

or V^{2+} . A striking feature of the data is that despite the fact that the rates of reaction differ little from case to case, the values of ΔH^\ddagger and ΔS^\ddagger do change considerably. In the inner-sphere reactions, quite rigid constraints are placed on the geometries of the activated complexes, and therefore on the distribution of electric charge within them, and as a result the values of ΔS^\ddagger do not vary capriciously. However, it may be that in the outer-sphere activated complex where such severe constraints do not exist a slight change in the distribution of charge in the Co(III) complex, for example, can call for a considerable change in the way oxidant and reductant are arranged in the activated complex, thus affecting ΔS^\ddagger .

An explanation of the variation of rate for the outer-sphere reactions with properties of the ligand will be difficult to develop because a satisfactory theory must account not only for the rates at a particular temperature but also for the way the rate pattern changes with temperature. We are in no position to offer such an

explanation and extensive discussion of the observations is therefore out of order. We do, however, wish to point to the comparison of the kinetic parameters for $C_2O_4H^-$ and $C_2O_4^{2-}$ as ligand. In accord with observations made for the reduction of an aquo *vs.* hydroxo ion by an outer-sphere mechanism,³ the rate for the protonated ligand is found to be greater than for the unprotonated one. Comparison of the values of ΔH^\ddagger for the two has shown, despite the inaccuracy of that recorded for the oxalate complex, that at a low temperature the rate for the oxalato complex will exceed that for the binoxalate. Thus the rate comparison for a complex containing a protonated ligand *vs.* that for a proton-free ligand must be used with caution in diagnosing mechanisms until the subject is better understood.

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Preparation of the Tris-Type Complexes of Cobalt(III) with Two Different Kinds of α -Amino Acids¹

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The complexes of carbonatobis(aminoacidato)cobaltate(III) have been prepared by the reaction of the tricarbonatocobaltate anion with an aminoacidate anion; the compounds obtained are $K[Co(gly)_2CO_3] \cdot H_2O$, $K[Co(L-ala)_2CO_3] \cdot 3H_2O$, and $K[Co(L-val)_2CO_3] \cdot 3.5H_2O$. The reaction of the carbonatobis(glycinato) complex with L-valine led to formation of a mixed amino acid complex, $[Co(gly)_2(L-val)]$, and three among the four possible isomers of the complex, *i.e.*, $\beta(+)_D$, $\beta(-)_D$, and $\alpha(+)_D$, have been isolated by means of the solubility difference. Using the other carbonate complexes, the following isomers were also obtained as water-insoluble forms: $\beta(+)_D-[Co(L-val)_2(gly)]$, $\beta(+)_D-[Co(L-val)_2(L-ala)]$, $\beta(-)_D-[Co(L-val)_2(D-ala)]$, and $\beta(+)_D-[Co(L-ala)_2(D-ala)]$. All of these isomers are characterized by the ORD and CD spectra, and the vicinal effect of optically active valine is also considered.

In our previous paper dealing with the preparation of tris(aminoacidato) complexes,² we concluded that the method using cobalt(III) hydroxide, which was originated by Ley and Winkler,³ is convenient for preparing the α (*trans* or peripheral) isomer, while the method using the hexaamminecobalt(III) cation, which was devised by Neville and Gorin,⁴ is advantageous for preparing the β (*cis* or facial) isomer. The third method using the tricarbonatocobaltate(III) anion was found to give both forms in about equal amounts. Dunlop and Gillard⁵ have recently used these three methods for the preparation and isolation of tris(L-alaninato)cobalt-

(III); the hydroxide method gives predominantly the α isomers, the hexaammine method gives only the water-insoluble $\beta(+)_D$ isomer, and the tricarbonato method gives all of the four isomers with a little predominance of the α isomers. Denning and Piper⁶ have obtained both (+) and (-) isomers of *trans*- α -tris(L-leucinato)cobalt(III) by using a slightly modified tricarbonato method and corresponding *cis*- β -isomers from the hexaammine method ((+) and (-) signs refer to the sign of the net rotational strength of the low-energy absorption band). They have also succeeded in separating three isomers of the possible four of tris(L-prolinato)cobalt(III), *i.e.*, *cis*- $\beta(+)$, *cis*- $\beta(-)$, and *trans*- $\alpha(-)$, from a reaction mixture of tricarbonatocobaltate(III) and L-proline. The method using hexaamminecobalt(III) failed to give any product. Before this,

(1) Presented at the 16th Symposium on Coordination Chemistry, Tokyo, Dec 1966.

