A 0.0033% solution of D-[FeTS$_2$]NO$_3$, obtained as before, gave α +0.018 ± 0.003°, $[\alpha]_D$ +545°.

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

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URBANA, ILLINOIS

[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 Forms[1]

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

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It has been observed that when a compound of the type *cis*-[Co^{III}ACl$_2$]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}AX$_2$]X, which has been isolated where X is OH, $^1/_2$CO$_3$ or Cl. The purity of the optical isomer obtained depends on the stability of the complex and the mode of operation. L-[Co^{III} en$_2$Cl$_2$]Cl[2] has been obtained as 25–30% resolved, whereas the L-[Co^{III} trien Cl$_2$]Cl seems to be optically pure, though there is no way to compare the purity, as [Co trien Cl$_2$]Cl could not be resolved by the classical method.

It has recently been shown[3] that there is a preferential coördination of the isomer of *d*-configuration when tartaric, chloropropionic, or lactic acid is introduced into [Co(*l*-propylenediamine)$_2$CO$_3$]Cl. The present authors have seen that the method is quite general in the following scheme

$$\text{D- or L-}[\mathrm{MA_n}] + 2m(dl\text{-B}) \rightleftarrows \text{D- or L-}[\mathrm{MA}_{n-m}(d\text{- or }l\text{-B})_m] + m\mathrm{A} + m(l\text{- or }d\text{-B})$$

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 coördination 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 coördination sphere, by *d*-antimonyl tartrate. The resulting 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°) 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 NH$_3$. 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} en$_2$NH$_3$Cl]Cl$_2$ 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 coördination sphere in the aqueous system.

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[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-[Co^{III} EDTA]$^-$ + 3en → D-[Co en$_3$]$^{+3}$ by F. P. Dwyer, private communication. L-[Co^{III} EDTA]$^-$ + 6(*dl*-pn) → L-[Co(*l*-pn)$_3$]$^{+3}$ + 3(*d*-pn) where ETDA = ethylenediamine tetraacetate. S. Kirschner, Thesis, University of Illinois, 1954. L-[Co en$_2$Cl$_2$]$^+$2*dl*-pn → L-[Co en$_2$*d*-pn]$^{+3}$ + *l*-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**, 4051 (1954).

We are planning further investigations to establish the mechanism of this induced asymmetry. It is hoped that this will lead to a general method of preparing optically active inorganic complexes of certain types, offering a quick, inexpensive method giving high yields.

Experimental

Triethylenetetramine, obtained from Eastman Kodak Co., was used without further purification. Analysis for carbon, hydrogen and nitrogen showed it to be sufficiently pure (85%) for preparatory work.

Silver *d*-antimonyl tartrate was prepared by the addition of silver nitrate in saturated solution to a cold solution of an equivalent amount of potassium *d*-antimonyl tartrate, filtering, washing several times with water and then with alcohol and acetone.

Reagent quality cobalt chloride hexahydrate was used throughout the work.

I. *cis*-Dichlorotriethylenetetraminecobalt(III) Chloride.—[Co^{III} trien Cl$_2$]Cl was prepared according to the method of Basolo.[6] Our efforts to resolve it by the classical methods, like those of Basolo, were unsuccessful.

Anal. Calcd.: C, 23.11; H, 5.78; N, 17.98; Co, 18.92. Found: C, 23.19; H, 5.55; N, 18.26; Co, 19.01.

The substance is violet, like all other *cis*-dichlorotetraminecobalt(III) compounds. With most of the dichloro compounds of this series, the *trans* form is more easily obtained than the *cis* isomer, but our attempts to prepare the *trans* form of this compound, like those of Basolo, were unsuccessful. It was observed, however, that a purple solution of this compound in methanol slowly changes to a light gray–violet color on standing. *cis*-[Co^{III} en$_2$ Cl$_2$] Cl in methanol solution gives a similar color change, ultimately becoming green. The visible and ultraviolet spectra of the fresh and few-hour old solutions in methanol showed that the color change is due to the conversion of the *cis* form to the *trans*, which goes all the way to the pure *trans* isomer (green) in the case of the bis-ethylenediamine compound, but only to an equilibrium mixture of about 40% *trans* and 60% *cis*, in the case of the triethylenetetramine compound. Evaporation of the methanol solution gives the purple *cis* compound in the case of [Co trien Cl$_2$]$^+$ and the green *trans*-isomer in the case of [Co en$_2$Cl$_2$]$^+$. The reason for the peculiar higher stability of the *cis*-isomer in the case of [Co trien Cl$_2$] Cl is difficult to explain.

