

ally are considerably weakened by the interposition of even a single methylene group between charged site and reaction site. The charge on an N^+ might orient an approaching dipolar molecule of butyl bromide into an unfavorable position for reaction with a neighbor, or possibly the field of a nearby N^+ can stabilize the $\geq N \cdot BrBu$ complex in its transition state, so that decomposition into $\geq N^+Bu$ and Br' becomes less probable. Finally, the intense field (megavolts/cm.) of a quaternized nitrogen might increase the density of the highly polar solvent in its neighborhood by electrostriction, and

thereby make access to the region by alkyl halide more difficult. One interesting consequence of the decelerating effect of partial quaternization should be mentioned. If there were no interaction, the distribution of quaternized sites among the chains would be a Bernoulli distribution around an average degree of quaternization. The interaction sharpens the distribution, because chains with more quaternized sites than the average will react more slowly with further alkyl halide, while those with less than the average will react more rapidly.

NEW HAVEN, CONN.

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

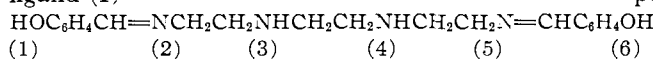
The Stereochemistry of Metal Chelates with Polydentate Ligands. Part I

BY BASUDEB DAS SARMA AND JOHN C. BAILAR, JR.

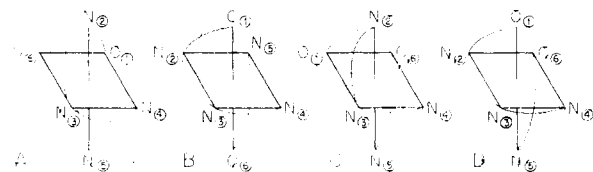
RECEIVED APRIL 25, 1955

This paper describes bis-salicylaldehyde-triethylenetetramine, the nitrogen analog of Dwyer and Lions' sexadentate 1,8-bis-(salicylideneamino)-3,6-dithioctane, as a chelating agent. The Schiff base offers six points of attachment and gives well defined, stable compounds with Co^{+3} , Co^{+2} , Fe^{+3} , Fe^{+2} , Al^{+3} , Cu^{+2} , Ni^{+2} , Pd^{+2} and the ions of other transition metals. The octahedral complexes of Co^{+3} , Fe^{+3} , Al^{+3} have been obtained in their optically active forms, only two of the eight possible isomers being obtained. The copper compound, which is tetra-coordinated and planar, has been obtained in optically active forms through a method of asymmetric synthesis. The tentative structures of the complexes have been described from the steric point of view and their infrared spectra. The Fe^{+3} compound is covalent with d^2sp^3 bonding and this has been resolved directly into the optical isomers.

Since the work of Dwyer and Lions¹ there has been a number of publications on complexes with sexadentate chelating agents.² The sexadentate ligand (I)



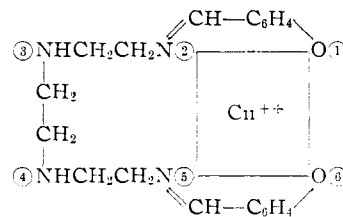
may span the octahedral positions around a metal ion in the following ways



together with the mirror images of each, as they are all asymmetric structures. But Fisher-Hirschfelder models show that the structures B, C and D are greatly strained and the models for them cannot be made. The angle $N-N-O$ tends toward 90° , as is the case with A. In all probability, therefore, these compounds have the structure represented by A.

The picture is slightly changed when all of the six coordinating positions are not utilized. For example, the cupric ion is normally reluctant to extend its coordination number of four, and is gener-

ally planar. If we assume that the two protons are replaced from the hydroxyl groups by cupric ion (like those of other Schiff bases, the compounds formed with a bivalent metal are non-electrolytes), and two of the four remaining nitrogens are coordinated to it, the structure



is still not symmetrical as the two benzene rings cannot lie in the plane of the complex. This gives rise to two active forms and of course, a *meso*-form. The classical method of resolution cannot be applied here, the chelate being a non-electrolyte. But if the compound is made from an optically active copper complex, such as the *d*-tartrate, it is obtained in optically active form. We have not yet been able to prepare the *meso*-form.

There is an alternate structure for this compound, with copper coordinated to N_3 and N_4 instead of N_2 and N_5 . This will require the stabilization of two nine-membered rings, instead of one large ring and two six-membered rings. This alternate structure is more difficult to make with a model. The infrared spectra of these compounds (Table I) show that when the secondary amine nitrogens, N_3 and N_4 , are coordinated, there is a multiplicity of the NH stretching vibrations in the region 3100-3600

(1) F. P. Dwyer and F. Lions, *THIS JOURNAL*, **69**, 2917 (1947).