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

(3) H. Ley and H. Winkler, *Ber.*, **42**, 3894 (1909).

(4) R. G. Neville and G. Gorin, *J. Am. Chem. Soc.*, **78**, 4895 (1956).

(5) J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.*, 6531 (1965).

(6) R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966).

Yasui, Hidaka, and Shimura⁷ obtained only the *cis*- $\beta(+)$ isomer by the reaction of diaquotetraamminecobalt(III) perchlorate with L-proline in the presence of activated charcoal. Recently, we have isolated four isomers of trihydrogen tris(L-aspartato)cobaltate(III) from a reaction mixture of tricarbonatocobaltate(III) with L-aspartic acid.⁸ Douglas and Yamada⁹ isolated all isomers of the cobalt(III) complexes of D- and L-alanine by the method of Ley and Winkler. The analogous four isomers with L-valine were also obtained by the same method in our laboratory.¹⁰

Thus, a number of geometrical optical isomers of the tris-type cobalt(III) complexes have been isolated. The absolute configuration of the *cis* isomers has been related to that of the diamine complex such as (+)-[Co(en)₃]³⁺ whose configuration was ascertained as D by the X-ray method.¹¹ For the *trans* isomers, an X-ray study¹² has determined the absolute configuration of (+) isomers as D form.

As far as we know, mixed complexes of cobalt(III) with two different kinds of aminoacidate anions have not been synthesized before, although some mixed complexes with amino acid and amine are known.¹³

Experimental Section

Preparation of Carbonatobis(aminoacidato)cobaltates(III).

(1) **Potassium Salt of Bis(glycinato)cobaltate(III)**, K[Co(gly)₂CO₃]·H₂O.—Cobalt chloride hexahydrate, 23.8 g (0.1 mole), in 50 ml of water and 16 ml of 30% H₂O₂ were mixed. This solution was added dropwise to an ice-cooled slurry of 65 g of KHCO₃ (0.65 mole) in 60 ml of water. Fifteen grams of glycine (0.2 mole) was added to the resulting tricarbonatocobaltate(III) solution, and the mixture was heated at 60–65° for 3 hr with stirring, whereupon the solution became violet in color. The solution was filtered, cooled to room temperature, and then adjusted to pH 7.2–7.5 with dilute acetic acid. After addition of a small amount of ethanol, the mixture was kept in a refrigerator overnight in order to precipitate salts such as potassium chloride and bicarbonate. After removal of the salts by filtration, about 200 ml of ethanol was added to the filtrate in the cold. When the walls of the beaker were scratched, red-violet crystals precipitated gradually. The precipitates were collected by filtration and recrystallized from water. The yield was approximately 12 g (40%). *Anal.* Calcd for K[Co(C₂H₄NO₂)₂CO₃]·H₂O: C, 18.50; N, 8.60; H, 3.09. Found: C, 18.33; N, 8.53; H, 3.34.

(2) **Carbonatobis(L-alaninato)cobaltate(III)**, K[Co(L-ala)₂CO₃]·3H₂O.—The potassium salt was obtained by the same procedure as the above except that acetone was used as the precipitant in place of ethanol; yield, 7 g. *Anal.* Calcd for K[Co(C₂H₅NO₂)₂CO₃]·3H₂O: C, 21.65; N, 7.21; H, 4.64. Found: C, 21.92; N, 7.53; H, 5.01.

(3) **Carbonatobis(L-valinato)cobaltate(III)**, K[Co(L-val)₂CO₃]·3.5H₂O.—Because of lower solubility than the corresponding glycinato complex, this was obtained by the concentration of a reacted solution under reduced pressure. Recrystallization of the complex was performed from methanol; yield, about 10 g.

(7) T. Yasui, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, **38**, 2025 (1965).

(8) M. Shibata, H. Nishikawa, and K. Hosaka, *ibid.*, **40**, 236 (1967).

(9) B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).

(10) M. Shibata, H. Nishikawa, and Y. Nishida, *Bull. Chem. Soc. Japan*, **39**, 2310 (1966).

(11) K. Nakatsu, *ibid.*, **35**, 832 (1962), and references therein.

(12) M. G. B. Drew, J. H. Dunlop, R. D. Gillard, and D. Rogers, *Chem. Commun.*, 42 (1966).

