

## 177. *The Preparative Chemistry of Cobalt(III) Complexes Starting from Tricarbonatocobaltate(III)*

### *Tricarbonato Method*

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**Introduction.** When cobalt(II) ion is oxidized by hydrogen peroxide in the presence of sodium hydrogencarbonate, a green coloration occurs indicating formation of a carbonato complex of cobalt (III). This reaction is known as the "Field-Durant reaction."<sup>1,2)</sup> In 1951 Laitinen and Burdett<sup>3)</sup> utilized this reaction in an iodometric method for cobalt analysis. In the course of a study aimed at modifying their method, we found that the presence of ammonium carbonate led to a change in the color from green via blue to red-violet of the carbonatotetraamminecobalt(III) complex.<sup>4)</sup> At that time we had an idea to use the green solution as a starting material for the syntheses of cobalt(III) complexes, and this idea was soon realized with the syntheses of carbonato-ammine series complexes.<sup>5)</sup> Since then we have extensively studied how to utilize this green solution for a great variety of syntheses, and we are now able to demonstrate its versatility.

**Starting material.** First<sup>5)</sup> we worked out a way to make the green solution on a preparative scale. The following description of an usual procedure provides a concrete illustration of our technique: Thirty-five grams of  $\text{KHCO}_3$  (0.35 mol) was introduced into 35 ml of water, and the resulting slurry was kept cool by immersion in a freezing mixture of ice and  $\text{NaCl}$ . Separately, 12 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.05 mol) was dissolved in 12 ml of hot water, and 20 ml of 30%  $\text{H}_2\text{O}_2$  was then mixed with the solution cooled in ice. The  $\text{Co}^{2+}$ - $\text{H}_2\text{O}_2$  mixture was added dropwise to the quenched slurry with constant stirring, and the resulting green solution was then quickly filtered by suction. The clear filtrate was again cooled in an ice-bath and used as the starting material. It was prepared anew for each run of the experiments. For convenience' sake, this starting material is hereinafter referred to simply as "the green solution." Various doubtful chemical formulas had been proposed for whatever complex comprised the green solution<sup>6),7)</sup> until we succeeded in obtaining potassium tricarbonatocobaltate(III) trihydrate,  $\text{K}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ .<sup>5)</sup>

A very similar starting material,  $\text{Na}_3[\text{Co}(\text{CO}_3)_3]\cdot 3\text{H}_2\text{O}$ , was reported by Bauer and Drinkard.<sup>8)</sup> At present both of these tricarbonatocobaltates(III) are useful as the starting material for the syntheses of cobalt(III) complexes. Thus, we suggest "the tricarbonato method" as a name for methods starting from "the green solution" or from  $\text{Na}_3[\text{Co}(\text{CO}_3)_3]\cdot 3\text{H}_2\text{O}$ .

**Dicarbonato complexes.** The tricarbonato method using "the green solution" is characterized by successive replacement of the carbonate in  $[\text{Co}(\text{CO}_3)_3]^{3-}$  with other ligands, and the first of the substitution steps yields a mixed ligand dicarbonato complex.

