geometrical purity of the various products was established. Also a preparation where no precipitate was formed gave the $\alpha/\beta$ ratio as 2.7 which established the $\alpha$ form as the thermodynamically stable form. This preparative procedure was assumed to be equilibrium controlled since in the analogous $[Co(en)_2(NO_2)_2]^+$ system either the *cis* or *trans* isomer can be precipitated depending on the anion present.

The visible and ultraviolet absorption spectra of the $\alpha$ and $\beta$ forms are very similar, Figure 11, and are of little use in distinguishing the isomers. However the infrared specta, Figure 12, confirm the $\alpha$ and $\beta$ assignments of configuration which have been made by converting the other complexes to the dinitro species with retention of configuration.[10] The NH absorptions $\sim$3300 $cm^{-1}$ are not well resolved, but the less symmetrical $\beta$ isomer gives a more complex spectrum which is consistent with the lower site symmetry of the $\beta$ NH groups. This is also evident in the infrared spectra of the deuterated complexes in the vicinity of 2400 $cm^{-1}$, Figure 12.

The $\alpha$ isomer was resolved with the $(-)[Co(en)(C_2O_4)_2]^-$ ion, and the $\beta$ isomer, with (+)antimonyl tartrate. The iodide, bromide, or perchlorate salts gave, for $\alpha$, $[M]_{546}$ $\pm 220°$ and, for $\beta$, $[M]_{546}$ $\pm 1100°$. The optical purities of these resolved complexes was confirmed by transforming the resolved dichloro and carbonato isomers to the dinitro salts with retention of configuration.

Careful fractionation of large amounts of these dinitro isomers failed to reveal any trace of the *trans* form. The infrared, visible, and ultraviolet spectra, powder diffraction patterns, and chromatographic behavior were always consistent with either the $\alpha$ or the $\beta$ isomer. The $\beta$-dinitro isomer, as well as being less stable than the $\alpha$ form, was also more reactive. An aqueous solution of the $\beta$ isomer lost 10% of its rotation in 5 hr at 50° whereas the $\alpha$ form showed no change in 30 hr under the same conditions.

**General Stability.**—It is apparent from the foregoing results that the relative stability of the $\alpha$ and $\beta$ isomers is a function of the substituent rather than of the possible strain associated with coordination of the secondary N atoms in the two configurations. The dichloro and dinitro complexes appear to favor the $\alpha$ form whereas the diaquo ion favors the $\beta$ configuration and there appears to be no obvious correlation between either the size or the electronic properties of these substituents to account for the variation in stability of the geometrical form.

**Assignment of Configuration.**—This has been discussed to some extent for each isomer in this paper and has been expounded also in a previous article.[10] The stereochemical detail in these systems will also be developed in subsequent papers for compounds in which the stereochemistry is closely related to the reactivity of the isomers.[5]

**Acknowledgment.**—The authors thank the Microanalytical Unit of the John Curtin School of Medical Research for the C, H, and N microanalyses and Dr. L. Durham for the 100-Mc pmr spectra.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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# Asymmetric Synthesis of Alanine *via* the Template Action of a Dissymmetric Cobalt(III) Complex

BY ROBERT G. ASPERGER[1] AND CHUI FAN LIU

*Received July 6, 1966*

The complex ion $\alpha$-amino-$\alpha$-methylmalonato-L,L-$\alpha,\alpha'$-dimethyltriethylenetetraminecobalt(III) has been isolated and decarboxylated in aqueous solution to yield the L-*cis*-$\beta$-[Co(L,L-$\alpha,\alpha'$-dimethyltrien)(L-alan)]$^{2+}$ ion. The configuration of the alanine is ascertained by decomposition of the complex ion, isolation of the resulting alanine, and measurement of its optical rotation. A high degree of stereospecificity in the formation of the alanine is indicated by the comparison of the ORD curve of the decarboxylated complex with those of the L-*cis*-$\beta$-[Co(L,L-$\beta,\beta'$-dimethyltrien)(L-alan)]$^{2+}$ and the L-*cis*-$\beta$-[Co(L,L-$\alpha,\alpha'$-dimethyltrien)(D-alan)]$^{2+}$ ions obtained from standard L-alanine and D-alanine, respectively.

