(1.0 g, 0.005 mole) and 1,10-phenanthroline (1.5 g, 0.0075 mole) in 80 ml of anhydrous pyridine was heated to reflux for 12 hr. The yellow product was washed with ethanol and ether and air dried, yield 2.2 g (90%). Purification was carried out as before: for a 0.2% aqueous solution, $\alpha^{25}\text{D}$ +0.004 ± 0.001, $[\alpha]^{25}\text{D}$ +20 ± 5°.

Anal. Calcd for $[CoC_{18}H_{20}N_6]Cl_3$: C, 43.96; N, 17.09; H, 5.33. Found: C, 44.22; N, 17.2; H, 5.14.

The ultraviolet spectrum (in aqueous solution) of D*-α-[Co(phen)(trien)]Cl_3 showed the following absorption maxima (10^3 cm^{-1} (log ε)); ν_1, 21.28 (2.10); ν_2, 28.49 (2.82); ν_3, 29.8 (3.01) (sh); ν_4, 31.47 (3.41) (sh); ν_5, 36.36 (4.18); ν_6, 44.64 (4.48). The infrared spectrum of D*-α-[Co(phen)(trien)]Cl_3 showed bands at 3050 (sh), 1610 (m), 1340 (sh), 1230 (w), 1140 (m), 1065 (s), 1045 (s), 1025 (m), 870 (sh), 850 (s), 792 (m), 776 (m), 695 (w), 645 (sh), 621 (w), 580 (w), 488 (s), 394 (w), 374 (w), 322 (w), and 306 (s).

Apparatus. The apparatus used was the same as described in an earlier paper.[1]

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The Stereochemistry of Complex Inorganic Compounds. XXXII. The Stereochemistry of the Ethylenediamine-2,2′-diaminobiphenylplatinum(II) Ion and the Bis(diaminobiphenyl)platinum(II) Ion

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Contribution from the William Albert Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois. *Received August 16, 1965*

Abstract: The ethylenediamine-2,2′-diaminobiphenylplatinum(II) ion has been resolved into optically active forms. The asymmetry arises from the noncoplanarity of the two phenyl rings, which is maintained by their attachment to the metal ion. Aqueous solutions of the isomers show no loss of optical activity in 140 min at room temperature. Dichloro-2,2′-diaminobiphenylplatinum(II) and its isomer, bis(diaminobiphenyl)platinum(II) tetrachloroplatinate(II), were prepared and characterized. The bis(diaminobiphenyl)platinum(II) ion might exist in both racemic and *meso* forms, but no evidence for the existence of such isomerism was seen. The ion proved to be too unstable for resolution.

It has long been known that derivatives of biphenyl having bulky substituents in the 2,2′, 6, and 6′ positions exist in the form of optical isomers because the two rings of the biphenyl cannot be in the same plane and are not free to rotate about their common axis. If there are substituent groups in only the 2 and 2′ positions, the rings can rotate and racemization is rapid.

If a metal ion is coordinated to substituents in the 2,2′ positions of the biphenyl derivatives, it should be possible to separate the resulting complex compound into optically active isomers, because coordination with the metal ion prevents rotation of the phenyl rings. McCollough and Bailar[1] prepared bis(ethylenediamine-2,2′-diaminobiphenyl)cobalt(III) chloride and resolved it into four isomeric forms, which can be designated as D*d*, D*l*, L*d*, and L*l*, the capital letters representing the optical activity inherent in the complex and the small letters the activity of the ligand. Although their evidence is quite clear, the demonstration of the asymmetry of the diaminobiphenyl group might be considered to be more solidly established if it were the only asymmetry in the complex, so it was decided to attempt the preparation and resolution of complexes of this type. The complexes chosen for study were the ethylenediamine-2,2′-diaminobiphenylplatinum(II) ion and the bis(2,2′-diaminobiphenyl)platinum(II) ion.