The action of  $(\text{NH}_4)_2\text{CO}_3$  on "the green solution" gave the hitherto unknown dicarbonatodiammine complex,  $\text{K}[\text{Co}(\text{CO}_3)_2(\text{NH}_3)_2]\cdot \text{H}_2\text{O}$ , but the action of aqueous ammonia gave known carbonatotetraammine complex.<sup>5)</sup> For the same reason, the solid material prepared by saturating ethylenediamine hydrate with  $\text{CO}_2$ , was used for the synthesis of the dicarbonatoethylenediamine complex,  $\text{K}[\text{Co}(\text{CO}_3)_2\text{en}]\cdot \text{H}_2\text{O}$ .<sup>9)</sup> The action of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  on "the green solution" yielded not the *bis*(oxalato)diammine,  $\text{K}[\text{Co}(\text{ox})_2(\text{NH}_3)_2]\cdot \text{H}_2\text{O}$ , but the carbonatooxalatodiammine complex,  $\text{K}[\text{CoCO}_3\text{ox}(\text{NH}_3)_2]\cdot \text{H}_4\text{O}$ , the former being derived from the latter by adding oxalic acid.<sup>9),10)</sup> Similar reactions were used for the syntheses of the corresponding ethylenediamine complexes.<sup>9),10)</sup> Those complexes other than  $[\text{Co}(\text{ox})_2(\text{NH}_3)_2]^{-11)}$  and  $[\text{Co}(\text{ox})_2\text{en}]^{-12)}$  were ones prepared for the first time. The structures of the diammine-type complexes were determined to be *cis*-forms on the basis of spectroscopic studies of the  $[\text{CoN}_2\text{O}_4]^{-}$ -type complexes.<sup>13)</sup> Optical resolutions of  $[\text{Co}(\text{CO}_3)_2\text{en}]^{-}$  and  $[\text{Co}(\text{ox})_2(\text{NH}_3)_2]^{-}$  complexes were achieved.<sup>10)</sup> The absorption spectral data for the newly synthesized complexes are summarized in Table I.

The reaction of "the green solution" with  $\text{KNO}_2$  yielded *cis*-dinitro complex,  $\text{K}_3[\text{Co}(\text{NO}_2)_2(\text{CO}_3)_2]\cdot \text{H}_2\text{O}$ .<sup>14)</sup> The related complexes,  $\text{K}_3[\text{Co}(\text{NO}_2)_2\text{CO}_3\text{ox}]$  and  $\text{K}_3[\text{Co}(\text{NO}_2)_2(\text{ox})_2]\cdot \text{H}_2\text{O}$ , were also prepared by the use of a starting material consisting of  $[\text{Co}(\text{CO}_3)_2(\text{ox})]^{3-}$  and  $[\text{Co}(\text{CO}_3)(\text{ox})_2]^{3-}$ .<sup>14)</sup> The action of acetylacetonone on  $[\text{Co}(\text{NO}_2)_2(\text{CO}_3)_2]^{3-}$  gave  $\text{K}_2[\text{Co}(\text{NO}_2)_2\text{CO}_3(\text{acac})]\cdot \text{H}_2\text{O}$ .<sup>15)</sup>

The action of KCN on "the green solution" resulted in a dicyano complex, and it was isolated as  $[\text{Co}(\text{en})_3][\text{Co}(\text{CN})_2(\text{CO}_3)_2]\cdot 2\text{H}_2\text{O}$ .<sup>16)</sup> From this complex, the related dicyano complexes,  $[\text{Co}(\text{CN})_2\text{CO}_3\text{ox}]^{3-}$ ,  $[\text{Co}(\text{CN})_2(\text{ox})_2]^{3-}$ , and  $[\text{Co}(\text{CN})_2(\text{mal})_2]^{3-}$ , were also derived.<sup>17)</sup> The *cis*- $[\text{Co}(\text{CN})_2(\text{CO}_3)_2]^{3-}$  thus obtained was of interest not only from the viewpoint of preparative chemistry, but also because of its absorption spectrum: A marked splitting of the first absorption band was observed (Table I).