## Introduction

In a previous paper[2] the synthesis of a new optically active tetradentate ligand L,L-$\alpha,\alpha'$-dimethyltriethylenetetramine[3] was reported. This ligand was found to form complexes with the cobalt(III) ion in a fashion analogous to that of triethylenetetramine.[4] The two *cis* isomers ($\alpha$ and $\beta$) were found to form in a stereospecific manner (with the D and L absolute configuration, respectively). Both of the *cis* isomers and the *trans* isomers were isolated, and their absolute configurations were assigned. In the present investigation the D-

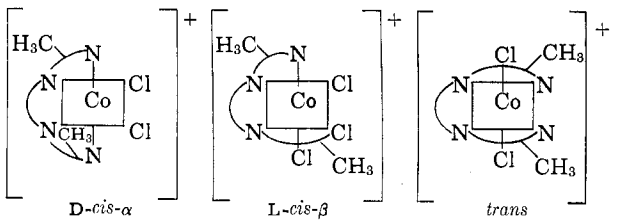
(1) Edgar C. Britton Research Laboratory, The Dow Chemical Co., Midland, Mich. 48640.

(2) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1395 (1965).

(3) Abbreviations used here are: 2,9-diamino-4,7-diazadecane (L,L-$\alpha,\alpha'$-dimethylethylenetetramine), L,L-$\alpha,\alpha'$-dimethyltrien; D-alanate, D-alan; L-alanate, L-alan; $(CH_3C(NH_2)(CO_2^-)_2H$, HMAM; the exact protonation site is not implied.

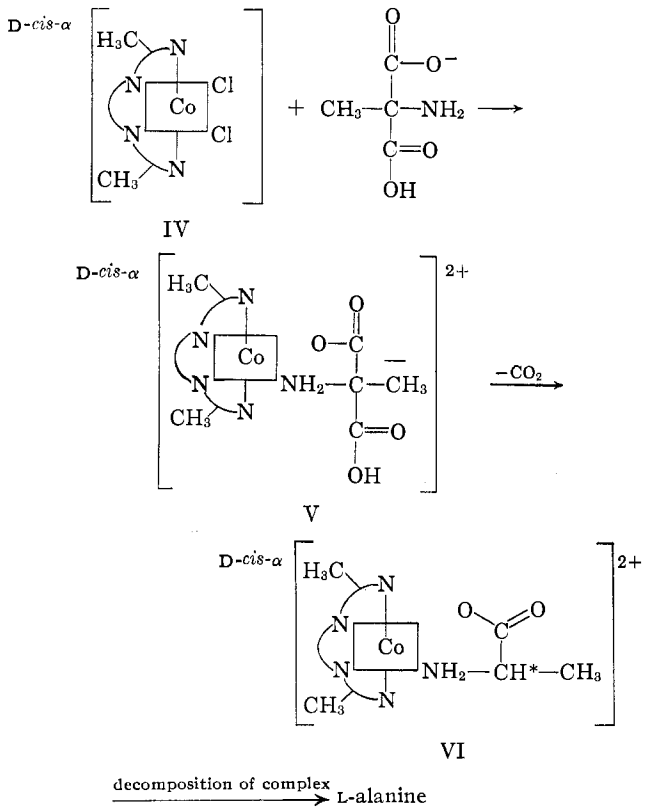
(4) A. M. Sargeson and G. A. Searle, *Inorg. Chem.*, **4**, 45 (1965).

*cis*-α-dichloro-L,L-α,α′-dimethyltriethylenetetraminecobalt(III) ion is chosen as the starting point for the




I II III

asymmetric synthesis of α-alanine. Originally, this synthesis was envisaged to proceed through the stereospecific decarboxylation of a coordinated malonate molecule according to the scheme shown below.




It was found that the alanine obtained as the final product was optically active and had an excess of the L antipode. However, compound VI in the above scheme was found to possess the L-*cis*-β configuration based on ORD and nmr studies of the L-*cis*-β and D-*cis*-α configurations of the ions [Co(L,L-α,α′-dimethyltrien)(aa)]$^{2+}$ where aa is the anion of L-alanine, D-alanine, or glycine.[5]

## Experimental Section

**ORD Measurements.**—Optical rotatory dispersion curves were measured on a Keston polarimeter attachment for a Beckman DU spectrophotometer. The attachment was manufactured by Standard Polarimeter Co., Hackensack, N. J. Some measurements were also made on a Jasco Model ORD-5, Durrum Instrument Corp., Palo Alto, Calif. Spectra of the same sample taken on both instruments were identical in all respects, within experimental error, except that the Jasco gave rotations at the peaks about 1.4% larger than the Keston. This is an expected difference owing to the higher degree of monochromaticity of the Jasco instrument.[6]

