

## Stereochemistry of Complex Inorganic Compounds. 37. Stereoselective Effects in Reactions of Cobalt Complexes Containing *d*- and *l*-Phenylethylenediamine

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The stereoselectivity of complex ions that depends upon the chiral nature of the ligands has been studied extensively with the hope of using it in the optical resolution of chiral ligands. Earlier studies have centered upon 1,2-propanediamine (pn) and stilbenediamine (stien). This paper is concerned with complexes containing phenylethylenediamine (phenen). The complexes of  $[\text{Co}(d\text{-phenen})_2(d\text{-tart})]^+$  and  $[\text{Co}(d\text{-phenen})_2(l\text{-tart})]^+$  react with  $\text{Pb}^{2+}$  and  $\text{Ba}^{2+}$  at quite different rates. This offers a method of separating the tartrate isomers.

### Introduction

In metal complexes in which bulky bidentate or multidentate ligands are attached to the central atom, the limited space around this atom tends to force the complexes to assume those configurations that minimize the interligand and the intraligand repulsive forces. This paper reports the results of an investigation of a stereoselective effect, as it applies to complexes with two optically active bidentate ligands in a complex of cis configuration.

One of the earliest observations of stereoselective effects in metal complexes was made by Tschugaeff and Sokoloff,<sup>1</sup> who reported the isolation of only one isomer of the propylenediamine (pn) complex  $[\text{Co}(l\text{-pn})_3]\text{I}_3 \cdot 2\text{H}_2\text{O}$ . Smirnoff<sup>2</sup> noted that three different methods of preparation, using racemic propylenediamine, yielded only the (+)- $[\text{Co}(l\text{-pn})_3]^{3+}$  and the (-)- $[\text{Co}(d\text{-pn})_3]^{3+}$  ions. Using racemic *trans*-1,2-diaminocyclopentane (cpn), Jaeger and Blumendal<sup>3</sup> obtained an equimolecular mixture of the *trans*- $[\text{Co}(l\text{-cpn})_2\text{Cl}_2]^+$  and *trans*- $[\text{Co}(d\text{-cpn})_2\text{Cl}_2]^+$  ions. An attempt to prepare  $[\text{Co}(l\text{-cpn})_2(d\text{-cpn})]^{3+}$  by reaction of *trans*- $[\text{Co}(l\text{-cpn})_2\text{Cl}_2]^+$  with *d*-cpn yielded only a 2:1 mixture of *D*- $[\text{Co}(l\text{-cpn})_3]^{3+}$  and *L*- $[\text{Co}(d\text{-cpn})_3]^{3+}$ . Like Smirnoff, Jaeger and Blumendal believed that the *lld* complex disproportionated according to the equation  $3[\text{lld}] \rightarrow 2[\text{lll}] + [\text{ddd}]$ . The driving force for such a reaction was thought to be the greater stability of the more symmetrical arrangement. However, Dwyer et al.<sup>4,5</sup> disagreed with the concept of disproportionation since this would necessitate the dismemberment and re-formation of the complex.

Bailar and McReynolds<sup>6</sup> observed interconvertibility of the two isomers of  $[\text{Co}(l\text{-pn})_2\text{CO}_3]^+$ , and by evaporating solutions of  $[\text{Co}(l\text{-pn})_2\text{CO}_3]\text{Cl}$  at room temperature and at 85–90 °C, Martinette and Bailar<sup>7</sup> obtained products that exhibited quite different rotations. In the hope that some differentiation could be seen, the reaction of  $[\text{Co}(l\text{-pn})_2\text{a}_2]^+$  (a = Cl or NO<sub>2</sub>) with racemic propylenediamine was studied. However, both isomers of the base reacted equally easily.<sup>8,9</sup> Jonassen, Bailar, and Huffman<sup>10</sup> treated *D,L*- $[\text{Co}(\text{en})_2\text{CO}_3]\text{Cl}$  with *d*-tartaric acid and obtained a material, which upon treatment with calcium nitrite, gave a 40% yield of *D*- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$ , after which the reaction stopped. This seems to indicate that both the *D* and *L* isomers of the tartrate complex were present in the mixture, but only one of them reacted with the calcium nitrite.

In  $[\text{Co}(l\text{-pn})_2(\text{tart})]^+$  (tart = tartrate), disproportionation does not take place, and both  $[\text{Co}(l\text{-pn})_2(d\text{-tart})]\text{Cl}$  and  $[\text{Co}(l\text{-pn})_2(l\text{-tart})]\text{Cl}$  are readily formed. Both react with *l*-propylenediamine, forming  $[\text{Co}(l\text{-pn})_3]^{3+}$ , but the latter reacts much more rapidly than the former.<sup>10</sup> Gott<sup>11,12</sup> obtained further evidence that the two tartrato complexes have different stabilities by measuring the pH of aqueous solutions of the metal complexes containing *l*-propylenediamine. The complex containing the *l*-tartrate ion hydrolyzes more rapidly than the one containing the *d*-tartrate ion.

