

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XIX. The Resolution of Bis-ethylenediamine-(2,2'-diaminobiphenyl)-cobalt(III) Chloride¹

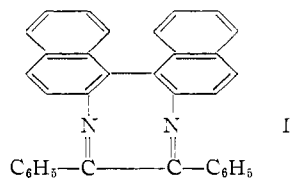
BY FRED McCULLOUGH, JR.,² AND JOHN C. BAILAR, JR.

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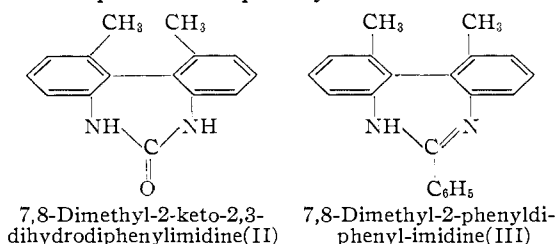
Derivatives of biphenyl which contain bulky groups in the 2,2',6,6'-positions are capable of being separated into optically active isomers. The source of this optical activity is the coaxial-non-coplanar configuration of the molecule caused by the restricted rotation of the benzene rings. Anything which prevents the coplanarity of the benzene rings should produce optical activity in the molecule. If the 2- and 2'-positions of a biphenyl derivative are linked in an organic ring of seven or eight members, the benzene rings are held out of coplanarity and the molecule shows optical activity. If a metal ion is coordinated to substituents in the 2,2'-positions of a biphenyl derivative, a seven-membered or larger ring results and by analogy to the above case, the complex should be optically active. In the present investigation, 2,2'-diaminobiphenyl was chosen as the ligand. Bis-ethylenediamine-(2,2'-diaminobiphenyl)-cobalt(III) chloride was resolved and four isomers (two *dl* pairs) were isolated. Bis-ethylenediamine-(2,2'-diaminobiphenyl)-cobalt(III) bromide was found to be resistant to racemization.

Certain derivatives of biphenyl, having bulky groups in the 2,2',6,6'-positions, are capable of being separated into optically active isomers. The source of this optical activity is believed to be the coaxial-non-coplanar configuration of the molecule caused by the mechanically restricted rotation of the benzene rings. Since the benzene rings are non-coplanar, non-superimposable mirror images are possible and optical isomerism results.

Anything which prevents the coplanarity of the benzene rings should produce optical activity in the molecule. If the 2- and 2'-positions in a resolvable biphenyl derivative are linked by rings larger than six-membered, the two nuclei of the molecule can still be non-coplanar and the potential optical activity remains. This is demonstrated by the condensation of *d*-2,2'-diamino-1,1'-dinaphthyl with benzil with the formation of a highly active product (I)^{3,4} in which the 2,2'-carbons are in an eight-membered ring.



Sako⁵ has reported the preparation from active 2,2'-dimethyl-6,6'-diaminobiphenyl of two derivatives (II, III) in which seven-membered rings are formed through the two amino groups. Both of these compounds are optically active.



If a metal ion is coordinated to substituents in

(1) This article is based upon a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois.

(2) Socony-Vacuum Laboratories Fellow in Chemistry 1954-1955.

(3) R. Kuhn and P. Goldfinger, *Ann.*, **470**, 183 (1929).

(4) E. Tauber, *Ber.*, **25**, 3287 (1892); **26**, 1703 (1893).

(5) S. Sako, *Mem. Coll. Eng. Kyushu Imp. Univ.*, **6**, 263 (1932).

the 2,2'-positions of a biphenyl derivative, a seven-membered or larger ring results and by analogy to the above cases, the complex should be optically active. In the present investigation, 2,2'-diaminobiphenyl was chosen as the ligand. Bis-ethylenediamine-(2,2'-diaminobiphenyl)-cobalt(III) chloride was prepared and resolved into four optical isomers.

