Preparation and Absorption Spectra of the Cobalt(III) Complexes of Amino Acids[1]

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There are two isomers, α (violet) and β (red), of trisglycinatocobalt(III). It has recently been ascertained from the absorption spectra by Shimura and Tsuchida[2] and also by Basolo et al.[3] that the more soluble α-form is a trans-cis isomer and that the other is a cis-cis isomer. This assignment is supported theoretically by Nakamoto et al.[4] Furthermore, Shimura[5] came to the same conclusion with trisalaninato cobalt(III).

The present research has two main purposes: one is an investigation on the preparation of these kinds of complexes, and the other an approach to the structures of the complexes by comparing their absorption spectra with those of model compounds having cis-cis and trans-cis structures. In addition, the thermal stability and the infrared spectra of the complexes are studied.

Experimental

Preparation.—i) *Method Using Cobalt(III) Hydroxide.*—This is essentially the same as the method of Ley and Winkler[6]. To a solution of the desired amino acid was added a slight excess of freshly prepared cobalt(III) hydroxide, and the mixture was heated on a water-bath until a dark red solution was obtained. The resultant solution was filtered once to remove unreacted hydroxide. The filtrate was evaporated on a water-bath almost to dryness. The residue was dissolved in a little hot water, and the solution was filtered, if necessary. On evaporating and then standing the solution, violet crystals of the α-form were obtained. The corresponding β-form was contaminated with the α-form, but the amount of contamination was very small. It was very easy to purify the α-form because of the great difference between the solubilities of the two isomers. By this method the α-isomers of glycine, *dl*-alanine and *l*-leucine were prepared with good yields. Therefore, this method may be recommended as a general method for the α-isomer.

Found: Co, 20.7; N, 14.8. Calcd. for α-[Co(gly)$_3$*]: Co, 20.9; N, 14.9%. Found: Co, 18.1; N, 12.8. Calcd. for α-[Co(ala*)$_3$]: Co, 18.2; N, 13.0%. Found: Co, 11.8; N, 18.4. Calcd. for α-[Co(leu*)$_3$]: Co, 12.8; N, 18.6%.

ii) *Method Using Hexamminecobalt(III) Chloride.*—This method was devised by us though a similar method was reported almost at the same time[7]; the principle is based on the following equation;

$$[Co(NH_3)_6]Cl_3 + 3NH_2CH_2COOH + 3KOH \rightarrow [Co(gly)_3] + 3KCl + 3H_2O + 6NH_3$$

A mixed solution of the desired amino acid with the hexamminecobalt(III) chloride was introduced

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[1] Part V: On the syntheses of metal complexes. Part IV. M. Mori, M. Shibata, E. Kyuno and Y. Okubo, This Bulletin, 31, 940 (1958). Partly presented at the 11 th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

[2] Y. Shimura and R. Tsuchida, This Bulletin, **29**, 311 (1956).

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

[4] K. Nakamoto, J. Fujita, M. Kobayashi and R. Tsuchida, *J. Chem. Phys.*, **27**, 439 (1957).

[5] Y. Shimura, This Bulletin, **31**, 173 (1958).

[6] H. Ley and H. Winkler, *Ber.*, **42**, 3894 (1909).

* The following abbreviations are used:
gly, $NH_2CH_2COO^-$; ala, $NH_2CH(CH_3)COO^-$;
leu, $(CH_3)_2CHCH_2CH(NH_2)COO^-$.

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

into a round flask with an air condenser, and a slight excess of 3 N potassium hydroxide was added to the mixture. The whole was heated until some crystalline materials appeared in it (it took more than 1 hr.). On cooling the contents by holding the flask in running water, fine violet crystals of the β-form separated out. In this step the α-form was not obtained even in traces, but it was produced with a poor yield on evaporating the mother liquor.

From the experiments with glycine, *dl*-alanine and *l*-leucine, it was found that this method was convenient for the preparation of the less soluble β-form.

Found: Co, 19.6; N, 13.8. Calcd. for β-[Co(gly)$_3$]: Co, 19.7; N, 14.0%. Found; Co, 18.5; N, 12.9. Calcd. for β-[Co(ala)$_3$]: Co, 18.2; N, 13.0%. Found: Co, 12.4; N, 8.8%; Calcd. for β-[Co(leu)$_3$]: Co, 12.6; N, 9.0%.

iii) *Method Using Potassium Tricarbonatocobaltate (III).*—The reaction to this method, which was also devised by us, is as follows:

$$K_3[Co(CO_3)_3]+3NH_2CH_2COOH+3CH_3COOH\rightarrow$$
$$[Co(gly)_3]+3CH_3COOK+3H_2O+3CO_2$$

