Studies on the Cobalt(III) Complexes Containing Only One Chelate Ring. I. Syntheses of $[Co(NH_3)_4gly]X_2$ *and* $[Co(NH_3)_4alan]X_2$[1].

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Limited number of cobalt(III) complexes which contain only one chelate ring are known, in contrast with the numerous series of those containing two chelate rings. The most familiar examples of such "mono-chelate cobalt(III) complexes" hitherto known are monocarbonato-tetrammine and monoxalato-tetrammine complexes. Mono(amino-acido)-tetrammine or monoethylenediamine-tetrammine cobalt(III) complexes were not known heretofore. Recently, Kuebler and Bailar[2] reported that the attempted replacement of the chloride ion or the sulfono group[3], respectively, in $[Co(NH_3)_4Cl_2]^+$ and $[Co(NH_3)_4(SO_3)_2]^-$ by *N, N*-diethylglycine was unsuccessful.

In the present paper, the syntheses of monoglycinato-tetrammine and mono-alaninato-tetrammine Co(III) complexes will be reported. Furthermore, the visible and ultraviolet absorption spectra of the (amino-acido)-ammine series of Co(III) complexes will be discussed mainly in relation to the geometrical structures of the complex ions.

Results and Discussion

Method of Syntheses.—For the first place, the reactions between sodium glycinate and $[Co(NH_3)_4(OH_2)_2]^{3+}$ or $[Co(NH_3)_4(OH_2)Cl]^{2+}$ were investigated. Evidences for the formation of some glycinato complexes were obtained, but the complexes were not isolated in pure state. Next, the use of decolorizing charcoal as catalyst[4] was examined. However, in the presence of charcoal glycinate radical gradually expelled the co-ordinated ammonia molecules and consequently the desired tetrammine complexes were not obtained.

Lastly, therefore, the reaction of $[Co(NH_3)_4(OH_2)Cl]SO_4$ with sodium glycinate was examined in the presence of decolorizing charcoal and of aqueous ammonia (see experimental part). This procedure produces a mixture of three or more species of the complex ions which belong to the glycinato-ammine series. From the mixture, $[Co(NH_3)_6]^{3+}$ was removed as the sparingly soluble chloride-sulfate, $[Co(NH_3)_6]Cl\cdot SO_4\cdot 3H_2O$, and the desired complex $[Co(NH_3)_4gly]^{2+}$ was separated as sulfate from the mother liquor*. The yield did not exceed 30%. As a by-product, $[Co(NH_3)_2gly_2]Cl$ was also obtained in a small yield.

The reaction between sodium alaninate and $[Co(NH_3)_4(OH_2)Cl]SO_4$ proceeds in a similar way. In this case an amount of tris-alaninato cobalt(III) complex also yielded.

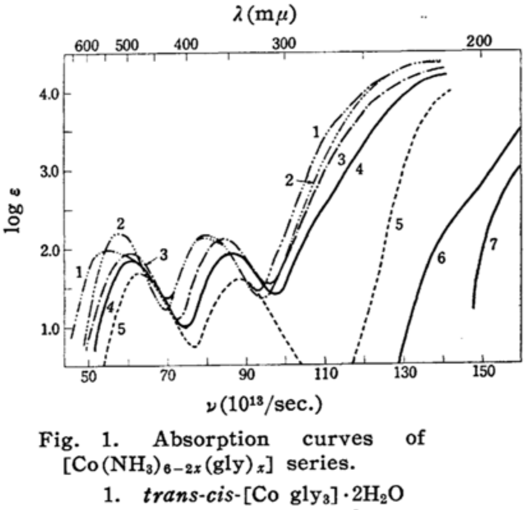

Fig. 1. Absorption curves of $[Co(NH_3)_{6-2x}(gly)_x]$ series.