(2) F. P. Dwyer, F. Lions and co-workers, *ibid.*, **72**, 1545 (1950); **72**, 5037 (1950); **74**, 4188 (1952); **75**, 2443 (1953). G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948). D. H. Busch and J. C. Bailar, Jr., *THIS JOURNAL*, **75**, 4574 (1953). A. K. Mukherjee, *Science and Culture*, **19**, 107 (1953).

cm.⁻¹, due to a salt-like character of the secondary amine.

Unlike the spectra of the complexes of Co⁺³, Fe⁺³, Al⁺³, those of the Cu^{II} and Co^{II} complexes show only one band in the same region, indicating that these nitrogens are not coordinated in the latter series.

The infrared spectra of the complexes and that of the tris-salicylaldehyde-triethylenetetramine were recorded with a Perkin-Elmer auto-recording infrared spectrophotometer using a sodium chloride crystal grating. The samples were run in nujol emulsions. From a study of them and the existing literature, some bands have been assigned to specific groups, as shown in Table I.

TABLE I

INFRARED BANDS SHOWN BY TRIS-SALICYLIDENEAMINOTRIETHYLENETETRAMINE AND SOME METAL DERIVATIVES OF BIS-SALICYLIDENEAMINOTRIETHYLENETETRAMINE

	[Co ^{III} - TS ₂] ⁺	[Fe ^{III} - TS ₂] ⁺	[Al ^{III} - TS ₂] ⁺	[Cu ^{II} - TS ₂]	[Co ^{II} - TS ₂]	
C=N (str.)	1635	1643	1630	1634	1637	1636
O-H (str.) (phenolic)	3440
N-H (str.)	..	3620	3610	3485	3150	3220
		3480	3510	3430		
		3408	3380	3300		
		3318	3170	3285		
		3160	3100	3120		
		3100				
C-N (str.)	1182	1205	1205	1207	1197	1192
	1152	1155	1154	1156	1153	1152
	1123	1131	1132	1133	1131	1129
C-O (str.)	1265	1314	1300	1315	1350	1344
O-substd. benzene C=C	1615	1605	1602	1607	1604	1602
	1585	1542	1542	1553	1538	1535
	1503					
C-H (Wag.)	761	762				
	755	755	755	743	758	757
C=C (aromatic)	1488	1475	1475	1480	1475	1473

As our knowledge of the infrared spectra of coordination compounds is still meager, the above assignments should be accepted as tentative. But some observations in this series are interesting. The C=N band of the Schiff base is very little changed on coordination of a metal to the nitrogen, which, however, is not surprising in view of the stronger force existing in the C=N group. But while the N-H stretching band is definitely multiplied in the hexa-coordinated compounds as compared to those where the secondary amine nitrogen is not coordinated, the band at 1152 cm.⁻¹, assigned to the H₂C-N stretching vibration, remains practically unchanged on coordination to various metals.

In the region 1100-1200 cm.⁻¹, there are two bands in addition to 1152-1159 cm.⁻¹ assigned to C-N stretching vibration. It has been shown by Bergmann and Pinchas³ that there are three bands in the region 1063-1190 cm.⁻¹ in the acetals and ketals in place of a strong band for C-O-C in ethers at 1130 cm.⁻¹. This is accounted for by the three types of vibrations of C-O-C-O-C grouping in acetals and ketals. According to them, no such

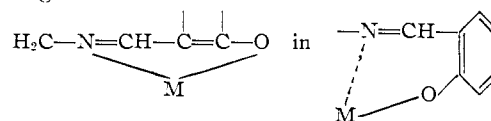
(3) E. D. Bergmann and S. Pinchas, *Rec. trav. chim.*, **71**, 161 (1951).

splitting of the ether band has been observed with C-O-C-O-C in glycol dialkyl ethers. There is a C-N-C-C-N-C grouping in all these compounds and a -N-C-C-N- group in the tris-salicylalde-

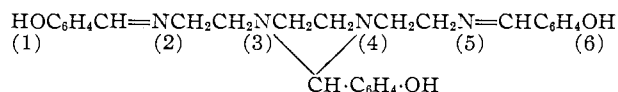
hyde base. The relative intensities of the three bands seem to show some correlation with the type of compound.

In the Schiff base TS₃H₃ the band at 1123 cm.⁻¹ is the strongest, while it is the weakest one in all of the complexes. The one at 1192-1207 cm.⁻¹ is strongest for the definitely hexa-coordinated complexes (Co⁺³, Fe⁺³), is almost of the same intensity in Al⁺³ and Ni⁺² complexes, and weaker than the band at 1152-1159 cm.⁻¹ for the tetra-coordinated complexes (Cu⁺², Co⁺²).

