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ENTITLED The Stereochemistry of Metal Chelates with Polydentate

Ligands.   Part II

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THE STEREOCHEMISTRY OF METAL CHELATES WITH

POLYDENTATE LIGANDS.   PART II

BY

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INTRODUCTION:

The ligand *bis-salicylaldehyde-triethylenetetramine* (I) forms six-coordinate complexes with the transition metal ions Co^{III}, Al^{III} and Fe^{III}, as well as four coordinate complexes with Pd^{II}, Co^{II} and Cu^{II}. In the six-coordinate complexes, these ligands can span the octahedral positions around a metal ion in several ways (see Fig. 1). These isomers exist in mirror image forms, making a total of eight possible isomers. Some of these structures are greatly strained, so the compounds probably have the structures represented by A. The *dextro-* and *levo-* stereoisomers of A can interconvert, making the two forms of the complex that are obtained.

There are several possible mechanisms of racemization. The goal of this work was to determine which mechanism is applicable to these compounds by separating the different isomers of these compounds, and comparing the rates and features of racemization of the various halides at different temperatures in the solid state. The chelate is a non-electrolite, so the conventional method of resolution into optically active isomers cannot be applied.[3] However, it is possible to separate the isomers as d-antimonyl tartrates, which can be converted to optically active chlorides, bromides and iodides. In addition, a sample of the cobalt complex is being submitted for an X-ray study to determine its absolute configuration.

HISTORY:

Sexadentate chelate compounds are a fairly recent discovery. The first such compound, a sexadentate chelate containing sulfur, was prepared by Dwyer and Lions in 1947.[1,2] Other compounds containing sulfur in their structures were investigated by Dwyer and Lions, such as *1,9-diamino-3,7-dithianonane*. A series of compounds of this general description, containing different lengths of hydrocarbon chains, were found to form sexadentate chelate compounds when condensed with salicylaldehyde.[5] Some of these compounds could be separated into optically active *d*- antimonyl

tartrates, *d*-tartrates, *d*-camphorsulfonates, *d*-α-bromocamphor-π-sulfonates and *d*-hydrogen tartrates. These compounds are notable for having extremely high optical molecular rotations, on the order of 50,000 degrees.[2]

The present compound was prepared by Ballar and Busch in 1954.[7] There are no sulfur atoms in the structure, as it is prepared from salicylaldehyde and triethylenetetramine (see Fig. 2). The compound was separated into optically active isomers by a number of methods, and the optical rotations were found to be much less than the compounds mentioned above. In addition, the approximate rates of racemization of these compounds in water and methanol were compared.[3] The absolute structure of these compounds was not determined by X-ray analysis, though they were thought to exist in only one of four possible forms (see Fig. 1).

DISCUSSION:

The attempt to prepare large quantities of optically active halides of the various complexes was not entirely successful (see Recommendations). However, a sample of the cobalt compound is being submitted for X-ray analysis to determine the absolute configuration. There were a number of results obtained from the procedure that warrant discussion. In addition, the basic procedure seems to be correct: only refinements in technique are needed to increase the yield to a useful value.

The elemental analyses of the compounds were close to the literature values. This indicates that the process to make the complexes outlined by Bailar and Das Sarma is correct.[3] The compounds formed in good yields. The original formation of the cobalt complex performed in this investigation used potash instead of potassium hydroxide. The cobalt complex formed in good yield with excellent purity, indicating that potassium hydroxide is not needed to make the reaction work. However, an attempt to make the aluminum complex using potash instead of potassium hydroxide produced no useful product. The formation of the aluminum complex seems to require a strongly basic solution to occur. The iron complex was synthesized only by the standard method.