Experimental Section

Preparation of Ethylenediamine-2,2′-diaminobiphenylplatinum(II) Chloride. Dichloroethylenediamineplatinum(II) was prepared by the method of Heneghan and Bailar,[2] and diaminobiphenyl by the method of Lloyd and McDougall.[3] From these two, ethylenediamine-2,2′-diaminobiphenylplatinum(II) chloride was prepared as follows. Diaminobiphenyl (4.65 g, 0.025 mole) and [Pt(en)Cl_2] (5.65 g, 0.025 mole) were placed in a flask containing 200 ml each of alcohol and water. The mixture was stirred mechanically at 75–85° for 2 hr on a steam bath. The suspended yellow crystals of [Pt(en)Cl_2] slowly dissolved to give a colorless solution. This solution was evaporated to dryness at 30° by use of a rotary evaporator. The crystals were washed with absolute alcohol and ether and air dried. They were then recrystallized from water, washed with alcohol and ether, and dried at 50° for 8 hr *in vacuo*. The resulting white crystalline product (yield 85.3%) melted with decomposition at 260°.

Anal. Calcd for [Pt(en)(dabp)]Cl_2: C, 32.95; H, 3.95; N, 10.98; Pt, 38.23; Cl, 13.89. Found: C, 33.00; H, 4.07; N, 11.29; Pt, 38.10; Cl, 14.40. The infrared spectrum of [Pt(en)(dabp)]Cl_2, which was taken on the Beckman IR5A, is given in Table I.

The Resolution of Ethylenediamine-2,2′-diaminobiphenylplatinum(II) Ion. Equimolar amounts of [Pt(en)(dabp)]Cl_2 (2.1 g or 0.041 mole) and silver tartrate[4] (1.5 g, 0.041 mole) were dissolved in 500 ml of water. The silver chloride was filtered off, and the filtrate was concentrated to saturation (200 ml). The desired [Pt(en)(dabp)][$C_4H_4O_6$] was then precipitated by adding alcohol, filtered, washed with alcohol, and dried at 50° *in vacuo* (yield 74.7%).

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[1] F. McCollough, Jr., and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 78, 714 (1956).

[2] L. F. Heneghan and J. C. Bailar, Jr., *ibid.*, 75, 1840 (1953).

[3] D. Lloyd and R. H. McDougall, *J. Chem. Soc.*, 4136 (1960).

[4] G. Brauer, *et al.*, "Handbuch der Präparative anorganischen Chemie," F. Enke, Stuttgart, 1960, p 922.

Table I. Infrared Spectrum of $[Pt(en)(dabp)]Cl_2$[a]

ν, cm⁻¹	Intensity	ν, cm⁻¹	Intensity	ν, cm⁻¹	Intensity
3257	m	1277	s	1030	w
3040	sh	1266	sh	1009	w
1613	s	1227	w	892.9	w
1577	vs	1205	s	878.0	m
1511	w	1170	s	838.9	m
1488	ms	1129	s	819.7	m
1332	m	1093	m	772.8	vs
1314	w	1105	s	732.6	s

[a] s, strong; m, medium; w, weak; sh, shoulder.

Anal. Calcd for $[Pt(en)(dabp)][C_4H_4O_6]\cdot H_2O$: C, 35.55; H, 4.31; N, 9.25; Pt, 32.07. Found: C, 35.18; H, 4.47; N, 9.25; Pt, 32.07.

