

Conclusion.—The features of secondary hydration which the structure of this compound has in common with those of two compounds $[MCl_2(OH_2)_4] \cdot 2H_2O$ are (i) the strong hydrogen bonding with the primary hydration sphere, and (ii) the ion-water association in cage formation. The secondary water-chloride ion hydrogen bonds appear to be relatively weak links in this structure. Continued existence of such cages when the solid is dissolved in water would provide a mechanism for the $[CrCl_2(OH_2)_4]^+ \cdot Cl^-$ ion-pair association suspected to occur in aqueous hydrochloric acid solution.²³

Acknowledgments.—I. G. D. gratefully acknowledges partial leave of absence granted by the N.S.W. Department of Mines, and the award of a C.S.I.R.O. Senior Studentship. The programs used for the computations on Silliac were devised by Drs. F. M. Lovell and J. G. Sime. The least-squares refinement was carried out on an IBM 7090 computer with the assistance of Mr. P. N. L. Goddard and the Mathematical Services Section, Weapons Research Establishment, Salisbury, South Australia.

(23) P. J. Elving and B. Zemel, *J. Am. Chem. Soc.*, **79**, 1281 (1957).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA 15213

Configurational and Vicinal Contributions to the Optical Activity of the Isomers of Tris(alaninato)cobalt(III)¹

BY BODIE E. DOUGLAS AND SHOICHI YAMADA

Received May 18, 1965

Four isomers of $[Co(L-ala)_3]$ (and the corresponding isomers of the D-alanine complex) have been isolated and characterized using circular dichroism (CD) data. Lifschitz's original assignment of the α' isomer as the opposite configuration to that of the α isomer (Δ) has been confirmed. The new β' isomer has been assigned as the opposite spiral configuration (Δ) to that of the β isomer (Δ). The vicinal and configurational contributions to the CD have been separated and demonstrated to be additive.

Introduction

Lifschitz² isolated three isomers from the reaction of $Co(OH)_3$ with D-alanine.³ He designated the red isomer as β and the two violet isomers α and α' . He believed α and β to be geometrical isomers. The α and α' isomers were believed to represent the two spiral configurations (right and left) of the chelate rings. This was supported by the optical rotatory dispersion (ORD) curves of these isomers which indicated opposite configurations, although the ORD curves were not quite mirror images, as indeed, the isomers are not mirror images since the ligands are all D. He believed the β isomer to be a racemic mixture, unresolved because of its very low solubility.

The assignments of α -tris(glycinato)cobalt(III) as the 1,2,6 (peripheral) isomer and the β complex as the 1,2,3 (facial) isomer have been made based on absorption spectra,^{4,5} infrared spectra,⁶ and the study of model compounds.^{7,8} Corresponding assignments were made of the α and β isomers of tris(alaninato)cobalt(III).⁹

Lifschitz's assumption concerning the configuration of α' -tris(alaninato)cobalt(III) seemed uncertain because this isomer, unlike the α and β isomers, is very soluble in water. This seemed inconsistent with the formulation of this as a neutral complex. He found that a cryoscopic molecular weight in water indicated that α' was a monomer. Swift¹⁰ found the conductivity of the α' isomer to be low enough for a neutral complex, but it was still possible that one chelate ring was opened with another group, e.g., H_2O , coordinated.

It has now been possible to isolate these three isomers (α , α' , and β) as well as a fourth isomer, β' , for the cobalt(III) complexes of D- and L-alanine. The study of the circular dichroism (CD) of these complexes makes it possible to assign their configurations and to separate the configurational and vicinal contributions to the optical activity as for other amino acid complexes.¹¹

Experimental

The L- and D-alanine were purchased from Nutritional Biochemicals Corporation, Cleveland, Ohio. All other chemicals were reagent grade.

α - and β -Tris(glycinato)cobalt(III).— α - and β - $[Co(gly)_3]$ were

(1) This work was supported by a research grant (GM10829-07) from the Division of General Medical Studies, Public Health Service.

(2) J. Lifschitz, *Z. physik. Chem.*, **114**, 493 (1925).

(3) Lifschitz did not give an observed rotation for D-alanine, but his results agree generally with our results using D-alanine, $[\alpha]_D -14.2^\circ$ in 1 N HCl solution.

(4) F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

(5) Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 311 (1956).