(13) T. Yasui, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, **39**, 2417 (1966).

Anal. Calcd for K[Co(C₅H₁₀NO₂)₂CO₃]·3.5H₂O: C, 29.13; N, 6.18; H, 6.10. Found: C, 29.02; N, 6.24; H, 6.09.

Preparation and Isolation of the Mixed Complex Bis(glycinato)-L-valinatocobalt(III), [Co(gly)₂(L-val)]·*n*H₂O.—The carbonatobis(glycinato) complex described above (6.4 g, 0.02 mole) was dissolved in 100 ml of water and 2.3 g of L-valine (0.02 mole) was added to the solution. The mixture was stirred at 55–60° for 7–8 hr. On cooling the solution, we obtained the first isomer insoluble in water, *i.e.*, the $\beta(+)$ D isomer. This was recrystallized from 50% sulfuric acid as red needles. When the filtrate after removal of the $\beta(+)$ D isomer was treated with ethanol (about 50 ml), the second isomer, $\beta(-)$ D, separated out. This was recrystallized from water as red needles. The remaining ethanolic solution was then evaporated to a small volume, and the third isomer, *i.e.*, $\alpha(+)$ D, was deposited as red-violet plates. The recrystallization was carried out with water. The final liquor from the above was evaporated to dryness and the residue was treated with methanol. The extracted methanolic solution was chromatographed on an alumina column; a violet band was observed on the column, but no material identifiable as the fourth $\alpha(-)$ D isomer was obtained because of its highly hygroscopic nature. The yields of these isomers were about 0.3 g ($\beta(+)$ D), 0.5 g ($\beta(-)$ D), and 1 g ($\alpha(+)$ D).

Anal. Calcd for $\beta(+)$ D-[Co(C₂H₄NO₂)₂(C₅H₁₀NO₂)]: C, 33.43; N, 13.00; H, 5.57. Found: C, 33.33; N, 13.20; H, 5.77.

Anal. Calcd for $\beta(-)$ D-[Co(C₂H₄NO₂)₂(C₅H₁₀NO₂)]: C, 30.85; N, 12.00; H, 5.14. Found: C, 30.53; N, 12.38; H, 5.36.

Anal. Calcd for $\alpha(+)$ D-[Co(C₂H₄NO₂)₂(C₅H₁₀NO₂)]: C, 30.06; N, 11.70; H, 6.13. Found: C, 30.19; N, 11.70; H, 6.09.

Preparation of the Others.—The procedure was essentially the same as above in each case of the mixed complexes. However, the isolation of the isomers was limited to only the water-insoluble β forms, *i.e.*, $\beta(+)$ D-[Co(L-val)₂gly]·1.5H₂O, $\beta(+)$ D-[Co(L-val)₂(L-ala)]·H₂O, $\beta(-)$ D-[Co(L-val)₂(D-ala)]·2H₂O, and $\beta(-)$ D-[Co(gly)₂(D-ala)]. A complex containing optically opposite ligands, *i.e.*, [Co(L-ala)₂(D-ala)], was also obtained as the water-insoluble $\beta(+)$ D isomer.

Anal. Calcd for $\beta(+)$ D-[Co(C₅H₁₀NO₂)₂(C₂H₄NO₂)]: C, 36.65; N, 10.70; H, 6.78. Found: C, 36.81; N, 10.94; H, 6.80.

Anal. Calcd for $\beta(+)$ D-[Co(C₅H₁₀NO₂)₂(C₃H₅NO₂)]: C, 39.29; N, 10.69; H, 7.05. Found: C, 39.00; N, 10.54; H, 6.95.

Anal. Calcd for $\beta(-)$ D-[Co(C₅H₁₀NO₂)₂(C₃H₅NO₂)]: C, 37.58; N, 10.11; H, 7.23. Found: C, 37.21; N, 10.13; H, 7.00.

Anal. Calcd for $\beta(-)$ D-[Co(C₂H₄NO₂)₂(C₅H₆NO₂)]: C, 28.52; N, 14.30; H, 5.07. Found: C, 28.69; N, 15.13; H, 4.65.

Anal. Calcd for $\beta(+)$ D-[Co(C₅H₆NO₂)₂(C₅H₆NO₂)]: C, 33.44; N, 13.01; H, 5.55. Found: C, 33.03; N, 13.58; H, 5.25.