**Elemental Analysis.**—All elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

**Preparation of Ammonium α-Methyl-α-aminomalonate (Modified Method of Lutz[7]).**—In 2 l. of anhydrous methanol was dissolved 340 g (1.73 moles) of methylbromomalonic acid. Gaseous ammonia was added to the solution in a 6-l. erlenmeyer flask, stirred with a magnetic stirrer, using an entry tube 2 cm in diameter (to prevent blockage by solid deposition). Concentrated ammonium hydroxide (750 ml) was added until the white solid first formed just dissolved. Then the solution was maintained at 45° and stirred for 10 days. Each day ammonia was added for 30 min. After the solution was evaporated to an oil using moving air at room temperature, 2.5 l. of technical methanol was slowly added. Crystallization was induced by seeding or scratching the inside surface of the flask and the solution was then cooled to 5°. A yield of 200 g representing 77% was obtained. Recrystallization three times from a hot, saturated aqueous solution by slow addition of methanol with seeding yielded pure product. *Anal.* Calcd for $NH_4(C_4H_6NO_4)$: C, 32.0; H, 6.72; N, 18.9. Found: C, 32.0; H, 6.76; N, 18.9.

**Preparation of Silver Methylaminomalonate Hemihydrate.**—To 16.8 g (0.112 mole) of ammonium α-methyl-α-aminomalonate dissolved in 100 ml of 50° water was added 20 g (0.118 mole) of silver nitrate dissolved in 50 ml of water; then 40 ml of a 1:1 acetone–ether mixture was added after cooling to room temperature. The resulting white solid and solution were cooled in an ice bath. The product was removed by filtration and recrystallized from hot water by the slow addition of absolute alcohol. *Anal.* Calcd for $AgC_4H_6NO_4 \cdot {}^1/_2H_2O$: Ag, 43.4. Found: Ag, 43.7, 43.6.

**Preparation of L-*cis*-β-[Co(L,L-α,α′-dimethyltrien)(D-alan)](NO$_3$)$_2$.**—A solution containing 0.172 g ($5.07 \times 10^{-4}$ mole) of D-*cis*-α-[Co(L,L-α,α′-dimethyltrien)Cl$_2$]Cl in 5 ml of water was aquated for 20 min by gently heating on a steam bath. Then 0.0452 g ($5.07 \times 10^{-4}$ mole) of D-alanine was added and the pH was adjusted to 8 using a dilute LiOH solution. This solution was then heated for 12 min on the steam bath with frequent stirring. The resulting red residue was dissolved in 10 ml of water and passed through 30 ml of Amberlite IRA 410 anion-exchange resin in the form of the nitrate, using water as eluent. The flow rate was 0.5 ml/min. The effluent was evaporated to dryness under moving air at room temperature. The residue was taken up in 3 ml of hot water followed by addition of hot absolute alcohol to the oil point. On cooling, a crop of crystals was removed by filtration. *Anal.* Calcd for [CoC$_{11}$H$_{28}$N$_5$O$_2$](NO$_3$)$_2$: C, 29.7; H, 6.34; N, 22.0. Found: C, 29.5; H, 6.37; N, 21.6.

**Preparation of L-*cis*-β-[Co(L,L-α,α′-dimethyltrien)(L-alan)](NO$_3$)$_2$.**—A solution containing 0.401 g ($5.94 \times 10^{-4}$ mole) of D-*cis*-α-[Co(L,L-α,α′-dimethyltrien)Cl$_2$]Cl dissolved in 5 ml of water was aquated for 20 min by gently heating on a steam path. Then 0.0529 g ($5.94 \times 10^{-4}$ mole) of L-alanine was added and the pH adjusted to 8 using a dilute LiOH solution. This solution was then heated for 20 min on a steam bath with frequent stirring. The resulting residue was then dissolved in 10 ml of water and passed through 30 ml of Amberlite IRA 410 anion-exchange resin in the form of the nitrate. It was eluted with water at a flow rate of 0.5 ml/min. The effluent from the nitrate column was evaporated to dryness under moving air at room temperature. The residue was taken up in 3 ml of hot water followed by addition of hot absolute alcohol to the oil point. On cooling, a crop of crystals was obtained which was removed by filtration. *Anal.* Calcd for [CoC$_{11}$H$_{28}$N$_5$O$_2$](NO$_3$)$_2$: C, 29.7; H, 6.34, N, 22.0. Found: C, 29.5; H, 6.49; N, 21.5.