Since it was expected that the tendency toward preferential coordination would increase as asymmetry within the coordination sphere increases, Williams<sup>13</sup> prepared complexes of 1,2-di-

phenylethylenediamine (stien) in the hope that the presence of two optically active centers would reinforce the stereoselective effect. However, this proved not to be the case. This failure was attributed to the great steric hindrance resulting from the large number of phenyl groups in this ion; this, it was thought, overshadowed the selectivity. Incidentally, it was observed that cobalt complexes containing two molecules of *meso*-1,2-diphenylethylenediamine are much less stable and more difficult to prepare than the corresponding ones containing the racemic ligand. These results are quite in accord with the results of conformational analysis<sup>14</sup> and gave hope that it would be possible to develop a method of optical resolution of chiral ligands based on this type of stereoselectivity.

For the study reported in the present paper, phenylethylenediamine (phenen) was chosen as the ligand. It was hoped that the large size of the phenyl group would enhance the stereoselectivity as compared with that of the ligand containing a methyl group (pn) but that the steric problems encountered with diphenylethylenediamine (stien) would be avoided.

### Experimental Section

The ligand, *d,l*-phenylethylenediamine, was prepared by three different methods: the third method was found to be best for our purposes although it suffers from the fact that nitrostyrene vapors are very irritating. Contact with the solid must be avoided, also.

**Method 1.** Steiger's<sup>15</sup> procedure was used to prepare *d,l*-(phenylamino)acetic acid (I) from benzaldehyde (yield 41%). Esterification of I according to the method of Marvel and Noyes<sup>16</sup> gave the *d,l*-ethyl (phenylamino)acetate hydrochloride (II), which was recrystallized from ethanol, washed with ether, and dried in air (yield 90%). A solution of II in methanol was cooled to 0 °C, and ammonia gas was passed into it. The ammonium chloride precipitate was removed by filtration, and the filtrate was treated with ammonia gas to give *d,l*-(phenylamino)acetamide (III),<sup>17</sup> which was recrystallized from methanol (yield 85%; mp 130 °C). Reduction<sup>18</sup> of (III) with  $\text{LiAlH}_4$  in a 3:2 mixture of ether and

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benzene or in tetrahydrofuran gave *d,l*-phenylethylenediamine (IV), which, when dissolved in a 2:1 mixture of benzene and absolute alcohol and saturated with HCl gas, crystallized as the *d,l*-phenylethylenediamine dihydrochloride (V). This was recrystallized from methanol, washed with ether, and dried in vacuo at 100 °C: yield 55%; mp 195–300 °C. Anal. Calcd for the dihydrochloride, C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>Cl<sub>2</sub>: C, 45.95; H, 6.75; N, 13.40. Found: C, 46.02; H, 6.75; N, 13.14.

**Method 2.** The method of Mannich and Hahn<sup>19</sup> was followed for the preparation  $\alpha$ -aminoacetophenone hydrochloride (VI): yield 52%; mp 186–187 °C dec. The reaction<sup>20</sup> of hydroxylamine hydrochloride with VI gave phenacylamine oxime (VII): yield 67%; mp 143–144 °C. Reduction of VII with LiAlH<sub>4</sub> yielded IV and thence V: yield 62%; mp 195–300 °C. Anal. Found: C, 45.86; H, 6.92; N, 13.07.

**Method 3.** The reaction of nitromethane with benzaldehyde gave nitrostyrene (VIII).<sup>21</sup> The yellow product was recrystallized from alcohol: yield 80%; mp 57–58 °C. *N*-(1-phenyl-2-nitroethyl)hydroxylamine (IX) resulted from the reaction of hydroxylamine with VIII:<sup>22</sup> yield 78.5%; mp 128.5–129.5 °C.

Fifteen grams (0.0825 mol) of *N*-(1-phenyl-2-nitroethyl)hydroxylamine (IX) was dissolved in 200 mL of absolute ethanol. To this solution were added 14.2 mL (~0.165 mol) of concentrated hydrochloric acid and 0.65 g of PtO<sub>2</sub>. The mixture was connected to a Parr hydrogenator, and reduction proceeded until 0.33 mol of hydrogen gas had been absorbed. During the hydrogenation, V precipitated, so 500 mL of hot methanol was added to redissolve it. After the platinum black was filtered off, the solution was concentrated until a white product began to precipitate. When the mixture became thick, the precipitate was filtered and washed with absolute ethanol and ether. The product, V, was recrystallized from methanol and dried under vacuum at 100 °C: yield 60.5%; mp 295–300 °C. Anal. Found: C, 45.90; H, 6.81; N, 13.12.

