1203. *Optically Active Co-ordination Compounds. Part II.*[1] *The Isomers of Tris-*L(+)*-alanine Complexes with Cobalt*(III) *and Rhodium*(III)

By J. H. Dunlop and R. D. Gillard

The four geometrical–optical isomers of tris-L(+)-alaninatocobalt(III) have been isolated, and their optical rotatory properties are described. A discussion is given of stereospecific effects in such complexes, and an explanation offered for the stereospecific formation of the β(+)-isomer. Two optically pure isomers of tris-L(+)-alaninatorhodium(III), β(+) and β(−), are described, and an optically impure α-isomer. These are the first amino-acid complexes of rhodium(III). The relative optical configurations of the β(−) rhodium and analogous β(+) cobalt complexes are presented, and a suggestion made concerning absolute configurations. Some interconversions of the cobalt(III) complexes are discussed, including a novel complete inversion of optical configuration.

When three molecules of an amino-acid form a complex with a metal of octahedral stereochemistry, two geometrical isomers are possible (Figure 1). When an excess of glycine reacts with cobalt(III), the two isomers are readily separable [2] through their differing solubilities in water. The red isomer, called β, *cis,cis*, or 1,2,3, is insoluble; the violet isomer, called α, *cis,trans*, or 1,2,6, is much more soluble.

The assignment of structure to the two geometrical isomers has relied [3,4] on their different symmetries. The β-isomer has a three-fold axis of rotation and belongs to the point group C_3, whereas the violet isomer has no elements of symmetry, and belongs to

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[1] Part I, K. Garbett and R. D. Gillard, *J.*, 1965, 6084.

[2] H. Ley and H. Winkler, *Ber.*, 1909, **42**, 3894.

[3] F. Basolo, J. Bjerrum, and C. J. Ballhausen, *Acta Chem. Scand.*, 1955, **9**, 810.

[4] G. Saraceno, I. Nakagawa, S.-I. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1958, **80**, 5018.

C_1. For a d^6 spin-paired complex, with complete octahedral symmetry, O_h, the spin-allowed transitions are ${}^1A_{1g} \longrightarrow {}^1T_{1g} + {}^1T_{2g}$. When the symmetry is lowered to C_3, both these triply degenerate transitions break down to ${}^1A \longrightarrow {}^1A + {}^1E$. For the C_1 point group, the corresponding transitions are ${}^1A \longrightarrow {}^1A + {}^1A + {}^1A$. Since the electronic spectrum of the α-isomer shows greater splittings for the longest-wavelength absorption band (Band I) than does the spectrum of the β-isomer, the structures α (1,2,6) and β (1,2,3) were assigned.[3] An exactly similar argument extends to complexes of optically active amino-acids such as L(+)-alanine; the electronic spectra of the α- and β-isomers of [Co{L(+)-alaninate}$_3$] are compared with those of the isomeric complexes of glycine in Figure 2. In a similar way, the infrared spectra [4] of β-isomers show more degeneracy than those of the α-isomers, which therefore have the richer spectra.

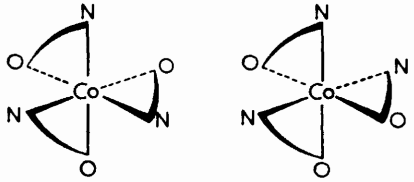

FIGURE 1. The geometrical isomers of [Co(glycinate)$_3$]

A number of tris-amino-acid complexes of cobalt(III) have recently been prepared [5] in geometrically isomeric forms. It appears that the original method,[2,6] using cobalt(III) oxide, leads to a mixture of α- and β-isomers, as does the use of the triscarbonatocobaltate(III) anion, whereas the synthesis using hexamminecobalt(III) cation leads largely to the red β-isomer. Until now, α and β geometrical isomers have been isolated only for complexes of cobalt(III). We have now prepared mixtures of isomers of trisalaninatorhodium(III) by reaction of hydrated rhodium(III) oxide with alanine, or, less satisfactorily, by reaction of rhodium tri-iodide with alanine. The isomers were separated in the same way as for the cobalt(III) complexes; the β(—)-isomer is extremely insoluble in water, the β(+)-isomer is sparingly soluble, and both α-isomers are quite soluble. Both β-isomers are off-white, anhydrous compounds; their electronic spectra are similar (Figure 3). The optical rotatory dispersion curve of the insoluble anhydrous β(—)-complex of rhodium(III) is similar in form to that of the insoluble β(+)-complex of cobalt(III). The rotatory dispersion curves of the more soluble β(+)-isomer of rhodium, and the β(—)-isomer of cobalt, are also similar. The infrared spectra of the β-isomers confirm the assignments given; details are given in the Experimental section. By continued fractionation of the more soluble complexes, α-isomers are obtained, characterised by their analyses (monohydrated) and infrared spectra. In this case, the small amplitude of the Cotton effects in rotatory

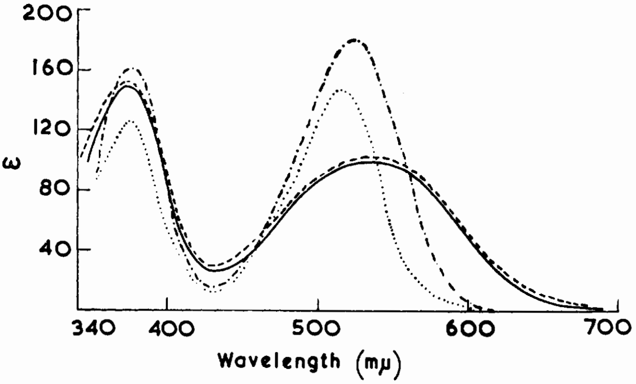

FIGURE 2. The electronic spectra of α- and β-isomers of [Co(amino-acid)$_3$]