Some data on the stereochemistry of the reaction also exist. Small amounts of weakly active complex halides were prepared. The most soluble iodide of the iron complex (d- $FeTS_2 \cdot I$) lost two thirds of its optical rotation after boiling off 13 ml of methanol. The iron compound appears to racemize quickly in methanol solution. The original iodide had an optical rotation of $+0.015^\circ$ ($+/-0.007^\circ$) as a 0.0045% solution in methanol (molecular rotation, sodium-D line, $+333^\circ$). However, measurement of these solutions was very difficult. The complexes were very dark (except for the aluminum compound) so the measurements were performed on extremely dilute solutions. An

attempt to use mercury vapor light for greater transmission in the iron complex was not successful. The instrument errors and the errors due to the design of the polarimeter tube (before March 25, after which a more precise instrument was used) often exceeded the measured rotations. The rotations measured were always on the order of 0.03 degrees or less. Many of the earlier data are suspect for this reason.

The optical rotation of the aluminum complex d- antimonyl tartrate is greater than the value reported by Ballar and Das Sarma.[3] The literature value of $[\alpha]$ D $^{\circ}$or D-$[AlTS_2]$-d- SbOtart is +44.8°, while the experimental value is +139°. Ballar and Das Sarma ment/ that the low measured activity of this fraction is due to low solubility: repeated fractionation could not be carried out. In this investigation, a large amount of the fraction was dissolved in a large amount of methanol; the complex that did not dissolve was measured.

Silver-d- antimonyl tartrate is not highly soluble in water or methanol. This presented the greatest difficulty in performing this reaction. The original technique of reacting the complex and silver-d- antimonyl tartrate (see Experimental) produced only rather low yields. Grinding with the complex was only partially successful, and only through increasing the dilution, time or temperature of the reaction were yields increased.

EXPERIMENTAL:

The synthesis of these ligands was performed in the method described by Bailar and Das Sarma.[3] Triethylenetetramine (10 ml, 75%, 0.05 mole), in methanol (50 ml); salicylaldehyde (12.1 g, 0.1 mole) in methanol (50 ml); potassium hydroxide (5.6 g, 0.1 mole); and 0.05 moles of a metal halide, nitrate or sulfate were mixed in rapid succession. The further details for each metal varied. This method was completely successful, and formed the coordination complexes in good yield. All starting materials were of reagent grade and did not require further purification. All microanalyses were performed by the Microanalytical Laboratory of the University of Illinois School of Chemical Sciences.

Bis-salicylaldehyde-Triethylenetetraminecobalt (III) Salts:

After adding the metal salt (cobalt chloride or cobalt sulfate) the mixture was oxidized by passing a strong current of air through it for one hour. Hydrochloric acid (1:1, 10 ml) was added, and the aeration was continued for twelve hours. Dark brown crystals separated, at times almost black. The product formed in good yield.

Anal. Calcd. for $[Co^{III}(C_{20}H_{24}N_4O_2)]Cl \cdot 2.5H_2O$: C, 49.00; H, 5.90; N, 11.56. Found: C, 48.88; H, 5.83; N, 11.56.

Isomeric separation was attempted by the method described by Bailar and Das Sarma: dissolving the complex (1 g) in methanol, adding an equal weight of silver-*d*-antimonyl tartrate, and stirring for one hour.[3] This method appears to be successful, but very inefficient. Very little of the complex reacted. Most of the silver-*d*-antimonyl tartrate could be filtered out, and fractions obtained from this method were too small to be of use. The isomeric separation was attempted under harsher conditions -- several grams of complex and a slightly greater than

equivalent weight of silver-d-antimonyl tartrate were dissolved in 400 ml of water. This mixture was stirred overnight, and boiled until brown crystals separated. Most of the silver-d-antimonyl tartrate appeared to react. The least soluble fraction was white or gray, being silver chloride. The second fraction of brown crystals was not optically active, and appeared to be unreacted complex. The rest of the complex which separated was dissolved in methanol and concentrated until fractions of dark brown, small crystals separated. There was white powder mixed in with the fractions, so the fractions were separated further by fractional crystallization in a minimum amount of warm water. The first fraction from the methanol solution was slightly

$levo$- rotatory: a 0.0283 % solution in water had a rotation of -0.006° (+/-0.005°), $[\alpha]$ D

42° (+/- 35°), so the compound was probably L-[Co(TS$_2$)]-d- SbOtart. The solution was evaporated to 5 ml, filtered, and evaporated to dryness to obtain the $dextro$- isomer. The d-SbOtartrates were dissolved in a minimum amount of water and a saturated solution of sodium halide was added. Small, dark brown crystals separated and were filtered.