Instrumental Measurements.—The absorption spectra and the optical rotatory dispersion (ORD) and circular dichroism (CD) curves were all recorded on a Jasco optical rotatory dispersion recorder, Model UV-5, with an attached CD recorder.

Results and Discussion

On the Preparation.—In several preparative studies^{2,14} dealing with tricarbonatocobaltate(III), we have found that it is relatively more difficult for another ligand to be substituted for the third carbonate ligand than for the first and second carbonate ligands. Using this fact, we prepared first carbonatobis(aminoacidato)cobaltate(III); this, through the reaction with another

(14) M. Mori, M. Shibata, E. Kyuno, and T. Adachi, *ibid.*, **29**, 883 (1956); M. Mori, M. Shibata, E. Kyuno, and Y. Okubo, *ibid.*, **31**, 940 (1958); M. Mori, M. Shibata, E. Kyuno, and F. Maruyama, *ibid.*, **35**, 75 (1962); M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964).

amino acid, led to the formation of desired mixed amino-acidato complex.

We have to consider an alternative reaction such as

$$3\text{K}[\text{Co}(\text{gly})_2\text{CO}_3] + 3\text{L-val-H} \longrightarrow 2[\text{Co}(\text{gly})_3] + [\text{Co}(\text{L-val})_3] + 3\text{KHCO}_3$$

If such a reaction takes place, the resulting product must be a mixture of two kinds of tris(aminoacidato) complexes. This doubt was dispelled by comparison of the X-ray diffraction pattern in powder for the product with that for a certain tris-type complex with a single amino acid.

Dwyer, Sargeson, and James¹⁵ confirmed the existence of the mixed-ligand complexes such as $\text{D-}[\text{Co}((+)\text{pn})_2((-)\text{pn})]^{3+}$ and $\text{L-}[\text{Co}((-)\text{pn})_2(+)\text{pn}]^{3+}$. Dunlop and Gillard⁵ also considered the formation of $\text{DL-}[\text{Co}(\text{L-ala})(\text{D-ala})_2]$ and/or $\text{DL-}[\text{Co}(\text{L-ala})_2(\text{D-ala})]$ in the reaction of hexaamminecobalt(III) with racemic alanine. We have now prepared the $\beta(-)\text{D}$ isomer of $[\text{Co}(\text{L-val})_2(\text{D-ala})]$, in addition to the $\beta(+)\text{D}$ isomer of $[\text{Co}(\text{L-val})_2(\text{L-ala})]$.

Characterization of the Complexes.—For the carbonatobis(aminoacidato) complexes, three geometrical isomers are possible, namely, (a) *cis(N)-cis(O)*, (b) *cis(N)-trans(O)*, and (c) *trans(N)-cis(O)*. Among these, (c) will be excluded because of nonsplitting of the first absorption band (Figure 1). Matsuoka, *et al.*,¹⁶

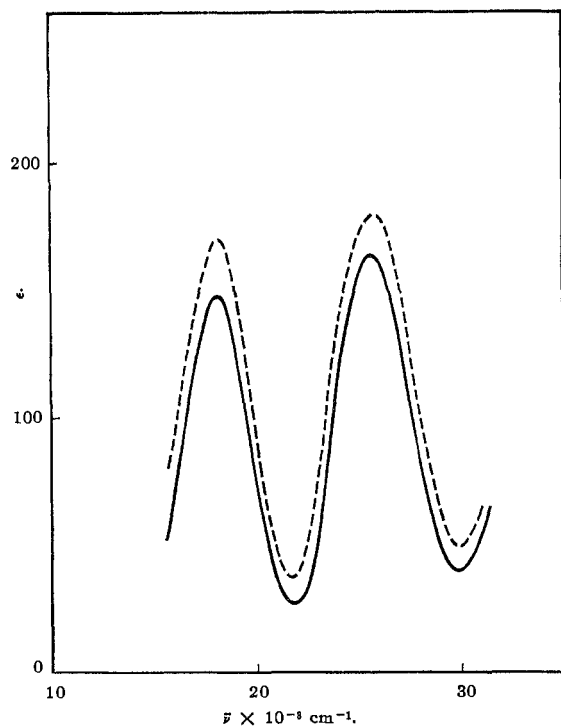


Figure 1.—Absorption curves for $\text{K}[\text{Co}(\text{gly})_2\text{CO}_3]$ (—) and $\text{K}[\text{Co}(\text{L-val})_2\text{CO}_3]$ (---) (in H_2O).

and Hidaka and Shimura¹⁷ have recently reported that *trans(N)*-oxalatobis(aminoacidato)cobalt(III) complexes show the splitting of the first absorption band.