(6) A. J. Saraceno, I. Mizushima, C. Curran, and J. Quagliano, *J. Am. Chem. Soc.*, **80**, 5018 (1958).

(7) H. E. Swift and B. E. Douglas, Abstracts of Papers Presented at the 138th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1960.

(8) M. Mori, M. Shibata, E. Kyuno, and M. Kanaya, *Bull. Chem. Soc. Japan*, **34**, 1837 (1961).

(9) Y. Shimura, *ibid.*, **31**, 173 (1958).

(10) H. E. Swift, Ph.D. Thesis, University of Pittsburgh, 1962.

(11) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

prepared from glycine and freshly prepared $\text{Co}(\text{OH})_3$ following the procedure of Ley and Winkler.¹²

Anal. Calcd. for $\text{CoN}_3\text{C}_9\text{H}_{12}\text{O}_6$: C, 25.63; H, 4.30; N, 14.95. Found for α isomer: C, 25.20; H, 4.70; N, 14.67. Found for β isomer: C, 25.21; H, 4.46; N, 14.59.

Partial Resolution of Tris(glycinato)cobalt(III). α Isomer. A starch column was prepared following the directions of Krebs and Rasche.¹³ A slurry of potato starch was poured into a column (70 \times 2.2 cm.) supported by a fritted glass disk covered with filter paper pulp. The column was washed for 7–8 hr. until the washings were clear (no Tyndall effect). Thirty ml. of a saturated solution of α -[Co(gly)₃] was then passed through the column and eluted with water. Twelve fractions (5 ml. each) were collected and the optical rotations examined. Fraction II was used for CD measurements. The concentration of the sample was determined from a Beer's law plot.

β Isomer.—Although the solubility of the β isomer in water is very low and its resolution was not attempted by Krebs and Rasche, it is sufficiently soluble in 10% KCl solution to be resolved partially. Thirty ml. of a saturated solution of the β isomer dissolved in 10% KCl solution was poured through a freshly prepared starch column and eluted with 10% KCl solution. Fraction II (5 ml.) was evaporated to about 2 ml. and used for CD measurements.

α -, α' -, β -, and β' -Tris(D- and L-alaninato)cobalt(III).—Following the general procedure of Ley and Winkler,¹² freshly prepared $\text{Co}(\text{OH})_3$ (1.9 g.) was washed into a beaker with D- or L-alanine (5.0 g.) and the volume adjusted to about 80 ml. The resulting mixture was stirred and heated for 5 hr. with the addition of water to replace that lost by evaporation. The violet-brown solid (α and β isomer and $\text{Co}(\text{OH})_3$) was removed from the hot mixture by filtration. The blue-violet filtrate, which contained the α , α' , and β' isomers, was evaporated to about 50 ml. on a water bath and then cooled. The α isomer which had crystallized was removed by filtration. The filtrate was evaporated almost to dryness and about 20 ml. of water added. The residue (α isomer) was removed by filtration. The addition of 20 ml. of 95% ethanol to the filtrate with stirring precipitated the β' isomer which was collected on filter paper and recrystallized from water by slow evaporation to give about 4 mg. of pink needles. On standing overnight at room temperature the α' isomer crystallized. It was recrystallized from water by adding 95% ethanol and allowing the solution to stand overnight.

The residue from the reaction mixture was suspended in a small amount of warm water and SO_2 gas was passed through the mixture until all of the $\text{Co}(\text{OH})_3$ dissolved. The α isomer was separated by repeated extraction of the residue with hot water until the washings were colorless. This isomer was recrystallized from water. The undissolved β isomer was recrystallized from 50% H_2SO_4 ; yields: α , 1.0 g.; α' , 1.5 g.; β , 0.8 g.; β' , 0.004 g. The corresponding isomers gave identical spectra using either D- or L-alanine.

Anal. Calcd. for $\text{CoN}_3\text{C}_9\text{H}_{18}\text{O}_6$: C, 33.44; H, 5.57; N, 13.00. Found for α -[Co(D-ala)₃]: C, 33.19; H, 5.60; N, 12.75. Found for α' -[Co(D-ala)₃]: C, 33.49; H, 5.96; N, 13.11. Found for β -[Co(L-ala)₃]: C, 33.49; H, 5.81; N, 13.21. Found for β' -[Co(D-ala)₃]: C, 33.34; H, 5.76; N, 12.87.