**Preparation of L-*cis*-β-[Co(L,L-α,α′-dimethyltrien)(D-alan)]Cl$_2$·2H$_2$O.**—A solution containing 0.201 g ($5.94 \times 10^{-4}$ mole) of D-*cis*-α-[Co(L,L-α,α′-dimethyltrien)Cl$_2$]Cl dissolved in 5 ml of

(5) R. G. Asperger and C. F. Liu, *J. Am. Chem. Soc.*, **89**, 708 (1967).

(6) See J. T. Yang in "Newer Methods of Polymer Characterization," B. Ke, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 130.

(7) O. Lutz, *Chem. Ber.*, **35**, 2553 (1902).

water was aquated for 20 min by gently heating on a steam bath. Then 0.0529 g ($5.94 \times 10^{-4}$ mole) of D-alanine was added and the pH was adjusted to 8 using a dilute LiOH solution. This solution was then heated for 12 min on a steam bath with frequent stirring. The solution was then cooled to 5° and the pH was adjusted to 7 using dilute HCl. After evaporation to dryness under moving air at room temperature, the residue was triturated with 200 ml of acetone in 100-ml batches. The residue was dissolved in 4 ml of methanol and allowed to stand covered for 4 hr at room temperature and then cooled to 5° and filtered. The filtrate was heated and hot 2-propanol was added to the oil point. The crystals obtained by long standing and then cooling to 5° were recrystallized from hot methanol *via* the same technique. *Anal.* Calcd for $[CoC_{11}H_{28}N_5O_2]Cl_2 \cdot 2H_2O$: C, 30.9; H, 7.54; N, 16.4; Cl, 16.6. Found: C, 31.0; H, 7.28; N, 16.3; Cl, 16.5.

**Preparation of L-*cis*-β-[Co(L,L-α,α′-dimethyltrien)(L-alan)]-$Cl_2 \cdot 2H_2O$.**—A solution containing 0.214 g ($6.31 \times 10^{-4}$ mole) of D-*cis*-α-[Co(L,L-α,α′ dimethyltrien)$Cl_2$]Cl dissolved in 5 ml of water was aquated for 20 min by gently heating on a steam bath. Then 0.0562 g ($6.31 \times 10^{-4}$ mole) of L-alanine was added and the pH was adjusted to 8 using a dilute LiOH solution. This solution was heated for 20 min on a steam bath with frequent stirring. It was then cooled to 5° and the pH was adjusted to 7 using dilute HCl. After evaporation to dryness under moving air at room temperature, the residue was triturated with 200 ml of acetone in 100-ml batches. The residue was dissolved in 4 ml of methanol and allowed to stand covered for 4 hr at room temperature. The methanol solution was then heated and hot 2-propanol was added to the oil point. Crystals were obtained on long standing, then cooled to 5°. They were recrystallized from hot methanol *via* the same technique. *Anal.* Calcd for $[CoC_{11}H_{28}O_2]Cl_2 \cdot H_2O$: C, 30.9; H, 7.54; N, 16.4; Cl, 16.6. Found: C, 31.0; H, 7.27; N, 16.4; Cl, 16.6.

**Preparation of L-*cis*-β-[Co(L,L-α,α′-dimethyltrien)(HMAM)]-$Cl_2 \cdot 3H_2O$.**—A total of 0.742 g ($2.19 \times 10^{-3}$ mole) of D-*cis*-α-[Co(L,L-α,α′-dimethyltrien)$Cl_2$]Cl in 10 ml of water was heated on the steam bath for 10 min, then cooled to below 60°. An aqueous saturated solution containing 0.525 g (0.00219 mole) of silver methylaminomalonate at 60° was then added. The mixture was allowed to digest for 2 hr at room temperature with occasional stirring. Then the silver chloride was removed either by centrifugation or by filtering through Celite No. 535. The red filtrate was then heated on the steam bath for 40 min followed by evaporation to dryness at room temperature under moving air. Then the red residue was recrystallized from 10 ml of hot water–absolute ethanol–methanol (1:1:1) plus 1 drop of dilute HCl by the addition of hot isopropyl alcohol to the oil point followed by slow cooling. Additional crops were obtained from the filtrates by heating and adding more isopropyl alcohol to the oil point. *Anal.* Calcd for $[CoC_{12}H_{28}N_5O_4]Cl_2 \cdot 3H_2O$: C, 29.4; H, 7.00; N, 14.3; Cl, 14.5. Found: C, 29.4; H, 6.69; N, 14.7; Cl, 14.5.