(15) F. P. Dwyer, A. M. Sargeson, and L. B. James, *J. Am. Chem. Soc.*, **86**, 590 (1964).

(16) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, in press.

(17) J. Hidaka and Y. Shimura, *ibid.*, in press.

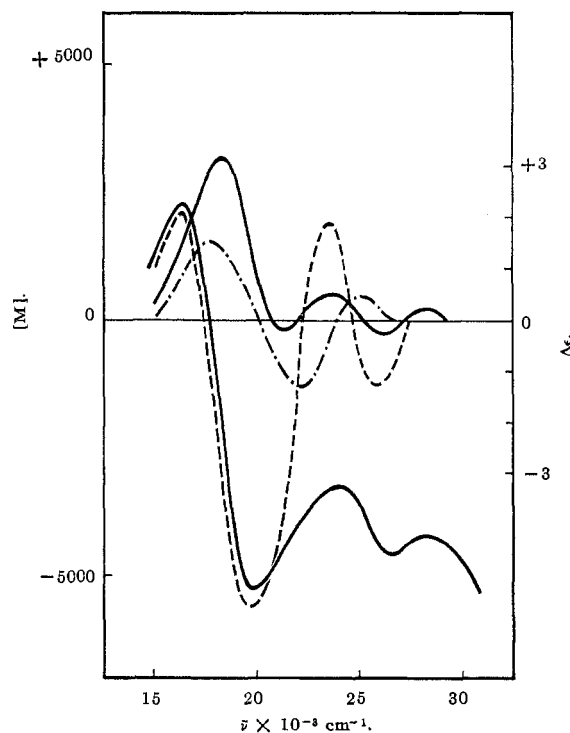


Figure 2.—ORD (—) and CD (— · —) curves for $(+)\text{D-K}[\text{Co}(\text{L-val})_2\text{CO}_3]$ and ORD (---) and CD (· · ·) curves for $(-)\text{D-}[\text{Co}(\text{en})_2(\text{NO}_2)_2] \cdot (+)\text{D-}[\text{Co}(\text{gly})_2\text{CO}_3]$ (in H_2O).

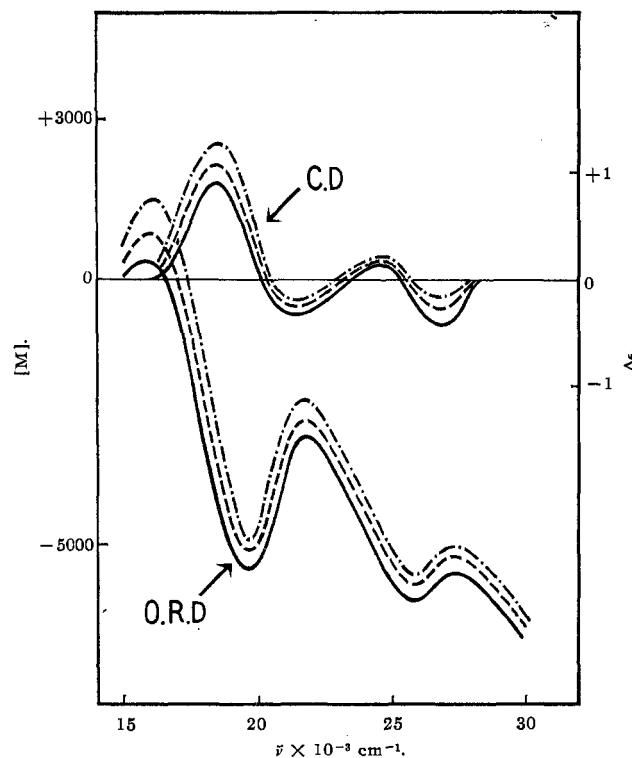


Figure 3.—ORD and CD curves for $\beta(+)\text{D-}[\text{Co}(\text{gly})_2(\text{L-val})]$ (— · —), $\beta(+)\text{D-}[\text{Co}(\text{gly})(\text{L-val})_2]$ (---), and $\beta(+)\text{D-}[\text{Co}(\text{L-val})_3]$ (—) (in 50% H_2SO_4).

It is still uncertain which structure, (a) or (b), is correct for the present carbonato complexes.