The C-O stretching vibration band at 1265 cm.⁻¹ shifts to a higher wave number in the complexes, indicating possibly a slightly stronger than normal single bond in C-O, presumably by a resonance in the ring



It has been shown already⁴ that salicylaldehyde reacts with triethylenetetramine to give tris-salicylideneaminotriethylenetetramine (II)



which, however, loses a molecule of salicylaldehyde when it coordinates to metal ions. Examination of models shows that when positions (3) and (4) are coordinated to a metal, the salicylaldehyde across them has to split off. Salicylaldehyde is actually liberated by the reaction of a cobalt salt and the tris-salicylidene compound in the presence of air. In the case of four-coordinate metals like Pd⁺², Cu⁺² and Co⁺², the third salicylaldehyde may remain in place if positions (1), (2), (5) and (6) are utilized in coordination, but the structure is still somewhat strained. The reaction product with Pd⁺² could not be purified, but the product approaches the calculated composition for a molecule containing triethylenetetramine condensed to three salicylaldehyde molecules. Infrared spectra for this product indicate that there is no NH band and the presence of OH is exhibited.

Experimental

II.—As Mukherjee^{2d} has found, attempts to prepare the sexadentate ligand I by the condensation of triethylenetetramine (1 mole) and salicylaldehyde (2 moles) in different solvents and under different conditions lead only to product II. In the presence of sodium acetate, however, another product was obtained, which did not contain any nitrogen and could not be identified. II can be obtained in best yield by the slow addition of 40 g. of 71.5% triethylenetetramine (0.2 mole) in 100 cc. of cold methanol to a cooled solution of 73.2 g. of salicylaldehyde (3 moles) in 300 cc. of methanol. When the mixture is gradually warmed to room temperature, yellow crystals separate. The crude yellow

(4) B. Das Sarma and J. C. Bailar, Jr., *THIS JOURNAL*, **76**, 4051 (1954).

product can be recrystallized from warm absolute alcohol or dilute methanol. It melts at 105–106°, is highly soluble in acetone, fairly soluble in methanol and practically insoluble in water; yield 80%.

Anal. Calcd. for $C_{27}H_{30}O_3N_4$: C, 70.74; H, 6.55; N, 12.23. Found: C, 70.56; H, 6.47; N, 12.32.

Attempts to prepare I by the removal of copper sulfide from a methanol solution of the corresponding copper compound were unsuccessful.

III. Bis-salicylaldehyde-triethylenetetraminecobalt(II). $[Co^{II}TS_2]$.—Cobalt(II) bis-salicylaldehyde was prepared by the addition of 11.9 g. cobalt chloride hexahydrate in 100 cc. of water to 12.2 g. of salicylaldehyde in 100 cc. of methanol, followed by the dropwise addition of 5.6 g. of caustic potash in 50 cc. of cold water (with constant stirring). The yellow brown product was washed with water and recrystallized from hot dilute ethanol and dried.

Seven and a half grams of cobalt(II)-bis-salicylaldehyde (0.025 mole) was dissolved in 30 cc. of hot methanol and 50 cc. of a 7.3% solution of trimethylenetetramine (0.025 mole) was added to it. The flask containing the mixture was immediately closed and the contents shaken well. The light yellowish-brown product which separated was collected by filtration, washed thoroughly with water and recrystallized from warm ethanol, taking care to avoid excessive exposure to air. A little of it was oxidized during recrystallization, but this did not contaminate the product, for the oxidized compound is soluble in both water and ethanol and was filtered off as a red brown solution. The product was dried in a vacuum at room temperature. It is insoluble in water and soluble in alcohols.

Anal. Calcd. for $[Co^{II}(C_{20}H_{24}N_4O_2)] \cdot 0.5H_2O$: C, 57.13; H, 5.95; N, 13.33; Co, 14.03. Found: C, 57.54; H, 6.14; N, 13.29; Co, 14.15.

The magnetic susceptibility, measured with a modified Curie balance, was found to be 2.01 B.M.

IV. Bis-salicylaldehyde-trimethylenetetraminecobalt(III) Salts, $[Co^{III}TS_2]X$.—These can be prepared in three different ways.

A. To a suspension of 4.1 g. of the cobalt (II) complex (0.01 mole) in 100 cc. of water 10 cc. of *N* hydrochloric acid was added gradually while air was passed through the suspension (12 hours). During this time the Co(III) complex went into solution. The deep red-brown solution was filtered and concentrated at room temperature. The deep brown-black hexagonal prisms which separated were collected by filtration and dried *in vacuo*, yield 4 g.

B. The following were mixed in the order given in quick succession: (1) 10 cc. of 71.5% triethylenetetramine (0.05 mole) in 50 cc. cold methanol; (2) 12.1 g. of salicylaldehyde (0.1 mole) in 50 cc. cold methanol; (3) 5.6 g. of caustic potash (0.1 mole) in 20 cc. cold water; (4) 11.9 g. of cobalt chloride hexahydrate (0.05 mole) in 75 cc. of cold water. The mixture was then oxidized by passing a strong current of air through it for one hour, after which 10 cc. of 1:1 HCl was added. The aeration was continued for 12 hours and the dark solution was filtered, concentrated and cooled. Dark brown-black crystals separated and were dried as before; yield 18.9 g.