Bis-salicylaldehyde-Triethylenetetraminealuminum (III) Salts:

The equivalent quantity of aluminum chloride, dissolved in a mixture of water and methanol, was added to the reaction mixture. The mixture was stirred for one hour and the white precipitate was filtered off. A saturated solution of potassium iodide was added to the filtrate and the aluminum complex was precipitated as the iodide. This was found to be more soluble in water than alcohol.

The most successful method of separating the isomers of this complex involved dissolving several grams of the complex, along with a slightly greater than equivalent amount of silver-d-antimonyl tartrate, in 300 ml of water and allowing the

mixture to react over a period of days. The water was removed by boiling under aspirator vacuum (the compound is subject to a slow hydrolysis, so boiling under normal pressure is not advisable) and the residue was dissolved in methanol. The solution was concentrated by boiling under aspirator vacuum. The first fraction separated around 50 ml. Nothing further separated until the volume was greatly reduced. The first fraction was d-Al-TS$_2$-d-Sb-O-tart. a 0.16% solution in water had an optical rotation (Sodium-D line) of +0.223° [α] D +139.375°. This dissolves very slowly in methanol.

The halides were made by dissolving the d-antimonyl tartrates of the complex in a minimum amount of water, and adding a saturated solution of sodium halide. The complex in solution was precipitated by adding a small amount of methanol; white crystals appeared in the solution. The *levo-* isomer can be obtained by concentrating the methanol solution of the d-antimonyl tartrate to 1 or 2 ml, filtering, diluting to 10 ml with methanol, concentrating (in vacuo), and repeating the procedure twice. This isomer may be percipitated as the less soluble halide more easily than the d- isomer because of the greater solubility of the d-antimonyl tartrate.

Bis-salicylaldehyde-triethylenetetramineiron(III) compounds:

This compound was made in the same way as the corresponding cobalt(III) and aluminum compounds. The compound was much more soluble in alcohol than in water.

Anal. Calcd. for [Fe(C$_{20}$H$_{24}$N$_4$O$_2$)]I·1.5H$_2$O: C, 42.70; H, 4.80; N, 9.99. Found: C, 42.77; H, 4.43; N, 9.87.

Resolution of the iron complex was accomplished by mixing equal weights of the complex iodide and silver-*d*-antimonyl tartrate in a large amount of water (900 ml when 5 g of the complex was used), stirring overnight, and boiling the water off. Brownish oxide appeared to form on the sides of the vessel. About half of the *d*-antimonyl tartrate reacted, and the solution was filtered, evaporated to dryness and dissolved in methanol. The first fraction separated out at about 50 ml (when 5 g was used) and this was dissolved in methanol and the least soluble fraction was collected. The original methanol solution was concentrated to a few ml, filtered, and the filtrate evaporated to dryness. This was dissolved in methanol and the least soluble fraction was collected.

The optically active halides were prepared by dissolving the *d*-antimonyl tartrates in a minimum amount of methanol and adding a few drops of saturated potassium halide solution. The complex iodide was found to lose two thirds of its optical activity in boiling methanol after a few minutes, so care must be taken when concentrating these solutions.

RECOMMENDATIONS:

This project was not entirely successful. However, it is the opinion of the author that the project can be completed with refinements on technique and many repetitions of the procedure to accumulate optically active compounds. The basic method for making and separating the complexes is sound. The yield, however, was rather low. Care must be taken to prevent the racemization of the iron and aluminum compounds when the optically active halides are being prepared.

