

shown<sup>4</sup> that graphite on oxidation with nitric acid and alkaline permanganate furnishes mellitic and carbonic acids exclusively and studies on the behavior of mellitic acid in the bomb, under the same conditions which were used for the oxidation of graphite, showed that 97% of the carbon of a 25-g. sample was converted to carbon dioxide in twenty-four hours.

The method used for isolation of the individual acids, barium salt fractionation, followed by esterification and vacuum fractionation of the esters, was essentially the same as applied to the acids prepared by the action of alkaline permanganate on the Pittsburgh Seam coal. As in that work, it was found that a significant fraction of the methyl esters will not distil under conditions where the least volatile of the esters of the benzene carboxylic acids, the hexamethyl mellitate, distils rapidly.

#### Summary

Several types of carbonaceous materials, rang-

ing in rank from an Illinois bituminous coal to artificial graphite, have been oxidized to simple acids by oxygen at elevated pressures, at temperatures of 200 to 250°, in the presence of aqueous alkali. With the lower rank materials a significant fraction of the carbon can be recovered as simple organic acids. From the materials of rank higher than a low temperature coke, decreasing recoveries of organic acids are obtained, and with graphite the soluble products consist almost exclusively of carbonic acid. The effects of temperature, time, oxygen partial pressure, catalysts, surface, and nature of the alkali on the course of the oxidation of a Pittsburgh Seam coal have been studied. Oxalic, trimellitic, pyromellitic, prehnitic, and terephthalic acids have been identified. A significant fraction of the acids forms non-distillable methyl esters, indicating the presence of structures more complex than the benzenecarboxylic acids.

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### The Stereochemistry of Complex Inorganic Compounds. IV. The Introduction of Racemic Organic Molecules into Some Optically Active Complex Ions of Cobalt and Chromium<sup>1</sup>

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The penetration of a molecule of an optically active diamine, dibasic acid or amino acid into an optically active complex of the type  $[MA_2X_2]^{2+}$  offers several stereochemical possibilities. In some cases, all of the possible stereoisomers of the reaction product are realized. Thus, levo-1,2-*trans*-diaminocyclopentane reacts with racemic dichlorodiethylenediaminocobaltic chloride,  $[Coen_2Cl_2]Cl$ , to give both the D and the L forms of  $[Coen_2-l-Cptdn]Cl_3$ .<sup>3</sup>

Sometimes, however, the entrance of the new group takes place only in certain preferred ways; this gives part, but not all, of the possible stereo-

(1) Abstracted from portions of the doctorate theses of C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman.

(2) The following symbols are used in this paper: M = metal ion, A = coordinating group occupying two corners of the octahedron, X = an acido group occupying one corner, en = ethylenediamine, pn = propylenediamine, Cptdn = 1,2-*trans*-diaminocyclopentane, Hala = alanine, Hleu = leucine. D and L refer to the dextro and levo configurations of the complex ion, and *d* and *l* to the configurations of the "A" groups.

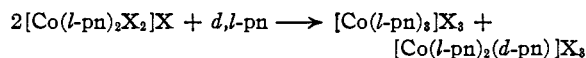
(3) Jaeger and Blumenthal, *Z. anorg. allgem. Chem.*, **175**, 161-230 (1928).

isomers. The reaction of racemic diaminocyclopentane with racemic dichlorodiethylenediaminocobaltic chloride gives only two of the four possible isomers; each of the antipodes of the  $[Coen_2Cl_2]Cl$  reacts preferentially with one form of the diaminocyclopentane. This effect is certainly not absolute, and may be very slight. It suggests, however, that the reaction between an optically active complex and an *excess* of a racemic coordinating substance might be selective to some extent—that is, that the complex might accept one antipode of the coordinating material preferentially, thus effecting a resolution. Some studies of this possibility are reported here. The results indicate that the preference of the complex for one antipode over the other is slight in these reactions.

The reactions studied were those of propylenediamine and alanine with cobalt complexes containing two molecules of levo-propylenediamine, that of leucine with dichlorodiethylenediaminocobaltic chloride, and that of phenylalanine with

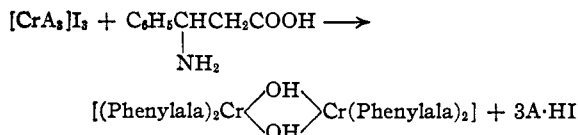
$[\text{Cr}(l\text{-pn})_3]\text{I}_3$  and optically active  $[\text{Cren}_3]\text{I}_3$ . The complex compounds containing levo-propylenediamine may offer an advantage over those of ethylenediamine because they do not racemize; the optically active diamine forces a definite configuration upon the complex ion.