The carbonato complex of L-valine shows distinctive ORD and CD spectra as is seen in Figure 2. This indicates the stereospecific formation of $(+)\text{D}$ isomer was caused by its water insolubility. For the carbonato

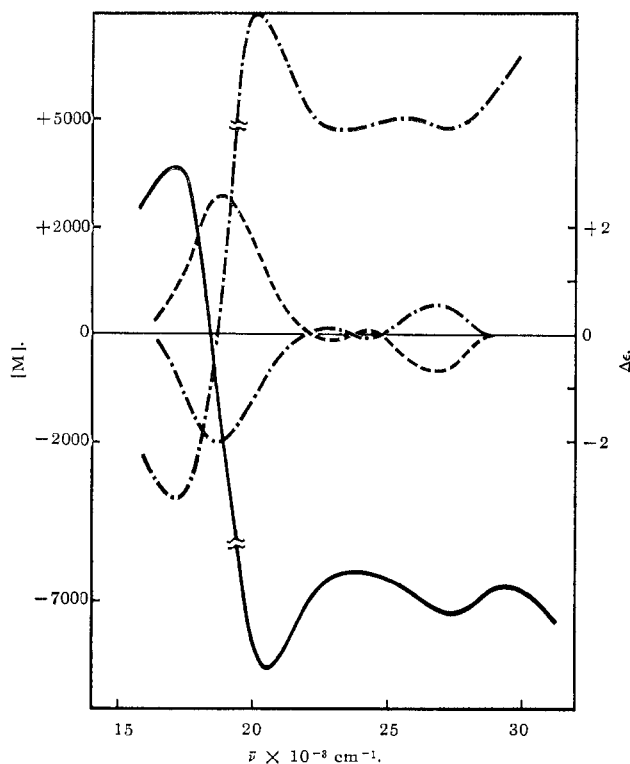


Figure 4.—ORD (—) and CD (---) curves for $\alpha(+)$ -D-[Co(gly)₂(L-val)] and ORD (- · -) and CD (- · -) curves for $\beta(-)$ -D-[Co(gly)₂(L-val)] (in H₂O).

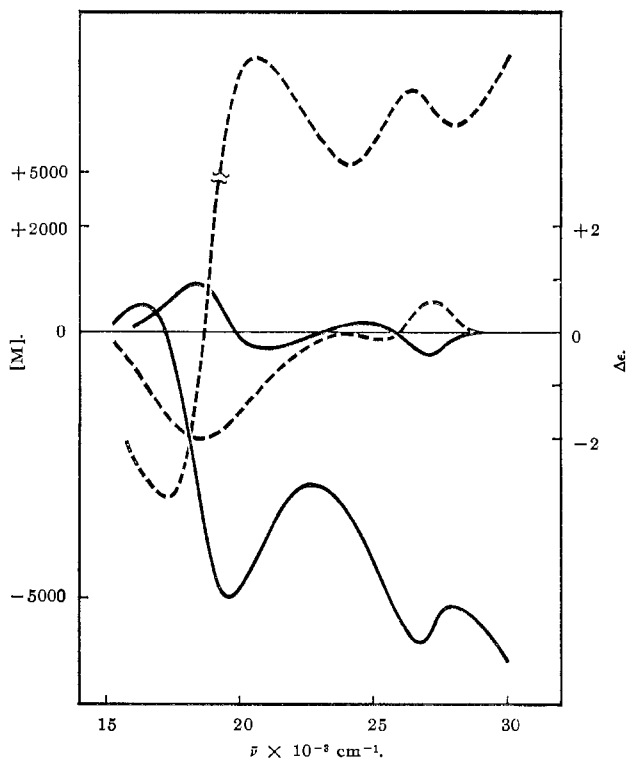


Figure 5.—ORD and CD curves for $\beta(+)$ -D-[Co(L-val)₂(L-ala)] (—) and $\beta(-)$ -D-[Co(L-val)₂(D-ala)] (- - -) (in 50% H₂SO₄).

complex of L-alanine, such stereospecific precipitation of one diastereoisomer was not observed. The resolution of the carbonato complex of glycine was successfully attained by the use of $(-)$ -D-[Co(en)₂(NO₂)₂]⁺ as a