C. A solution of 9.4 g. of I (0.02 mole) in 100 cc. of acetone was added to a solution of 4.8 g. of $CoCl_2 \cdot 6H_2O$ (0.02 mole) in 50 cc. of water. A little activated carbon was added. The mixture was oxidized with a current of air for 5–6 hours and 20 cc. of 2 *N* caustic soda was added. Aeration was continued for another two hours, the mixture was cooled in an ice-bath, and filtered. The complex chloride, together with carbon, was obtained as the residue. This was treated with 100 cc. of hot water and filtered. On concentration and cooling, the filtrate gave brown-black crystals of the complex chloride. These products were all found to be diamagnetic as expected.

Anal. Calcd. for $[Co^{III}(C_{20}H_{24}N_4O_2)]Cl \cdot 2.5H_2O$: C, 49.00; H, 5.90; N, 11.43; Co, 12.01; Cl, 7.24. Found: C, 49.79, 49.73; H, 5.85, 5.86; N, 11.49, 11.13; Co, 12.03, 12.06; Cl, 7.15, 7.28.

The material melts at 240°. It has a red-brown color in concentrated aqueous solution, and greenish brown in dilute solution. It was found to be quite stable in aqueous solution, as an attempt to decompose the complex with excess of aqueous sodium sulfide gave practically no cobalt sulfide, but the complex sulfide crystallized out.

Calcd. for $[Co^{III}(C_{20}H_{24}N_4O_2)]_2S \cdot 6H_2O$: C, 49.91; H, 6.23; N, 11.64. Found, C, 49.92; H, 5.88; N, 11.41.

Even on heating on the steam-bath in the presence of excess sulfide, very little cobalt sulfide was formed.

Resolutions into Optically Active Forms.—The rotations recorded in this paper were taken on aqueous solutions in a one-dm. tube, using a high-precision polarimeter reading to 0.001°. All readings were taken at the *D*-line of sodium unless otherwise stated.

The resolution was attempted through *d*-tartrate, *d*-camphorsulfonate, *d*-bromocamphorsulfonate and by adsorption on *d*-quartz.

There was no effective resolution as the *d*-tartrate or *d*-camphorsulfonate.

With *d*-Bromocamphor- π -sulfonate.—A sample of 0.5 g. of the complex cobalt chloride was dissolved in methanol (20 cc.) and ground with 0.43 g. of silver *d*-bromocamphorsulfonate. The silver chloride was filtered and the filtrate was concentrated *in vacuo*. When the volume was 5–6 cc. a dark oil separated. The solution was decanted, evaporated and taken up with a minimum quantity of water (a). The oil obtained previously was also dried *in vacuo* and dissolved in water (b). The least soluble fraction from (b) and the most soluble fraction from (a) were dissolved in water and precipitated with a saturated solution of potassium iodide, filtered, washed with cold water and dried; iodide from the least soluble fraction (0.01% solution), $\alpha -0.023 \pm 0.003^\circ$, $[\alpha]_D -230^\circ$; iodide from the most soluble fraction, $\alpha +0.022 \pm 0.003^\circ$, $[\alpha]_D +220^\circ$.

With *d*-Antimonyl Tartrate.—To a solution of 1.0 g. of the complex chloride in 50 cc. of methanol was added 1 g. of silver *d*-antimonyl tartrate. The mixture was stirred for an hour and filtered. On concentration of the filtrate, the first fraction contained a little silver salt and was rejected. The second fraction (about 0.3 g.) was collected and dissolved in water. On fractional crystallization, this gave about 0.1 g. of $L-[CoTS_2] \cdot d-SbO_4$. For the dextro fraction of the complex, the filtrate, after collecting the first fraction from methanol solution, was concentrated until 0.8–0.9 g. of the complex separated. The filtrate from this operation was evaporated to dryness, dissolved in water and precipitated as the iodide; least soluble fraction as iodide (0.01% solution), $\alpha -0.025 \pm 0.003^\circ$, $[\alpha]_D -250^\circ$, most soluble fraction, as iodide (0.01% solution), $\alpha +0.026 \pm 0.003^\circ$, $[\alpha]_D +260^\circ$.

With *d*-Quartz.—A solution of the complex chloride in 50 cc. of water was stirred for 15–20 minutes with 1 g. of finely powdered *d*-quartz. The mixture was filtered and the filtrate was diluted until its rotation could be read in the polarimeter. The concentration, as obtained by estimation of the chlorine content was about 0.01%; $\alpha -0.030 \pm 0.003^\circ$, $[\alpha]_D -300^\circ$.