Table I. Absorption spectral data on carbonato complexes

Carbonato complex	$\nu_1 10^{13} \text{s}^{-1} (\log \epsilon)$	$\nu_{II} 10^{13} \text{s}^{-1} (\log \epsilon)$
$[\text{Co}(\text{CO}_3)_3]^{3-}$	46.5 (2.19)	68.2 (2.22)
<i>cis</i> - $[\text{Co}(\text{CO}_3)_2(\text{NH}_3)_2]^-$	52.2 (2.14)	76.8 (2.40)
$[\text{Co}(\text{CO}_3)_2 \text{en}]^-$	52.6 (2.17)	76.9 (2.33)
<i>cis</i> - $[\text{CoCO}_3 \text{ox}(\text{NH}_3)_2]^-$	53.1 (2.09)	77.2 (2.18)
$[\text{CoCO}_3 \text{ox en}]^-$	53.5 (2.17)	78.5 (2.30)
<i>cis</i> - $[\text{Co}(\text{NO}_2)_2(\text{CO}_3)_2]^{3-}$	54.8 (2.34)	—
<i>cis</i> - $[\text{Co}(\text{NO}_2)_2 \text{CO}_3 \text{ox}]^{3-}$	56.0 (2.26)	—
<i>cis</i> - $[\text{Co}(\text{NO}_2)_2 \text{CO}_3 \text{acac}]^{2-}$	56.1 (2.18)	—
<i>cis</i> - $[\text{Co}(\text{CN})_2(\text{CO}_3)_2]^{3-}$	54.9 (1.96), 67.5 (2.03)	82.5 (2.20)
<i>cis</i> - $[\text{Co}(\text{CN})_2 \text{CO}_3 \text{ox}]^{3-}$	56.1 (1.90), 69.0 (2.07)	84.3 (2.25)
<i>cis</i> - $[\text{Co}(\text{CO}_3)_2(\text{py})_2]^-$	52.8 (2.25)	76.5 (2.40)
<i>trans</i> - $[\text{Co}(\text{CO}_3)_2(\text{py})_2]^-$	54.6 (2.00)	72.0 (sh), 80.7 (2.03)
$[\text{CoCO}_3(\text{NO}_2)_3 \text{NH}_3]^{2-}$	63.6 (2.34)	—
<i>mer-cis</i> - $[\text{CoCO}_3(\text{gly})(\text{NH}_3)_2]$	54.0 (2.13)	79.5 (2.25),
<i>mer-trans</i> - $[\text{CoCO}_3(\text{gly})(\text{NH}_3)_2]$	56.0 (1.93)	72.0 (sh), 81.8 (1.35)
<i>fac</i> - $[\text{CoCO}_3(\text{gly})(\text{NH}_3)_2]$	56.2 (2.16)	80.1 (2.22)
<i>mer</i> - $[\text{CoCO}_3(i\text{-dtma})]$	58.1 (2.12)	74.5 (sh), 82.3 (1.98)
<i>cis, cis</i> - $[\text{Co}(\text{CN})_2 \text{CO}_3(\text{NH}_3)_2]^-$	60.1 (1.96), 69.5 (2.02)	ca. 89.1 (sh)

In one of our earliest papers<sup>5)</sup> we reported a blue variety and a violet variety of the  $[\text{Co}(\text{CO}_3)_2(\text{NH}_3)_2]^-$  complex, assuming the former to be the *cis* isomer and the latter the *trans*. Later, for the violet variety the formation itself was denied.<sup>18)</sup> Very recently, however, we found that the reaction between "the green solution" and pyridine resulted in not only the *cis* isomer but also the *trans* in the case of the  $[\text{Co}(\text{CO}_3)_2(\text{py})_2]^-$  complex.<sup>19)</sup> Both were isolated as  $\text{K}[\text{Co}(\text{CO}_3)_2(\text{py})_2] \cdot 3\text{H}_2\text{O}$ . In this connection, the complex  $[\text{CoCO}_3(\text{py})_4]\text{ClO}_4$  had been isolated via the reaction of "the green solution" and pyridine.<sup>20)</sup> It is an established fact<sup>21)</sup> that in a *trans* isomer of the  $[\text{CoN}_2\text{O}_4]^-$ -type complex, marked splitting of the first absorption band into Ia and Ib bands occurs, while no appreciable splitting of the second band into IIa and IIb is observed. The present *trans* isomer showed only a maximum in the first absorption band region and an explicit shoulder and a maximum in the second band region (Table I). View in the light of Yamatera's predictions,<sup>22)</sup> these three bands were assignable to Ib, IIa, and IIb, respectively.