The absorption spectra were measured on a Cary Model 14 recording spectrophotometer. Optical rotations for the ORD curves were obtained using a Rudolph Model 8006 polarimeter with quartz optics and a photoelectric attachment. The light sources were a 100-watt zirconium arc lamp and a Rudolph Model 614 xenon arc lamp (below 400 $m\mu$) with a Bausch and Lomb grating monochromator. The CD curves were recorded with a Roussel-Jouan Dichrograph.

Results and Discussion

Circular Dichroism of the Four Isomers.—The CD, ORD, and absorption curves are given for the four

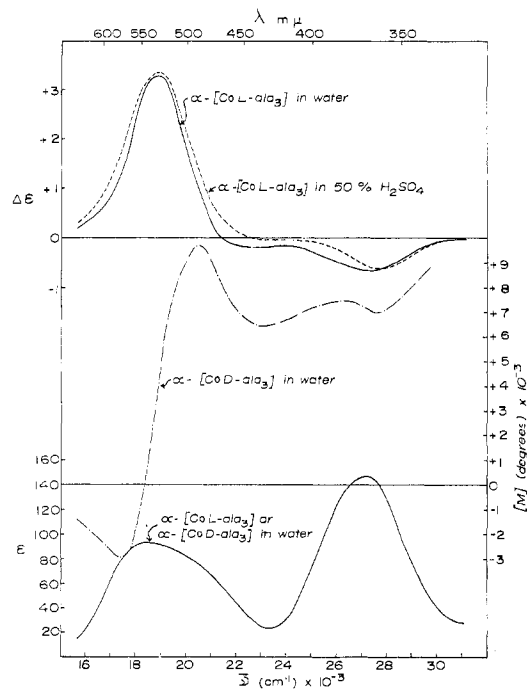


Figure 1.—Absorption, ORD, and CD curves for α -[Co(L- or D-ala)₃].

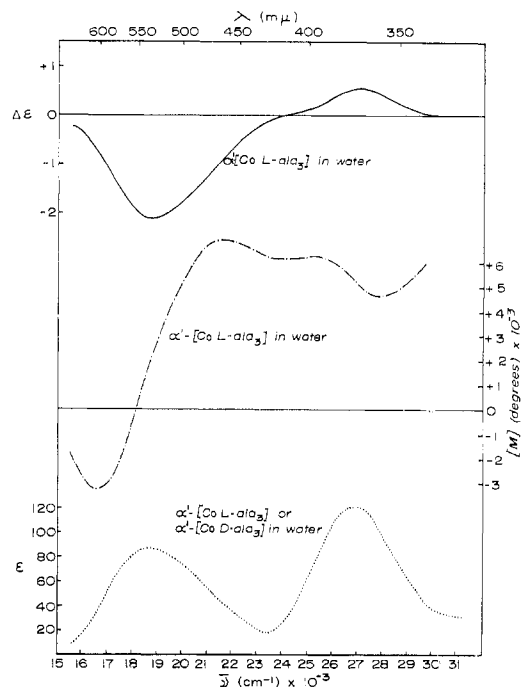


Figure 2.—Absorption, ORD, and CD curves for α' -[Co(L-ala)₃].

isomers in Figures 1–4. In each case only one absorption curve is given since the curves are the same for the corresponding D- and L-alanine complexes. For the α and α' complexes ORD and CD data are given for the complex containing only one configuration of alanine. The curves for the corresponding compounds containing alanine of the opposite configuration are mirror images of these. The ORD curves for the isomers which are mirror images are shown for comparison for β (Figure 3) and the CD curves for the mirror images are shown for β' (Figure 4).

(12) H. Ley and H. Winkler, *Ber.*, **42**, 3900 (1909); **45**, 375 (1912).

(13) H. Krebs and R. Rasche, *Z. anorg. allgem. Chem.*, **276**, 273 (1954).