Before the tartrate was exchanged with other anions, [Pt(en)(dabp)][tart] was fractionally crystallized. About 3.6 g of [Pt(en)(dabp)][tart] was dissolved in 400 ml of warm water. The solution was concentrated by use of a rotary evaporator until it seemed to be saturated (300 ml). Then the solution was put into a vacuum desiccator, and [Pt(en)(dabp)][tart] was fractionally crystallized by evaporation at room temperature. The rotations of the fractions which were collected are given in Table II. The rotations of the fractions were taken on a Bendix-Ericsson ETL-NPL Automatic polarimeter Type 143A equipped with a Sargent recorder, Model S-72180-50. This was checked against solutions of tartaric acid. Since a solution of tartaric acid containing the same tartrate ion concentration as the solutions listed in Table II gave $[\alpha]^{28}D$ +9.6, it appears that in fractions 1 and 2 the cation is racemic. However, fractions 3 and 4, which have smaller specific rotations, contain the *l* isomer, while fractions 5 and 6 contain the *d* isomer. Fractions 3 and 4 were combined, as were fractions 5 and 6, and were designated as fractions A and B, respectively. The crystals of both of these fractions were treated with lead nitrate to convert the tartrate salt to the nitrate. Fraction A (1.14 g or 0.0019 mole) was treated with lead nitrate (0.73 g or 0.0021 mole) in 100 ml of water. After filtering off the lead tartrate, the solution of $[Pt(en)(dabp)](NO_3)_2$ was concentrated in a vacuum desiccator to about 5 ml. The crystals of *l*-$[Pt(en)(dabp)](NO_3)_2$ were filtered off, washed with alcohol, and dried *in vacuo* at room temperature, yield 77.2%.

Table II. Rotation Data on Fractions

Fraction	Wt of fraction, g	Wt of sample, mg/5 ml (1%)	Obsd rotation, deg	$[\alpha]^{28}D$, deg
1	1.4	50	+0.0080	+8.0
2	0.2	50	+0.0096	+9.6
3	1.0	50	+0.0032	+3.2
4	0.2	50	+0.0024	+2.4
5	0.3	50	+0.0104	+10.4
6[a]	0.5	50	+0.0120	+12.0

[a] To dryness.

Anal. Calcd for *l*-$[Pt(en)(dabp)](NO_3)_2$: C, 29.84; H, 3.55; N, 14.91; Pt, 34.64. Found: C, 29.89; H, 3.65; H, 14.75; Pt, 34.45.

The infrared spectrum of *l*-$[Pt(en)(dabp)](NO_3)_2$ is given in Table III. The compound showed no loss of optical activity upon standing in solution at room temperature for 140 min. The optical stability is great enough to allow the compound to be recrystallized at room temperature. After three recrystallizations from water, the specific rotation of this compound was $[\alpha]^{28}D$ −3.8°. Fraction B was treated in the same way.

Anal. Calcd for *d*-$[Pt(en)(dabp)](NO_3)_2$: C, 29.84; H, 3.55; N, 14.91; Pt, 34.64. Found: C, 29.79; H, 3.66; N, 14.63; Pt, 33.60.

The infrared spectrum of *d*-$[Pt(en)(dabp)](NO_3)_2$ was the same as that of the *l* compound. After the three recrystallizations, the specific rotation of the *d* complex was $[\alpha]^{28}D$ +4.0°.

Table III. Infrared Spectrum of *l*-$[Pt(en)(dabp)](NO_3)_2$ (Nujol)[a]

ν, cm⁻¹	Intensity	ν, cm⁻¹	Intensity	ν, cm⁻¹	Intensity
3484	w	1418	vs	881.1	w
3195	sh	1309	vs	836.1	w
3115	s	1200	m	824.4	m
1626	sh	1157	s	811.0	w
1610	s	1060	w	775.2	s
1567	sh	1043	m	760.5	s
1484	sh	1024	w	732.1	m
1449	vs	952.4	w		

[a] s, strong; m, medium; w, weak; sh, shoulder.

Bis(2,2′-diaminobiphenyl)platinum(II) chloride was prepared according to the reaction scheme

$$K_2PtCl_4 + dabp \longrightarrow [PtCl_2(dabp)] + dabp \longrightarrow [Pt(dabp)_2]Cl_2$$

Dichloro-2,2′-diaminobiphenylplatinum(II) was prepared as follows. An alcohol solution of diaminobiphenyl (0.25 g, 0.0014 mole) in 20 ml of alcohol was slowly dropped into a solution of potassium tetrachloroplatinate(II) (0.42 g, 0.001 mole) in a mixture of 20 ml of water and 10 ml of alcohol. The solution was stirred for 6 hr at room temperature. The red solution of potassium tetrachloroplatinate(II) gradually became colorless and a beige, crystalline precipitate formed. It was found that these crystals were of two kinds. One kind is soluble in acetone, and the solution, upon evaporation, gives yellow crystals; the other, which is beige, is not soluble in acetone or in water. Elemental analyses of these two materials indicate that they have the same composition.