1. *trans-cis*-$[Co\,gly_3]\cdot 2H_2O$
2. *cis-cis*-$[Co\,gly_3]\cdot H_2O$
3. $[Co(NH_3)_2gly_2]Cl$
4. $[Co(NH_3)_4gly]SO_4\cdot H_2O$
5. $[Co(NH_3)_6](ClO_4)_3$
6. $NH_2CH_2CO_2Na$[5]
7. NH_3[5]

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[1] Partly presented at the Symposium on Co-ordination Compounds, Tokyo, October 28, 1956.

[2] J. R. Kuebler, Jr. and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **74**, 3535 (1952).

[3] The "sulfono group" is $SO_3^=$ radical bound to the central metal ion by the sulfur atom: See Y. Shimura, This Bulletin, **25**, 46 (1952).

[4] J. C. Bailar, Jr. and J. B. Work, *J. Am. Chem. Soc.*, **67**, 176 (1945).

* The following abbreviations are used: am, amino-acid radical in general; gly, $NH_2\cdot CH_2\cdot CO_2^-$; alan, $NH_2\cdot CH(CH_3)\cdot CO_2^-$.

TABLE I

ABSORPTION DATA OF $[Co(NH_3)_{6-2x}(gly)_x]$ AND $[Co(NH_3)_{6-2x}(alan)_x]$ SERIES.

Complex ion	First absorption band				Second absorption band				$\Delta(\nu_{max})$[e]	$(\log \varepsilon_{max})$[f]
	ν_{max} (10^{13} /sec.)	$\log \varepsilon_{max}$	l[b] (10^{13} /sec.)	δ[c] (10^{13} /sec.)	ν_{max} (10^{13} /sec.)	$\log \varepsilon_{max}$	l[b] (10^{13} /sec.)	δ[c] (10^{13} /sec.)		
$[Co(NH_3)_6]^{3+}$	62.9	1.68	10.3	0.5	88.3	1.60	12.5	0.35	25.4	−0.08
$[Co(NH_3)_4gly]^{2+}$	60.8	1.86	11.3	0.55	86.4	1.93	12.3	0.35	25.6	+0.07
$[Co(NH_3)_2gly_2]^+$	60.4	1.94	11.3	0.25	84.3	2.11	11.8	0.5	23.9	+0.17
cis-cis-$[Co\ gly_3]$[d]	57.7	2.20	9.1	0.55	80.2	2.14	12.7	0.6	22.5	−0.06
trans-cis-$[Co\ gly_3]$	55.2[a]	1.99	—	—	80.4	2.16	12.1	0.35	—	—
$[Co(NH_3)_4alan]^{2+}$	61.5	1.87	11.0	0.6	86.7	1.90	12.8	0.4	25.2	+0.03
cis-cis-$[Co\ alan_3]$[d]	57.9	2.27	9.0	0.6	80.3	2.21	11.7	0.7	22.4	−0.06
trans-cis-$[Co\ alan_3]$[d]	55.6[a]	2.00	—	—	80.9	2.18	12.3	0.5	—	—

a: This band splits into two or more components (see Figs. 1 and 2).

b: l=half-value width. This corresponds to $\{\delta(+)+\delta(-)\}$ in Jørgensen's notation[6)].

c: δ=inclination parameter[7)] or Inklination (in German)[8)]. This parameter corresponds to $\frac{1}{2}\{\delta(+)-\delta(-)\}$ in Jørgensen's notation[6)], and is defined by the equation $\delta=\frac{1}{2}\{\nu_k+\nu_l\}-\nu_{max}$, where ν_k and ν_l are the two frequencies where the formal extinction coefficients are equal to the half of ε_{max}.

d: Measured in 60 % perchloric acid.

e: Frequency difference between the maxima of the second and the first absorption band.

f: Difference between $\log \varepsilon_{max}$'s of the second and the first band.