Phenylethylenediamine dihydrochloride is very soluble in water, somewhat soluble in methanol, and slightly soluble in absolute ethanol. When crystallized from water, it contains water that is removed only by long heating in a vacuum.

The reduction of IX gave cyclohexylethylenediamine (X) when the reduction was permitted to continue until no more hydrogen uptake was observed: yield 88%; mp 261–266 °C. Anal. Calcd for C<sub>8</sub>H<sub>18</sub>N<sub>2</sub>·2HCl: C, 44.66; H, 9.37; N, 13.02; Cl, 32.95. Found: C, 44.30; H, 9.49; N, 13.10; Cl, 32.67.

**Resolution of *d,l*-Phenylethylenediamine.** A modification of the procedure of Reihlen et al.<sup>23</sup> was used. To freshly prepared silver *d*- or *l*-tartrate (80 g, 0.22 mol) was added 46 g (0.22 mol) of phenylethylenediamine dihydrochloride in enough water to allow easy mixing. After 1.5 h, the mixture was filtered, and the silver chloride precipitate was washed with water, which was added to the filtrate. By passing filtered air over the solution, it was concentrated to 200 mL. It was then heated and kept just below the boiling point while methanol (about 300 mL) was added slowly until the solution was faintly cloudy. The clear, hot solution was permitted to cool slowly. The resulting white precipitate was filtered, washed with 75% methanol solution, absolute alcohol, and ether, and dried in the air. Yield of (+)-*l*-phenylethylenediammonium *d*-tartrate (XI) was 22.4 g (71%). After recrystallization, the melting point was 210 °C,  $[\alpha]^{29}_D = +40.7^\circ$ . From the filtrate, the other diastereoisomer, (–)-*d*-phenylethylenediammonium *l*-tartrate (XII), was obtained: mp 210 °C;  $[\alpha]^{27.5}_D = -41.0^\circ$ .

The tartrates were converted to dihydrochlorides by dissolving them in water and adding the equivalent amount of CaCl<sub>2</sub>·2H<sub>2</sub>O. After filtration, the dihydrochloride was precipitated by concentration and addition of absolute alcohol; mp 301 °C.  $[\alpha]^{29}_D$  for the *l*-phenen salt (XIII) is +29.5° (lit.<sup>24</sup> +28.9°); for the *d* salt (XIV) it is –29.2°.

**trans-Dichlorobis(phenylethylenediamine)cobalt(III) chloride (XV)** was prepared by an adaptation of the method used to prepare the *trans*-dichloro complexes of ethylenediamine<sup>25</sup> and propylenediamine.<sup>26</sup> To 11.9 g (0.05 mol) of CoCl<sub>2</sub>·6H<sub>2</sub>O in 500 mL of water was added 13.08 g (0.0625 mol) of V. After being heated to 70 °C, the solution was made basic (pH 8) by the slow addition of sodium hydroxide. A vigorous stream of air was bubbled through the solution for 24 h. The tan precipitate, which began to form almost immediately, was filtered. The

filtrate was treated with 150 mL of concentrated HCl, and the volume was reduced to about 40 mL. The resulting mixture was filtered, and the solid was washed with concentrated HCl. The green precipitate was dissolved in 500 mL of absolute ethanol, and 75 mL of concentrated HCl was added. The solution was concentrated, and the precipitated green complex was washed with absolute alcohol and dried under vacuum at 65 °C: yield 5.5 g (40%); mp 263–265 °C. Anal. Calcd for [Co(phenen)<sub>2</sub>]Cl: Co, 13.46; C, 43.90; H, 5.52; N, 12.81. Found: Co, 13.32; C, 43.87; H, 5.66; N, 12.33.

Attempts to convert the *trans* to the *cis* isomer by heating the dry salt or an aqueous solution<sup>11,25</sup> were unsuccessful.