Anal. Calcd for $[PtCl_2(dabp)]$: C, 32.01; H, 2.68; N, 6.22; Cl, 15.74; Pt, 43.33. Found (yellow crystals): C, 32.31; H, 2.88; Cl, 15.74; Pt, 42.18. Found (beige crystals): C, 32.52; H, 2.96; N, 5.57; Cl, 14.98; Pt, 43.05.

Both forms of the material are hygroscopic. The infrared spectra (Table IV) show that they are different from each other. Because of the solubility relationships and the infrared spectra, it is thought that the yellow crystals are dichloro-2,2′-diaminobiphenylplatinum(II) and the beige crystals are bis(diaminobiphenyl)platinum(II) tetrachloroplatinate(II).

Table IV. Infrared Spectra of Yellow and Beige Crystals

ν, cm⁻¹	Intensity	ν, cm⁻¹	Intensity	ν, cm⁻¹	Intensity
		Yellow Crystals			
3425	w	1534	sh	946.1	m
3279	w	1488	s	838.2	m
3165	sh	1418	sh	813.0	w
3077	s	1416	w	806.5	w
2304	w	1272	w	794.3	w
1613	sh	1208	w	771.6	s
1577	s	1160	s	761.0	sh
1563	sh	1144	vs	754.7	vs
1541	w	1086	m	729.9	s
		Beige Crystals			
3425	w	1538	w	836.8	w
3165	sh	1534	sh	807.1	sh
2315	w	1488	s	792.4	w
1650	sh	1418	sh	763.9	s
		1342	sh		
1618	m	1236	m	732.1	m
1592	m	1198	m		
1560	sh	1093	w		

Bis(2,2′-diaminobiphenyl)platinum(II) chloride was prepared as follows. A mixture of diaminobiphenyl (0.368 g, 0.002 mole), dichloro-2,2′-diaminobiphenylplatinum(II) (0.45 g, 0.001 mole), and 20 ml of acetone was stirred mechanically at 60° for 3 hr. The yellow solution gradually became colorless and yielded white crystals; these were washed with alcohol and ether, yield 82.7%. These crystals were soluble in water but not in alcohol or in acetone, and were hygroscopic.

Anal. Calcd for $[Pt(dabp)_2]Cl_2$: C, 45.43; H, 3.81; N, 8.82; Pt, 30.75. Found: C, 45.92; H, 3.85; N, 8.51; Pt, 30.28.

Table V. Infrared Spectrum of [Pt(dabp)$_2$]Cl$_2$

ν, cm^{-1}	Intensity	ν, cm^{-1}	Intensity	ν, cm^{-1}	Intensity
3390	m	1538	w	1164	w
3086	sh	1508	sh	1117	w
2315	w	1490	s	1085	w
1647	sh	1418	sh	840.3	w
1618	sh	1342	sh	814.3	w
1590	s	1239	m	768.6	s
1563	sh	1199	m	735.3	m

The compound gave almost the same infrared spectrum as the beige crystals, as shown in Table V.

All attempts to convert [Pt(dabp)$_2$][PtCl$_4$] to [Pt(dabp)$_2$]Cl$_2$ by reaction with diaminobiphenyl according to the equation

$$[\mathrm{Pt(dabp)_2}][\mathrm{PtCl_4}] + 2\ \mathrm{dabp} \longrightarrow 2[\mathrm{Pt(dabp)_2}]\mathrm{Cl_2}$$

were unsuccessful, probably because of the insolubility of [Pt(dabp)$_2$][PtCl$_4$]. The resolution of [Pt(dabp)$_2$]Cl$_2$ by means of tartrate was attempted, but the solution of [Pt(dabp)$_2$][tart] decomposed, giving a reddish brown color before any crystals separated.