In order to solve the problem of yield, the time or the temperature of the reaction of the complexes with silver-*d*- antimonyl tartrate must be increased. The cobalt complex is very stable, so refluxing the complex in boiling water with a slight excess of silver-*d*- antimonyl tartrate is suggested. If the reaction is refluxed in a large amount of water (300 ml for 5 g of the complex) for two or three days, most of the complex will react. Repeated combination and recrystallization of optically active fractions of the *d*- antimonyl tartrate will give optically active compounds that can be combined and added to the optically active compounds obtained by repetitions of this procedure. The procedure, repeated several times, will give enough optically active cobalt compound to complete the experiments.

The iron and aluminum compounds must be treated more gently. The aluminum compound is subject to a slow hydrolysis, and should not be boiled. The aluminum complex was successfully separated by mixing several grams of the complex with a slightly greater weight of silver-*d*- antimonyl tartrate, dissolving in 500 ml of water, and letting the water evaporate. Since the aluminum complex is more soluble in water than in methanol, the complex halides were made by dissolving the complex-*d*-antimonyl tartrate in a minimum amount of water. A saturated solution of sodium halide was added and the complex halide was precipitated by adding methanol. Care

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must be taken not to precipitate the sodium halide or the potassium-*d*- antimonyl tartrate; these are indistinguishable from the aluminum complex on casual inspection. The aluminum complex racemizes very quickly in water, so care must be taken to prevent the racemization of the halides while they are being made.[3] Fortunately, since the aluminum complex does not absorb light strongly, accurate optical rotation measurements are easily made with concentrated solutions.

The iron compound also seems to react in boiling water. Brownish scale formed on the side of the reaction vessel when an aqueous solution of the iron complex and silver-*d*- antimonyl tartrate was boiled. The iron compound is much more soluble in methanol than water, so the procedure for separating the aluminum complex can be applied here if methanol is substituted for water and the reaction is carried out in a sealed flask to prevent evaporation of the methanol before the compounds have a chance to react. The solution in the flask should be stirred to encourage the silver-*d*-antimonyl tartrate to react; it is not very soluble in methanol. The solution should be stirred for approximately a week. Halides can be formed by dissolving the separated complex *d*- antimonyl tartrate in a minimum amount of methanol (carefully, since it dissloves very slowly) and adding a slightly greater than equivalent amount of potassium halide solution in methanol. The iron complex halide, if it does not percipitate, can be recovered by adding ether dropwise.

After the complexes are separated, the best procedure is to heat a large number of samples in an Abderhalden apparatus for widely varying periods of time to establish a "ballpark" time for racemization. Afterwards, when the time for racemization is estimated, a second trial of several samples can be heated to produce a racemization curve. Theoretically, the optical rotation should decrease with time. However, some mechanisms of racemization would give an *increase* in rotation at

first. One likely mechanism is one in which the oxygens on the end of the molecule let go and switch places (see Fig. 3). This may involve a change in a bond angle from 90° to 60° if the oxygens are on the same side of the metal ion, but no change in bond angle if the oxygens are on opposite sides of the metal ion. In the first case (Fig. 3 A), one of the isomers would be more stable than the other. Tho optical rotation would reach an equilibrium value different from zero. In the second case (Fig. 3 B) the rotation would stabilize at zero.

In another possible mechanism of rotation, the halide attached to the complex would attach itself to the metal ion while the complex rearranges. The rate in this case would depend on the type of halogen involved. Iodine, being the heaviest, would give the fastest reaction, chlorine would give the slowest. Flourine is the least active of the halogens in this respect, and the complex flouride should not racemize if this mechanism is the one involved. So, one suggestion would be to make the complex flouride and see if it racemizes when heated. Flourine and flouride salts, however, are very toxic. If this procedure is performed, proper precautions must be taken. This procedure would disprove the theory that the halogen attaching to the metal is the cause of the reaction.