The ultraviolet and visible spectra of methanol solutions of the complex were determined on a Cary 14 recording spectrophotometer.

wavelength ( $\lambda$ ), nm	log $\epsilon$
599	1.63
445	1.63
380	1.85
252	3.95

These results are in agreement with the data for the ethylenediamine and propylenediamine analogues.<sup>27,28</sup>

**Tris(phenylethylenediamine)cobalt(III) chloride (XVI)** was prepared by modifications of the methods for Work,<sup>29</sup> Schlessinger,<sup>30</sup> and Dwyer and co-workers<sup>4,5</sup> for similar complexes. Into 500 mL of water were dissolved 5.95 g (0.025 mol) of CoCl<sub>2</sub>·6H<sub>2</sub>O and 15.7 g (0.075 mol) of V. The solution was heated to 70 °C, and the pH was adjusted to 8. The cobalt was oxidized by bubbling air through the solution for 15 h. Evaporation of the solution to dryness gave a dark gum like substance, which was dissolved in hot ethanol. The filtered solution, on concentration, gave a dull yellow precipitate (XVI). After recrystallization from water, the yield was 7.9 g (55%); mp 224–227 °C. Anal. Calcd for [Co(phenen)<sub>3</sub>]Cl<sub>3</sub>: Co, 10.26; C, 50.23; H, 6.32; N, 14.64. Found: Co, 10.66; C, 49.97; H, 6.32; N, 14.29.

The preparations of tris(phenylethylenediamine)cobalt(III) chloride containing the *l* and *d* isomers (XVII and XVIII, respectively) were carried out similarly. XVIII was also prepared by the method of Lifschitz and Dijkema.<sup>31</sup> Absorption spectra of aqueous solutions of [Co(*d*-phenen)<sub>3</sub>]Cl<sub>3</sub> show a peak at 470 nm ( $\epsilon = 112$ ) and a shoulder at 352 nm ( $\epsilon = 107$ ). These data are in agreement with those for analogous complexes of ethylenediamine and propylenediamine.<sup>30,32</sup> Fractional crystallization of XVII gave three samples, as follows: A, 1.54 g,  $[\alpha]^{32}_D = -75^\circ$ ; B, 0.92 g,  $[\alpha]^{32}_D = -61.3^\circ$ ; C, 0.54 g,  $[\alpha]^{32}_D = -38.4^\circ$ . The two samples from XVIII were D, 0.9 g,  $[\alpha]^{32}_D = +103.2$ , and E, 2.3 g,  $[\alpha]^{32}_D = +68.4$ .

Chromatography, using silica gel plates as the stationary phase and ethanol as the eluent or filter paper and wet butanol, gives two spots, indicating, again, the presence of at least two isomers.

**(Carbonato)bis(*d*-phenylethylenediamine)cobalt(III) chloride (XIX)** was prepared by the action of XIV on potassium tris(carbonato)cobaltate (III).<sup>33,34</sup> Anal. Calcd for [Co(*d*-phenen)<sub>2</sub>CO<sub>3</sub>]Cl: C, 47.84; H, 5.67; N, 13.15. Found: C, 47.90; H, 5.79; N, 12.91.

Theoretically, this compound can consist of several isomers, the most apparent of which depend upon the relative positions of the phenyl groups in the complex (*cis-cis*, *cis-trans*, and *trans-trans*). Treatment with ammonium *d*- $\alpha$ -bromocamphor- $\pi$ -sulfonate precipitated two fractions, the less soluble of which showed  $[\alpha]^{28}_D = -498^\circ$  and the more soluble of which showed  $[\alpha]^{28}_D = +40^\circ$ . Recrystallization of the former gave  $[\alpha]^{28}_D = -526^\circ$ , which was not changed by further recrystallization.

**The preparations of (*d*-tartrato)- and (*l*-tartrato)bis(*d*-phenylethylenediamine)cobalt(III) chlorides** were carried out by adding 1.758 g (1.17 mmol) of *d*- or *l*-tartaric acid to solutions of 5.00 g (1.17 mmol) of XIX. This gives the diaquo complexes. After the solutions are evaporated to dryness and heated for a long time, the tartrate ion displaces the water molecules in the coordination sphere, but the *d*-tartrato salt (XX) has to be heated very much longer (60 h in our case) than the *l*-tartrato salt (XXI) to reach constant weight.