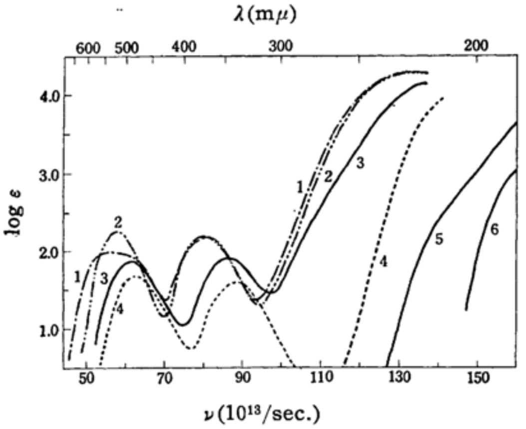


Fig. 2. Absorption curves of $[Co(NH_3)_{6-2x}(alan)_x]$ series.

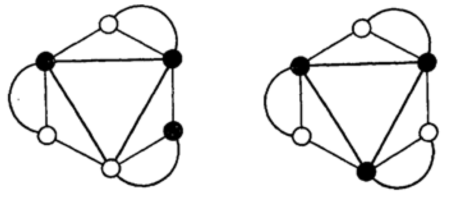
1. *trans-cis*-$[Co\ alan_3]$
2. *cis-cis*-$[Co\ alan_3]$
3. $[Co(NH_3)_4alan]SO_4$
4. $[Co(NH_3)_6](ClO_4)_3$
5. $NH_2CH(CH_3)CO_2Na$[5)]
6. NH_3[5)]

The aqueous solutions of the $[Co(NH_3)_4\ am]X_2$-type complexes are rather unstable. These complexes can be recrystallized from warm water, but hot water decomposes the complexes.

Absorption Spectra.—The absorption curves of the cobalt(III) complexes which belong to the glycinato-ammine and the alaninato-ammine series are shown in Figs. 1 and 2. The numerical data of the first and the second absorption bands of these complexes are summarized in Table I.

As is seen in the figures and the table, the successive substitution of ammonia ligands in those complexes by the glycinate or the alaninate ions causes the regular red-shifts of the band maxima and the regular increase in the absorption intensities. The alaninate ion has a slightly higher position in the spectrochemical series[9),10)] than the glycinate ion.

The two isomers, α(violet) and β(red), are known for the complexes of $[Co^{III}am_3]$ type. The two forms correspond to the geometrical isomers, *cis-cis* and *trans-cis* forms (Fig. 3). As will be seen



α (*trans-cis*, violet) β (*cis-cis*, red)

Fig. 3. Two geometrical isomers of $[Co^{III}am_3]$. (white circle, oxygen atom; black circle, nitrogen atom)

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5) H. Ley and B. Arends, *Z. physik. Chem.*, **B 17**, 117 (1932).

6) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).

7) Y. Shimura and R. Tsuchida, This Bulletin, **28**, 572 (1955).

8) H. Siebert and M. Linhard, *Z. physik. Chem.*, *N. F.*, **11**, 318 (1957).

9) R. Tsuchida, This Bulletin, **13**, 388, 436 (1938).

10) Y. Shimura and R. Tsuchida, ibid., **29**, 311 (1956).

in Figs. 1 and 2, the main difference between the absorption curves of the two isomers occurred in the first absorption bands. Thus the first band of the β-isomer has a normal pseudo-parabolic form, while that of the α-form distinctly shows an indication of splitting. This splitting may be considered as a proof of the *trans-cis* structure of the α-form, since a similar splitting was reported for the first band of *trans* isomer of $[Co(NH_3)_4(OCOCH_3)_2]ClO_4$ and not for that of the corresponding *cis* isomer[11]. The above conclusion was reported briefly in a previous report[10]. Independently, Basolo et al.[12] came to the same conclusion. The assignment is also supported by the semi-empirical molecular orbital calculations by Nakamoto et al.[13] and by Yamatera[14].

Five geometrical isomers are possible for the complex ion, $[Co(NH_3)_2 gly_2]^{2+}$ (Fig. 4). In the present study only one species was obtained. Since the first band of the species has no indication of splitting, it has probably a *cis* structure concerning the two oxygen atoms of the two glycinate ligands, i. e., one of (a), (c) or (d) in Fig. 4.