II.—The compound [Co^{III} trien (*d*-SbO tart)$_2$] (*d* SbO tart) was prepared as follows: 27.6 g. (0.08 mole) of silver *d*-antimonyltartrate was suspended in about 250 cc. of water and the mixture was stirred mechanically while 6.2 g. (0.02 mole) of [Co trien Cl$_2$]Cl was added to it in small quantities. The next batch of complex was added when the solution changed from purple to pink. After the addition of the whole of the cobalt complex, the stirring was continued for a couple of hours. The mixture was cooled in an ice-bath and was filtered after 3–4 hours. To the red-pink solution was added 100 cc. of methanol whereupon most of the L-[Co trien(*d*-SbO tart)$_2$] (*d*-SbO tart) separated as a pinkish red powder. This was separated by filtration and purified by repeatedly dissolving in water (it takes a long time to redissolve, the powdery mass forming a red oil at the bottom at first) and reprecipitating by the addition of methanol. The product was finally washed successively with methanol, ethanol and acetone and dried in a vacuum; yield 16 g. The analysis of the product varied a little, depending upon the mode of preparation and drying.

Anal. Calcd. for [Co trien (SbO tart)$_2$] (SbO tart): C, 20.34; H, 2.83; N, 5.27; Co, 5.55; Sb, 34.41. Calcd. as [Co trien (SbO tart)$_2$] (SbO tart)·2CH$_3$OH: C, 21.35; H, 3.38; N, 4.98; Co, 5.24; Sb, 32.47. Found: C, 21.11; H, 3.93; N, 5.04; Co, 5.31; Sb, 32.18.

$[\alpha]^{25}\text{D}$ + 120–125° for a 0.1% solution in water.

III.—For the preparation of the carbonato complex, L-[Co trien CO$_3$]$_2$ CO$_3$, 10 g. of L-[Co trien (*d*-SbO tart)$_2$] (*d*-SbO tart) was dissolved in 200 cc. of cold water and a slight excess of a saturated solution of barium hydroxide was added to it with constant stirring. A voluminous precipitate of barium *d*-antimonyl tartrate separated. This was filtered under suction and carbon dioxide was passed into the filtrate until it was no longer alkaline. The solution was then evaporated at room temperature by blowing a stream of air over it. The residue was taken up with methanol and filtered from the insoluble barium carbonate, and the filtrate was again evaporated at room temperature and taken up with methanol. On evaporation, a deep red product was obtained. This was dried in a vacuum desiccator. The product was hygroscopic, highly soluble in water and methanol and insoluble in acetone; yield 2.2 g.

Anal. Calcd. for [Co trien CO$_3$]$_2$CO$_3$: C, 30.51; H, 7.00; N, 18.99; Co, 20.00. Calcd. for [Co trien CO$_3$]$_2$-CO$_3$·CH$_3$OH: C, 31.19; H, 6.72; N, 17.12; Co, 18.04. Found: C, 31.68; H, 6.17; N, 17.35; Co, 18.09.

The specific rotation for a 0.1% solution in water $[\alpha]^{25}\text{D}$ −85 to −90°.

The carbonato compound was also prepared from L-[Co trien Cl$_2$] Cl and silver carbonate by grinding them in the solid state and then with methanol. This mixture was filtered when the methanol solution did not give any test for the presence of chloride ion. On evaporation the filtrate yielded a deep red powder which was dried at 80–85° *in vacuo*. It was highly soluble in water and methanol.

Anal. Calcd. for [Co trien CO$_3$]$_2$CO$_3$·2CH$_3$OH: C, 31.19; H, 6.72; N, 17.12; Co, 18.04. Found: C, 30.66; H, 6.25; N, 17.04; Co, 18.30.

A 0.1% solution in water gave $[\alpha]^{25}\text{D}$ −135°.