The quartz was then shaken with methanol. The solution gave a rotation of $+0.015 \pm 0.002^\circ$.

V. Bis-salicylaldehyde-Triethylenetetraminecopper(II). $[CuTS_2]$.—The copper compound was made by the addition of triethylenetetramine (4 g. of a 71.5% solution) to a suspension of 6 g. of copper bis-salicylaldehyde in a mixture of 100 cc. of water and 100 cc. of methanol. The bluish green solution was concentrated and cooled. The bluish green prismatic needles which separated were recrystallized from water containing about 25% methanol. The product melted at 78–79°, but lost some water *in vacuo* at room temperature to yield green crystals, which decomposed.

levo-Compound.—To a solution of 8.5 g. of copper chloride dihydrate (0.05 mole) in 100 cc. of water was added 34.5 g. of sodium *d*-tartrate (0.15 mole). Copper tartrate precipitated. The mixture was cooled in ice and cold 2 *M* KOH was added with constant stirring until the green copper tartrate went into solution with a deep blue color. To this solution was added a cold solution of 12.2 g. of salicylaldehyde (0.1 mole), 10 cc. of 71.5% triethylenetetramine (0.05 mole) and 5.6 g. of caustic potash (0.1 mole) in 150 cc. of methanol and 25 cc. of water. The mixture was stirred and kept in ice for two hours and was then filtered from the separated sodium and potassium salts. Three hundred cubic centimeters of methanol was added to the filtrate, which was filtered again if a precipitate formed. When the solution was concentrated by a stream of air, the copper compound separated as greenish blue crystals. The product was collected by filtration, washed with a little cold water and recrystallized from 25% methanol. It turned green in a desiccator.

Anal. Calcd. for $[\text{Cu}^{\text{II}}(\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2)]$: C, 57.76; H, 5.78; N, 13.47; CuO, 19.13. Found: C, 58.23; H, 6.16; N, 13.13; CuO, 19.24.

A 0.04% solution in water gave a rotation of $-0.020 \pm 0.002^\circ$ against the solution of the racemic compound as blank; $[\alpha]_{\text{D}} -50^\circ$.

Another fraction of the copper complex made from disodium copper(II) bis-*levo*-glutamate, instead of copper *d*-tartrate, gave a rotation of $+0.032 \pm 0.003^\circ$ for a 0.05% solution; $[\alpha]_{\text{D}} +64^\circ$. It is interesting to note that *l*-glutamic acid apparently has a structure opposite to that of *d*-tartaric acid and, by these asymmetric processes, give the copper isomers of opposite rotations. *d*-Tartaric acid, *d*-tartrates and copper *d*-tartrate all have dextrorotation. *levo*-Glutamic acid is dextrorotatory.

VI. Bis-salicylaldehyde-Triethylenetetraminealuminum(III) Iodide, $[\text{AlTS}_2]\text{I}$.—As in the preparation of the cobalt(III) compound (method B), the following were quickly mixed in the order given: (a) 20 g. of 71.5% triethylenetetramine (0.1 mole) in 75 cc. of methanol; (b) 24 g. of salicylaldehyde (0.2 mole) in 100 cc. of cold methanol; (c) 11.2 g. of caustic potash (0.2 mole) in 50 cc. of cold water; (d) 37.5 g. of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1 mole) in a mixture of 200 cc. of water and 100 cc. of methanol.

The mixture was stirred for one hour and the white precipitate filtered off. To the cooled filtrate was then added a saturated solution of potassium iodide, whereupon the complex iodide separated. This was filtered and washed with acetone. The compound was purified by redissolving in warm water (the solution should not be boiled as there is a slow hydrolysis) and reprecipitated by the addition of potassium iodide solution and cooling in ice. The product was washed first with cold water and then with acetone and dried *in vacuo*. It forms white crystals, with a greenish tinge when the crystals are large. The iodide was found to be fairly soluble in water, very soluble in methanol and slightly soluble in acetone.

Instead of precipitating the less soluble iodide with potassium iodide, the nitrate can be isolated as hexagonal prisms by slow concentration at room temperature. Some of the crystals obtained in this way were as large as 0.5 cm. in length.

Anal. Calcd. for $[\text{Al}(\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2)]\text{I} \cdot 0.5\text{H}_2\text{O}$: C, 46.6; H, 4.85; N, 10.87; Al, 5.24. Found: C, 46.59; H, 4.77; N, 10.87; Al, 5.13.

Resolution of the Aluminum Complex.—One gram of the complex iodide in 50 cc. of methanol was allowed to react with 1 g. of silver-*d*-antimonyl tartrate, filtered, washed with methanol and the filtrate and washings concentrated *in vacuo*. There was a separation of solid (0.2 g.) when the volume was reduced to 20 cc. This is *D*- $[\text{AlTS}_2]\text{-d-SbOtart}$. A 0.25% solution in methanol gave $\alpha +0.112 \pm 0.002^\circ$; $[\alpha]_{\text{D}} +44.8^\circ$.