A desired amino acid was poured into a green solution of tricarbonatocobaltate(III) prepared by the method described in a previous paper⁸⁾, and the mixture was warmed on a water-bath for a little while, whereupon the color of the solution changed from green to blue. Then, 6 N acetic acid was added dropwise until the evolution of carbon dioxide ceased and the color of the solution became red-viotet. After filtering the solution, the filtrate was allowed to stand for some time in the cold. Crystals of the less soluble β-form were deposited, and then the α-form separated out on evaporating the mother liquor over sulfuric acid. This method was applied to the same materials as those in i) and ii), and α and β isomers were obtained in about equal amounts.

iv) *Ammoniatriacetatoethylenediaminecobalt(III)*, *[Co en(ata*)]·H_2O*.—About 3 g. of the α-K[Co(ata)(OH)(OH$_2$)]·2H$_2$O prepared by the method described in the previous paper⁹⁾ was suspended in 20 ml. of water, and 6 ml. of a 10% solution of ethylenediamine was added to the suspension. The mixture was warmed on a water-bath until a red-violet solution was obtained. On evaporating the resultant solution over sulfuric acid, dark violet crystals of the desired complex separated out gradually. Yield, about 3 g.

Found: Co, 17.8; N, 12.7. Calcd. for [Co en(ata)]·H$_2$O: Co, 18.1; N, 12.9%.

v) *Citratotriamminecobalt(III)*, *[Co(NH$_3$)$_3$cit**]·H_2O*.—About 5 g. of *cis-cis*-[Co(NH$_3$)$_3$(NO$_3$)$_3$] and 2 g. of potassium citrate were dissolved separately in a little hot water, and the solutions were mixed and warmed on a water-bath for a few minutes. Then, about three volumes of ethanol was added to the solution, whereupon a violet oily material went to the bottom. After removal of the material by a separating funnel, the solution was kept in a refrigerator until fine rosy crystals separated out. This was slightly hygroscopic. Yield, about 1.5 g.

Found: Co, 17.9; N, 12.7. Calcd. for [Co(NH$_3$)$_3$cit]·H$_2$O: Co, 18.6; N, 13.1%.

Of all the complexes prepared here, the ammoniatriacetatoethylenediamine- and the citratotriamminecobalt(III) are to be regarded as new complexes. The aqueous solutions of all the complexes are very stable against acids and heat. Their solubilities in water decrease in the order of the glycinato-, the alaninato- and the leucinato-complexes; while the leucinato-complex is soluble to a certain extent in ethanol, the glycinato-complex is sparingly soluble in it.

Thermal Decomposition and Absorption Spectra.—The thermal decomposition was performed by using a Shimadzu thermal-balance in the same manner as that described in a previous paper⁹⁾. The absorption spectra in solution were measured by a Hitachi EPU spectrophotometer, and the infrared spectra were obtained with a Koken DS 201 infrared spectrophotometer equipped with sodium chloride optics.

Results and Discussion

Thermal Decomposition.—The decomposition curves of the glycinato-, alaninato- and leucinato-complexes are shown in Figs. 1—2 in which the weight loss per formual weight was plotted against temperature. In the case of the β-glycinato-complex, there is a certain weight loss corresponding to one molecule of water at 100~150°C, but there is no such weight loss in the corresponding α-complex. It has been believed that the α-complex has two molecules of water of crystallization, but the compound obtained in the present study is anhydrous. The decompositions of both isomers begin at nearly 220°C, and the weight loss corresponding to three molecules of

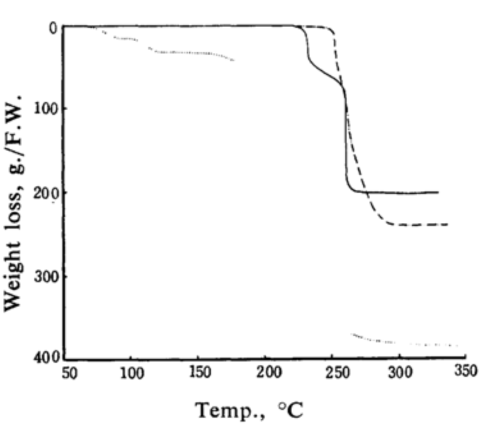

Fig. 1. Thermal decomposition curves of:
—— α-[Co(gly)$_3$]
-·-· α-[Co(ala)$_3$]
······ α-[Co(leu)$_3$]·2H$_2$O

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8) M. Mori, M. Shibata, E. Kyuno and T. Adachi, This Bulletin, 29, 883 (1956).