The reaction of racemic propylenediamine with the cobalt complexes is a simple penetration reaction, both antipodes of the base taking part with equal readiness



The mixed complex ion doubtless rearranges at once, as Smirnof<sup>4</sup> has shown. The compound formed when alanine reacts with  $[\text{Co}(l\text{-pn})_2\text{Cl}_2]\text{-Cl}$  is quite stable, and evidently has the formula  $[\text{Co}(l\text{-pn})_2(\text{ala})]\text{Cl}_2$ . Both the *d*- and the *l*-alanine react, and several stereoisomers of the product are possible. Their excessive solubility prevented their separation, however. The reaction of  $[\text{Coen}_2\text{Cl}_2]\text{Cl}$  with leucine was studied with the thought that each form of the amino acid might react selectively with one form of the complex ion. This would give rise to two mirror-image isomers,  $[\text{Coen}_2(\text{leu}')]\text{Cl}_2^{+}$  and  $[\text{Coen}_2(\text{leu}'')]\text{Cl}_2^{+}$ ,<sup>5</sup> which might be separated by resolution. The two forms of the amino acid could then be recovered from these complexes. Unfortunately, however, the salts are so soluble that all attempts at resolution failed.

The reaction of phenylalanine with the luteo chromic salts is more complicated, as the diamine molecules are completely expelled from the complex



The reaction must take place in steps, so at least the first phenylalanine molecules which react are subject to whatever stereochemical influences the complex may exert. The optically active luteochromic salts did not effect a resolution of the phenylalanine, but the reaction is of some interest because of the insolubility of the tetraphenylalanine-diol-dichromium. It might possibly be used in the separation of phenylalanine from other amino acids. Ley and Ficken<sup>6</sup> have prepared the

(4) Smirnof, *Helv. Chim. Acta*, **3**, 177-195 (1920).

(5) leu' and leu'' represent the two mirror image forms of leu.

(6) Ley and Ficken, *Ber.*, **45**, 380-382 (1912).

corresponding glycine and alanine compounds, and report them to be somewhat soluble in water.

### Experimental

**Preparation of  $[\text{Co}(l\text{-pn})_2\text{Cl}_2]\text{Cl}$ .**—The method of Werner and Frolich<sup>7</sup> was modified as follows: 50 g. of cobalt chloride hexahydrate is dissolved in 1200 cc. of water, containing 25 g. of *l*-propylenediamine. The base is resolved according to the directions of Bauman<sup>8</sup> except that calcium hydroxide is substituted for potassium hydroxide. Air is bubbled through the solution for sixteen hours, slowly at first, so as not to sweep out any of the uncoordinated propylenediamine. Twelve hundred cubic centimeters of concentrated hydrochloric acid is added, and the solution concentrated *in vacuo* (at a temperature not above 70°) to 200 cc. On standing at room temperature for a day, 30 g. of the green *trans*-dichloro salt separate. Evaporation of the filtrate to 150 cc. yields another 3 g. of slightly less pure material. The crystals may be purified by dissolving in alcohol and precipitating with ether. The *trans* salt readily may be changed to the gray-purple *cis* isomer by heating to 100° in an acid-free atmosphere. This was not necessary in these studies, as rearrangement to the *cis* form takes place when an amino acid or propylenediamine is introduced into the molecule. The dichloro salt may be changed to the dinitro or to the carbonato salt by treatment with the appropriate silver salt.

The reaction of alanine with  $[\text{Copen}_2\text{Cl}_2]\text{Cl}$  was adapted from the directions of Meisenheimer, Angermann and Holsten.<sup>9</sup> A solution of 1.5 g. of alanine in 20 cc. of water was added slowly and with stirring to a mixture of 5 g. of  $[\text{Co}(l\text{-pn})_2\text{Cl}_2]\text{Cl}$  and 2 g. of sodium acetate in 30 cc. of water. The solution became blood red at once, but was heated on the steam-bath for one-half hour to ensure completion of the reaction. The extremely soluble salt was obtained in crystalline form by evaporation to dryness, solution in absolute alcohol, and precipitation with ether. The red crystals were kept over phosphorus pentoxide for several days before analysis.

*Anal.* Calcd. for  $[\text{Co}(l\text{-pn})_2\text{ala}]\text{Cl}_2$ : C, 29.51; H, 7.15; N, 19.13. Found: C, 29.38; H, 7.52; N, 19.38.

In another experiment the  $[\text{Co}(l\text{-pn})_2\text{Cl}_2]\text{Cl}$  was allowed to react with twice the theoretical amount of racemic alanine. The unused alanine was precipitated as the double mercury salt,<sup>10</sup> freed from the mercury by hydrogen sulfide, and recrystallized from water. Slightly more than half of the alanine was recovered. It showed no optical activity.

The reaction of leucine with  $[\text{Coen}_2\text{Cl}_2]\text{Cl}$  was carried out in a similar manner. Five and eight-tenths grams of *trans*  $[\text{Coen}_2\text{Cl}_2]\text{Cl}$ ,<sup>11</sup> 3.49 g. of leucine and 1 g. of sodium carbonate were heated together on the steam-bath in 75 cc. of water. Carbon dioxide was evolved slowly, and the blood red color of the carbonato salt gave way to orange-red. After twelve hours, the reaction was apparently complete, and the mixture was evaporated to about 15 cc.