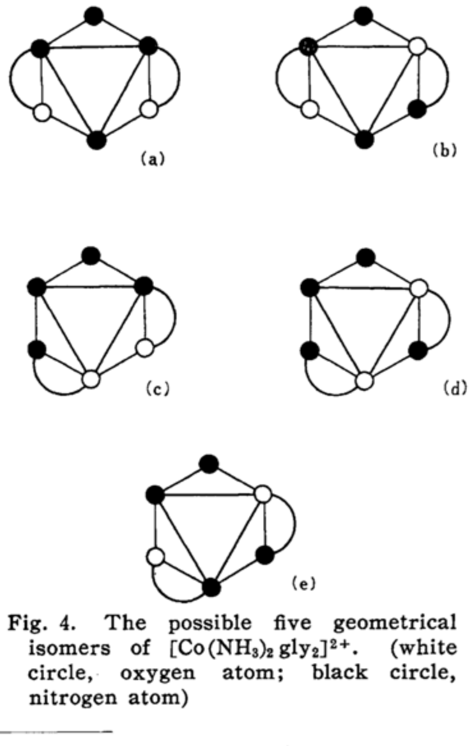

Fig. 4. The possible five geometrical isomers of $[Co(NH_3)_2 gly_2]^{2+}$. (white circle, oxygen atom; black circle, nitrogen atom)

Experimental

Glycinato-tetrammine cobalt(III) sulfate monohydrate, $[Co(NH_3)_4 gly]SO_4 \cdot H_2O$ — Two grams of glycine and one gram of Na_2CO_3 were dissolved in 6 ml. of warm water. To this solution were added 7.4 g. of $[Co(NH_3)_4(OH_2)Cl]SO_4$[15], 0.5 g. of decolorizing charcoal and 0.5 ml. of aqueous ammonia (28 %). The resulting mixture was evaporated on a water bath almost to dryness. The residue was treated with about 60 ml. of warm water and any sparingly soluble materials were filtered off by suction. Upon cooling, some amount of $[Co(NH_3)_6]SO_4 \cdot Cl \cdot 3H_2O$* separated from the filtrate in orange-yellow crystals. After removal of the orange-yellow crystals by filtration, a large amount of 95 % ethanol was added to the filtrate. The desired complex separated as the orange precipitate. This was separated by filtration from the red-colored mother liquor. (This mother liquor contains $[Co(NH_3)_2 gly_2]Cl$.) The crude product was much contaminated by the orange-yellow crystals above mentioned. Therefore it was recrystallized from warm water or by the addition of ethanol to the cold aqueous solution. Three or more recrystallizations were necessary to obtain the pure products. The pure crystals are orange-red plates and effloresced on exposure to the air. The freshly dried crystals were analyzed for water of crystallization.

Anal. Found: H_2O, 5.27 %. Calcd. for $[Co(NH_3)_4 gly]SO_4 \cdot H_2O$: H_2O, 5.72 %.

The analyses for the following components were performed by use of the salts dehydrated at 90–100°C.

Anal. Found: Co, 19.4; C, 8.40; H, 5.50; SO_4^{--}, 32.18 %; Calcd. for $[Co(NH_3)_4(NH_2CH_2Co_2)]SO_4$: Co, 19.83; C, 8.08; H, 5.43; SO_4^{--}, 32.32 %.

Bisglycinato-diammine cobalt(III) chloride, $[Co(NH_3)_2 gly_2]Cl$—The red colored mother liquor above mentioned was evaporated in vacuo over sulfuric acid at room temperature. The separated red precipitates were dissolved in hot water and filtered. After cooling, 99 % ethanol was added to the filtrate. The pure product was precipitated as red crystals.

Anal. Found: C, 17.45; H, 4.96; Cl, 12.4 %. Calcd. for $[Co(NH_3)_2(C_2H_4O_2N)_2]Cl$: C, 17.37; H, 5.10; Cl, 12.82 %.