**Monocarbonato complexes.** The second of the substitution steps yielded a mixed ligand monocarbonato complex. The reaction of "the green solution" with a diamine such as ethylenediamine,<sup>9)</sup> trimethylenediamine,<sup>23)</sup> or bipyridine<sup>24)</sup> readily resulted in the *bis*(diamine)-type complex. The reaction of "the green solution" with an  $\alpha$ -amino acid yielded *bis*(aminoacidato) complexes:  $\text{K}[\text{CoCO}_3(\text{gly})_2] \cdot 2\text{H}_2\text{O}$ ,<sup>25)</sup>  $\text{K}[\text{CoCO}_3(\text{L-ala})_2] \cdot 3\text{H}_2\text{O}$ ,<sup>25)</sup>  $\text{K}[\text{CoCO}_3(\text{L-val})_2] \cdot 3\text{H}_2\text{O}$ ,<sup>25)</sup> and  $\text{Ag}_3[\text{CoCO}_3-$

(L-asp)<sub>2</sub>·4H<sub>2</sub>O.<sup>26)</sup> In the case of the *bis* (glycinato) complex, its spontaneous resolution was achieved.<sup>27)</sup>

**Amino acid complexes.** In 1961 we<sup>28)</sup> investigated three different methods for synthesizing *tris* (aminoacidato) complexes and found that the method using [Co(CO<sub>3</sub>)<sub>3</sub>]<sup>3-</sup> is most suitable for obtaining *mer* and *fac* isomers in good yields. Later, similar investigation<sup>29)</sup> was carried out with L-alanine, and the tricarbonato method was recommended for obtaining four possible isomers (*A-fac*, *Δ-fac*, *A-mer*, and *Δ-mer*) in good yields. Moreover, a slightly modified procedure was developed.<sup>30)</sup> Complexes of L-aspartic acid<sup>31)</sup> and β-alanine<sup>32)</sup> were successfully prepared starting from [Co(CO<sub>3</sub>)<sub>3</sub>]<sup>3-</sup>. The *bis*-type complex of L-aspartic acid was also prepared.<sup>33),34)</sup> Thus, the method using [Co(CO<sub>3</sub>)<sub>3</sub>]<sup>3-</sup> was established as a general method for the synthesis of amino acid complexes.

We developed a method for the preparation of a *tris*-type complex with different kinds of α-amino acids:<sup>25)</sup> The reaction of "the green solution" with glycinate yielded the K[CoCO<sub>3</sub>(gly)<sub>2</sub>]·2H<sub>2</sub>O. Then the reaction of this complex with L-valine led to [Co(gly)<sub>2</sub>(L-val)], its three diastereoisomers, *A-fac*, *Δ-fac*, and *A-mer*, being isolated by means of solubility difference. The reaction was, of course, applicable to a complex containing the L- and D-form of an amino acid together.

When L-aspartate was allowed to react with [CoCO<sub>3</sub>(gly)<sub>2</sub>]<sup>-</sup> in the presence of active charcoal, a series of complexes of the [Co(gly)<sub>3-n</sub>(L-asp)<sub>n</sub>]<sup>n-</sup>-type (*n*=0~3) formed, and their diastereoisomers were isolated by means of ion-exchange chromatography.<sup>27)</sup> Similar reactions were applied to [Co(L- or D-ala)<sub>3-n</sub>(L-asp)<sub>n</sub>]<sup>n-35)</sup> and [Co(L-pro)<sub>3-n</sub>(L- or D-asp)<sub>n</sub>]<sup>n-36)</sup> series. These preparative methods for amino acid complexes have made valuable contributions to the development of coordination stereochemistry.

**Some novel complexes.** Through various experiments involving "the green solution," it could be discerned that the third-step replacement of the chelated carbonate ion with another ligand is more difficult than the first- and second-step replacements. Utilizing this fact we were able to obtain some novel complexes.