(7) Werner and Frohlich, *ibid.*, **40**, 2225 (1907).

(8) Bauman, *ibid.*, **28**, 1180 (1895).

(9) Meisenheimer, Angermann and Holsten, *Ann.*, **438**, 266 (1924).

(10) Neuberg and Kerb, *Biochem. Z.*, **40**, 498-513 (1912).

(11) Jørgensen, *J. prakt. Chem.*, **39**, 16 (1889); **41**, 448 (1890).

On cooling, a bright orange powder formed. This was washed with alcohol and ether.

*Anal.* Calcd. for  $[\text{Coen}_2\text{leu}]\text{Cl}_2$ : Cl, 18.66. Found: Cl, 19.26.

This salt was converted to the *d*-bromo-*pi*-camphorsulfonate through the action of the silver salt. Attempts to crystallize an active salt from water and water-alcohol solutions met with failure, as only glassy solids were formed.

**The Reaction between Racemic Propylenediamine and Optically Active Cobalt Salts.**—Racemic propylenediamine was added in 100% excess to solutions of  $[\text{Co}(l\text{pn})_2\text{Cl}_2]\text{Cl}$ ,  $[\text{Co}(l\text{pn})_2(\text{NO}_2)_2]\text{NO}_2$ , and  $[\text{Co}(l\text{pn})_2\text{CO}_3]_2\text{CO}_3$  at various temperatures and concentrations. Complete reaction took place in every case. The excess propylenediamine was recovered (by vacuum distillation or steam distillation) as the racemic base, so the two isomers must have entered the complex at equal rates.

**The Preparation and Reactions of the Luteo Chromamines.**—Triethylenediamine chromic chloride<sup>12</sup> was resolved and converted to the active iodide as described by Werner.<sup>13</sup> The iodide in 0.5% solution showed  $[\alpha]^{25}_D +67^\circ$ , somewhat higher than the  $+60^\circ$  reported by Werner.

Tri-*levo*-propylenediamine chromic chloride may be prepared in the same way or by the method of Pfeiffer.<sup>14</sup> The latter method gives a good yield only if concentrated (80% or more) propylenediamine is used. The luteo chloride may be converted readily by metathetical reactions to the less soluble and more stable bromide, iodide, or thiocyanate. The iodide was recrystallized from boiling water.

*Anal.* Calcd. for  $[\text{Cr}(l\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2)_3]\text{I}_3 \cdot \text{H}_2\text{O}$ , 56.61% iodide. Found, 56.43%. For a 0.55% solution,  $[\alpha]^{25}_D -26.04^\circ$ .

The two luteo salts react with phenylalanine in the

(12) Balthis and Ballar, *THIS JOURNAL*, **58**, 1474 (1936). A much better method of preparing these salts has been devised since this work was done. It will be described in a forthcoming article.

(13) Werner, *Ber.*, **45**, 866 (1912).

(14) Pfeiffer, *Z. anorg. Chem.*, **24**, 286 (1900).

same way, so only one experiment need be described. To 6 g. of phenylalanine in 250 cc. of water was added 5 g. of  $[\text{Cren}_3]\text{Br}_3 \cdot 3\text{H}_2\text{O}$ , and the mixture was heated on the steam-bath for six hours. The lavender precipitate which formed was filtered from the pink solution and washed with hot water. The yield is nearly quantitative.

*Anal.* Calcd. for  $(\text{C}_6\text{H}_5\text{ala})_2\text{Cr} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{array} \text{Cr}(\text{C}_6\text{H}_5\text{ala})_2$ :

Cr, 13.10; N, 7.05. Found: Cr, 13.41; N, 7.23.

The compound is insoluble in hot or cold water and the usual organic solvents. It is easily soluble in nitric acid, but only slightly soluble in hydrochloric and 50% sulfuric acids. The acid solutions slowly turn green, indicating decomposition. In the attempted resolutions, a 100% excess of phenylalanine was allowed to react with *d* $[\text{Cren}_3]\text{I}_3 \cdot \text{H}_2\text{O}$  or  $[\text{Cr}(l\text{pn})_3]\text{I}_3 \cdot \text{H}_2\text{O}$ . The precipitated tetraphenylalanine-diol-dichromium was examined for optical activity in 50% sulfuric acid. None was observed in any case. The filtrate from the lavender precipitate was made basic, the ethylenediamine or *levo*-propylenediamine steam distilled out, and the residual phenylalanine examined for optical activity. In every case, it was inactive.

### Summary

1. The possibility of using optically active complex ions of cobalt and chromium in the resolution of diamines, dibasic acids and amino acids has been investigated. Positive results have not yet been obtained.

2. An improved method of preparing dichlorodipropylenediaminocobaltic chloride is described.

3. The reaction of luteo chromic salts with phenylalanine has been investigated. This is apparently a new type of reaction, and leads to the formation of tetraphenylalanine-diol-dichromium. The insolubility of this compound suggests the possibility of its use in the separation of phenylalanine from other amino acids.

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