———— α-[Co(glycinate)$_3$]
– – – – – (α(+)-[Co(L-alaninate)$_3$]
· · · · · · · β-[Co(glycinate)$_3$]
—·—·— β(+)-[Co(L-alaninate)$_3$]

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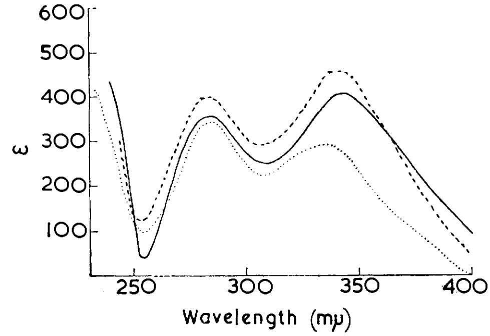
[5] M. Mori, M. Shibata, E. Kyono, and M. Kanaya, *Bull. Chem. Soc. Japan*, 1961, **34**, 1838.
[6] I. Lifschitz, *Proc. k. ned. Akad. Wetenschap.*, 1924, **15**, 721.

dispersion suggests that the crystals obtained are a mixture of the α(+)- and the α(−)-isomers.

Optical Isomerism.—Both α- and β-isomers of [M(amino-acidate)$_3$] are resolvable (Figure 4). The further optical isomerism arising from any asymmetry which may be present in the amino-acid ligand itself is considered later. For the present, the existence of four optical–geometrical isomers is the point at issue. We denote their absolute configurations as shown because left-handed helicity about the three-fold axis is characteristic of the D(+)-trisethylenediaminecobalt(III) cation; our Dβ-isomer is that isomer with such left-handed helicity. It might also be called $S(C_3)$-β or Λβ. By analogy, the α-isomers are called Dα and Lα.

FIGURE 3. The electronic spectra of α- and β-isomers of [Rh-L(+)-alaninate-$_3$]
——— β(−)-[Rh(L-alaninate)$_3$]
– – – – β(+)-[Rh(L-alaninate)$_3$]
· · · · · α[Rh(L-alaninate)$_3$]



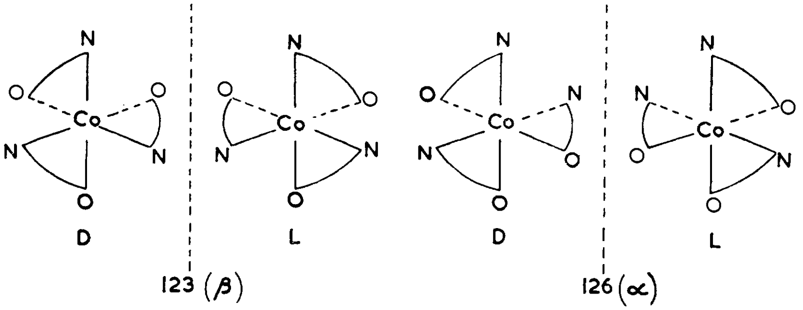


FIGURE 4. The four optical isomers of [Co(glycinate)$_3$]

There has been some doubt as to whether all four isomers have ever been obtained for complexes of any optically active amino-acid with cobalt(III). There is, of course, no doubt that the four isomers of the trisglycine complex exist, since both DLα- and DLβ-[Co(glycinate)$_3$] have been resolved by means of starch columns.[7] In this case, of course, the stabilities of Dα and Lα are equal, as are those of Dβ and Lβ. However, in complexes involving such optically active amino-acids as L(+)-alanine, the Dα- and Lα-isomers are no longer enantiomers but diastereoisomers, as are Dβ and Lβ, and there is now no reason why the stabilities of these pairs should be equal. The question arises therefore of how many isomers of [Co(L-amono-acidate)$_3$] are known. Lifschitz studied both L-alanine[6] and D-glutamic acid, and claimed to have obtained three isomers [(+)α, (−)α, and (+)β] in the case of alanine, and all four in the case of glutamic acid. (In the absence of information on absolute configurations, signs of rotation at the sodium D-line are used to denote isomers.) However, inspection of the rotatory dispersion curves given[8] for these alleged isomers revealed that, in the case of glutamic acid, confusion had arisen between geometrical and optical isomerism, so that the problem remained open.

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[7] H. Krebs and H. Diewald, *Z. anorg. Chem.*, 1956, **287**, 98.

[8] I. Lifschitz, *Proc. k. ned. Akad. Wetenschap.*, 1936, **27**, 1192.

We have now succeeded in obtaining all four isomers of [Co(L-alaninate)$_3$], and absorption spectra, optical rotatory dispersion curves, and circular dichroism data are presented in Figures 5—8. Clearly, the absorption spectrum is characteristic in distinguishing

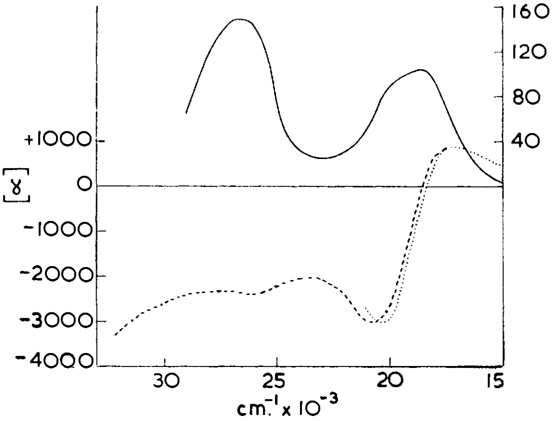

FIGURE 5. Properties of
(+)α-[Co(L-ala)$_3$]
——— Absorption spectrum
– – – – optical rotatory dispersion
· · · · · optical rotatory dispersion[5]

