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THE ISOLATION OF TRANS AND CIS ISOMERS OF DICARBONATOBIS-(PYRIDINE)COBALTATE(III)

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Two isomeric compounds, trans- and cis-$K[Co(CO_3)_2(py)_2]\cdot3H_2O$, have been isolated from a reaction mixture of the $[Co(CO_3)_3]^{3-}$ ion with pyridine. The absorption spectrum of the trans complex revealed distinct splitting of the second absorption band.

One of the present authors and his co-workers$^{1)}$ reported once two isomers of the dicarbonatodiamminecobaltate(III) as products from the reaction between the green solution of potassium tricarbonatocobaltate(III) and ammonium carbonate. In that paper, they assumed that the blue product formed at an earlier stage of the reaction has cis-structure and the violet one formed through the blue one has trans-structure. The cis-structure was then supported by the studies of absorption spectra of the $[Co\ N_2\ O_4]^-$-type complexes$^{2)}$ and also by the optical resolution of related dicarbonatoethylenediamine complex.$^{3)}$ For the violet product, however, the formation itself was denied by Hyodo and Archer$^{4)}$ who came to the conclusion that the violet product is not trans-diammine complex but is a mixture of several cobalt(III) complexes.

Under the circumstances, our efforts have been continued to isolate a trans-diammine type complex and now rewarded with success; the reaction between the tricarbonatocobaltate(III) and pyridine gave not only cis isomer but also trans one of potassium dicarbonatobis(pyridine)cobaltate(III). Recently, carbonatotetrakis(pyridine)cobalt(III) perchlorate has been isolated via the reaction of the tricarbonatocobaltate(III) and pyridine,$^{5)}$ and its crystal structure has been reported.$^{6)}$

To a cold, green solution of potassium tricarbonatocobaltate(III) ($Co(NO_3)_2\cdot 6H_2O$, 15 g (0.05 mol) scale), was added pyridine (8 mℓ, 0.1 mol) and the mixture was stirred at 15°C for 40 min, whereby precipitation resulted and the solution became violet. After the whole was kept in an ice-bath for a while, the precipitates colored red-violet were collected by filtration. The yield of this crude product was about 2 g. On the other hand, the filtrate was evaporated to dryness with the aid of a rotary vaccume evaporator, and the residue was then extracted with a minimum amount of ethanol. In keeping the extracted solution in a refrigerator, violet crystals deposited. The yield of this crude product was about 0.5 g. The red-violet product (assigned later as the trans isomer) was recrystallized three times from water, while the violet one (assigned later as cis) was recrystallized two times from ethanol. The elemental analyses of these two products corresponded well with the formula $K[Co(CO_3)_2(py)_2]\cdot 3H_2O$.

Found for red-violet product: C, 33.80; H, 3.51; N, 6.51%. Found for violet product: C, 33.41; H, 3.66; N, 6.71%. Calcd for $K[Co(CO_3)_2(C_5H_5N)_2]\cdot 3H_2O$: C, 33.50; H, 3.75; N, 6.51%.

The absorption spectra of these isomeric products in aqueous solutions are shown in Fig. 1. The short vertical lines in the figure indicate the band positions calculated by Yamatera's predictions$^{7)}$ (the big lines stand for doubly degenerate components (truely or accidentally) and the fine lines, for non-degenerate ones); in the calculation cis-structure was assumed for the violet complex and trans-structure for the red-violet one. Moreover, the parameters concerning the first and second absorption bands, δ^{I} and δ^{II}, were treated as $\delta^{I} = \delta^{I}_{\sigma} + \delta^{I}_{\pi}$ and $\delta^{II} \approx \delta^{II}_{\sigma}$. The numerical values were estimated from the absorption maxima of the $[CoCO_3(py)_4]^{+}$ $^{5)}$ and $[Co(CO_3)_3]^{3-}$ $^{1)}$ complexes (δ^{I} = 5,060 cm^{-1}; δ^{II} = 5,460 cm^{-1}).