A study of atomic models of the two complex ions, [Pt(en)(dabp)]$^{2+}$ and [Pt(dabp)$_2$]$^{2+}$, shows that there is a slight distortion in the model of [Pt(dabp)$_2$]$^{2+}$. Some of the hydrogen atoms which surround the platinum atom are so close together that they interfere with each other. This may explain why [Pt(dabp)$_2$]$^{2+}$ is not stable enough to be resolved. In the case of [Pt(en)(dabp)]$^{2+}$, there is no distortion. In any event, it is clear the diaminobiphenyl is the only seat of the optical activity. We hope, at a later time, to study the kinetics and mechanism of the racemization of [Pt(en)(dabp)]$^{2+}$.

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Reactions of Coordinated Ligands. XIII.

Cobalt(III)-Promoted Hydrolysis of Glycine Esters[1a]

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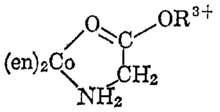
Abstract: Metal ion promoted hydrolysis of α-amino esters is a matter of significance. The investigation of cobalt(III) systems has provided insight into the nature of this accelerated hydrolysis. The glycine ester containing complexes, *cis*-[Co(en)$_2$(NH$_2$CH$_2$CO$_2$R)X]X$_2$, where en is ethylenediamine, R is CH$_3$, C$_2$H$_5$, or *i*-C$_3$H$_7$, and X is Cl or Br, are relatively inert with respect to hydrolysis in aqueous solution. However, in acid solution, mercury(II) ion reacts readily with each of the complexes, resulting in hydrolysis of the ester and formation of glycinatobis(ethylenediamine)cobalt(III) as the sole final product. Spectrophotometric studies reveal that the coordinated halide is removed by the mercury(II) in a first step, and that hydrolysis of the ester occurs in a subsequent step. Infrared spectral data strongly suggest that the intermediate is the chelated ester complex



The hydrolysis of the chelated ester is very much more rapid than the hydrolysis of the ester bound through the amino group alone. The rate of reaction of the intermediate is insensitive to hydrogen ion concentration below pH 4. However, a study of the reaction in a number of buffer systems has shown that the reaction is subject to general nucleophilic or general base catalysis.

Divalent transition metal ions are known to promote the hydrolysis of esters of α-amino acids.[2a] The nature of the hydrolytic process is of special interest because of its possible relationship to similar enzymatic processes occurring in biological systems. With this in mind Bender and Turnquest[2b] have studied in some detail the copper(II)-promoted hydrolysis of certain of these esters. On the basis of oxygen-18 exchange data and kinetic studies, they have proposed a mechanism for the promotion which involves formation of a complex in which the ester is chelated to the metal ion through the amino group and the carbonyl oxygen. The accelerated hydrolysis is then explained on the assumption that the polarization of the carbonyl group makes the carbon more susceptible to nucleophilic attack.

The earlier studies do not exclude the possibility of mechanisms other than that summarized above, for example, one involving attack of the dangling ester function by coordinated water or hydroxide ion. Resolution of such problems relating to the mechanism is extremely difficult using the systems previously studied because of the labile nature of the complexes involved. The present investigation utilizes relatively inert cobalt(III) complexes in order to permit preparation and characterization of intermediates and isolation of the steps in the complicated over-all rate process. The glycine ester containing complexes, *cis*-[Co(en)$_2$(NH$_2$CH$_2$CO$_2$R)Cl]Cl$_2$, where en is ethylenediamine and R is CH$_3$, C$_2$H$_5$, and *i*-C$_3$H$_7$, described elsewhere,[3] together with the corresponding bromo complexes, have proved useful in this connection.

In addition to the elucidation of the hydrolytic process, the studies involving these compounds have

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(1) (a) From the Ph.D. Thesis of M. D. A.; (b) Ethyl Corporation Fellow, 1962-1963; American Oil Company Fellow, 1963-1964.

(2) (a) H. Kroll, *J. Am. Chem. Soc.*, 74, 2036 (1952); (b) M. L. Bender and B. W. Turnquest, *ibid.*, 79, 1889 (1957).

(3) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, in press.