**Preparation of L-*cis*-β-[Co(L,L-α,α′-dimethyltrien)(alan)]-$(NO_3)_2$ *via* Decarboxylation of L-*cis*-β-[Co(L,L-α,α′-dimethyltrien)-(HMAM)]$Cl_2 \cdot 3H_2O$.**—In 20 ml of water was dissolved 0.10 g ($2 \times 10^{-4}$ mole) of L-*cis*-β-[Co(L,L-α,α′-dimethyltrien)-(HMAM)]$Cl_2 \cdot 3H_2O$. The pH was adjusted to 7.5–8.0 using dilute LiOH and the solution was heated at boiling for 10 min. After cooling to 5° in an ice bath, dilute HCl was used to adjust the pH to 7. The solution was evaporated to dryness under moving air at room temperature and triturated with 200 ml of hot acetone in 100-ml batches. The residue was dissolved in 10 ml of water and passed through 25 ml of Amberlite IRA 410 in the form of the nitrate at a flow rate of 1–2 ml/min. The effluent was evaporated to 10 ml under moving air at room temperature and then recycled through the freshly nitrated IRA 410 column.

This last effluent was evaporated to dryness under moving air at room temperature. The residue was recrystallized from 2 ml of water by cooling the solution to 5°, adjusting the pH to 1 with dilute $HNO_3$, adding 250 ml of acetone, and then allowing long standing (7 days) in a 250-ml sealed erlenmeyer flask. *Anal.* Calcd for $[CoC_{11}H_{28}N_5O_2](NO_3)_2$: C, 29.7; H, 6.34; N, 22.0. Found: C, 30.0; H, 6.43; N, 19.94.

**Isolation and Characterization of the Asymmetrically Synthesized Alanine.**—Isolation of the L-alanine from the complex after decarboxylation was accomplished by the addition of excess sulfide ion to 1.0 g ($2.34 \times 10^{-3}$ mole) of the red-orange complex in solution. The color rapidly turned an intense red-brown. This colored species was stable in acid at a pH of less than 1. The breakdown of the very stable intermediate, reduction of the cobalt(III) to cobalt(II), and precipitation were accomplished by repeated very slow addition of a saturated solution containing 0.566 g (0.00294 mole) of $CoCl_2 \cdot 6H_2O$. The resulting precipitate was separated from the solution by centrifugation and decantation. The process was repeated if the supernatant had any remaining color of the complex. Excess sulfide ion was removed from solution as $H_2S$. The solution was made acid with HCl and air was bubbled through for 5 min. Dowex 3 (20–50 mesh) was used to isolate the alanine. The neutral alanine solution was passed through 20 ml of the resin in the chloride form. After careful rinsing with 1.5 l. of water, 1.5 l. of 2 *N* HCl was used to elute the alanine. The alanine was isolated from the effluent by evaporation to dryness at room temperature. The residue was stored under high vacuum for 8 hr. It was then recrystallized from several drops of water by the addition of acetone. The yield was 0.1244 g or 60% of the theoretical value.

The infrared spectrum of this precipitate was identical with that of authentic alanine. The optical rotation for the sample dissolved in 2 ml of 1.57 *N* HCl was $\alpha_{obsd}D$ +0.027 ± 0.001°, $[\alpha]^{23}D$ +2.2°. This solution was evaporated to a dryness and then recrystallized from 0.5 ml of water–alcohol (50:50) and 1 drop of concentrated HCl by the very slow addition (50 ml) of ether during 1 day. *Anal.* Calcd for $C_3H_7NO_2 \cdot HCl$: C, 28.70; H, 6.42; N, 11.2. Found: C, 28.6, 28.6; H, 6.39, 6.50; N, 11.2, 11.2.

**Isolation of L-Alanine from a Comparison Standard Complex.**—To a solution of 0.175 g ($3.93 \times 10^{-4}$ mole) of L-*cis*-β-[Co(L,L-α,α′-dimethyltrien)(L-alan)]$(NO_3)_2$ in 30 ml of water was added 2 ml of concentrated $NH_4OH$. An electrolytic cell using a finely fritted glass bridge was used electrolytically to reduce the cobalt(III) ion to cobalt(II) ion. The ammoniacal complex solution was placed in the working electrode chamber and supporting electrolyte (0.1 *M* $NH_4OH$) was placed in the other chamber. The reduction was run at a constant voltage of 0.87 v for 15 hr with constant stirring. Platinum electrodes were used.