Anal. Calcd. for $[\text{Al}(\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2)]\text{SbC}_4\text{H}_4\text{O}_7$: C, 43.30; H, 4.21; N, 8.42; $\text{Al}_2\text{O}_3 + \text{Sb}_2\text{O}_3$, 29.60. Found: C, 43.25; H, 4.81; N, 8.76; $\text{Al}_2\text{O}_3 + \text{Sb}_2\text{O}_3$, 29.30.

D- $[\text{AlTS}_2]\text{NO}_3$, obtained from the methanol solution of the complex antimonyl tartrate and slightly greater than the equivalent quantity of silver nitrate, gave $[\alpha]_{\text{D}} +20^\circ$ (0.167% solution in methanol).

The filtrate, after separation of the first fraction, was concentrated to 1-2 cc. *in vacuo*, filtered, diluted with 25 cc. of methanol and again concentrated to 2 cc. This was repeated twice. The final filtrate was evaporated to dryness *in vacuo*.

0.086 g. of this *L*- $[\text{AlTS}_2]\text{-d-SbOtart}$ was dissolved in 20 cc. of methanol and the rotation observed; $\alpha -0.255 \pm 0.002^\circ$ (concentration 0.43%), $[\alpha]_{\text{D}} -59.3^\circ$.

Anal. Calcd. for $[\text{Al}(\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2)]\text{SbC}_4\text{H}_4\text{O}_7 \cdot \text{H}_2\text{O}$: C, 42.16; H, 4.39; N, 8.21; $\text{Al}_2\text{O}_3 + \text{Sb}_2\text{O}_3$, 28.82. Found: C, 41.81; H, 4.43; N, 7.92; $\text{Al}_2\text{O}_3 + \text{Sb}_2\text{O}_3$, 28.47.

Silver nitrate (0.022 g.) was dissolved in a drop of water and the methanol solution (20 cc., 0.43%) of the complex antimony tartrate was added to it. The volume was made up to 25 cc., the solution was shaken well and filtered directly into the polarimeter tube. The observed rotation (15 minutes after mixing) was $-0.285 \pm 0.003^\circ$. The concentration of the solution in terms of $[\text{AlTS}_2]\text{NO}_3$ was 0.229%; $[\alpha]_{\text{D}} -124.4^\circ$.

The precipitate obtained with silver nitrate from either *D*-

or *L*- $[\text{AlTS}_2]\text{-d-SbOtart}$ was found to give dextrorotation by reaction with dilute hydrochloric acid.

The difficulty experienced in obtaining a higher activity of the dextro fraction was due to the low solubility and slow rate of dissolution. Repeated fractionation, therefore, could not be carried out.

Both isomers of $[\text{AlTS}_2]\text{NO}_3$ underwent rapid racemization in methanol (half-life 1.5 to 4 hours depending on the solvent and other factors). A solution of *rac*- $[\text{AlTS}_2]\text{-d-SbOtart}$ in methanol was found to change rotation with time, while *D*- and *L*- $[\text{AlTS}_2]\text{-d-SbOtart}$ were found to be very slow in racemization. In the solid form, they were found to retain about 50-80% of their activity after seven months. The rate of racemization of all the aluminum compounds in aqueous solution was too rapid to follow. The solids as well as the solutions slowly turn yellowish on exposure to air and possibly also to light. The solutions of the active nitrates should be kept in the dark and out of contact with air. If the slight excess of silver salts present in these solutions be removed there is no need to keep them in the dark. The details of the rate and possible mechanism of racemization will be published in a separate paper.

VI. Bis-salicylaldehyde-Triethylenetetramineiron(III) Compounds $[\text{Fe}^{\text{III}}\text{TS}_2]\text{X}$.—These were made in the same way as the corresponding aluminum and cobalt(III) compounds (method B), by the reaction of ferric nitrate hexahydrate (25 g. in 100 cc. of water), and a cold mixture of triethylenetetramine (10 g. of 71.5% solution in 100 cc. of 50% methanol), salicylaldehyde (12.2 g. in 100 cc. of methanol) and potassium hydroxide (5.6 g. in 20 cc. of cold water). On cooling and concentration, dark purple plates of the complex nitrate separated. This compound was recrystallized from warm water and dried *in vacuo*. It was found to be more soluble in alcohol than in water.

Anal. Calcd. for $[\text{Fe}(\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2)]\text{NO}_3 \cdot \text{H}_2\text{O}$: C, 49.18; H, 5.33; N, 14.34; Fe_2O_3 , 16.40. Found: C, 49.04; H, 5.23; N, 13.76; Fe_2O_3 , 16.11.