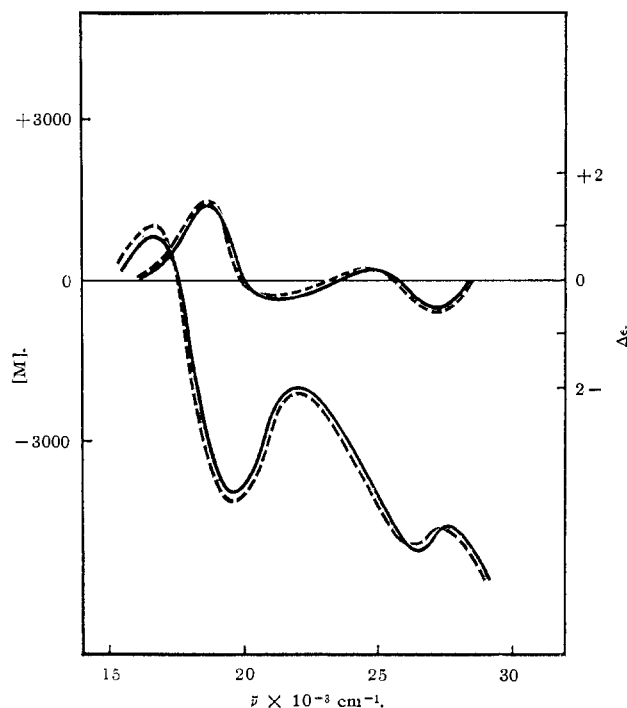


Figure 6.—ORD and CD curves for $\beta(+)$ -D-[Co(gly)₂(L-ala)] (---) and $\beta(+)$ -D-[Co(L-ala)₂(D-ala)] (—) (in 50% H₂SO₄).

resolving agent. The precipitated diastereoisomer was $(-)$ -D-[Co(en)₂(NO₂)₂] · $(+)$ -D-[Co(gly)₂CO₃] · 2H₂O (Figure 2).

The four isomers of tris(glycinato)cobalt(III) have been resolved partially because of their enantiomerism.^{9,18} An introduction of an optically active ligand into the coordination sphere instead of a glycinate ligand generates diastereoisomerism, and thus, three isomers of [Co(gly)₂(L-val)] have been separated. The ORD and CD curves of $\beta(+)$ -D-[Co(gly)₂(L-val)] and [Co(gly)(L-val)₂] are shown in Figure 3 with the curves of $\beta(+)$ -D-[Co(L-val)₃].¹⁰ Figure 4 shows the ORD and CD spectra of $\beta(-)$ -D and $\alpha(+)$ -D isomers for [Co(gly)₂(L-val)]. The ORD and CD of the bis(L-valinato) complexes containing another ligand L- or D-alanine are shown in Figure 5. Figure 6 shows the spectra of $\beta(+)$ -D-[Co(gly)₂(L-ala)] and $\beta(+)$ -D-[Co(L-ala)₂(D-ala)]. All numerical data for the CD spectra of the mixed-ligand complexes are given in Table I.

Douglas and Yamada⁹ have shown that the vicinal and configurational effects of the CD can be separated and are exactly additive for the β isomers of tris(alaninato)cobalt(III). For the corresponding α isomers, they observed some deviation from the additivity of the effects. Using the Douglas treatment, we inspected the additive rule for our complexes. The calculated curves of circular dichroism for $\beta(+)$ -D-[Co(gly)₂(L-val)] and $\beta(+)$ -D-[Co(gly)(L-val)₂] from the data for $\beta(+)$ -D- and $\beta(-)$ -D-[Co(L-val)₃] are shown in Figure 7. The values of $(\epsilon_1 - \epsilon_2)_{\max}$ in the region of the first absorption band were calculated to be +1.19 for the former and +1.01 for the latter isomer. On the other

(18) H. Krebs and H. Diewald, *Z. Anorg. Allgem. Chem.*, **287**, 98 (1956).