The compound may also racemize by a "twist" reaction. One face of the octahedron may turn to form a trigonal bipyramid momentarily.[6] In this mechanism, none of the atoms would need to detatch from the metal ion. The rate of this reaction would depend on the size of the metal ion. The rate would seem to depend less on the halogen substituted than in the other mechanisms.

REFERENCES:

(1)   Dwyer, F. P.; Lions, F.; J. Am. Chem. Soc., 1947, 69, 2917-2918.

(2)   Dwyer, F. P.; Lions, F.; J. Am. Chem. Soc., 1950, 72, 1545-1550.

(3)   Das Sarma, B.; Bailar, J. C.; J. Am. Chem. Soc., 1955, 77, 5476-5480.

(4)   Dwyer, F. P.; Gill, N. S.; Gyarfas, E. C.; J. Am. Chem. Soc., 1953, 75, 2443-2446.

(5)   Dwyer, F. P.; Gill, N. S.; Gyarfas, E. C.; J. Am. Chem. Soc., 1952, 74, 4188-4193.

(6)   Busch, D. H.; Bailar, J. C.; J. Am. Chem. Soc., 1953, 75, 4574-4575.

(7)   Das Sarma, B.; Bailar, J. C.; J. Am. Chem. Soc., 1954, 76, 4051-4052.