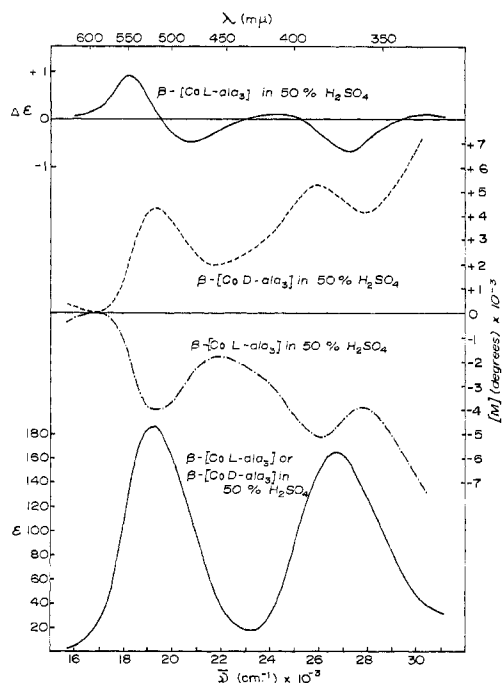


Figure 3.—Absorption, ORD, and CD curves for β -[Co(L-ala)₃] and ORD curve for β -[Co(D-ala)₃].

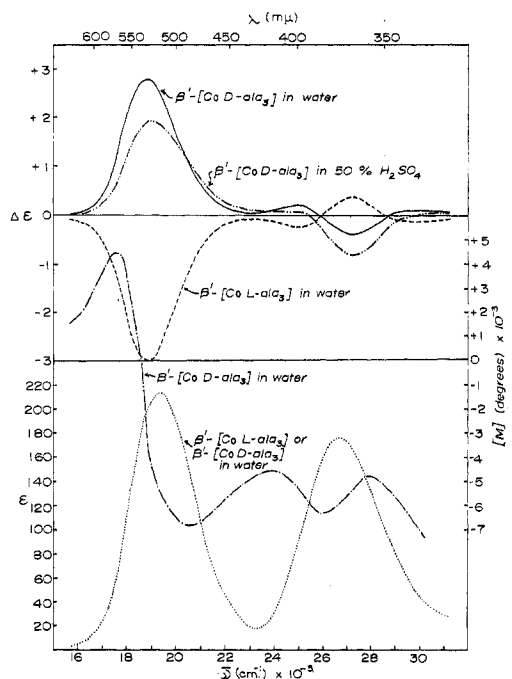


Figure 4.—Absorption, ORD, and CD curves for β' -[Co(D-ala)₃] and CD curve for β' -[Co(L-ala)₃].

All data for the β complex are for 50% H_2SO_4 as a solvent because of its low water solubility. Water was used as the solvent for the other isomers except for some measurements made in 50% H_2SO_4 to demonstrate that the absorption curves are essentially the same in both solvents and for comparison of β and β' . The slight effect of the solvent change on the CD curve for the α isomer is shown in Figure 1 and the extent of changes in intensity of the CD peaks for the β' isomer is shown in Figure 4.

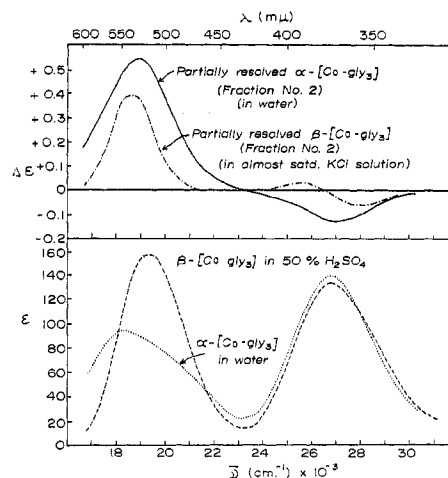


Figure 5.—Absorption curves for α - and β -[Co(gly)₃] and CD curves for the complexes partially resolved on a starch column.

The absorption spectrum of the β isomer of glycine (Figure 5) has been interpreted as indicating an effectively cubic crystal field about the cobalt⁴ since the bands show no splitting. The curves for β -[Co(ala)₃] (Figure 3) and β' -[Co(ala)₃] (Figure 4) are very similar to that for β -[Co(gly)₃] except for changes in intensity and slight shifts in peak heights. Corresponding similarities are observed for the α and α' complexes (Figures 1, 2, and 5).