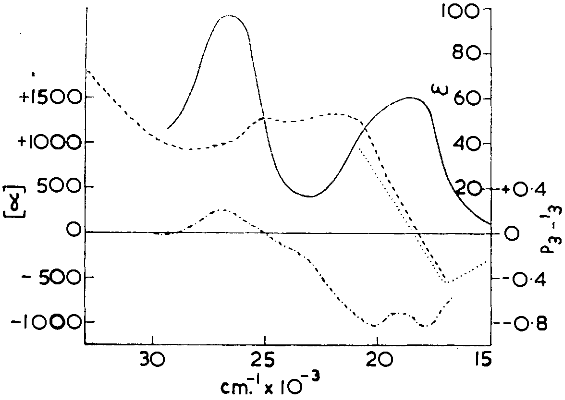

FIGURE 6. Properties of
(—)α-[Co(L-ala)$_3$]
———— Absorption spectrum
– – – – – – optical rotatory dispersion
· · · · · · · · optical rotatory dispersion[5]
— · — · — circular dichroism

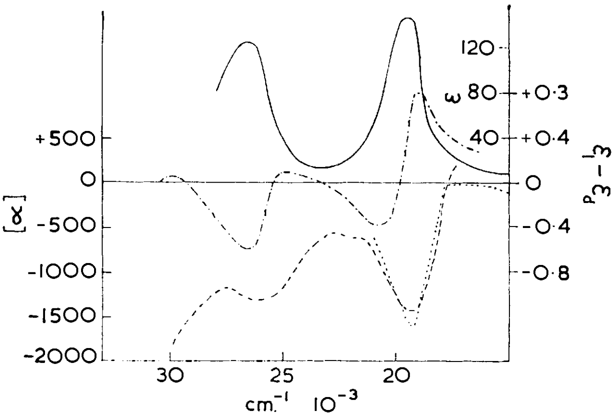

FIGURE 7. Properties of
(+)β-[Co(L-ala)$_3$]
——— Absorption spectrum
– – – – – optical dispersion
· · · · · · · optical rotatory dispersion[5]
— · — · – circular dichroism

between geometrical isomers, and the rotatory dispersion curves are required in distinguishing optical isomers. The three isomers of [Co(L-ala)$_3$] described[6] by Lifschitz are in fact, pure (+)β, pure (+)α, and impure (—)α (which he called α′). The rotatory dispersion curve of this isomer and of the pure (—)α-isomer are compared in Figure 6. The rotatory dispersion curve of the enantiomer of α-[Co(glycinate)$_3$], which is less adsorbed on a starch column, is shown in Figure 9 with that of (+)α-[Co(L-ala)$_3$] for comparison. These two compounds obviously have related geometrical and optical configurations.

The four isomers of [Co(L-ala)$_3$] are obtained in the following way. One of the isomers, red (+)β, is completely insoluble in water, and can thus be separated from the other three, which remain in the violet filtrate. We believe that this (+)β-isomer is optically pure because samples prepared by different methods have identical rotatory dispersion curves. Further, fractions obtained by dissolving the water-insoluble material in concentrated sulphuric acid and partially precipitating with water are again identical. The remaining three isomers were separated by fractional crystallisation; the first four fractions obtained were violet, with very similar rotations, $[\alpha]_{476} = -2750°$. The sixth fraction, however, had $[\alpha]_{476} = +1190°$, and the most soluble fraction was taken up in aqueous ethanol and chromatographed on alumina, giving a dextrorotatory violet crop ($[\alpha]_{476} = +623°$) and a fairly small amount of the second red isomer, with $[\alpha]_{476} = +1700°$. Further fractionation of this (−)β-isomer did not change its properties. We have shown in this way that all four isomers of tris-L(+)-alaninatocobalt(III) can be obtained; comment on the relative amounts is made later.

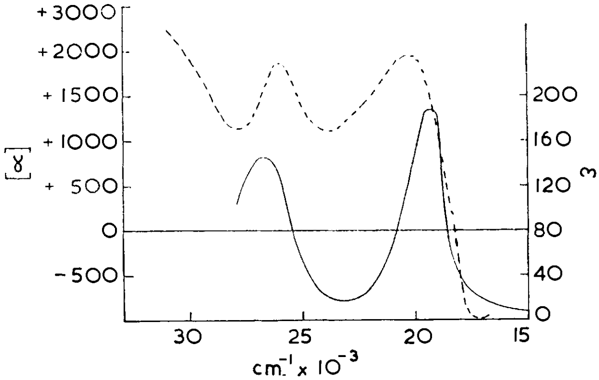

FIGURE 8. Properties of (−)β-[Co(L-ala)$_3$]
——— Absorption spectrum
- - - - optical rotatory dispersion

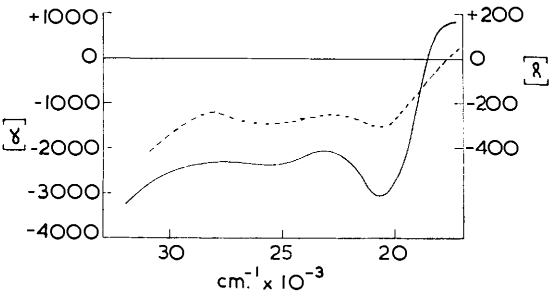

FIGURE 9. Optical rotatory dispersion curves for (+)α-[Co(aminoacidate)$_3$]
——— (+)α[Co(L-ala)$_3$] (left-hand scale)
- - - - (+)α-[Co(glycinate)$_3$] (right-hand scale)

