\iota}$$

$$\downarrow \text{refractionation}$$

$$\underset{30°}{\text{S}\kappa,} \ \underset{35°}{\text{S}\lambda}$$

$$\text{conversion to} \downarrow \text{bromide}$$

$$\underset{-80°}{\text{B}}$$

$$\underset{46°}{\text{S5,}} \ \underset{41°}{\text{S6,}} \ \underset{44°}{\text{S7}} \xrightarrow{\text{refractionation}} \underset{41°}{\text{S}\mu,} \ \underset{51°}{\text{S}\nu,} \ \underset{43°}{\text{S}\xi}$$

$$\text{conversion to} \downarrow \text{bromide}$$

$$\underset{8°}{\text{C}}$$

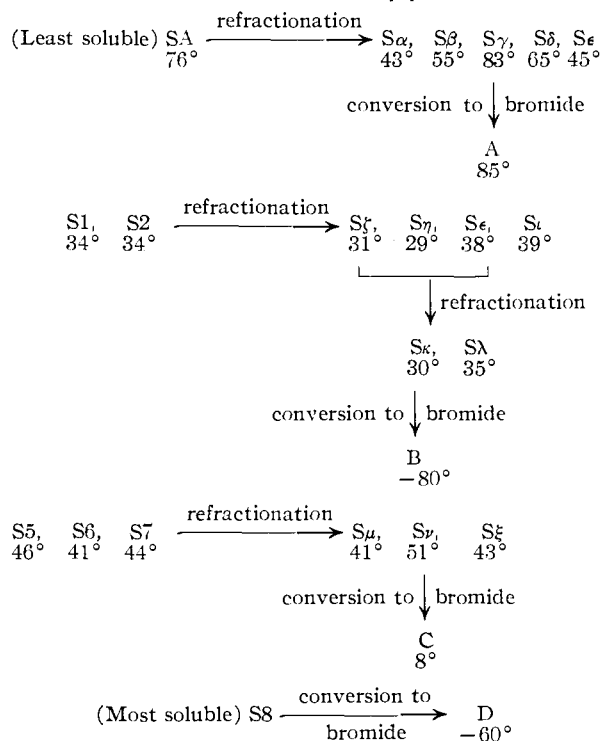$$\text{(Most soluble) S8} \xrightarrow[\text{bromide}]{\text{conversion to}} \underset{-60°}{\text{D}}$$

Figure 4 is the distribution diagram for fractions U1-U10. The maxima and two minima of the curve point to the presence of four isomers. Equal distribution among the isomers would cause the maxima and minima to fall on the vertical dotted lines. They do not, of course, but the deviations are not extreme. We conclude that the amounts of the four isomers are reasonably similar. No better estimate of the distribution was possible,

Table II

Fractionation Leading to the Four Isomers of cis-[Co en ibn (NO₂)₂]Br

Numerical values are $[\alpha]_D^{25}$
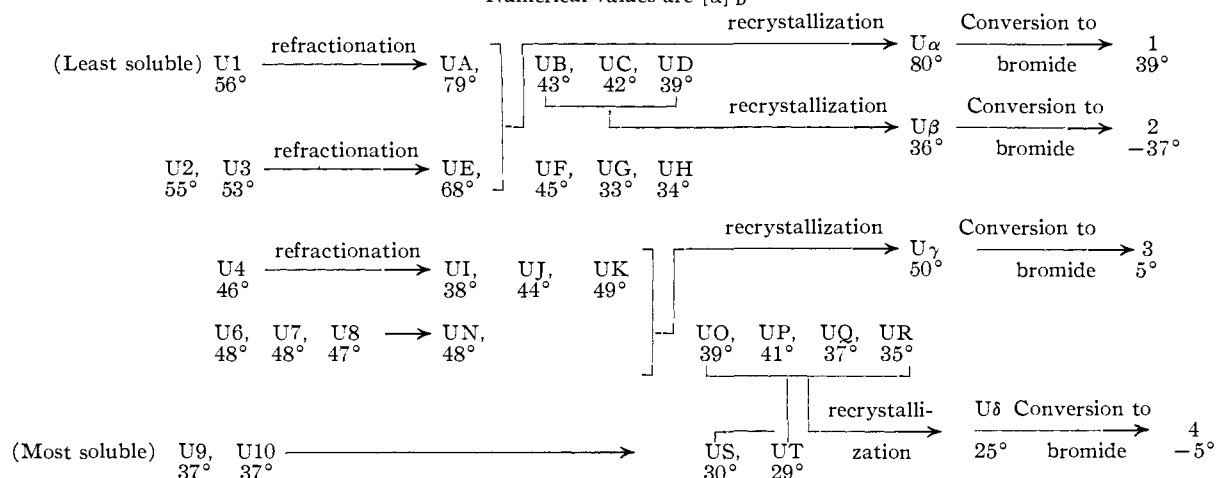
for the ensuing fractionation of a mixture with a small solubility range resulted in final fractions that were very small.

The important parts of the further fractionations are summarized in Table II. The most striking contrast between the processes for these isomers and the double optical isomers was that no pronounced racemization appeared in this group. Rotations of the solutions changed practically not at all on standing. No other evidence of preferential stability was found. Apparently variable stability is characteristic of double optical isomerism but not of optical-geometric isomerism.

Crystal Appearance.—The extremely small crystals of bromides 1–4 were poorly formed and not immediately distinguishable. Recrystallization from water at 40° on the hot stage of the polarizing microscope showed that 1 and 2 formed rhombic prisms, while 3 and 4 formed needles. No detailed crystallographic study was attempted. If we name the four isomers by analogy to cis-[Co en pn (NO₂)₂]Br,[7] without implying anything about absolute configurations, isomers 1, 2, 3 and 4 become isomers Dα, Lα, Dβ and Lβ, respectively. Bromides A–D, the double optical isomers, did not exhibit any crystal differences. These observations are in accord with the fact that geometric isomers may have marked physical differences, whereas optical isomers are generally identical except for the direction of asymmetry.

Absorption Spectra.—Basolo[15] has pointed out the separation between absorption maxima of cis- and trans-dinitro complexes of cobalt(III). The spectrum of a methanol–water solution of the least soluble fractions of [Co en ibn (NO₂)₂]NO₂, before conversion to the bromide, was compared with that of the most soluble fractions and with Basolo's figures for analogous complexes. A good parallel appears in the data, and we infer that the less soluble form is the cis form. The inference is justified by the actual separation of four optically active isomers of the less soluble (cis) form.

Complex	λmax, mμ	
cis-[Co(NH₃)₄(NO₂)₂]⁺	238	327
trans-[Co (NH₃)₄(NO₂)₂]⁺	255	356
cis-[Co en₂(NO₂)₂]⁺	240	325
trans-[Co en₂(NO₂)₂]⁺	250	347
Least soluble [Co en ibn (NO₂)₂]⁺	240	327
Most soluble [Co en ibn (NO₂)₂]⁺	248	338

The absorption spectra of cis- and trans-[Co en bn (NO₂)₂]⁺ were determined and used qualitatively to show that their absorption maxima, solubilities and cis–trans isomerism are in the same order as the properties of [Co en ibn (NO₂)₂]⁺.