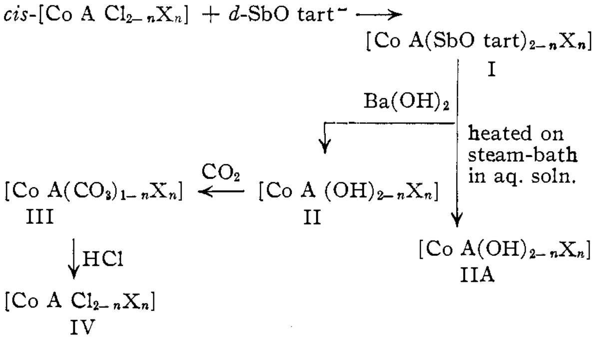
IV.—The dichloro complex, L-[Co trien Cl$_2$] Cl, was prepared as follows. One gram of the *l*-carbonato complex was ground to a fine powder in a mortar and then treated with acetone containing 0.5% HCl. The acetone–HCl was poured off after some time and replaced with a fresh solution. After the red mass turned purple, it was suspended in 200 cc. of acetone containing a drop or two of concentrated hydrochloric acid and shaken from time to time for 24 hours. The solid was filtered and washed with acetone and then with ether and dried *in vacuo*. It then had the characteristic violet color of the *cis*-dichlorocobalt(III) compounds.

Anal. Calcd. for [Co trien Cl$_2$]Cl: C, 23.11; H, 5.78; N, 17.98. Found: C, 23.19; H, 5.55; N, 18.26.

A 0.05% solution in water gave $[\alpha]^{25}\text{D}$ −85 to −90°.

The dichloro complex was also prepared directly from L-[Co trien(*d*-SbO tart)$_2$] (*d*-SbO tart) by grinding with acetone containing 0.5–1% hydrochloric acid. The reaction required 2–3 days, but ultimately an almost purple powder was obtained. It gave $[\alpha]\text{D}$ −100° for a 0.05% aqueous solution.

The following outline represents the results of subjecting a series of [Co^{III} AClX] complexes to the same sequence of operations (X is a Cl or NH$_3$).



The rotations of the various products were all made at the D-line of sodium, at approximately 25° at concentrations of 0.05–0.1% in aqueous or water–methanol solutions, and calculated in terms of initial concentration of the starting compound I except for IV. They are collected in Table I.

D-[Co en$_2$Cl$_2$] Cl.—Exactly in the same way as in the case of triethylenetetramine compound, 2.9 g. of *cis*-[Co en$_2$Cl$_2$] Cl was treated with 13 g. of silver *d*-antimonyl tartrate. The resulting light red complex was treated with barium hydroxide, filtered, treated with carbon dioxide, and filtered again. Finally, the red carbonato compound was converted into [Co en$_2$Cl$_2$] Cl by treatment with HCl–acetone, washed with acetone and then with ether and dried in a vacuum.

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[6] F. Basolo, This Journal, **70**, 2634 (1948).

TABLE I

	Specific rotations, degree				
	I	IIA[a]	II	III	IV
[Co trien Cl]$_2^+$	+120	0 to +5	−111	−100	−85
[Co en$_2$Cl$_2$]$^+$	+111	+ 57	− 21	...	−60
[Co en$_2$NH$_3$Cl]$^{++}$	+ 98.5	+103	−5∼0	...	...
[Co pn$_2$Cl$_2$]$^+$	+131	+ 53	− 10	...	...
K-*d*-SbO tart	+143	+143	0	...	...

[a] The rotations in column IIA include that due to the ionic SbO tart$^-$.

Anal. Calcd. for [Co en$_2$ Cl$_2$]Cl·H$_2$O, C, 15.81; H, 5.93; N, 18.41; Co, 19.41. Found: C, 15.87; H, 5.68; N, 18.37; Co, 18.99.

The rotation of a 0.05% aqueous solution was −0.035° at the D-line of sodium. Different samples of 0.05% solutions of L-[Co en$_2$Cl$_2$]Cl resolved by the standard *d*-bromocamphorsulfonate method gave rotations +0.11 to +0.134 for different samples.

A similar approach is under way using other stable metal complexes of the same type containing metal ions other than cobalt(III).