The circular dichroism results for the β(+)- and the α(−)-isomers may be interpreted in the light of the symmetries of the complexes. The β-isomer has C_3 symmetry, and all four transitions, $^1A \longrightarrow {}^1E$ and ^1A of Band I, and $^1A \longrightarrow {}^1E$ and ^1A of Band II are magnetic-dipole-allowed, so that four components are expected in the circular dichroism spectrum. Further, the transition $^1A \longrightarrow {}^1A$ of Band I is parallel to the three-fold axis, whereas $^1A \longrightarrow {}^1E$ is perpendicular to this axis, so that opposite signs of rotational strengths are expected for the two components of Band I, just as in complexes like [Co en$_3$]$^{3+}$ of D_3 symmetry. From Figure 7, it is clear that this expectation is borne out. For Band II, the rather large rotational strength of the negative component at 368 mμ may be attributed to intensity borrowing from the charge-transfer transition with a negative Cotton effect at 220 mμ. An interesting point is that a third component is just apparent under Band II; this may be due to the presence of some species of symmetry lower than C_3, formed by opening one chelate ring of β-[Co(L-ala)$_3$]. A similar situation is found[9] for the trisoxalatocobaltate(III) ion, where more transitions occur under Band II than can arise from the ion of D_3 symmetry. On the other hand, the α-isomers have C_1 symmetry, so that three Cotton effects are expected for each absorption band. These are observed for Band II of α(−)-[Co(L-ala$_3$] at 415, 367, and 330 mμ, but under Band I, apparently two negative Cotton effects occur. The detailed analysis of this spectrum is shown in Figure 6. It seems at least possible that one transition with a negative Cotton effect at *ca.* 525 mμ lies between two positive transitions at *ca.* 490 and 550 mμ. It is not uncommon for less components to be observed than are predicted, as in *cis*-dichlorobisethylenediaminecobalt(III) chloride.[10]

Stereospecific effects in optically active co-ordination compounds are well known.[11] In particular, for complexes of optically active diamines, there are striking differences in the thermodynamic stabilities of diastereoisomers. For example, in a complex with three molecules of (+)-propylenediamine, D-[M(+ pn)$_3$]$^{n+}$ is favoured rather than L-[M(+ pn$_3$]$^{n+}$, and this has been used[12] to derive absolute configurations in diamine complexes. The current explanation of such stereospecific effects in diamine complexes rests[11] on the puckered nature of the chelate rings. For complexes of amino-acids, where the chelate rings are less puckered, little stereospecificity is predicted for *trans*-bis-complexes, and in the copper(II)-α-alaninate system, no stereospecificity was found.[13] A recent study[14] of copper(II) bisglycinate has shown that the puckering of chelate rings formed by α-amino-acids is larger than had been thought, and consequently, in the tris-amino-acid systems, the optically active chelate rings might be expected to interact so as to give Dβ-[M(L-ala)$_3$] greater stability than Lβ-[M(L-ala)$_3$], the difference being of the order of 1 kcal./mole. A smaller effect, involving at most a few hundred calories per mole, is predicted for the α-isomers, which are more nearly akin to the bis-active-diamine complexes.

We have attempted to establish the size of any stereospecific effects in our synthetic mixtures by isolating the pure geometrical–optical isomers, and by using their rotatory properties to analyse mixtures. Unfortunately, several difficulties arise. The insoluble red β(+)-isomer appears to be formed stereospecifically; there is very little, if any, β(−) formed initially. This enormous preponderance of β(+) over β(−) is probably due not so much to an intramolecular steric effect as to the extremely small solubility of the β(+)-isomer displacing the equilibrium completely. This theory is supported by the fact that in attempts to equilibrate either the α(+)- or the α(−)-isomer, using active charcoal, the sole product was the insoluble β(+)-isomer. One reaction is, of course, a complete inversion of optical configuration, since the scheme may be written:

$$\alpha(+)\text{-[Co(L-ala)}_3] \longrightarrow \beta(+)\text{-[Co(L-ala)}_3] \longleftarrow \alpha(-)\text{-[Co(L-ala)}_3]$$

This is the first inversion of configuration in a reaction of a cobalt complex in which complete inversion has occurred. A similar case is the resolution[15] of the trisethylenediaminecobalt(III) cation by (+)-tartrate in the presence of cobalt(II) ions, where the equilibrium set up by the cobalt(II) is displaced by the crystallisation of the less soluble diastereoisomer, (+)-[Co en$_3$]Cl (+)-tartrate hydrate. There is other evidence supporting the idea that the stereospecific formation of the β(+)-isomer is caused by its insolubility. For example, in the case of glutamic acid, where the complexes in the product are water-soluble, different preparative procedures gave different relative amounts of isomers. However, in the alanine system, using any of our four synthetic methods [air-oxidation of cobalt(II), or reaction with triscarbonatocobaltate(III), cobalt(III) oxide, or hexamminecobalt(III) cation] the red

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[9] A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 1962, 388.
[10] R. D. Gillard, *Nature*, 1963, **198**, 580.
[11] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **82**, 2620.
[12] J. H. Dunlop, R. D. Gillard, and G. Wilkinson, *J.*, 1964, 3160.
[13] R. D. Gillard, H. M. Irving, R. M. Parkins, N. C. Payne, and L. D. Pettit, *Chem. Comm.*, 1965, 81.
[14] H. C. Freeman, M. R. Snow, I. Nitta, and K. Tomita, *Acta Cryst.*, 1964, **17**, 1463.
[15] D. H. Busch, *J. Amer. Chem. Soc.*, 1955, **77**, 2747.

β(+)-isomer obtained always had the same properties, and virtually no red β(—)-isomer was detected. Other cases of displacement of equilibrium by the crystallisation of one isomer are known; for example, L-[Co(—pn)$_2$CO$_3$]I can be obtained [16] from the DL-mixture by slow crystallisation. For the α-isomers of [Co(L-ala)$_3$] prepared from sodium triscarbonatocobalt(III), the fractional crystallisation procedure was followed by optical rotatory dispersion, and each fraction was weighed. The final weights of the two isomers were almost equal, (+)α being formed in slightly larger amounts than (—)α. However, using the preparation from cobalt(III) oxide, the proportions were reversed. Any stereospecificity is therefore small and variable.