From a reaction mixture of "the green solution" with NH<sub>4</sub>Cl and NaNO<sub>2</sub>, an interesting complex, K<sub>2</sub>[CoCO<sub>3</sub>(NO<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>]·H<sub>2</sub>O, was obtained, and action of KNO<sub>2</sub> on this carbonato complex resulted in a novel monoammine complex, K<sub>2</sub>[Co(NO<sub>2</sub>)<sub>5</sub>NH<sub>3</sub>].<sup>37)</sup> We also obtained [CoCN(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub> and *mer*-[Co(CN)<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub>] by the method of first letting KCN react with "the green solution" and then letting NH<sub>4</sub>Cl and NH<sub>3</sub> react with the product in the presence of active charcoal.<sup>37)</sup> Later, *fac*-[Co(CN)<sub>3</sub>(NH<sub>3</sub>)<sub>3</sub>] was also synthesized from "the green

solution" by other workers.<sup>38)</sup>

The reaction of *cis*-[Co(CO<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>-</sup> with glycine resulted in a non-electrolyte-type complex, [CoCO<sub>3</sub>(gly)(NH<sub>3</sub>)<sub>2</sub>], and its three geometrical isomers—*mer* (with respect to N or O atoms) *cis* (with respect to NH<sub>3</sub>), *mer-trans*, and *fac*—were isolated by means of solubility difference and ion-exchange chromatography.<sup>39)</sup> The reaction was successfully applied to other amino acids such as  $\alpha$ -alanine,  $\beta$ -alanine, and valine.<sup>40)</sup> The reaction between "the green solution" and *N, N*-bis(2-aminoethyl)glycine (*i*-dtmaH) yielded not only the known *fac*(N)-isomer<sup>41)</sup> but also the unknown *mer*(N)-isomer of the [CoCO<sub>3</sub>(*i*-dtma)] complex.<sup>42)</sup> With the *mer-trans* isomers of the glycinato,  $\alpha$ -alaninato, and valinato complexes, and also with *mer* isomer of the *i*-dtma complex, the spectra revealed a clear shoulder in the second absorption band region (Table I). The shape of the spectrum is quite similar to that for the *trans*-[Co(CO<sub>3</sub>)<sub>2</sub>(py)<sub>2</sub>]<sup>-</sup>.<sup>20)</sup>

The reaction of the *cis*-[Co(CN)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>]<sup>3-</sup> species<sup>16)</sup> with NH<sub>4</sub>ClO<sub>4</sub> and NH<sub>3</sub> resulted in *cis-cis*-[Co(CN)<sub>2</sub>CO<sub>3</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>-</sup> species, being resolved into an optically active form with (-)<sub>589</sub>-[Coox(en)<sub>2</sub>].<sup>43)</sup> Acid-hydrolysis of the *cis*-[CoCO<sub>3</sub>(ox)(NH<sub>3</sub>)<sub>2</sub>]<sup>-</sup> complex<sup>10)</sup> with nitric acid yielded [Co(ox)(H<sub>2</sub>O)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> species, being resolved into an optically active form with (+)<sub>546</sub>-[Co(edta)]<sup>-</sup>.<sup>43)</sup> To date little attention has been given to such complexes that derive their dissymmetry solely from the distribution of unidentate ligands about a central metal ion. Our reactions mentioned above hold promise for contributing to future developments in this field.

Lastly, we report the preparation of heteropolyelectrolytes containing cobalt(III) and tungsten(VI): When "the green solution" was allowed to react with a slightly acidified solution of Na<sub>2</sub>WO<sub>4</sub>, two kinds of tungstocobaltates, K<sub>4</sub>H[CoW<sub>6</sub>O<sub>22</sub>]·7H<sub>2</sub>O and K<sub>7</sub>H<sub>2</sub>[CoO<sub>6</sub>H<sub>2</sub>O<sub>4</sub>W<sub>11</sub>O<sub>30</sub>]·15H<sub>2</sub>O, were obtained.<sup>10)</sup> Of these, the discovery of the 11-tungstocobaltate(III) led to the preparation of various other compounds belonging to a new structural type of heteropolyelectrolyte.<sup>44)</sup>

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