Our best thanks are due to the University of Illinois and to the National Science Foundation for providing funds to one of us (Das Sarma) and also to the kind help and coöperation of Mr. Josef Nemeth, Mrs. E. L. Fett and Mrs. L. Chang for the microanalysis for carbon, hydrogen and nitrogen.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MALAYA]

Compounds of Chromium(III) with Alanine

BY R. W. GREEN AND K. P. ANG

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The Van Slyke manometric method for determination of amino groups has been used to demonstrate the presence of N-coördinated alanine in solutions of alanine and chromium(III) salts. This has been combined with spectroscopic and isopiestic studies to show that solutions near *p*H 4.5 contain complexes in which each chromium atom is united to three alanine residues, of which one is in the form of a chelate ring and the other two are coördinated by their carboxyl groups only. It is possible to prepare solutions at *p*H 7–8 in which two alanine residues are chelated to each chromium atom, but higher degrees of chelation produce very sparingly soluble derivatives.

The first compound of chromium and alanine was prepared by Tchougaeff and Serbin,[1] who boiled together solutions of chloropentamminochromium(III) chloride and excess alanine until most of the ammonia had been driven off. The resulting deep red, faintly ammoniacal solution deposited rose colored needles whose composition corresponded to the formula Cr[CH$_3$·CH(NH$_2$)·COO]$_3$. Hugouneng and Morel[2] boiled concentrated solutions of amino acids with freshly precipitated chromium(III) hydroxide and obtained two products containing, respectively, two and three molecules of amino acid per chromium atom. In the same year, Ley and Ficken,[3] by adding three moles of sodium hydroxide to a hot solution of one mole chromium(III) chloride and three moles alanine, prepared two very sparingly soluble crystalline solids, one red and one violet, to which they gave the formulas, Cr(C$_3$H$_6$O$_2$N)$_3$ and Cr(C$_3$H$_6$O$_2$N)$_2$(OH)·H$_2$O. The same two solids, which, on account of their insolubility and inertness, are generally regarded as chelate compounds, were again prepared by Volshtein.[4] In each case, the amount of alkali present or added during the preparation was equivalent to the total chlorine of the chromium(III) chloride, so that the solutions from which the solids separated were approximately neutral in reaction.

More acid solutions have been studied by Shuttleworth,[5] who interpreted conductimetric evidence as indicating that the amino groups of glycine and alanine were not coördinated by chromium in dilute solutions, even on boiling. On the other hand, Serfass, Wilson and Theis[6] showed by spectrophotometric measurements that glycine reacted with chromium(III) ions much more readily than did acetate. Indeed, they found it to be more readily coördinated than any other substance they studied, except oxalic acid, which is well known to cause chelation. This paper describes the use of analytical, isopiestic and spectrophotometric methods to investigate the nature of chromium(III)–alanine solutions.

Experimental Methods

Chromium was determined in solution by oxidizing with sodium peroxide and comparing the optical density at 373 mμ with that of standard chromate solutions. Chromium(III) chloride and sulfate solutions were analyzed in this way for chromium, gravimetrically for chloride and sulfate, and also by titration of the hot solution with alkali in the presence of phenolphthalein.

Basic chromium(III) chloride solutions free from other electrolytes were made by adding to boiling chromium(III) sulfate solution the calculated quantities of barium chloride and barium hydroxide.

Absorption spectra were measured with a Beckman model DU spectrophotometer. Because solutions usually contained more than one chromium complex of unknown molecular formula, results are given as atomic extinction coefficients

$$\epsilon = 1/cd \log_{10}(I_0/I)$$

where c is the concentration in g. atom Cr per liter. All the chromium solutions examined had two absorption maxima (Fig. 6), one near 400 mμ and one near 540 mμ. We shall use ϵ_1 and λ_1 to denote the atomic extinction coefficient and wave length of the first maximum, and ϵ_2 and λ_2 for the second maximum.

A Beckman *p*H meter was used for all *p*H determinations.

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(1) L. Tchougaeff and E. Serbin, *Compt. rend.*, **151**, 1361 (1910).

(2) L. Hugounenq and A. Morel, *ibid.*, **154**, 119 (1912).

(3) H. Ley and K. Ficken, *Ber.*, **45**, 377 (1912).

(4) L. M. Volshtein, *Compt. rend. acad. sci. (U.S.S.R.)*, **54**, 321 (1946).

(5) S. G. Shuttleworth, *J. Intern. Soc. Leather Trades' Chem.*, **32**, 116 (1948).

(6) E. J. Serfass, C. D. Wilson and E. R. Theis, *J. Amer. Leather. Chem. Assoc.*, **44**, 647 (1949).