Unfortunately, then, we have not been able to draw any firm conclusions about the possible stereospecificity in these systems; tentatively, we place the pairs of isomers in the order of stabilities $\beta(+) > \beta(-)$, and $\alpha(+) \simeq \alpha(-)$. Using the order of stabilities predicted from stereospecific considerations, βD-[Co(L-ala)$_3$] > βL-[Co(L-ala)$_3$], we arrive at the

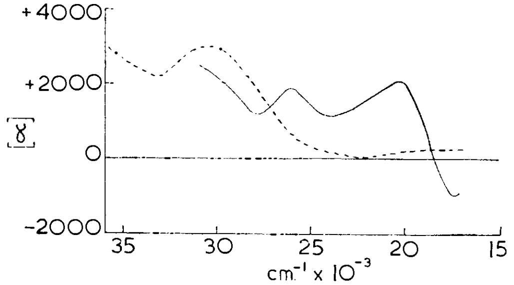

FIGURE 10. Optical rotatory dispersion curves for Lβ-[M(L-ala)$_3$]

——— (—)β-[Co(L-ala)$_3$],
– – – – (+)β-[Rh(L-ala)$_3$]

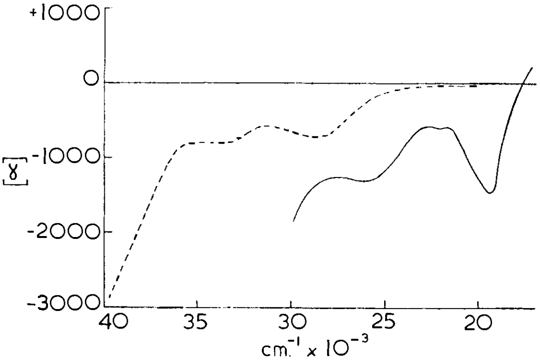

FIGURE 11. Optical rotatory dispersion curves for Dβ-[(M(L-ala)$_3$]

——— (+)β-[Co(L-ala)$_3$]
– – – – (—)β-[Rh(L-ala)$_3$]

absolute configuration Dβ(+)-[Co(L-ala)$_3$]. In the D-configuration, for C_3 complexes, $^1A \longrightarrow {}^1E$ will have a positive rotational strength; the circular dichroism band observed at 547 mμ may therefore be assigned to $^1A \longrightarrow {}^1E$, and that at 483 mμ to $^1A \longrightarrow {}^1A$. It is interesting that the splitting of Band I deduced here for the complex of C_3 symmetry, $^1A \longrightarrow {}^1E$ at lower energy, and $^1A \longrightarrow {}^1A$ at higher energy, is similar to that in such complexes as D(+)-[Co en$_3$]$^{3+}$, where $^1A_1 \longrightarrow {}^1E_a$ occurs at lower energy than $^1A_1 \longrightarrow {}^1A_2$.

In the hope that complexes of rhodium(III) are more kinetically inert than the analogous complexes of cobalt(III), we have fractionally crystallised both α- and β-isomers of tris-L(+)-alaninatorhodium(III). The optical rotatory properties of the insoluble β(—)-isomer from both methods of preparation are identical, and we feel that it is probably optically pure because of its insolubility. We also suggest that its absolute configuration is the same as that of the insoluble β(+)-isomer of cobalt(III); this is essentially an application of the method of less-soluble diastereoisomers, though the present case is the first application to non-electrolytic complexes. In the case of the soluble isomers, the less soluble fraction, β(+), can readily be recrystallised to constant optical rotation, which suggests that our material is optically pure. The mother-liquors certainly contain both α-isomers, since, on fractionation, a number of crops are obtained which vary regularly in optical rotation. We have not succeeded in obtaining either α-isomer pure, because both are very soluble in water. The rotatory dispersion curves of the two pairs of analogous β-complexes are given in Figures 10 (L-configuration) and 11 (D-configuration).

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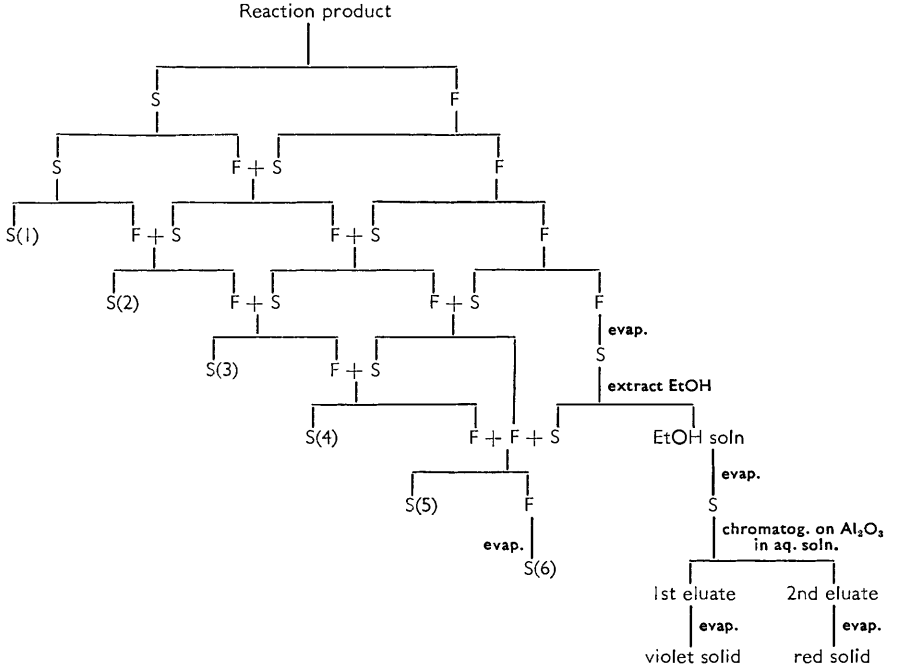
[16] F. P. Dwyer and T. E. McDermott, *Inorg. Chem.*, 1963, **2**, 871.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory of this Department. Absorption spectra were determined using a Perkin-Elmer model 350 spectrophotometer. Optical rotatory dispersion data were obtained, using a Bendix Spectropolarmatic spectropolarimeter with a direct read-out X–Y plotter.