To a solution of the nitrate in warm water was added a saturated solution of potassium iodide. On cooling in ice, shining, almost black crystals of the complex iodide separated. This material was washed with cold water and dried in air. It gave a deep purple solution.

Anal. Calcd. for $[\text{Fe}(\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2)]\text{I} \cdot 1.5\text{H}_2\text{O}$: C, 42.70; H, 4.80; N, 9.99; Fe_2O_3 , 14.14. Found: C, 42.99; H, 5.38; N, 9.99; Fe_2O_3 , 14.14.

The iodide melts at 117-118°. The magnetic susceptibility was found to be 1.81 Bohr magnetons at 27°. Generally Fe^{III} complexes give a much higher value⁵ compared to the theoretical 1.73 for one unpaired electron. Only in rare cases like Fe^{III} -heme is the value so close to theory. This suggests a strong covalent d^2sp^3 bonding.

Resolution of most optical isomers of Fe^{III} compounds cannot be obtained directly,⁶ but only through oxidation of the optically active Fe^{II} complexes. This complex, however, has been resolved into optical isomers directly.

One gram of the complex iodide was dissolved in 100 cc. of methanol and 1 g. of silver *d*-antimony tartrate was added to it. The mixture was stirred for 0.5 hour, filtered and concentrated *in vacuo*. The first fraction (A) was collected as shining black crystals (0.7 g.), rejecting the scales formed on the sides of the vessel. No more solids separated when the volume of the filtrate was concentrated to 20 cc. This was then evaporated to dryness *in vacuo* (residue B).

(A) and (B) were dissolved separately in 50-cc. portions of methanol, and the least soluble fraction from (A) and most soluble fraction from (B) collected.

(A) **Least Soluble Fraction, *L*- $[\text{FeTS}_2]\text{-d-SbOtart}$.**—A 0.005% solution in methanol gave a rotation of $-0.005 \pm 0.003^\circ$; $[\alpha]_{\text{D}} -100^\circ$.

Anal. Calcd. for $[\text{Fe}(\text{C}_{20}\text{H}_{24}\text{N}_4\text{O}_2)]\text{SbC}_4\text{H}_4\text{O}_7$: C, 41.5; H, 4.04; N, 8.07. Found: C, 41.87; H, 4.17; N, 7.93.

L- $[\text{FeTS}_2]\text{NO}_3$, obtained by the action of silver nitrate on the solution of the complex antimonyl tartrate (0.0033% in methanol), gave a rotation of $-0.017 \pm 0.003^\circ$, $[\alpha]_{\text{D}} -515^\circ$.

(B) **Most Soluble Fraction, *D*- $[\text{FeTS}_2]\text{-d-SbOtart}$.**—A 0.005% solution in methanol gave a rotation of $+0.022 \pm 0.004^\circ$, or $[\alpha]_{\text{D}} +440^\circ$.

(5) M. Calvin and C. H. Barkeley, *THIS JOURNAL*, **68**, 2267 (1946); R. S. Nyholm, *J. Chem. Soc.*, 851 (1950).

(6) F. P. Dwyer and E. C. Gyrfas, *THIS JOURNAL*, **74**, 4699 (1952).

A 0.0033% solution of D -[FeTS₂]NO₃, obtained as before, gave $\alpha +0.018 \pm 0.003^\circ$, $[\alpha]_D +545^\circ$.

Further work on this and other polydentate ligands is in progress.

The authors' best thanks are due to the University of Illinois and to the National Science Foundations for providing funds to one of them (Das Sarma).

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

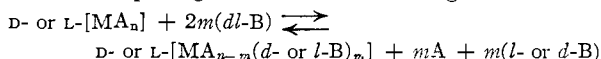
The Stereochemistry of Complex Inorganic Compounds. XVIII. A New Method for the Preparation of Inorganic Complexes in their Optically Active Forms¹

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RECEIVED APRIL 25, 1955

It has been observed that when a compound of the type *cis*-[Co^{III}AX₂]Cl (where A is equivalent to two bidentate amines or a tetradentate amine), is treated with silver *d*-antimonyl tartrate, there is an induced asymmetric synthesis of the cobalt complex, to give L-[CoA(*d*-SbOtart)₂](*d*-SbOtart) during the replacement of chloride by the *d*-antimonyl tartrate. When the *d*-antimonyl tartrate is replaced subsequently, there is obtained an L-[Co^{III}AX₂]X, which has been isolated where X is OH, 1/2CO₃ or Cl. The purity of the optical isomer obtained depends on the stability of the complex and the mode of operation. L-[Co^{III}en₂Cl₂]Cl² has been obtained as 25-30% resolved, whereas the L-[Co^{III}trienCl₂]Cl seems to be optically pure, though there is no way to compare the purity, as [Co^{III}trienCl₂]Cl could not be resolved by the classical method.