FIGURE 1: Configuration of Ligands

$$HOC_6H_4CH=NCH_2CH_2NHCH_2CH_2NHCH_2CH_2N=CHC_6H_4OH$$
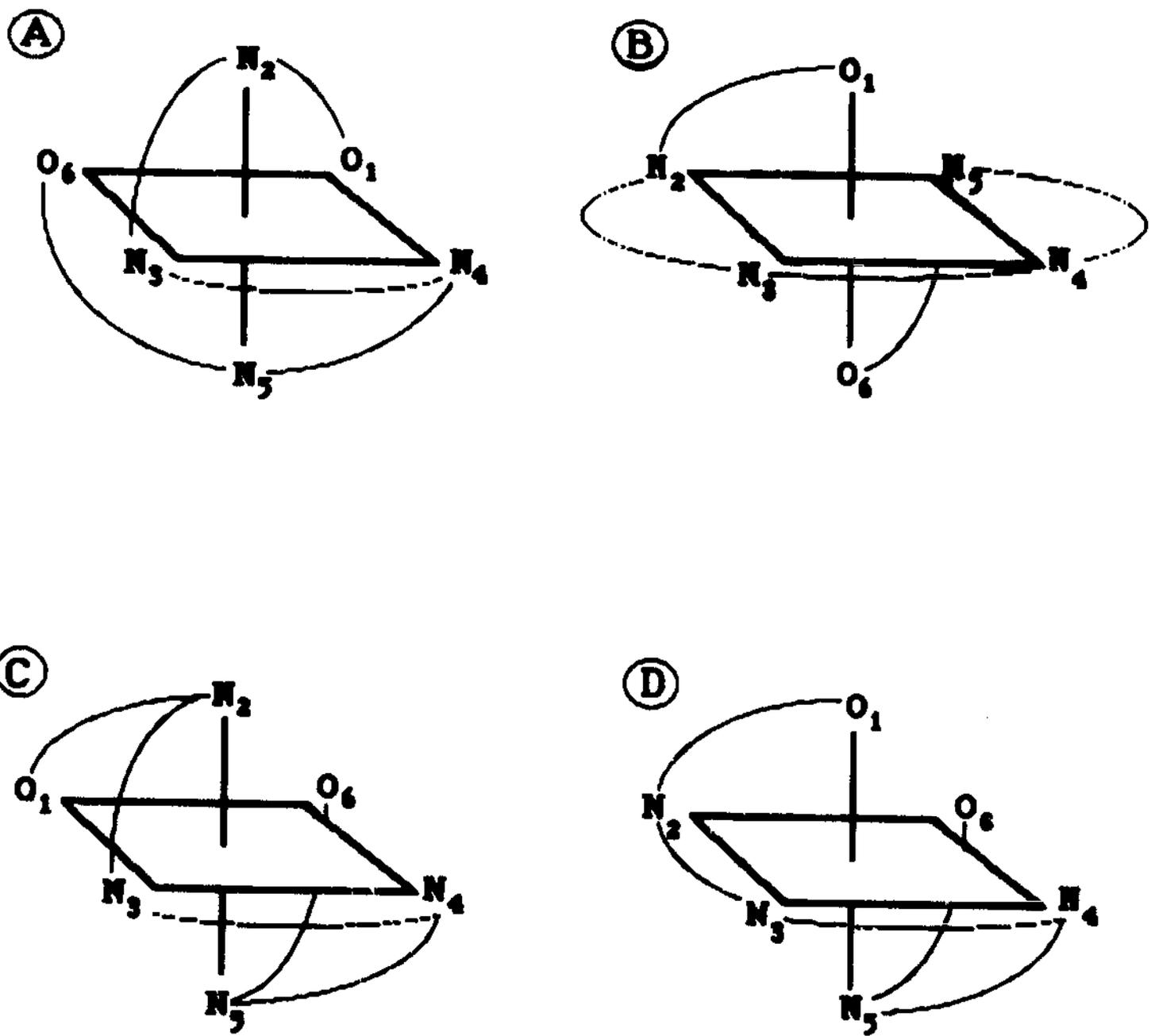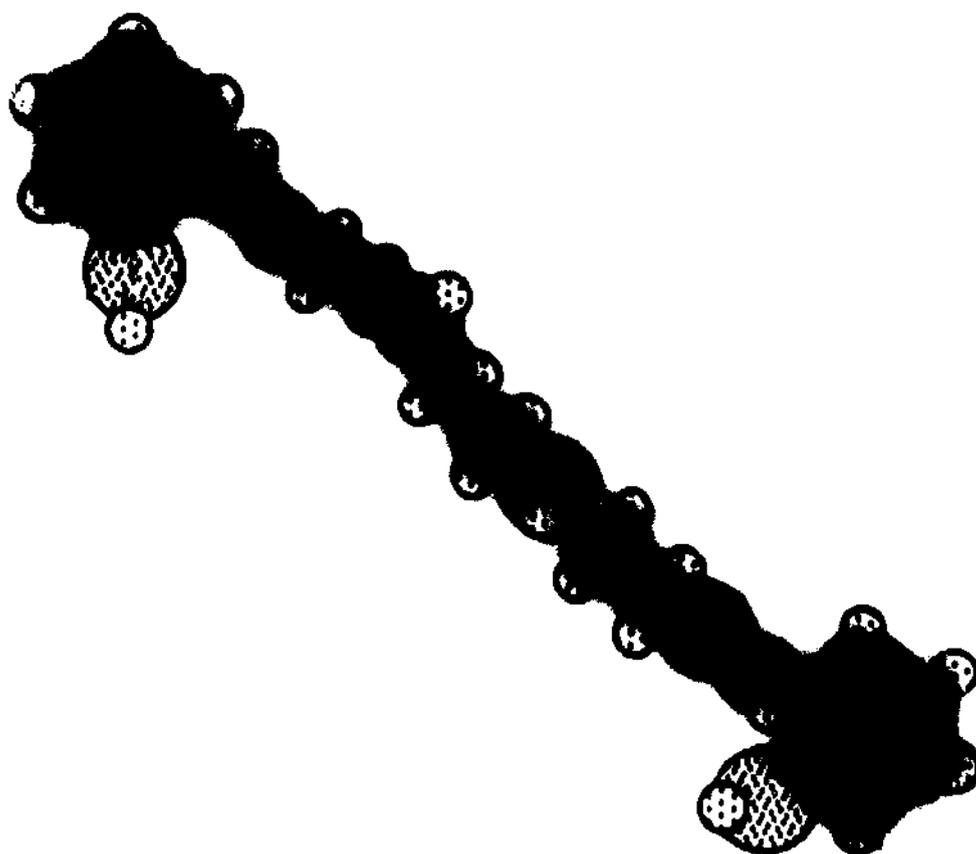
Metal	⬤	C	⬤	H	⊕
		N	⬤	O	▦