Trisglycinatocobalt(III).—The violet α-isomer was prepared [2] from cobalt(III) hydroxide. Its properties agreed well with those reported.[3] A saturated aqueous solution (10 ml.) of this isomer was chromatographed on a column of potato starch (400 g.). Krebs has mentioned [7] this method of resolution. The first eluate contained α(+)-Co(glycine)$_3$, whose optical rotatory dispersion curve is shown in Figure 9. The red β-isomer was prepared from hexamminecobalt(III) chloride, following the literature method.[5]

Tris-L-*α-alaninatocobalt*(III).—The following preparative methods were used; the details were as given.[5] (a) *From cobalt*(III) *hydroxide.* This method gives predominantly the violet isomers. (b) *From hexamminecobalt*(III) *chloride.* This method gives only the water-insoluble β(+)-isomer. The filtrate, after the β(+)-isomer had been removed, was examined. Only cobalt(II) compounds were detected. Strangely, when racemic alanine was used in this preparation instead of Lα-alanine, considerable amounts of an α-isomer were isolated, which we suppose to contain optically mixed ligands, *i.e.*, DL-[Co(L-ala)(D-ala)$_2$] and/or DL-[Co(L-ala)$_2$(D-ala)]. (c) *From sodium triscarbonatocobaltate*(III). All four isomers can be isolated from the reaction products. However, the two violet isomers predominate.



Isolation of the Isomers.—(a) β(+)-*Tris*-L*α-alaninatocobalt*(III). This water-insoluble pink microcrystalline solid was separated from the other isomers by filtration. It was recrystallised from 50% sulphuric acid. The solid was reprecipitated from the acid solution by the addition of water. Several fractions were obtained by this method, $[\alpha]_{500} = -1060$, -850, and -793. The specific rotation of the acid solution before precipitation was $[\alpha]_{500} = -1255$. We attribute the slight variations in optical properties of this isomer to various degrees of polymerisation. (b) *The violet α-isomers.* The solid product from the preparation using sodium triscarbonatocobaltate(III) was extracted with large volumes of boiling water. The violet isomers and the red β(−)-isomer were thus dissolved. The resulting solution was fractionally crystallised according to the scheme shown, where S = solid, and F = filtrate.

To ascertain the optical purity of the α(−)-isomer we re-fractionated the entire fraction 6, dissolved in 50% aqueous ethanol, by successive addition of, first, acetone and subsequently ether. The properties of the fractions, which were thus precipitated, are (solvent and $[\alpha]_{476}$): original material (Fraction 6), +1340; 1, acetone, +1190; 2, acetone, +1180; 3, ether; 4, ether, +1220; 5, ether, +1330.

β(−)-*Tris*-Lα-*alaninatocobalt*(III). This water-soluble isomer was separated from the alcohol-soluble α(−)-isomer by chromatography on alumina. In aqueous solution the red isomer is more strongly absorbed and is thus eluted after the violet isomer. The aqueous solution of this red β(−)-isomer was evaporated to a small volume. Ethanol was added to this solution and the solution was again evaporated to a small volume. Fine red crystals of the β(−)-isomer were formed on standing at low temperature. The crystals were removed from the solution by filtration. They were washed with alcohol and with ether and were then dried in a vacuum desiccator.

Properties of the Isomers.—α(+)-*Tris*-Lα-*alaninatocobalt*(III) *monohydrate.* A violet crystalline solid sparingly soluble in water (Found: C, 31·7; H, 5·85; N, 12·3. Calc. for $C_9H_{20}CoN_3O_7$; C, 31·65; H, 5·85; N, 12·3%), $[\alpha]_D$ +847, $[\alpha]_{546}$ *ca.* 0, $[\alpha]_{476}$ −2960 (lit.,[5] +845, ca. 0, −2750, respectively), $\lambda_{\text{max.}}$ 375 and 545 mμ (ε 151 and 104).

α(−)-*Tris*-Lα-*alaninatocobalt*(III) *hydrate.* A violet non-crystalline powder which is very soluble in water and is sparingly soluble in alcohol; $\nu_{\text{max.}}$ at 3500 cm.$^{-1}$ confirms the presence of a molecule of water of crystallisation. A crystalline *sample* was obtained from ethanol (Found: C, 31·65; H, 5·45; N, 12·7%) (Lifschitz's α′-isomer was allegedly anhydrous), $[\alpha]_D$ −660, $[\alpha]_{546}$ *ca.* 0, $[\alpha]_{476}$ +1352 (lit.,[5] for α′-isomer, −590, −50, +900, respectively (Lifschitz demonstrated by cryoscopy that his α′-isomer was monomeric), $\lambda_{\text{max.}}$ 375 and 540 mμ (ε 96 and 60).