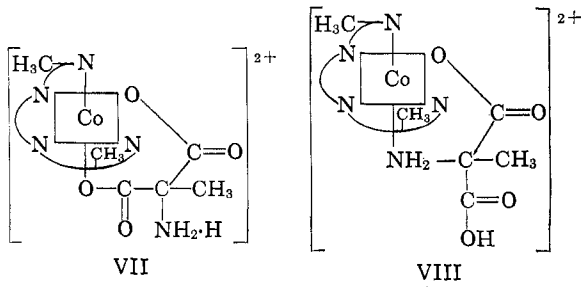
Excess hydrogen sulfide was bubbled into the cobalt(II) solution in an erlenmeyer flask. The resulting cobalt(II) sulfide was removed by centrifugation and the excess $H_2S$ was removed by aeration. The L-alanine was isolated by use of an ion-exchange column as described for the above isolation of the synthetic L-alanine.

The resulting L-alanine, 0.0215 g ($2.4 \times 10^{-4}$ mole), 61% of the theoretical yield, was dissolved in 2 ml of 1.57 *N* HCl and had the following optical rotation: $\alpha_{obsd}D$ +0.0095 ± 0.0005°; $[\alpha]^{23}D$ +4.4°.

**Optical Rotation of Pure L-Alanine.**—The optical rotation of a solution of 0.1191 g ($1.34 \times 10^{-3}$ mole) of pure L-alanine dissolved in 2 ml of 1.57 *N* HCl was $\alpha_{obsd}D$ +0.182 ± 0.0005; $[\alpha]^{23}D$ +15.2.

## Results and Discussion

The coordination of α-methyl-α-aminomalonate to the complex ion can result in linkage isomers VII and VIII. The coordinated malonate ion is asymmetric in either case. The infrared spectrum of the complex [Co(L,L-α,α′-dimethyltrien)(HMAM)]$Cl_2 \cdot 3H_2O$ shows a single carboxyl peak at 1650 $cm^{-1}$ and no bands in the region where carboxylic acids generally absorb. Therefore, the complex probably has structure VII (though there



VII VIII

is a possibility that a small amount of the complex still has the D-*cis*-$\alpha$ configuration at this point). Also supporting this structural assignment is the fact that this complex has a first absorption band Cotton effect very similar in magnitude and sign (negative) to those observed for complexes with the configuration L-*cis*-$\beta$[8,9] containing oxalate or carbonate.

The mechanism of the decarboxylation step is not known. It is entirely possible that the complex rearranges to structure VIII before decarboxylation as there is a pronounced change in color of the solution (from red to orange) before evolution of carbon dioxide is observed.

The alanine from the decarboxylated complex was isolated and characterized using infrared spectra, elemental analysis, and optical rotation. The specific rotation of $+2.2°$ represents a 14% excess of L-alanine over the D isomer in the mixture. The ORD data suggest, however, that the reaction is possibly much more stereospecific than the above percentage would indicate. The ORD curve of the L-*cis*-$\beta$-[Co(L,L-$\alpha,\alpha'$-dimethyltrien)(D-alan)]$(NO_3)_2$ (Figure 1) is quite different from that of the L-*cis*-$\beta$-[Co(L,L-$\alpha,\alpha'$-dimethyltrien)(L-alan)]$(NO_3)_2$ (Figure 2), especially in the near-ultraviolet region. The ORD curve of the L-*cis*-$\beta$-[(Co(L,L-$\alpha,\alpha'$-dimethyltrien)(alan)]$(NO_3)_2$ derived from the decarboxylation reaction (Figure 3) is very similar to that of the standard L-alanine adduct particularly in the near-ultraviolet region. A possible explanation for the relatively low specific rotation of the L-alanine obtained from the decarboxylation reaction is that racemization occurred in one of the isolation steps This explanation was made more plausible by the observation that the alanine isolated from the standard L-alanine adduct has undergone racemization as the specific rotation was only $+4.4°$.

This loss of activity is not totally unexpected since racemization of L-alanine in aqueous solution containing the metal ions $Al^{3+}$ and $Cu^{2+}$ has been reported in the literature.[10] In that work the alanine to metal ratio was 10 and the racemization efficiency was 3; *i.e.*, 3 mmoles of D-alanine/mmole of metal ion was obtained in 10 min at 100°. We have shown that a 1:1 mixture of $Co^{2+}$ and L-alanine, protected from air, loses optical activity during standing at room temperature.[9] This occurred without the complications of hydroxide ion or electron transfer during reduction from $Co^{3+}$ to $Co^{2+}$ as is the case in methods for liberating the complexed alanine required by these complexes.