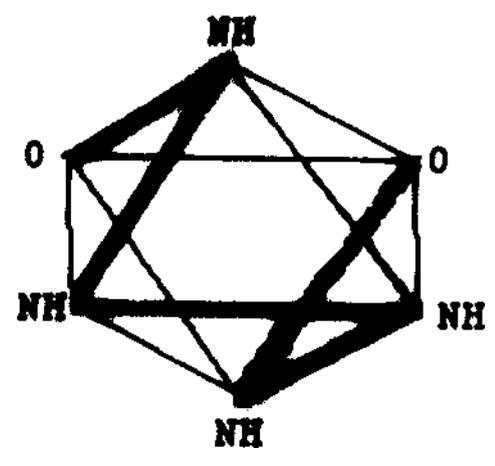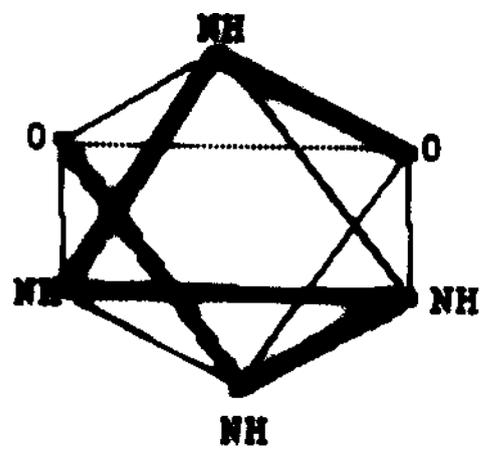**FIGURE 3: Possible Mechanisms for Racemization**
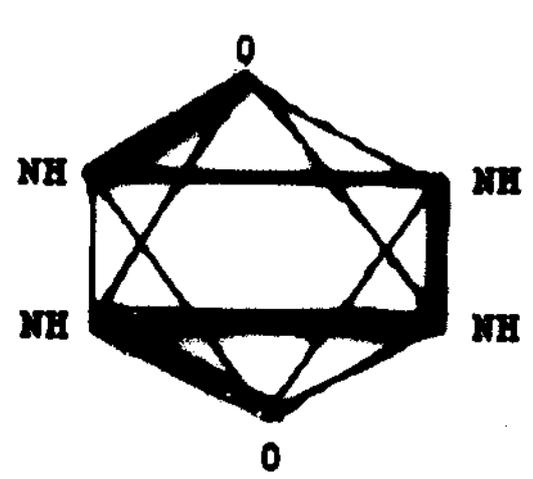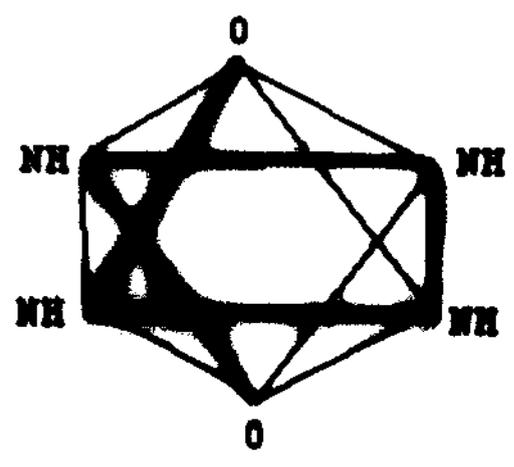
Figure 3 A: Oxygens on same side of metal atom

Figure 3 B: Oxygens on opposite sides of the metal atom