Configurational and Vicinal Effects.—It has been shown that the configurational effect (the contribution from the right or left spiral of the chelate rings) and the vicinal effect (the contribution from an asymmetric ligand) can be separated and are additive¹¹ for complex ions of the type [Co(en)₂ala]²⁺. If these effects are additive for complexes such as [Co(D-ala)₃] then they can be separated since the β and β' isomers differ in the spiral arrangements (assume left and right, as assigned later) but not in the configuration of alanine. From this assumption the following relationships follow

$$\begin{aligned} \text{optical activity } (\beta) &= \text{config. effect (left spiral)} + \text{vicinal effect (D)} \\ \text{optical activity } (\beta') &= \text{config. effect (right spiral)} + \\ &\quad \text{vicinal effect (D)} \end{aligned}$$

and, since the effects of the left and right spirals are equal in magnitude and opposite in sign

$$\text{optical activity } (\beta) + \text{optical activity } (\beta') = 2 \text{ vicinal effect (D)}$$

Figure 6 is the result of applying this relationship to the CD data for β and β' . This calculated curve is the same as that obtained by mixing equimolar quantities of the β and β' isomers in 50% H_2SO_4 [labeled (vicinal effect)_{exp} in Figure 6]. When this curve is subtracted from the CD curves for β and β' (both in H_2SO_4), the resultant curves (taken to represent the configurational effects) are mirror images. Further, these resultant curves are remarkably similar to the CD curve for β -[Co(gly)₃] (Figure 5) where the only contribution is from the spiral of the chelate rings, since glycine is optically inactive.

This process was repeated for the α and α' isomers with the results shown in Figure 7. Here the experi-

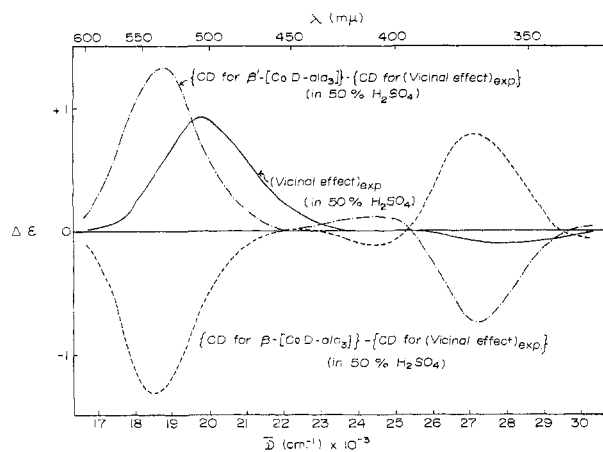


Figure 6.—Vicinal effect curve obtained from the CD curves of β - and β' -[Co(D-ala)₃] or by mixing equimolar amounts of the two isomers in 50% H₂SO₄; configurational effect curves for β - and β' -[Co(D-ala)₃] (experimental CD curves — vicinal effect curve).

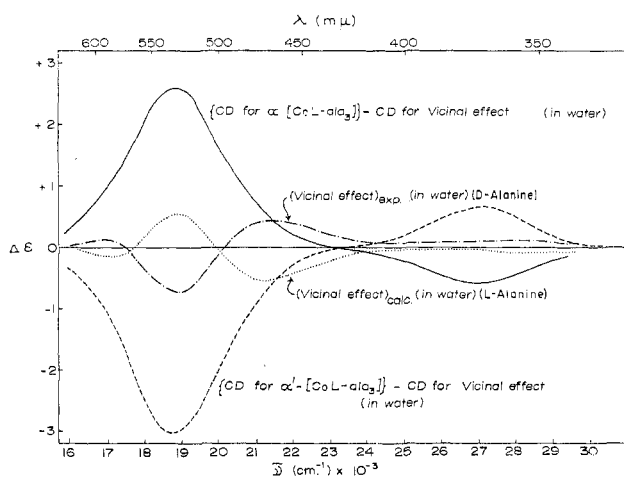


Figure 7.—Vicinal effect curves calculated from CD curves for α - and α' -[Co(L-ala)₃] and from an equimolar mixture of α - and α' -[Co(D-ala)₃]; configurational effect curves for α - and α' -[Co(L-ala)₃] (experimental CD curves — experimental vicinal effect curve).

mental and calculated curves (shown for D- and L-alanine, respectively, for comparison) differ slightly in peak heights, and hence the resultant curves, using the experimental vicinal curve (but for L-alanine), differ slightly. This could indicate some deviation from additivity of the effects for α and α' . This might be the result of the interaction of two methyl groups for one isomer (later assigned α') and not the other. There is no interaction of substituents for either β or β' and the effects were additive. The resultant curve for α -[Co(L-ala)₃] corresponds very well to the curve for α -[Co(gly)₃].