It has recently been shown³ that there is a preferential coordination of the isomer of *d*-configuration when tartaric, chloropropionic, or lactic acid is introduced into [Co(*l*-propylenediamine)₂-CO₃]Cl. The present authors have seen that the method is quite general in the following scheme



where

M = Co^{III}, Cu^{II}, Ni^{II}

A = (*d* or *l*)-propylenediamine, *d*-tartaric acid, *d*-gluconic acid, *l*-glutamic acid

B = propylenediamine, alanine, tartaric acid

It has further been observed that when A is not optically active, but the complex [MA_n] is, a similar process occurs which results in active [MA_{n-m}-B_m] and B.⁴

The presence of an optically active ligand does not completely fix the configuration of the complex of which it is a part, but it is known that the stabilities of *D*-[M(*l*-A)_n] and *L*-[M(*l*-A)_n] are generally quite different, and a forced asymmetry is induced. The same effect of asymmetric induction is also observed when the environment is asymmetric in nature or there is an exchange between asymmetric groups in the coordination sphere.⁵

In the present investigation, *cis*-dichlorotriethylenetetraminecobalt(III) chloride was treated with silver *d*-antimonyl tartrate. This replaced the chloride, both inside and outside the coordination sphere, by *d*-antimonyl tartrate. The resulting

(1) Presented at the Cincinnati meeting of the American Chemical Society, April 5, 1955.

(2) The following abbreviations have been used in this article: en = ethylenediamine; pn = propylenediamine; trien = triethylenetetramine; *d*-SbO tart = *d*-antimonyl tartrate.

(3) A. D. Gott and J. C. Bailar, Jr., *THIS JOURNAL*, **74**, 4820 (1952); J. C. Bailar, Jr., H. B. Jonassen and A. D. Gott, *ibid.*, **74**, 3131 (1952).

(4) $D\text{-}[Co^{III}EDTA]^- + 3en \rightarrow D\text{-}[Co en_3]^{+3}$ by F. P. Dwyer, private communication. $L\text{-}[Co^{III}EDTA]^- + 6(dl\text{-}pn) \rightarrow L\text{-}[Co(dl\text{-}pn)_3]^{+3} + 3(d\text{-}pn)$ where EDTA = ethylenediamine tetraacetate. S. Kirschner, Thesis, University of Illinois, 1954. $L\text{-}[Co en_2Cl_2] + 2dl\text{-}pn \rightarrow L\text{-}[Co en_2d\text{-}pn]^{+3} + l\text{-}pn$ by present authors, to be communicated.

(5) H. B. Jonassen, J. C. Bailar, Jr., and E. H. Huffman, *THIS JOURNAL*, **70**, 256 (1948); N. R. Davies and F. P. Dwyer, *J. Proc. Roy. Soc., N. S. Wales*, **86**, 64 (1953); B. Das Sarma and John C. Bailar, Jr., *THIS JOURNAL*, **76**, 4071 (1954).

solution gave no indication of separation of optical isomers on fractional crystallization or precipitation. On the other hand, the specific rotation ($[\alpha]_D +110$ to 125°) decreased rapidly to a very low value (0 to $+5^\circ$) when the aqueous solution was heated on the steam-bath with accompanying increase in acidity. As the *d*-antimonyl tartrate is highly dextrorotatory there must be some levorotatory component present to reduce the rotation almost to zero, as the racemization of antimonyl tartrate is highly improbable under these conditions. Treatment with barium hydroxide converts the product presumably into dihydroxytriethylenetetraminecobalt(III) hydroxide, which in turn can be converted into carbonato- or dichlorotriethylenetetraminecobalt(III) ion. These are all levorotatory ($[\alpha]_D = -80$ to -150°). Thus asymmetry is induced by the presence of the *d*-antimonyl tartrate which can then be replaced and the active complex containing only optically inactive ligands can be isolated easily.

A similar approach has been attempted on a series of cobalt(III) compounds of the type [CoAClX], where A is a tetradentate amine or two moles of a bidentate amine and X is either Cl or NH₃. The results indicate that there is an induced asymmetric synthesis only if both Cl and X are replaced by *d*-antimonyl tartrate. *cis*-Dichloro-bis-ethylenediaminecobalt(III) ion gives the same results as the triethylenetetramine analog. The dichloro-bis-propylenediamine complex gives a doubtful result; in this case the matter is more complicated due to the presence of *d*- and *l*-propylenediamine in the complex. With compounds like [Co^{III}en₂NH₃-Cl]Cl₂ there is no asymmetric synthesis, because there is only one replaceable group.

In order to see whether the effect is the same with other active components in the place of *d*-antimonyl tartrate, silver *d*-bromocamphorsulfonate and silver *d*-camphorsulfonate were employed. The induced synthesis of the active isomer is very feeble, if it exists at all. The reason here may be the inability of the camphorsulfonates to replace the chloride ion in the coordination sphere in the aqueous system.