Experimental and Discussion of Results

Preparation of Bis-ethylenediaminediaminobiphenyl-cobalt(III) Chloride.—The method described by Middleton⁶ was used. One and four-tenths grams of $[\text{Coen}_2\text{Cl}_2]\text{Cl}$ and nine-tenths gram of diaminobiphenyl were placed in a flask and 25 ml. each of alcohol and water were added. Half a gram of charcoal was added and the flask was stoppered and shaken for two days. The charcoal was then filtered off and the filtrate was mixed with 75 ml. of absolute alcohol. Seventy-five milliliters of ether was added and the mixture was allowed to stand for three hours. The product was then filtered off and washed with absolute alcohol and ether and air-dried. It was recrystallized by dissolving it in 40 ml. of 50% alcohol and reprecipitating it by adding, successively, 3 ml. of concentrated hydrochloric acid, 50 ml. of absolute alcohol and 30 ml. of ether. The precipitate was washed as before and dried at 110° for seven hours. *Anal.* Calcd. for $[\text{Coen}_2 \text{dabp}]\text{Cl}_3$: C, 40.90; H, 5.97; N, 17.90. Found: C, 40.82; H, 6.64; N, 17.17. This molecule has two centers of asymmetry—the cobalt atom and the biphenyl. It, therefore, has four optical isomers.

The Resolution of Bis-ethylenediaminediaminobiphenyl-cobalt(III) Chloride.—The procedure used in the resolution

TABLE I
ROTATIONAL DATA OF FRACTIONS IN SERIES I

Fraction	Wt. of fraction, g.	Wt. of sample, mg.	Obsd. rotation, deg.	$[\alpha]_D$, deg.
1	0.11	52	-0.395	-76
2	.12	52	- .382	-73
3	.13	49	- .149	-30
4	.24	48	+ .217	+45
5	.18	53	- .022	- 4
6	.17	52	+ .318	+61
7	.23	52	+ .209	+40
8	.12	52	+ .327	+63
9	.11	49	+ .162	+33
10	.11	50	+ .102	+20
11	.11	51	+ .051	+10
12	.10	50	- .102	-20
13	.08	51	+ .464	+91
14	.10	50	+ .100	+20
15 (to dryness)	.20	50	+ .064	+13

(6) E. B. Middleton, Ph.D. Thesis, University of Illinois, 1938.

is similar to that described by Cooley.⁷ Equimolar amounts of $[\text{Coen}_2\text{dabp}]\text{Cl}_3$ and silver tartrate were ground in a mortar with a little water and the silver chloride was filtered off. The filtrate was evaporated and the $[\text{Coen}_2\text{dabp}]\text{Cl}$ tart was fractionally crystallized by evaporation of the solution at room temperature. The rotations of the fractions are given in Table I. The rotations were taken on a Schmidt and Haensch polarimeter graduated in thousandths of degrees.

Series I was refractionated by combining fractions one and two, recrystallizing them and using the filtrate as solvent for the next fraction, etc. Fractions ten and eleven, and fourteen and fifteen were also combined and treated as single fractions. The rotations of the fractions in series II are given in Fig. 1. The number of maxima and minima indicate the number of isomers present.

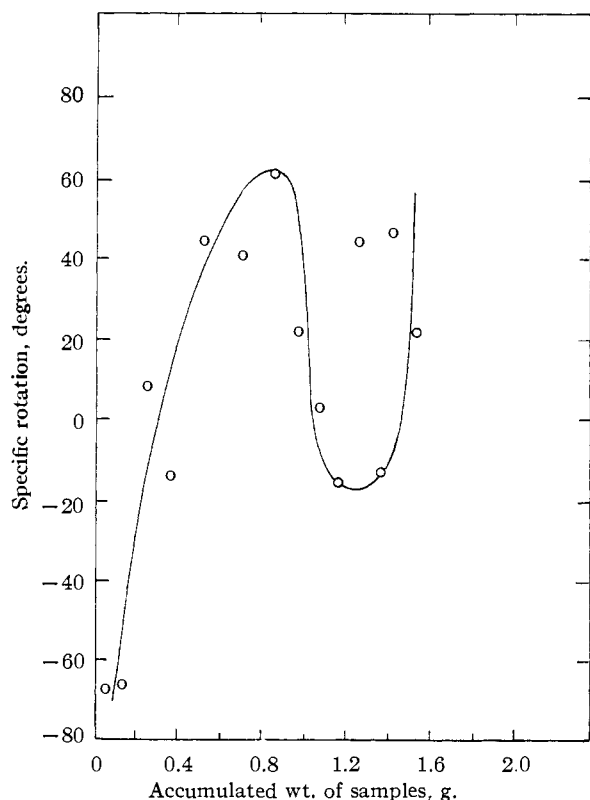


Fig. 1.—Distribution of rotation among the fractions (series II).

