Studies on the Synthesis of Metal Complexes. IV[1]. *The Cobalt(III) Complexes of Ammoniatriacetic Acid*

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It is commonly known that ammoniatriacetic acid (ATA) acts as a tetradentate donor in combining with metal ions, and this has been proved by Schwarzenbach and his co-workers[2] by the titration of the acid with a base in the presence of a number of metal ions. In the event that one molecule of ATA co-ordinates to a cobalt(III) ion having a co-ordination number six, it is to be expected that two positions around the cobalt ion, not occupied by the chelating agent, are filled by solvent molecules or other donors in the solution. On the other hand, if two molecules of ATA combined with the ion, it would be expected that the two nitrogen atoms and four of the carboxyl groups participate in the bonding, and the remaining two carboxyl groups are uncomplexed. It was the purpose of this investigation to ascertain whether ATA could behave in this way. A few complexes containing only one ammoniatriacetate ion per cobalt(III) as a quadrivalent ligand have been isolated and identified by chemical analysis, thermal decomposition, absorption spectroscopy etc. The attempt to prepare a complex containing

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[1] Presented at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April 6, 1957. For a previous paper in this series see M. Mori, M. Shibata, E. Kyuno and K. Hoshiyama, This Bulletin, **31**, 291 (1958).

[2] G. Schwarzenbach et al., *Helv. Chim. Acta*, **28**, 828 (1945); G. Schwarzenbach and W. Biedermann, ibid., **31**, 331 (1948).

TABLE I
ANALYTICAL RESULTS (amounts in %)

	Co		N		K		H_2O	
	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.	calcd.	obsd.
α-K[Co ata(OH)(OH_2)]$\cdot 2H_2O$	16.5	16.1	3.86	3.75	10.9	10.4	10.1	10.3
β-K[Co ata(OH)(OH_2)]$\cdot 3H_2O$	15.7	16.0	3.75	3.66	10.4	9.8	14.4	14.0
K_2[ataCo$(OH)_2$Co ata]$\cdot 6H_2O$	16.5	16.0	3.97	3.89	10.9	10.9	15.2	15.5
K_2[Co ata(CO_3)]$\cdot H_2O$	14.6	14.2	3.47	3.19	19.3	19.0	4.5	4.7
K_2[Co ata(C_2O_4)]$\cdot H_2O$	13.6	13.4	3.24	—	18.1	17.9	4.2	4.2

two ammoniatriacetate ions was unsuccessful.

Experimental

Synthesis. — 1) *α-Form of potassium hydroxoammoniatriacetatoaquocobaltate(III)*, α-K[Co ata(OH)(OH_2)]$\cdot 2H_2O$*. — To a solution of 4 g. of ATA in 25 ml. of 2.5 N potassium bicarbonate were added 5 g. of cobalt chloride hexahydrate and 1 ml. of 30% hydrogen peroxide, and the mixture was placed in an ice-bath until blue crystals separated out (about 5 hr.). The crystals were filtered, washed several times with a little cold water, dissolved in a little hot water containing potassium acetate and then recrystallized by the usual procedure. The product was washed with ethanol and ether in turn. Yield, about 1 g. This complex will hereafter be referred to as α-form. It is slightly soluble in water and is converted into another variety (β-form) by heating the solution or acidifying it with acetic acid.

2) *β-Form of potassium hydroxoammoniatriacetatoaquocobaltate(III)*, β-K[Co ata(OH)(OH_2)]$\cdot 3H_2O$.—This was prepared from a filtrate in 1); after the filtrate was acidified with 6N-acetic acid (about 10 ml.), a large amount of ethanol was added to it, and the solution was kept overnight in a refrigerator. The reddish violet crystals deposited were collected and recrystallized from the cooled solution by the addition of ethanol. The final product was washed with ethanol and ether. Yield, about 2.5 g.