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**Table I.** Difference in the Reaction Rates between the Reactions of XX and XXI with Lead Acetate

time, h	wt of lead <i>d</i> -tartrate from XX, g		wt of lead <i>l</i> -tartrate from XXI, g	
	each weighing	cumulative	each weighing	cumulative
	1.17	0.7398		0.3252
4.33	0.1191	0.8589	0.1954	0.5206
10.50	0.0653	0.9242	0.2499	0.7705
21.75	0.0423	0.9665	0.1402	0.9107
45.75	0.0433	1.0098	0.1162	1.0269
93.75	0.0431	1.0529	0.0486	1.0755
heated	0.2328	1.2857	0.2321	1.3076

**Table II.** Results from the Second Experiment

time, h	wt of lead ( <i>R</i> )-tartrate from XX, g	wt of lead ( <i>S</i> )-tartrate from XXI, g
1.67	0.0610	0
3.17	0.0575	0
7.33	0.0636	0
15	0.0684	0.0066
24	0.0592	0

Theoretically, the tartrate ion can coordinate with a metal ion in several different ways, forming both coordination and ring-size isomers. However, the general preference for the formation of five-membered rings leads to the conclusion that the coordination is through a carboxyl and the adjacent hydroxy group. This is supported by the work of Pyatnitskii and Hendler<sup>35</sup> and of Fialkov and Davidenko.<sup>36</sup> The absolute configuration of *d*-tartaric acid, as shown by X-ray studies,<sup>37</sup> is designated as *R* and that of *d*-phenen as *S*. Thus, [Co(*d*-phenen)<sub>2</sub>(*d*-tart)]Cl is [Co(*S*-phenen)<sub>2</sub>(*R*-tart)]Cl and [Co(*d*-phenen)<sub>2</sub>(*l*-tart)]Cl is [Co(*S*-phenen)<sub>2</sub>(*S*-tart)]Cl.

**The Reaction of (*d*-Tartrato)- and (*l*-Tartrato)bis(*d*-phenylethylenediamine)cobalt(III) Chlorides with Lead Acetate.** Two experiments were performed to determine the difference in the stabilities of these two isomers. In each case, a weighed amount of cobalt complex was dissolved in a mixture of acetone and water at a fixed temperature. Any undissolved material was removed, dried, and weighed in order to give the exact amount of material in solution. Each solution was stirred for 40 min to allow for any aquation that might take place. In the first experiment, a 9-fold excess of lead acetate was added all at once; in the

**Table III.** Reactions of XX and XXI with Barium Hydroxide

time, h	wt of barium <i>d</i> -tartrate from XX, g		wt of barium <i>l</i> -tartrate from XXI, g	
	each weighing	cumulative	each weighing	cumulative
	0.25	0.4791		0.3611
0.83	0.1131	0.5922	0.1597	0.5208
2.25	0.0648	0.6570	0.0880	0.6088
5.25	0.0420	0.6990	0.0539	0.6627
24	0.0693	0.7683	0.0883	0.7510
heated	0.0348	0.8031	0.0412	0.7922

second experiment, a similar excess was added, but in increments (one-fifth of it each time) at designated time intervals. The precipitated lead tartrate was filtered at intervals and washed, dried, and weighed. The results from the first experiment are shown in Table I; those of the second experiment are shown in Table II. It is evident that aquation does not play a determining role. Additional heating did not yield any more lead tartrate. The calculated values of 1.3506 and 1.3606 g would be expected for complete reaction of the (*R*)- and (*S*)-tartrato complexes, respectively. It is evident that both complexes lose essentially all of the combined tartrate, but the one containing (*R*)-tartrate does so much more rapidly than its isomer. In Table II the calculated amount of lead tartrate from each mixing of the portions was 0.1158 g. The complex containing (*R*)-tartrate yielded about half that much; the one containing (*S*)-tartrate yielded almost none. This offers a method of separating the *R* and *S* isomers almost completely.

The reactions between the (*R*)-tartrato and (*S*)-tartrato complexes and barium hydroxide were performed in a similar way and led to the same conclusion (Table III). Solutions of XX and XXI containing 1.4500 g (2.816 mmol) of complex in 200 mL of a 1:3 acetone-water mixture were allowed to stand 40 min, filtered, and treated with 4.45 g (14.1 mmol) of Ba(OH)<sub>2</sub>·8H<sub>2</sub>O in 50 mL of warm water. In each case a precipitate began to form immediately. After 15 min, more barium (*R*)-tartrate had formed than barium (*S*)-tartrate. The difference in weight between these two precipitates, however, was not as large as in the previous experiment because the reaction of the complex with barium hydroxide is much faster than with lead acetate. At intervals thereafter the samples were centrifuged, and the precipitates were dried and weighed. Constant weight was achieved only after long heating. No further precipitation was observed after 24 h, so the solutions were heated to 60 °C for 1 day. Practically all of the tartrate was precipitated in each case, but XX reacted more rapidly than XXI.

### Conclusions

Although the stereoselectivity shown by complexes containing chiral ligands is only relative, the results reported here indicate that, under some circumstances, it may be used in the resolution of chiral chelating materials. For practical use, it is essential that the material being resolved can be retrieved without destruction of the complex, which can then be used repeatedly.

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