The fractions of Series II were combined as follows

Fractions (series II)	$[\alpha]_D$, deg.	Fraction (series III)
1, 2	-67, -66	A (not refractionated in this series)
3, 4	+8, -14	B (refractionated into 4 fractions)
5, 6	+44, +41	C (refractionated into 3 fractions)
7	+61	D (not refractionated in this series)
8, 9	+21, +2	E (refractionated into 3 fractions)
10, 12	-16, -13	F (not refractionated in this series)
11, 13	+44, +46	G (not refractionated in this series)
14	+22	H (refractionated into 2 fractions)

The fractions in series III were combined as follows

Fractions (series III)	$[\alpha]_D$, deg.	Fractions (series IV)
A, B1, B2	-66, -78, -49	A'
B3, B4, C2, C3	+25, +33, +34, +36	B'
C1, D	+62, +60	C'
E1, F	-5, -15	D'
E2, E3, H2	+27, +38, +24	E'
G, H1	+45, +78	F'

(7) W. E. Cooley, Ph.D. Thesis, University of Illinois, 1954.

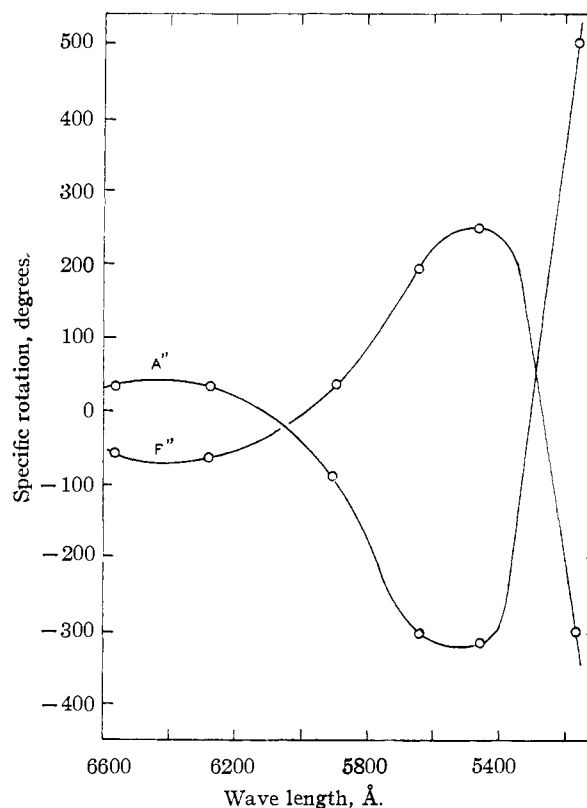


Fig. 2.—Rotatory dispersion curves (solutions A'' and F'').

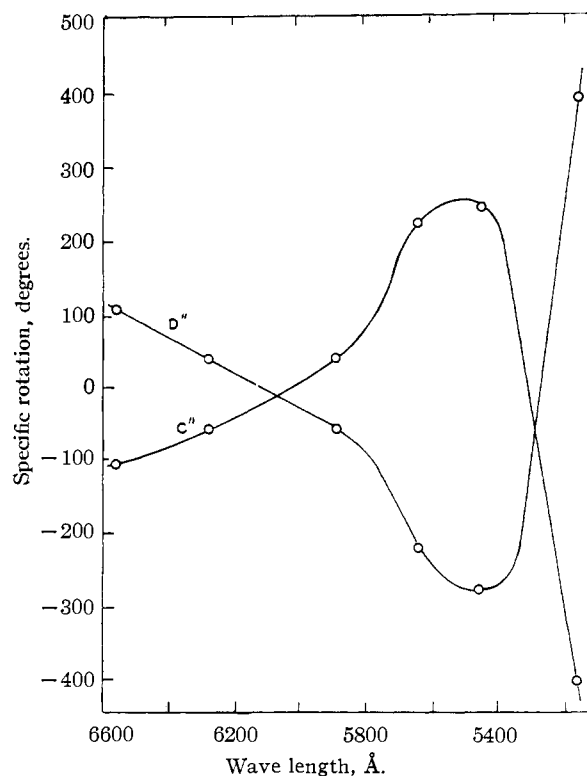


Fig. 3.—Rotatory dispersion curves (solutions C'' and D'').

Fractions A', C', D' and F' evidently contain the four isomers of the complex, while fractions B' and E' contain mixtures of A', C' and D', F', respectively. Fractions A',

C', D' and F' were recrystallized twice. The rotations of the fractions are given in Table II.