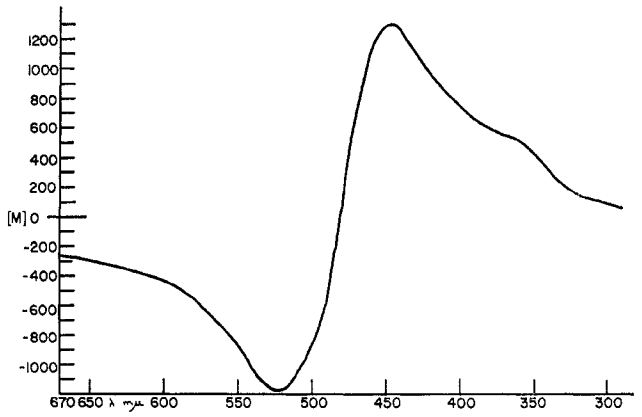



Figure 1.—ORD of L-*cis*-$\beta$-[Co(L,L-$\alpha,\alpha'$-dimethyltrien)(D-alan)]$(NO_3)_2$.

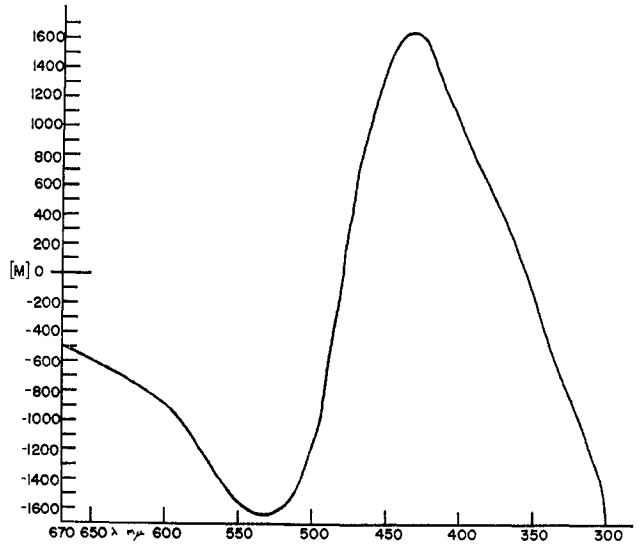



Figure 2.—ORD of L-*cis*-$\beta$-[Co(L,L-$\alpha,\alpha'$-dimethyltrien)(L-alan)]$(NO_3)_2$.

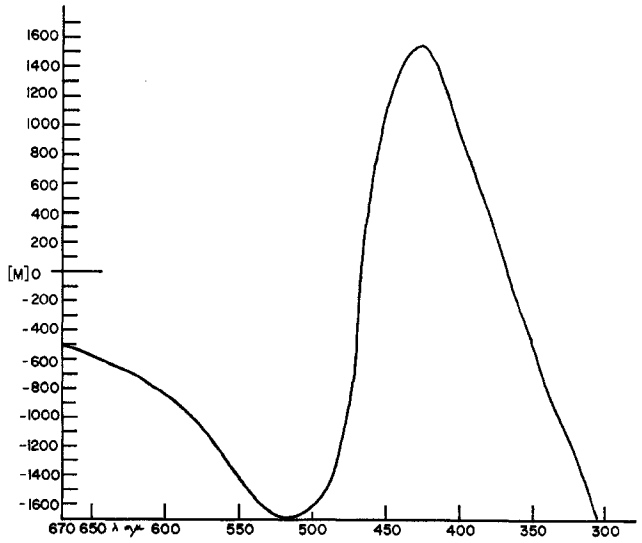



Figure 3.—ORD of L-*cis*-$\beta$-[Co(L,L-$\alpha,\alpha'$-dimethyltrien)(alan)]$(NO_3)_2$ derived from decarboxylation.

(8) E. Kyuno and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **88**, 1120 (1966).
(9) R. G. Asperger and C. F. Liu, unpublished results.
(10) J. Olivard, D. E. Metzler, and E. E. Snell, *J. Biol. Chem.*, **199**, 669 (1952).