3) *Potassium bis-(ammoniatriacetato)-μ-dioldicobaltate(III)*, K_2[ata Co$(OH)_2$Co ata]$\cdot 6H_2O$. — This also was prepared from a separate filtrate in 1); after the filtrate was acidified with 1 N-hydrochloric acid (about 5 ml.), the solution was heated on a boiling water-bath until a pink solution appeared. On cooling, pink precipitates began to appear, which were collected and dissolved in hot water and reprecipitated by cooling and washed with ethanol and ether in turn. Yield, about 2 g.

4) *Potassium carbonatoammoniatriacetatocobaltate(III)*, K_2[Co ata(CO_3)]$\cdot H_2O$. — Approximately 4 g. of ATA was added to a cold green solution of potassium tricarbonatocobaltate(III) prepared from 20 g. of $KHCO_3$ and 10 g. of $CoCl_2\cdot 6H_2O$ $-$5 ml. of 30% H_2O_2 by the previous method[3]. The mixture was warmed on a water-bath until the green color of the solution changed into violet (about 10 min.). After the solution was cooled, about an equal volume of ethanol was added to it and the whole was kept overnight in a refrigerator. The crystals were recrystallized from water in the hot. They were brilliant violet in color. Yield, about 2.5 g.

5) *Potassium oxalatoammoniatriacetatocobaltate (III)*, K_2[Co ata(C_2O_4)]$\cdot H_2O$.—About 3.5 g. of the α-form obtained in 1) was dissolved in 25 ml. of 2 N-potassium acetate solution containing 1.3 g. of oxalic acid. The solution was warmed on a water-bath until the color changed to reddish violet, and then cooled and about 12 ml. of ethanol was added, whereupon crystallization of the substance took place. It was recrystallized in the form of bright, reddish-violet needles. This was also obtained by using the β-form or the carbonato-complex obtained in 4).

Determination of the Chemical Formulae. —For this purpose, chemical analysis, thermal decomposition, coagulation of ferric oxide sol and spectroscopic measurement were used in the same manner as described in the previous papers[3,4].

Results and Discussion

Chemical Analysis. — The numerical values are given in Table I. The water of crystallization was estimated from the weight loss in the thermal decomposition. For the determination of cobalt and potassium, the residues from the thermal decompositions of the complexes were used as samples. The nitrogen content was determined by Kjeldahl's method.

Thermal Decomposition. — When a sample was heated with gradual elevation of temperature up to nearly 300°C, decomposition took place in several steps, and finally a residue containing an oxide of cobalt (perhaps, Co_2O_3) and potassium carbonate was left behind. Decomposition curves showing the weight loss per millimole vs. temperature are shown in Fig. 1.

It may be noted that the weight loss of the β-form at 150∼190°C corresponds closely to one molecule of water (curve

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* "ata" stands for ammoniatriacetate ion.

[3] M. Mori et al., This Bulletin, **29**, 883 (1956).

[4] M. Mori et al., This Bulletin, **31**, 291 (1958).

2). In fact the product had exactly the same pink color as the diol-complex reported in the previous syntheses. However, the weight loss of the α-form in the same temperature range is too great for one to assume the formation of the diol-complex and it is at present unknown what happens in that stage (curve 1). In the case of the carbonato- and the oxalato-complexes, the weight loss corresponding to removal of a carbonate or an oxalate ion from each of the complexes was observed prior to the final decomposition (curves 4 and 5).