TABLE II
ROTATIONAL DATA OF FINAL FRACTIONS

Fraction	Wt. of sample, mg.	Obsd. rotation	$[\alpha]_D$, deg.
A''	10	-0.068°	-68
C''	10	+ .072	+72
D''	10	- .060	-60
F''	10	+ .061	+61

The specific rotations of succeeding fractions were diverging and this is further evidence of the presence of four fractions.

Thirty-milligram samples of fractions A'', C'', D'' and F'' were dissolved in water and 30 mg. of 48% hydrobromic acid (10% excess) was added to each solution. The solutions were filtered and evaporated to small volume at room temperature, and acetone was added to precipitate the complex bromide, $[\text{Coen}_2\text{dabp}]\text{Br}_3$. This was washed with acetone and dried.

The rotatory dispersion curves for the four isomers of the bromide are plotted in Figs. 2 and 3.

It can be seen from the rotatory dispersion curves that the samples are not completely pure since the rotations do not pair up exactly.

The complex bromide is reasonably stable to racemization. Solutions of isomers A'' and C'' were made up in approximately equal concentrations—0.05 and 0.045%—and the rate of loss of optical activity was determined. There is very little difference in the rate of change in the two isomers (Table III).

TABLE III
RACEMIZATION DATA

Time, hr.	A''		C''	
	Obsd. rotation, deg.	Specific rotation, deg.	Obsd. rotation, deg.	Specific rotation, deg.
0	-0.040	-77	+0.030	+67
5	- .040	-77		
24	- .031	-60	+ .030	+67
48	- .025	-48	+ .020	+44
70			+ .010	+22
96			+ .005	+11
121			+ .001	~ 0

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[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XX. The Tetradentate and Bidentate Complexes of Ethylenediaminetetraacetic Acid

BY DARYLE H. BUSCH AND JOHN C. BAILAR, JR.

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Two types of ethylenediaminetetraacetic acid complexes may be prepared with platinum(II) and palladium(II). In one, the ligand acts as a bidentate group and in the other, as a tetradentate group. The complex compounds have been characterized on the basis of analysis, equivalent weight, pK_{av} of the free acids, infrared spectra and isomer studies. These compounds provide proof that the hexafunctional ethylenediaminetetraacetic acid may use only a few of its donor atoms in the formation of certain complexes.

Introduction

In an earlier paper,¹ the authors confirmed the ability of ethylenediaminetetraacetic acid (EDTA) to act as a hexadentate and as a pentadentate donor molecule when combined with cobalt(III). It is commonly assumed that this ligand acts as a tetradentate donor in combination with metal ions having a coordination number of four. This has not been proven, however, and it was the purpose of this investigation to determine whether or not EDTA utilizes four or fewer groups in the formation of coordinate bonds in such cases. The dipositive ions of platinum and palladium were chosen for these studies since an invariable coordination number of four is best established for them. In the event that EDTA acts as a tetradentate chelate, in combination with platinum(II) or palladium(II), it is to be expected that the two nitrogen atoms and two of the carboxyl groups will be involved in the bonding. Since these metal ions normally form square planar complexes, the two carboxyl groups involved in bond formation must be parts of acetate groups attached to the two different nitrogen atoms. The resulting complex might be expected to exist in racemic and *meso* forms as a result of the asymmetry of the two nitro-

gen atoms. Study of the Fisher-Hirschfelder-Taylor models shows that the *meso* isomer is strained. It would be expected that the *meso* form would find its greatest stability in the acid form since a slight attraction might be gained through hydrogen bonding of the two carboxyl groups, while the two charges of the dinegative anion would cause the carboxyl groups to be strongly repelled from each other. The acids derived from the two geometrical isomers should differ greatly in their pK_1 and pK_2 values since they are comparable to the *cis* and *trans* forms of an unsaturated dicarboxylic acid.²

Palladium(II) and platinum(II) complexes of EDTA have not previously been prepared, and only recently has it been realized that complexes are formed in solutions of these substances.³ In the present study, it has been found that EDTA reacts in a stepwise manner with platinum(II) chloride, palladium(II) chloride, tetrachloroplatinate(II) ion or tetrachloropalladate(II) ion, first replacing two chlorides with the two nitrogen atoms and then replacing the remaining two chlorides with two carboxyl oxygen atoms. Free acids of both

(2) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 396.

(3) W. M. MacNevin and O. H. Krieger, *Anal. Chem.*, **26**, 1768 (1954).

(1) D. H. Busch and J. C. Bailar, Jr., *THIS JOURNAL*, **75**, 4574 (1953).