* Abbreviation ata stands for ammoniatriacetate ion.

9) M. Mori, M. Shibata, E. Kyuno and Y. Okubo, This Bulletin, 31, 940 (1958).

** Abbreviation cit stands for citrate ion.

ammonia is clearly observed at the first stage of decomposition. In the cases of the α- and the β-alaninato-complex there is no evidence for the existence of water of crystallization and the decomposition temperatures are about 250°C. For the α-isomer of the leucinato-complexes, the removal of water takes place in two steps and the total amounts correspond to $2H_2O$. On the other hand, the β-isomer may be anhydrous because no distinct weight loss is observed. The decomposition temperatures are in the neighborhood of 180°C. In general, it may be said that the α-forms are less stable than the corresponding β-forms, though the difference in the decomposition temperature is not very large.

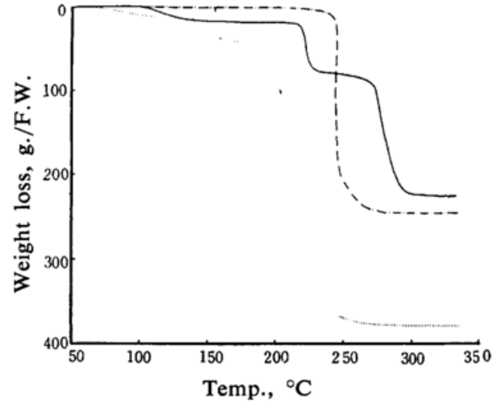


Fig. 2. Thermal decomposition curves of:
—— β-$[Co(gly)_3]\cdot H_2O$
-·-· β-$[Co(ala)_3]$
······ β-$[Co(leu)_3]$

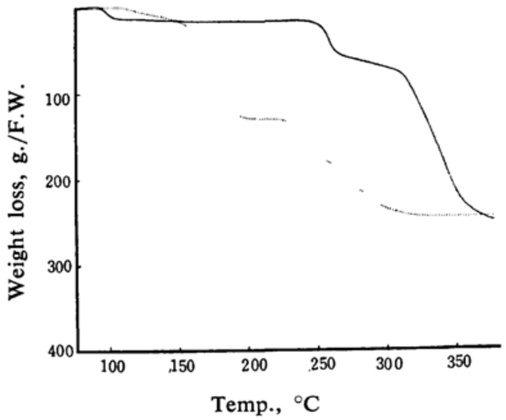


Fig. 3. Thermal decomposition curves of:
—— $[Co\,en(ata)]\cdot H_2O$
······ $[Co(NH_3)_3cit]\cdot H_2O$

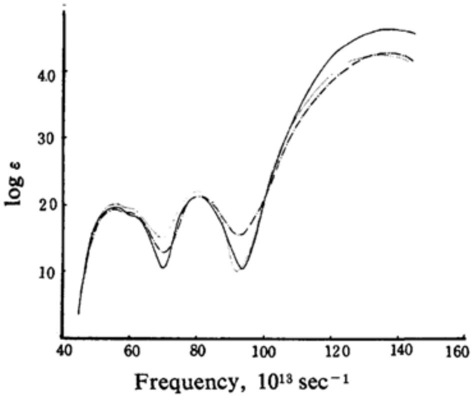


Fig. 4. Absorption spectra of:
—— α-$[Co(gly)_3]$
-·-· α-$[Co(ala)_3]$
······ α-$[Co(leu)_3]\cdot H_2O$

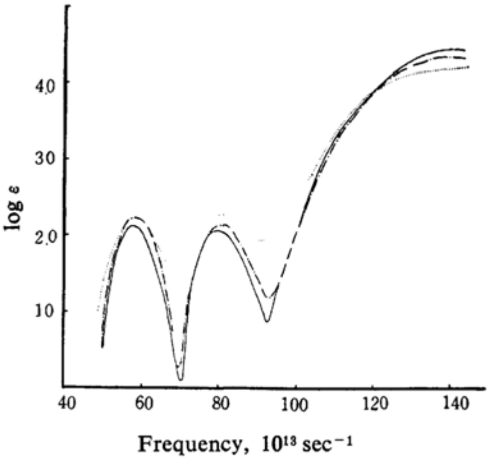


Fig. 5. Absorption spectra of:
—— β-$[Co(gly)_3]$
-·-· β-$[Co(ala)_3]$
······ β-$[Co(leu)_3]\cdot H_2O$

TABLE I. ABSORPTION MAXIMA AND log ε (10^{13}/sec.)