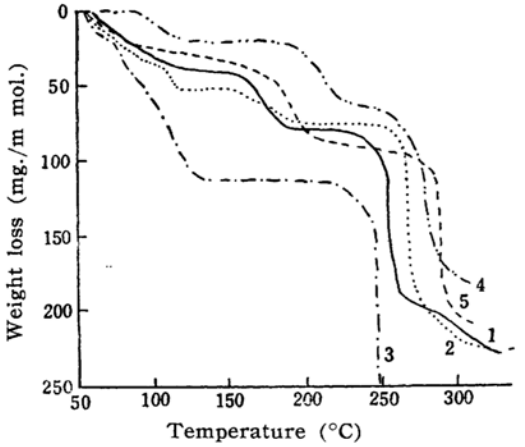
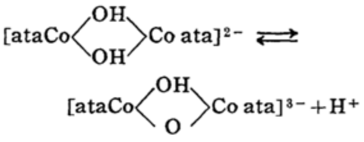


Fig. 1. Thermal decomposition curves of:
1. α-K[Co ata(OH)(OH$_2$)]$\cdot$2H$_2$O
2. β-K[Co ata(OH)(OH$_2$)]$\cdot$3H$_2$O
3. K$_2$[ataCo(OH)$_2$Co ata]$\cdot$6H$_2$O
4. K$_2$[Co ata(CO$_3$)]$\cdot$H$_2$O
5. K$_2$[Co ata(C$_2$O$_4$)]$\cdot$H$_2$O

Coagulation Value.—Nakahara and coworkers[5] have given 6.6 mF and 0.48 mF as the average values for uni- and bivalent complex anions respectively, but the values obtained in the present experiment deviated from the average to a considerable extent. Namely, (i) α-K[Co ata(OH)(OH$_2$)]...2 mF, (ii) β-K[Co ata(OH)(OH$_2$)]... 0.6 mF, (iii) K$_2$[Co$_2$(ata)$_2$(OH)$_2$]...0.2 mF, (iv) K$_2$[Co ata(CO$_3$)]...0.3 mF, (v) K$_2$[Co ata(C$_2$O$_4$)]...0.3 mF.

Among these, the values for the species of the β-form and the diol-salt are too low for a uni- or a bivalent anion respectively, but they may be explained by assuming the following reactions;

$$[\text{Co ata(OH)(OH}_2)]^- \rightleftarrows [\text{Co ata(OH)}_2]^{2-}+\text{H}^+$$



$$[\text{ataCo}\overset{\text{OH}}{\underset{\text{OH}}{\langle\,\rangle}}\text{Co ata}]^{2-} \rightleftarrows [\text{ataCo}\overset{\text{OH}}{\underset{\text{O}}{\langle\,\rangle}}\text{Co ata}]^{3-}+\text{H}^+$$

As an evidence for these equilibria, it was found that the pH values of the β-form and the diol-salt were 5.8 and 3.6 in the M/500 solutions. The coagulation value for the α-form is also lower than the average, but this deviation may be attributed to partial conversion into the β-form, because the sample solution was prepared by heating.

Visible and Ultraviolet Absorption Spectra.—All the absorption curves are shown in Figs. 2 and 3, and the numerical data are given in Table II. As is seen in Fig. 2, the curves 1 and 2 have shoulders at about 100×10^{13}/sec. probably owing to the ligand OH$^-$ in the complex radicals. This is supported by the fact that the shoulder disappears in an acidified solution but remains in an alkaline solution, as are illustrated by the curves 3 and 4.

The curve 1 in Fig. 3 also has a shoulder at nearly the same frequency as the above and this may be considered as a specific band of diol-bond, because a similar band has been found in octammine-μ-diol-dicobalt(III) salt[6].

For the carbonato- and the oxalato-complex, the absorption curves are similar to each other in appearance (Figs. 3-2 and 3). It may be noted that both complexes are perhaps the first examples represented by the general type [CoNO$_5$].

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

	ν_1	log ε_1	ν_2	log ε_2	ν_s	log ε_s	ν_3	log ε_3
α-K[Co ata(OH)(OH$_2$)]$\cdot$2H$_2$O	54.25	2.28	74.62	2.48	ca 100	3.54	132.74	4.21
β-K[Co ata(OH)(OH$_2$)]$\cdot$3H$_2$O	55.56	1.72	73.89	1.73	ca 100	2.94	134.53	3.69
K$_2$[ataCo(OH)$_2$Co ata]$\cdot$6H$_2$O	58.36	1.65	—	—	ca 100	2.54	—	—
K$_2$[Co ata(CO$_3$)]$\cdot$H$_2$O	53.19	2.22	77.32	2.18	—	—	123.97	4.09
K$_2$[Co ata(C$_2$O$_4$)]$\cdot$H$_2$O	54.55	2.30	77.32	2.29	—	—	127.12	4.33

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[5] S. Nakahara et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 488 (1953).