β(+)-*Tris*-Lα-*alaninatocobalt*(III). A pink crystalline solid, which is insoluble in water and only soluble in 50% sulphuric acid. Cryoscopic studies in concentrated sulphuric acid have produced ambiguous results owing to the possibility of a polymeric structure for this isomer, which is also suggested by the small variations in [α] values found (Found: C, 33·4; H, 5·4; N, 12·85. Calc. for $C_9H_{18}CoN_3O_6$: C, 33·45; H, 5·55; N, 13·0%), $[\alpha]_D$ +285, $[\alpha]_{546}$ −770, $[\alpha]_{500}$ −1255 (lit.,[5] −45, −690, −1220, respectively), $\lambda_{\text{max.}}$ 375 and 516 mμ (ε 127 and 149). Although slight differences were found for the rotations of samples obtained in different ways, we think that this arises from the probable polymeric nature of the compound.

β(−)-*Tris*-Lα-*alaninatocobalt*(III). A pink crystalline *compound*, which is soluble in water and sparingly soluble in ethanol (Found: C, 33·05; H, 5·5; N, 13·0%), $[\alpha]_D$ −990, $[\alpha]_{546}$ *ca.* 0, $[\alpha]_{500}$ +1870, $\lambda_{\text{max.}}$ 376 and 516 mμ (ε 148 and 192). All four tris-Lα-alaninatocobalt(III) complexes are stable in acid solutions but are decomposed on warming in alkaline solution.

Interconversions and Equilibria.—α(+)-*Trisglycinatocobalt*(III). A dilute solution (10 ml.) of this compound ($[\alpha]_{476}$ −300) was boiled with a very small amount of activated charcoal. The optical activity had disappeared after 2 minutes' boiling. Therefore, equilibration is achieved in a short time. The unresolved compound (0·5 g.) in water (25 ml.) was then boiled for 3 hr. with activated charcoal. There was no change in the visible spectrum. Although small amounts of cobalt(II) compounds were detected in the final solution, no red isomer had formed, so that the equilibrium is almost entirely on the side of the violet isomer.

β-*Trisglycinatocobalt*(III). A dilute aqueous solution of this compound was boiled for 3 hr. with a small amount of activated charcoal. The visible spectrum of the final solution showed that the β-isomer had been largely converted into the α-isomer.

α-*Trisalaninatocobalt*(III). When this compound is boiled with activated charcoal the β-isomer is quickly precipitated. The filtrate contains cobalt(II) compounds. The two diastereoisomers of the violet α-complex were therefore treated in the same way to see which β-isomer was produced. The results are indicated below.

$$\alpha(+)\text{-}[\mathrm{Co}(\mathrm{L}\alpha\text{-ala})_3]\ ([\alpha]_{476}\ -2960) + \mathrm{C} \xrightarrow{\text{boil}} \beta(+)\text{-}[\mathrm{Co}(\mathrm{L}\alpha\text{-ala})_3]\ ([\alpha]_{500}\ -1116)$$

$$\alpha(-)\text{-}[\mathrm{Co}(\mathrm{L}\alpha\text{-ala})_3]\ ([\alpha]_{476}\ +1350) + \mathrm{C} \xrightarrow{\text{boil}} \beta(+)\text{-}[\mathrm{Co}(\mathrm{L}\alpha\text{-ala})_3]\ ([\alpha]_{500}\ -1280)$$

$$\alpha(+)\text{-}[\mathrm{Co}(\mathrm{L}\alpha\text{-ala})_3]\ ([\alpha]_{476}\ -2960) + 0{\cdot}05\mathrm{CoCl}_2 \xrightarrow[\text{24 hr.}]{\text{reflux}} \alpha(+)\text{-}[\mathrm{Co}(\mathrm{L}\alpha\text{-ala})_3]\ ([\alpha]_{476}\ -2850)$$

The α(+)-isomer is therefore almost unaffected by boiling in water for 24 hr. in the presence of cobalt(II) ions.

Also, in case the small amount of β(−)-isomer obtained by chromatography in ethanol on alumina was an artefact, we treated both α(+)- and α(−)-isomers in aqueous ethanol with alumina, but no isomerisation occurred.

Determination of Equilibrium Amounts.—(a) *From the preparation using sodium triscarbonatocobaltate*(III). The fractions from the fractional crystallisation were weighed (see Scheme) and the amounts of the two diastereoisomers were calculated using the relationship:

$$[\mathrm{Co}][\alpha] = [\mathrm{Co_D}][\alpha_\mathrm{D}] + [\mathrm{Co_L}][\alpha_\mathrm{L}]$$

$$[\mathrm{Co_D}]/[\mathrm{Co_L}] = ([\alpha_\mathrm{L}] - [\alpha])/([[\alpha] - [\alpha_\mathrm{D}])$$

where [Co], $[\mathrm{Co_D}]$, and $[\mathrm{Co_L}]$ are the concentrations of the original unfractionated material and the optically pure D- and L-compounds, respectively, and [α], $[\alpha_\mathrm{D}]$, and $[\alpha_\mathrm{L}]$ are their specific rotations at 476 mμ. The results of these calculations are given in Table 1.

TABLE 1

Fractional crystallisation of α-[Co(L-alanine)$_3$]

Fraction	$[\alpha]_{476}$	Weight (g.)	Composition α(+) (g.)	Composition α(−) (g.)
1	−2960	1·163	1·163	0·000
2	−2850	0·674	0·660	0·014
3	−2570	0·443	0·402	0·041
4	−2750	0·318	0·303	0·015
5	+435	0·527	0·116	0·410
6	+1190	1·560	0·160	1·400
Alcohol-soluble	+1350	0·380	0·000	0·380
	Totals	5·065	2·804	2·260

Whence α(+)/α(−) = 55·5/44·5.