Alaninato-tetrammine cobalt(III) sulfate, $[Co(NH_3)_4 alan]SO_4$—One gram of sodium carbonate and 2.4 g. of *dl*-α-alanine were dissolved in 6 ml. of warm water. To this solution were added 7.4 g. of $[Co(NH_3)_4(OH_2)Cl]SO_4$[15], 0.5 g. of decolorizing charcoal and 0.4 ml. of aqueous ammonia (30 %). The resulting mixture was evaporated on a water bath almost to dryness. The residue was treated with about 100 ml. of

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[11] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **264**, 321 (1951).

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

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

[14] H. Yamatera, presented at the Symposium on Coordination Compounds, Osaka, October 30, 1955.

[15] S. M. Jørgensen, *J. prakt. Chem.*, **42**, 211 (1890).

* *Anal.* Found: Co, 17.4; H_2O, 15.85%. Calcd. for $[Co(NH_3)_6]SO_4 \cdot Cl \cdot 3H_2O$: Co, 17.00; H_2O, 15.53%.

warm water and any sparingly soluble materials** were filtered off by suction. When the filtrate was cooled, some amount of orange-yellow crystals, $[Co(NH_3)_6]SO_4 \cdot Cl \cdot 3H_2O$, separated. After removal of the orange-yellow crystals by filtration, a large amount of 95 % ethanol was added to the filtrate. The crude complex was obtained as orange precipitate. This was separated by filtration from the red mother liquor. The product was much contaminated by the orange-yellow crystals above mentioned. Therefore, this was dissolved in warm water and fractionally precipitated by addition of ethanol. The contaminants were concentrated in the first fraction. The second and the following fractions were put together and precipitated twice more by the same manner. The orange red crystals obtained were washed with 95 % ethanol and dried in air. The crystals dried in air contained 1—1.5 moles of water of hydration. This was completely dehydrated by heating at about 100°C.

Anal. Found: SO_4^{--}, 31.30 %. Calcd. for $[Co(NH_3)_4(C_3H_5O_2N)]SO_4$: SO_4^{--}, 30.87 %.

By evaporation of the red mother liquor above mentioned, a small amount of red crystals separates, and this is probably $[Co(NH_3)_2\,alan_2]Cl$. Further studies were not intended for this complex, since only a small amount of the sample was available.

trans-cis-[Co gly_3]$\cdot 2H_2O$, ***cis-cis***-[Co gly_3]$\cdot H_2O$, ***trans-cis***-[Co $alan_3$] and *cis-cis*-[Co $alan_3$] were prepared by the method of Ley and Winkler[16] with reference to the report of Holtzclaw and Sheetz[17]. $[Co(NH_3)_6](ClO_4)_3$ was prepared by the method of Linhard[18].

Absorption Measurement.—The absorption spectra of *cis-cis*-[Co gly_3] and the two isomers of [Co $alan_3$] were measured in 60 % perchloric acid. The aqueous solutions were used for the other complexes. The concentrations of the solutions varied from 1.0×10^{-2} to 0.5×10^{-4} gram complexion per liter. The absorption measurements were made by a Beckman DU spectrophotometer at room temperature.

Summary

The three new complexes, $[Co^{III}(NH_3)_4\,gly]SO_4 \cdot H_2O$, $[Co^{III}(NH_3)_4\,alan]SO_4$ and $[Co^{III}(NH_3)_2\,gly_2]Cl$, have been synthesized by the reaction of $[Co(NH_3)_4(OH_2)Cl]SO_4$ with the amino-acid radicals in the presence of ammonia and decolorizing charcoal.

The visible and the ultraviolet absorption spectra of the glycinato-ammine and alaninato-ammine series of cobalt(III) complexes have been measured and discussed in relation to the geometrical structures of the complex ions.

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** This is a mixture of decolorizing charcoal and the two isomers of [Co^{III} $alan_3$].

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

[17] H. F. Holtzclaw, Jr. and D. P. Sheetz, *J. Am. Chem. Soc.*, **75**, 3053 (1953).

[18] M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).