Both β - and β' -[Co(ala)₃] have C_3 symmetry (E and A for each band) as for D_3 . On this basis the CD peaks for β -[Co(L-ala)₃] in 50% H₂SO₄ (Figure 3) are tentatively assigned as follows¹⁴: E_a (+0.80, 18,250), A (-0.44, 20,600), E_b (+0.13, 24,600), and A (-0.61, 27,150). The remaining weak peak at about 30,200

(14) ($\Delta\epsilon$, $\bar{\nu}$ in cm.⁻¹).

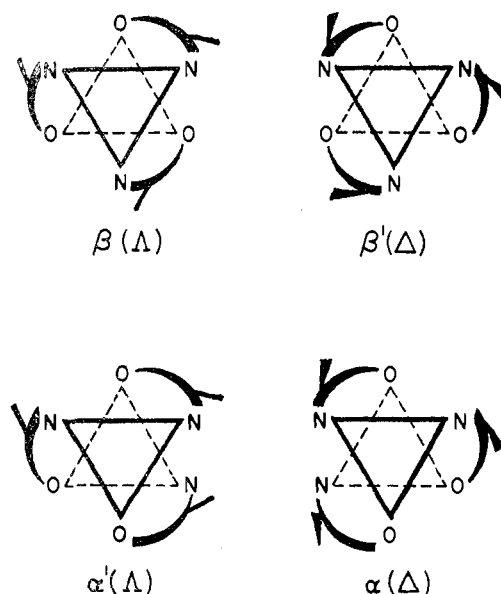


Figure 8.—Representations of β - and α' -[Co(L-ala)₃] (methyl groups equatorial), β' -[Co(L-ala)₃] (methyl groups axial and pointed up), and α -[Co(L-ala)₃] (methyl groups axial, two pointed up and one down).

cm.⁻¹ is unassigned since only two peaks are expected for each band region. This peak is very weak for a ligand transition and it is at higher energy than is expected for a spin-forbidden transition. The intensity of E_a is greatly reduced by the vicinal effect (Figure 6). For β' -[Co(L-ala)₃] in water (Figure 4) the tentative assignments are¹⁴: E_a (-3.0, 18,900), A (not resolved), E_b (-0.26, 25,100), and A (+0.4, 27,250). The weak peak at about 29,800 cm.⁻¹ is also unassigned in this case. Here E_a is enhanced by the vicinal effect to the extent that it cancels A.

The configuration of (+)-[Co(en)₃]³⁺ is Λ and the CD peaks in the low-frequency region are E_a (+) and A₂ (-). Based on the similar splitting for D_3 and C_3 and the signs of the CD peaks in this region, the configurations of the L-alanine complexes can be tentatively assigned as Λ for β and Δ for β' .

The α and α' isomers have C_1 symmetry so that three CD peaks are expected for each band region. The CD peaks observed for α -[Co(L-ala)₃] in water (Figure 1) are¹⁴: (+3.33, 18,850); (-0.2, 22,650, broad), and (-0.67, 27,150, broad); and for α' -[Co(L-ala)₃] in water (Figure 2)¹⁴: (-2.32, 18,650), (shoulder?), and (+0.56, 27,000, broad). The vicinal effect curve (Figure 7) shows the expected three peaks in the first band region. The center peak is of opposite sign to the other two so it can be considered to be of A₂ (D_3) parentage and the other two of E_a (D_3) parentage. This is the dominant peak for both isomers as was noted for complexes of the type [Co(en)₂am]²⁺ (am = amino acid anion).¹¹ Based on the sign of this peak, assumed to be of A₂ parentage, the configurations of the L-alanine are tentatively assigned as Δ for α and Λ for α' .

The isomers (from L-alanine) are represented in Figure 8. The methyl groups are equatorial for β and

point clockwise as shown while the chelate rings spiral to the left. On this basis it is reasonable that the configurational and vicinal effects are of opposite sign in the low-frequency band region, partially cancelling one another to give two weak peaks of opposite sign. The resultant optical activity in the visible region is so weak that the effect of the contribution from the stronger ultraviolet transitions causes the ORD curve of $\beta\text{-[Co(L-ala)}_3\text{]}$ to be entirely negative in the visible region.