TABLE I
THE CD DATA AND ABSOLUTE CONFIGURATIONS

Complex	Isomer	Circular dichroism		Config ^a (C ₂)
		λ_{\max} , cm ⁻¹	$(\epsilon_1 - \epsilon_2)_{\max}$	
[Co(gly) ₂ (L-val)]	$\beta(+)$ D	18,500	+1.30	Δ
		20,900	-0.20	
	$\beta(-)$ D	18,800	-2.00	Δ
	$\alpha(+)$ D	18,860	+2.60	Δ
		22,200	-0.01	
[Co(L-val) ₂ (gly)]	$\beta(+)$ D	18,510	+1.08	Δ
		20,900	-0.03	
[Co(L-val) ₂ (L-ala)]	$\beta(+)$ D	18,500	+0.92	Δ
		20,900	-0.02	
[Co(L-val) ₂ (D-ala)]	$\beta(-)$ D	18,860	-2.00	Δ
[Co(gly) ₂ (L-ala)]	$\beta(+)$ D	18,510	+1.36	Δ
		20,900	-0.02	
[Co(L-ala) ₂ (D-ala)]	$\beta(+)$ D	18,500	+1.33	Δ
		20,900	-0.03	

^a The symbols Δ and Λ are based upon the convention proposed by T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

hand, the observed values are +1.30 and +1.08, respectively. The magnitude of the vicinal effect of L-valine was also calculated from the data for $\beta(+)$ D-[Co(L-val)₂(L-ala)] and $\beta(-)$ D-[Co(L-val)₂(D-ala)], but the value was a little higher than that obtained from the data for the tris(valinato) complexes. From these, we conclude that Douglas' additive rule is essentially true, but not exactly in the case of our complexes containing optically active valine.

The absolute configuration for β isomers of the tris(aminoacidato) complex has been related to that of the

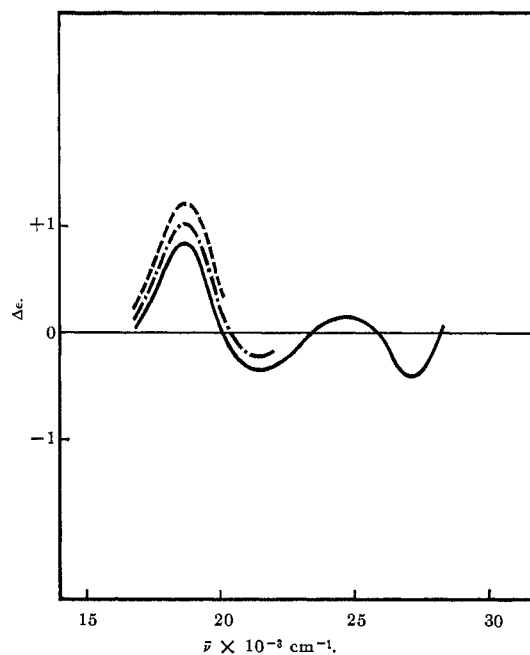


Figure 7.—Calculated CD curves for $\beta(+)$ D-[Co(gly)₂(L-val)] (---) and $\beta(+)$ D-[Co(gly)(L-val)₂] (- · -) and the observed CD curve for $\beta(+)$ D-[Co(L-val)₃] (—) (in 50% H₂SO₄).

tris(ethylenediamine)cobalt cation, while the absolute configuration for α isomers has been determined directly by an X-ray study.¹² By relating our CD spectra to the known data, we can assign the absolute configuration for the present isomers as is seen in Table I.

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An Electron Spin Resonance Study of a Low-Spin, Five-Coordinated Complex of Cobalt

By E. E. GENSER

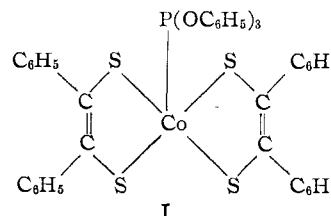
Received September 27, 1967

The electron spin resonance study of a five-coordinated cobalt complex with $S = 1/2$ has been shown to be consistent with the geometry of a rectangular-based pyramid. The ligand hyperfine structure permitted a principal symmetry axis in the complex to be identified and thus helped to establish the configuration of the unpaired electron in the complex. An interpretation of the magnitude of the measured esr parameters is given which suggests that a significant amount of 3d-4p hybridization of the cobalt orbitals occurs in addition to the effects of covalency.

Introduction

Extensive studies of the square-planar bis-dithiodiketone complexes of transition metals have been reported.¹⁻⁴ Recently, the preparation of some five-coordinated derivatives of the bis compounds of iron and cobalt has been reported.⁵ In this report the

results of esr studies of the uncharged complex (I) of cobalt are given:



(1) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

(2) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *ibid.*, **84**, 3596 (1962).

(3) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *ibid.*, **86**, 4580 (1964).

(4) G. N. Schrauzer and V. P. Mayweg, *ibid.*, **87**, 1483 (1965).

(5) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *ibid.*, **88**, 4606 (1965).