(b) *From cobalt*(III) *hydroxide.* The stereospecificity was calculated from the rotation of the filtrate, which contained all the α-isomers, before the fractional crystallisation was carried out. The unreacted cobalt(III) hydroxide was boiled with water for a considerable time (*ca.* 3 hr.) to make sure that all the insoluble α(+)-isomer is taken into solution. This solution will contain the β(−)-isomer also but its amount, less than 2% of α-isomer, is too small to affect the result. The total amount of the α-isomers in solution was determined by gravimetric analysis for cobalt using 1-nitroso-2-naphthol. The solution of the complex was evaporated to dryness. A small sample of the solid was dissolved in concentrated hydrochloric acid to see if any cobalt(II) compounds were present. No cobalt(II) was detected. Therefore, the analytical result of 0·4213 g. of cobalt in 1000 ml. of solution was taken with the specific solution of the mixture, $[\alpha]_{476}$ −706, to calculate that the ratio of the α(+)-isomer to the α(−)-isomer in the initial mixture was 47·7 : 52·3.

Tris-Lα-*alaninatorhodium*(III).—(a) *From rhodium*(III) *hydroxide.* Rhodium(III) chloride trihydrate (2·67 g.) was dissolved in water (30 ml.), and sodium hydrogen carbonate (3 g.) was added to this solution until there was no effervescence and a yellow precipitate had formed on warming the solution. Lα-Alanine (2·7 g.) was then added, and the mixture was refluxed for 2 hr., when the reaction was assumed to be complete. The white crystalline solid which had formed was collected. It was extracted with boiling water (4 × 200 ml.), which after removal of the water-insoluble compound (final weight 0·60 g.) was added to the original filtrate. The filtrate was then fractionally crystallised. This gave four fractions of an off-white solid (total 1·16 g.). A yellow solution remained, from which no further solids could be crystallised. The visible spectrum and optical rotatory dispersion of this solution showed that it contained only unreacted starting material. (b) *From rhodium*(III) *iodide.* This preparation was similar to the method above. Rhodium(III) iodide and anhydrous sodium carbonate were used instead of the rhodium(III) chloride and sodium hydrogen carbonate. The two compounds, which have been designated the β(−)- and β(+)-isomers of tris-L-alaninatorhodium(III), were separated by the method described above.

Properties of the Isomers.—β(+)-*Tris*-Lα-*alaninatorhodium*(III). An off-white *solid* which is sparingly soluble in water (Found: C, 29·55; H, 4·7. $C_9H_{18}N_3O_6Rh$ requires C, 29·45; H, 4·8%), $[\alpha]_\mathrm{D}$ +256°, $[\alpha]_{546}$ +223°, $[\alpha]_{300}$ +2230°, $\lambda_{\max.}$ 339 and 284 mμ (ε 440 and 382). The infrared spectrum is very similar to that of the β(−)-isomer (Table 3).

TABLE 2

Fractional crystallisation of water-soluble isomers of Rh(L-alanine)$_3$

Fraction	$[\alpha]_{300}$	Nature	Fraction	$[\alpha]_{300}$	Nature
1	+2230	$\beta(+)$	4	+195	Mixed α
2	+840	Mixed α	Pure alanine	+74	
3	+490	,,	Water-insoluble	−795	$\beta(-)$

TABLE 3

Infrared spectra (cm.$^{-1}$) of isomers of [M(L-ala)$_3$]

α(+)-[Co(L-ala)$_3$]	α(±)-[Rh(L-ala)$_3$] *	β(+)-[Co(L-ala)$_3$]	β(−)-[Rh(L-ala)$_3$]
3500m	3450s		
3200s	3200s	3250s	3200s
3100sh	3100s	3120s	3100s
1660vs	1652vs	1650vs	1640vs
1600sh	1600s	1590s	1580s
1400s			
1370vs	1365vs	1380vs	1360vs
1340s	1340s	1360vs	1340s
1300s	1295sh		
1280s	1280s	1275vs	1260s
1265s	1278sh	1255m	1240m
1230s	1238m		
1210s	1205m	1200m	1190m
1155m			
1120s	1115m	1110m	1100m
1085m	1085w		
1070m	1065w		
1035m			
1020w	1020w	1030w	1010w
935m	925m	925m	920m
870s	863s	860s	855s
835w	845sh		
810w	820w	815w	820m
785w		785w	
760s	760s	745w	755sh
735m	735m	730m	740m

* This is fraction 4 from Table 2.

β(−)-*Tris*-Lα-*alaninatorhodium*(III). An off-white crystalline *solid*, which is completely insoluble in water but dissolved in 50% sulphuric acid (Found: C, 28·8; H, 5·0; N, 11·5%), $[\alpha]_{500}$ −92, $[\alpha]_{300}$ −795°, $\lambda_{\text{max.}}$ 340 and 283 mμ (ε 400 and 345).

α(+)-*Tris*-Lα-*alaninatorhodium*(III). A pale yellow *solid*, readily soluble in water (Found: C, 28·0; H, 4·8. $C_9H_{20}N_3O_7Rh$ requires C, 28·05; H, 5·2%), $\lambda_{\text{max.}}$ 335 and 287 mμ (ε 265 and 322).

Fractional Crystallisation of α-*Tris*-L-*alaninatorhodium*(III).—This was carried out in the same way as the fractional crystallisation of α(+)-tris-L-alaninatocobalt(III). Table 2 gives the specific rotations of the fractions of α-isomer, with those of previously removed β-isomers for comparison. The rapid decrease of $[\alpha]_{300}$ suggests that the later fractions are either a mixture of the two α-diastereoisomers, or, less likely, of one α-isomer and free alanine. The two types of crystal in fraction 4 could be seen clearly under the microscope. The infrared spectra supported the mixed diastereoisomer formulation (the spectrum of Fraction 4 is given in Table 3; all the bands observed may be assigned to an α-isomer). The assignment of isomeric structures to the complexes of rhodium(III) is supported by infrared spectra as shown in Table 3.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, SHEFFIELD 10. [*Received, June 11th,* 1965.]