[6] Y. Inamura and Y. Kondo, ibid., **74**, 627 (1953).

Fig. 4 is a diagram in which the frequency values for the first band of the complexes belonging to the types $[CoN_5O]$, $[CoN_3O_3]$ and $[CoNO_5]$ are plotted against the number of nitrogen atoms co-ordinated.

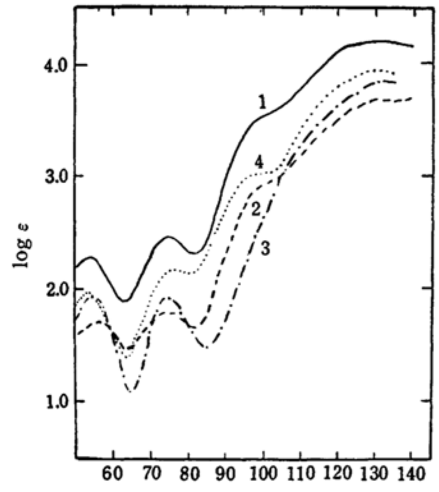

Fig. 2. Absorption spectra of:
1. α-K[Co ata(OH)(OH_2)] (aqueous sol.)
2. β-K[Co ata(OH)(OH_2)] (aqueous sol.)
3. β-K[Co ata(OH)(OH_2)] (at pH 2.6)
4. α-K[Co ata(OH)(OH_2)] (at pH 13.3)

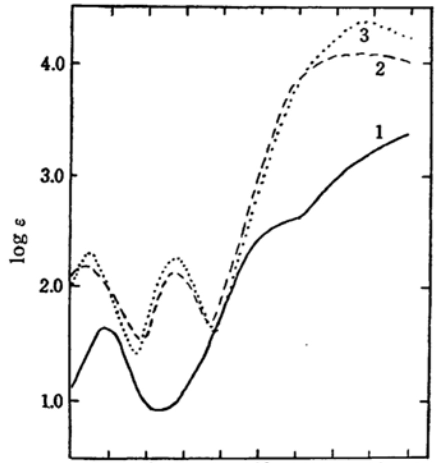

Fig. 3. Absorption spectra of:
1. K_2[ataCo$(OH)_2$Co ata]
2. K_2[Co ata(CO_3)]
3. K_2[Co ata(C_2O_4)]

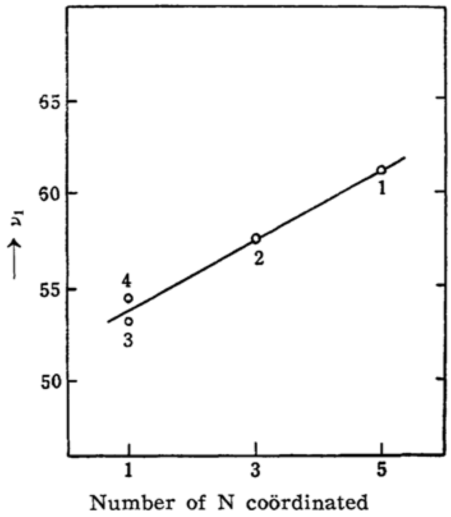

Fig. 4. Frequency position of:
1. $[Coen_2(gly)]ClO_4$[7]
2. β-$[Co(gly)_3]$[7]
3. K_2[Co ata(CO_3)]
4. K_2[Co ata(C_2O_4)]

Infrared Spectra.—These were measured in order to confirm the fact that the three carboxyl groups in the chelate agent were complexed. Strong split bands were observed at 1718 and 1735 cm^{-1} for the free acid. On the other hand, the α-form shows bands at 1672 and 1618 cm^{-1}, the β-form at 1667 cm^{-1} and the diol-salt at 1600 cm^{-1}. It is obvious that these bands are due to the co-ordinated carboxyl groups since such an assignment has been best established for the EDTA-complexes[8].