The methyl groups are axial for the β' isomer and point in the same direction as shown (horizontal component clockwise) as the spiral of the chelate rings. The configurational and vicinal contributions are in the same direction and add to give a single, more intense peak than for β .

The peaks for the vicinal effect are displaced so much to higher frequencies compared to the configurational effect that it is apparent that the dominant components are not the same for the two effects. This was also true for the $[\text{Co(en)}_2\text{am}]_2\text{I}_2$ compounds. For the α and α' compounds the dominant CD peak overshadows the others, but from the vicinal effect the corresponding peak can be seen to be the center peak (of three) of comparable intensity to one of higher frequency ($21,400\text{ cm.}^{-1}$).

The methyl groups are equatorial for α' , corresponding to β with one chelate ring reversed. Two of the methyl groups point in the opposite direction (as shown) to the left spiral and one points in the same direction. Thus the vicinal effect is smaller than for β and β' . The vicinal effect curve can be seen to have the effect of lowering the maximum and broadening the resultant (experimental) curve for α' . The methyl groups are axial for α with the horizontal component in the same direction as shown (clockwise) for only two of the groups. The third methyl group points down and

counterclockwise. The sign combination of peaks for the vicinal effect when added to the configurational effect curve gives the sharp positive peak flanked by the weak negative peak of the experimental curve for α (Figure 1).

It is apparent that for complexes with three chelate rings the contribution to the optical activity from the configurational effect is larger than that from the vicinal effect. The vicinal effect is reduced when the substituents are oriented in such a way as to cancel partially their effects, as for the α and α' isomers. The two effects contribute to different extents to the intensities of different CD components in the low-frequency region and the vicinal effect has little effect in the higher frequency band region.

The lower solubility of $\beta\text{-[Co(ala)}_3\text{]}$ compared to $\alpha\text{-[Co(ala)}_3\text{]}$ is not so surprising since the molecules of the β isomer might be expected to interact strongly through intramolecular hydrogen bonding which would be possible if the molecules were stacked directly above one another. Models do not reveal any significant differences in the opportunities for hydrogen bonding to water. The great increases in water solubilities caused by changing the methyls from equatorial positions (α' and β) to axial positions (α and β') is surprising. The difference is especially great for β and β' . Framework molecular models show that the axial methyl groups for the β' isomer project up far enough so that they might interfere with intramolecular hydrogen bonding and thus increase solubility.

Acknowledgment.—The authors wish to thank Dr. Harold E. Swift for background work on the glycine and alanine complexes and Mr. Noel J. Farrier for some preliminary CD measurements on some of the complexes.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
EMORY UNIVERSITY, ATLANTA, GEORGIA

Studies on the Interconversion of $trans\text{-Dichlorotetraammineplatinum(IV)}$ and $trans\text{-Dibromotetraammineplatinum(IV)}$ Cations

BY R. R. RETTEW AND RONALD C. JOHNSON

Received June 18, 1965

The reactions of bromide ion with $trans\text{-Pt}(\text{NH}_3)_4\text{Cl}_2^{2+}$ and $trans\text{-Pt}(\text{NH}_3)_4\text{ClBr}^{2+}$ and the reverse reactions of chloride with $trans\text{-Pt}(\text{NH}_3)_4\text{ClBr}^{2+}$ and $trans\text{-Pt}(\text{NH}_3)_4\text{Br}_2^{2+}$ exhibit a first-order rate dependence in the reactant platinum(IV) complex, in the entering halide ion, and in $\text{Pt}(\text{NH}_3)_4^{2+}$. These rate data are consistent with a mechanism involving a bridged activated complex, Pt-X-Pt . Rate constants and activation parameters for the four reactions were measured. Reactions in which a bromine atom is *trans* to the leaving halide are much more rapid than those in which the *trans* ligand is chloride. Equilibrium constants for the reactions were evaluated from the kinetic data and from independent spectrophotometric studies.

Introduction

A mechanism involving a bridged activated complex is consistent with the rate data for several substitution reactions of complex cations such as $trans\text{-Pt}(\text{NH}_3)_4\text{X}_2^{2+}$

and $trans\text{-Pt}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{X}_2^{2+}$.^{1,2} All reactions for which kinetic data are available show third-order

- (1) W. R. Mason and R. C. Johnson, *Inorg. Chem.*, **4**, 1258 (1965).
- (2) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 35 (1961).