	ν_1	log ε_1	ν_2	log ε_2	ν_3	log ε_3	$\nu_{2\,\text{calcd}}$	Δ
α-$[Co(gly)_3]$	55.4	1.97	80.4	2.15	136.4	4.64	79.18	+1.22
α-$[Co(ala)_3]$	55.6	1.96	80.7	2.16	135.8	4.34	79.42	+1.28
α-$[Co(leu)_3]\cdot 2H_2O$	55.6	2.04	80.0	2.23	135.8	4.30	79.42	+0.58
$[Co\,en(ata)]\cdot H_2O$	57.5	2.20	82.0	2.24	133.9	4.59	81.68	+0.32
β-$[Co(gly)_3]\cdot H_2O$	57.7	2.16	79.6	2.08	140.2	4.45	81.92	−2.32
β-$[Co(ala)_3]$	58.0	2.22	80.4	2.21	—	—	82.27	−1.87
β-$[Co(leu)_3]\cdot H_2O$	58.0	2.27	80.4	2.26	—	—	82.27	−1.87
$[Co(NH_3)_3cit]\cdot H_2O$	56.4	1.58	79.8	1.92	—	—	80.37	−0.57

TABLE II. INFRARED ABSORPTION

Assignment	α-[Co(gly)$_3$]	β-[Co(gly)$_3$]	α-[Co(ala)$_3$]	β-[Co(ala)$_3$]
st NH$_2$	3106(sh)	3356(sh) 3106(sh)	3460(w) 3125(s)	3096(sh)
st-a CO$_2$	1618(vs)	1621(vs) 1585(vs)	1629(vs)	1634(vs) 1582(vs)
st-s CO$_2$	1351(sh)	1350(sh)	1344(sh)	1344(sh)
d, w NH$_2$	1299(m)	1302(s)	1282(s)	1274(vs)
st-a CCN	1233(m)	1205(s)	1238(w)	1250(w)
d, t CH$_2$	1181(s)	1174(s)	1190(m)	1190(m)
d, t NH$_2$	1036(w)	1030(w)	1024(w)	1028(w)
d, r CH$_2$ or d, r NH$_2$	955(w)	963(m)	—	—
st-s CCN	911(m)	919(m)	924(m)	923(m)
d, r NH$_2$ or d, r CH$_2$	819(m) 778(w)	821(m) 776(m)	864(s) 821(w) 806(w)	858(s) 821(sh) 807(m)
d CO$_2$	753(m)	759(w) 755(w)	763(w)	761(w)
?	1133(s)	1149(s)	1126(s)	1124(sh) 1109(m)

* K. Nakamura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 80, 113 (1959). The abbreviations used in the first column of the table of assignments are: st, bond stretching vibration; d, deformation vibration; r, rocking vibration; w, wagging vibration; t, twisting vibration; ?, assignment uncertain; -s, symmetric vibration; -a, asymmetric vibra-

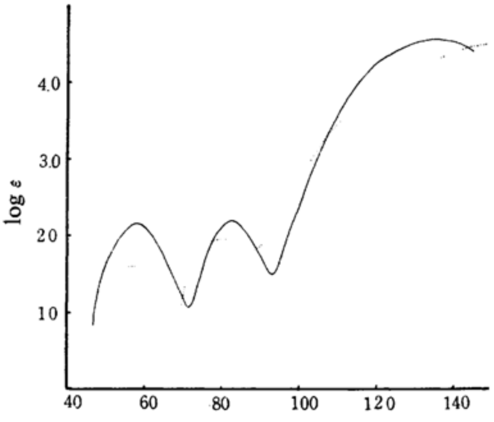


Fig. 6. Absorption spectra of:
—— [Co en(ata)]·H$_2$O
…… [Co(NH$_3$)$_3$cit]·H$_2$O

The decomosition curves for the ammoniatriacetato- and the citrato-complex are shown in Fig. 3. The former complex loses one molecule of water at a temperature below 100°C and begins to decompose at about 240°C. The latter is dehydrated at about 150°C and then decomposed when the temperature is raised.

Visible and Ultraviolet Absorption Spectra.— The absorption spectra of the α- and the β-forms are summarized in Figs. 4 and 5 respectively. The characteristic difference between them is seen in the first and the third bands; all of the first bands of the α-forms are more or less splitted, while those of the β-forms are normal and sharp. The third bands for the α-forms are sharper than those for the β-forms.

The absorption curves of the ammoniatriacetato- and the citrato-complex are shown in Fig. 6. The former complex has a somewhat split first band and a distinct third band, but the latter has a sharp first band and no maximum in the region of the third band.