Structure. — The structures of the complexes must be considered on the basis of the above discussion. In the case of the α- and the β-form, a type of isomerism illustrated by formula I and II in Fig. 5 is possible and to the other complexes the structures illustrated by formula III, IV and V may be assigned. It is hard to say conclusively, which of the formulae, I or II, is the α-form and which the β-form, but an assumption is possible based upon the following discussion.

In the previous paper[3], the authors reported that the absorption maximum of the first band for the blue variety of potassium dicarbonatodiamminecobaltate $K[Co(NH_3)_2(CO_3)_2]$, shifted to a somewhat longer wave length than that for the corresponding violet variety, and the former variety may be *cis*- and the latter *trans*-form. The same relationship exists in the present case, too; the α-form has a maximum at longer wave length than the β-form (Table II). In addition to this, when the fact that ligands H_2O and NH_3 stand in a near position and ligands OH^- and CO_3^{2-}

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[7] Y. Shimura and R. Tsuchida, This Bulletin, **28**, 573 (1955).

[8] D. H. Bush and J. C. Bailar *J. Am. Chem. Soc.*, **75**, 4574 (1953); **78**, 716 (1956).

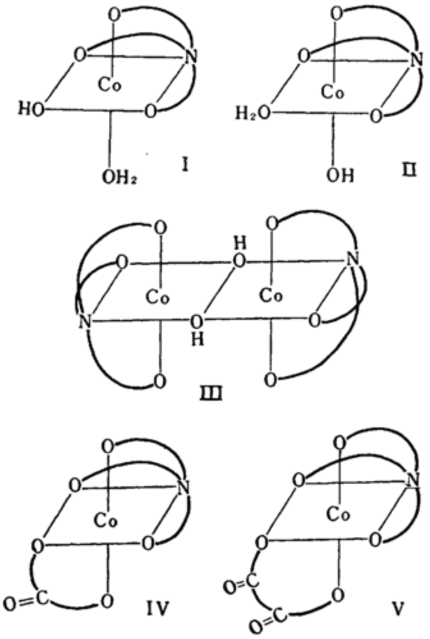

Fig. 5. Structural formulae.

in almost the same position of the spectrochemical series is taken into consideration*, formula I in which ligand H_2O is cis to the co-ordinated nitrogen atom will be assigned to the α-form.

Summary

The cobalt(III) complexes containing ammoniatriacetato group (ata) as a quadridentate ligand are newly prepared:

i) α-K[Co ata(OH)(OH$_2$)]$\cdot 2H_2O$
ii) β-K[Co ata(OH)(OH$_2$)]$\cdot 3H_2O$
iii) K_2[ataCo(OH)$_2$Co ata]$\cdot 6H_2O$
iv) K_2[Co ata(CO$_3$)]$\cdot H_2O$
v) K_2[Co ata(C$_2$O$_4$)]$\cdot H_2O$

In order to determine the structural formulae of these complexes, their visible, ultraviolet and infrared spectra were measured, as well as their thermal decomposition and their potency to coagulate ferric oxide sol.

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* NO_2^- SO_3^{2-} en NH_3 $\begin{matrix}ONO^-\\NCS^-\\OH_2\end{matrix}$ $C_2O_4^{2-}$ $\begin{matrix}ONO_2^-\\OSO_3^{2-}\end{matrix}$
$\begin{matrix}OCHO^-\\OH^-\\CO_3^{2-}\\OCOR^-\end{matrix}$ ………………