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# β-Diketone Complexes of Cobalt(III). II. The Solvolysis Products of Sodium *trans*-Dinitrobis(acetylacetonato)cobaltate(III)[1]

BY BRILLE P. COTSORADIS AND RONALD D. ARCHER[2]

*Received November 4, 1966*

The solvolysis stereochemistry of sodium *trans*-dinitrobis(acetylacetonato)cobaltate(III), $Na[Co(acac)_2(NO_2)_2]$ (acac = anion of acetylacetone), has been investigated in neutral and basic aqueous solutions as well as in dimethyl sulfoxide and methanol. The *trans*-dinitro ion rapidly hydrolyzes to the *trans*-nitroaquo complex. Equilibrium is established between the two species almost immediately, even below room temperature. The second hydrolysis step is several orders of magnitude slower. The visible spectrum of the base hydrolysis products indicates a mixture of products. Evidence for solvolyzed species also has been obtained in methanol and dimethyl sulfoxide. The *trans*-$[Co(acac)_2(NO_2)(H_2O)]$ and *cis*-$Na[Co(acac)_2(NO_2)_2]$ complexes have been prepared from *trans*-$Na[Co(acac)_2(NO_2)_2]$ using ion-exchange, freeze-drying, and solvent extraction procedures. A third complex, *cis*-$Na[Co(acac)_2(OH)_2]$, has been isolated in small yields from the base hydrolysis of sodium *trans*-dinitrobis(acetylacetonato)cobaltate(III). The configurations have been assigned to the complexes by correlation of pmr (pmr = proton magnetic resonance), infrared, visible, and ultraviolet spectra.

## Introduction

A detailed study of bis(β-diketonato)cobalt(III) complexes[1b] has been initiated in this laboratory in order to determine the effect of ligand field strength on the reaction rates and product stereochemistry of cobalt(III) complexes. The absence of acidic protons on the donor atoms of the ligands makes the base hydrolysis reactions particularly interesting.

Sodium dinitrobis(acetylacetonato)cobalt(III) has recently been used by us[1b] and by other investigators[3] in the preparation of several new bis(acetylacetonato)cobalt(III) complexes. In order to elucidate the mechanisms which are important in reactions of this useful complex, a solvolysis study has been initiated. As a result of this investigation, several new complexes have been isolated and characterized.

## Results and Discussion

**Synthesis.**—As noted below, the only previously reported[1b,3,4] isomer of $[Co(acac)_2(NO_2)_2]^-$ hydrolyzes rapidly in aqueous solution. Therefore, ion-exchange procedures have proven useful for the separation of the *trans*-nitroaquo ion of this series. Dissolution of the dinitro ion in cold water was followed by passage through a chloride-form ion-exchange column. The column exchanges chloride ions for unhydrolyzed $[Co(acac)_2(NO_2)_2]^-$, nitrite, and hydroxide ions. The exchange of nitrite ions prevents the reverse reaction of the equilibrium

$$trans\text{-}[Co(acac)_2(NO_2)_2]^- + H_2O \rightleftharpoons trans\text{-}[Co(acac)_2(NO_2)(H_2O)] + NO_2^- \quad (1)$$

Concentration by freeze drying prevented further hydrolysis of the green solid, which was recrystallized from 95% ethanol and ether solutions.

The hydrated sodium *cis*-dihydroxobis(acetylacetonato)cobaltate(III) has been prepared from slightly basic solutions of *trans*-nitrobis(acetylacetonato)aquocobalt(III). The cold solutions were evaporated to dryness *in vacuo*. A green species was extracted from the resulting residues with chloroform and precipitated by the addition of ether. In aqueous solution, the green dihydroxo complex is adsorbed by anion ion-exchange resins. Since the anionic complex is soluble in chloroform as well as in water, ion-pair formation is apparent.

Sodium *cis*-dinitrobis(acetylacetonato)cobaltate(III) has been separated from the mixture of hydrolysis products which results when aqueous solutions of sodium *trans*-dinitrobis(acetylacetonato)cobaltate(III) are allowed to stand 1 week at room temperature. The *cis*-dinitro isomer was extracted with acetone and ethanol from the freeze-dried mixture of hydrolysis products of the *trans*-dinitro complex. The new isomer was recrystallized from acetone.

**Proton Magnetic Resonance Spectra.**—The proton magnetic resonance spectra of the *trans*-dinitro and the

(1) (a) Extracted in part from the Ph.D. Dissertation of B. P. Cotsoradis, Tulane University, 1965; (b) part I of this series: R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965).

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(3) L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).

(4) A. Rosenheim and A. Garfunkel, *Ber.*, **44**, 1865 (1911). The isomer under discussion was originally prepared by these chemists. The *trans* configuration of the isomer was first postulated by Boucher and Bailar[3] on the basis of the infrared spectrum and chemical reaction product configurations.