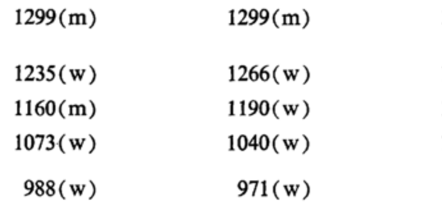
As mentioned above, the ammoniatriacetato-complex is taken as a model for the trans-cis configuration and the citrato-complex for the cis-cis configuration, because ammoniatriacetate ion acts as a tetradentate donor and citrate ion is a tridentate ligand; consequently the most probable structures of the two complexes are thought to be those given in Fig. 7. From the similarity of the absorption spectra, it may be concluded that all the α-forms have the trans-cis structure and the β-forms, the cis-cis. The same conclusion has been reached by others[2,3,5] but a somewhat different approach was adopted in our study.

The numerical data of the absorption spectra of these complexes are summarized in Table I; the absorption maxima for the second bands reveal a general relationship between the α- and β-isomers. In the last two columns of

BANDS(cm^{-1}) FOR AMINOACIDS COMPLEXES

α-[Co(leu)$_3$]	β-[Co(leu)$_3$]	[Co en(ata)]·H_2O	[Co(NH_3)$_3$cit]·H_2O	NH_2-CH_2-COOH*
		3413(w)	3425(sh)	
3175(sh)	3175(sh)	3145(m)	3175(sh)	
	1639(vs)			
1634(vs)	1613(vs)	1631(vs)	1577(vs)	1572(vs)
1325(sh)	1333(s)	1323(m)	1328(s)	1412(s)
1299(m)	1299(m)	1266(m)	1271(m)	1133(m)
				1109(m)
1235(w)	1266(w)	1229(w)	1232(s)	1034(s)
1160(m)	1190(w)	1198(w)	1170(w)	
1073(w)	1040(w)	1059(m)	1067(s)	
988(w)	971(w)	957(w)	938(w)	909(sh)
926(w)	924(w)	913(s)	914(w)	892(s)
847(m)	843(m)	849(sh)	862(s)	
821(w)	820(w)		820(sh)	
794(w)	777(w)			
758(w)	727(s)	758(s)	727(s)	696(s)
1127(w)	1134(w)	1152(s)	1140(s)	

tion. The abbreviation used in the body of the table of assignments to indicate the relative intensities of the absorption are; vs, very strong; s, strong; m, medium strong; w, weak; sh, shoulder.



[Co en(ata)] [Co(NH_3)$_3$cit]

Fig. 7. Probable structures.

the table, the values calculated by a Sone's equation[10] and the differences (Δ) of the calculated values from the observed maxima are given. All of the trans-cis isomers show positive difference and the cis-cis isomers, negative difference.

Infrared Spectra.—The numerical data of the infrared spectra are summarized in Table II, in which the assignment is carried out with reference to papers of Nakamura and others[11]. A distinctive difference between the absorption of α- and β-isomers is observed in the region of 1580~1630 cm^{-1}; there is only one peak for the α-isomer, but the β-isomer has two split absorption peaks. Among the isomers of the same type, the absorption maxima shifted to longer wavelengths in the following order: the leucinato-, the alaninato- and the glycinato-complexes.

Preparation.—It is very interesting that the methods mentioned in the Experimental section above have preferential properties for the production of cis-cis and trans-cis isomers; the cobalt(III) hydroxide method favors the trans-cis, the hexammine method is advantageous for the cis-cis, and the tricarbonato method gives both isomers in the about the same amount. Therefore, somewhat different mechanisms may be involved in these methods and perhaps in the formation of the isomers; the decisive factor is which of the nitrogen and oxygen atoms of the incoming donor attacks the objects first.

Summary

Three different methods were investigated of the preparation of trisglycinato-, trisalaninato- and trisleucinato-cobalt(III). The method using cobalt(III) hydroxide is convenient for the α-form, the method using hexamminecobalt(III) salt is advantageous for the β-form, and the method using tricarbonatocobaltate(III) gives both forms of the complexes. In addition, two new isomers of [Co en(ata)]·H_2O and [Co(NH_3)$_3$cit]·H_2O having trans-cis and cis-cis

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[10] K. Sone, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **71**, 270 (1950).

[11] K. Nakamura, ibid., **80**, 113 (1959): S. Mizushima and I. Nakagawa, ibid., **80**, 124 (1959).

configurations with respect to the coordinated atoms were synthesized.

By comparing the visible and the ultraviolet absorption spectra, it was concluded that the α-form is a trans-cis isomer and that the β-form is a cis-cis isomer. Thermal decomposition of the complexes was performed in order to estimate the water of crystallization and the stability. The infrared spectra of the complexes were also measured.

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