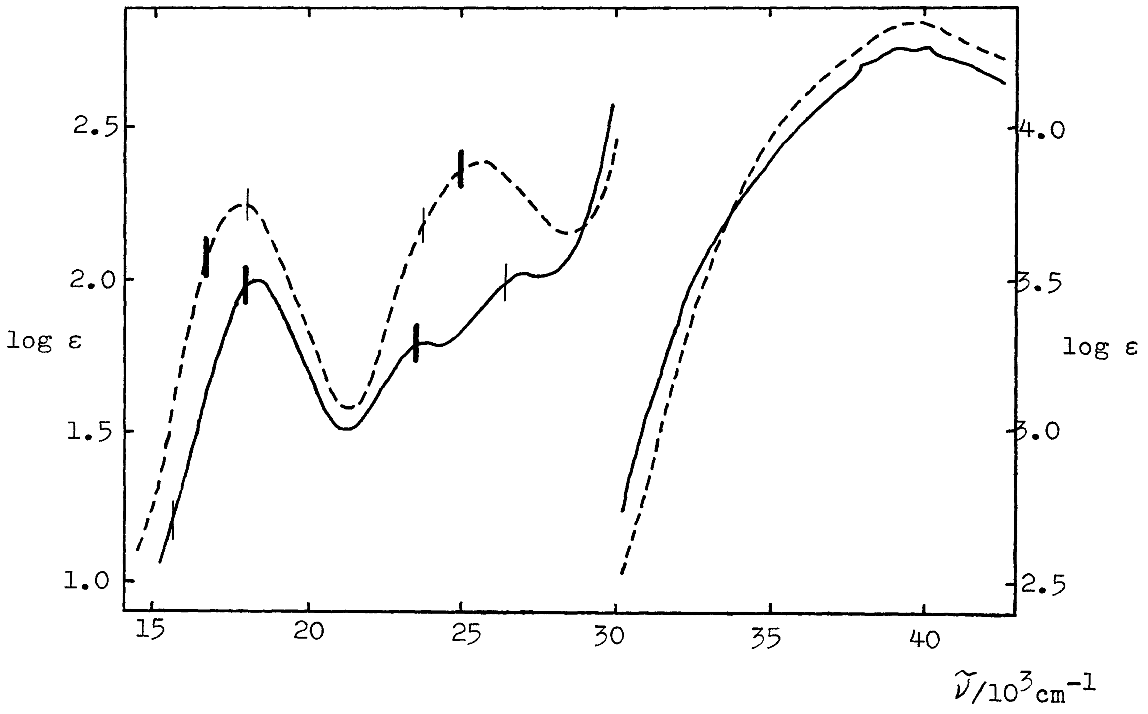

Fig.1 Absorption spectra of the red-violet (———) and violet (-----) complexes

As for the violet compound, the maxima of the first and second absorption bands ($\tilde{\nu}_{I}$ and $\tilde{\nu}_{II}$) are at 17,600 (log ε = 2.25, half-width ca. 3,400) and 25,500 cm^{-1} (log ε = 2.40), respectively. These values are in rough accord with those for the cis-$[Co(CO_3)_2(NH_3)_2]^{-}$ complex; $\tilde{\nu}_{I}$ = 17,800 (log ε = 2.14), $\tilde{\nu}_{II}$ =

25,600 cm^{-1} (log ε = 2.40).1) Regarded from the fact that the ligands py and NH$_3$ rank at the same position in the spectrochemical series,8) it is reasonable to regard this complex as the cis one. In fact the observed maxima correspond fairly well to the predicted positions.

The red-violet complex shows its $\tilde{\nu}_{I}$ at 18,200 cm^{-1} (log ε = 2.00, half-width ca. 3,200 cm^{-1}). In the second band region, an explicit shoulder and a maximum are observed at ca. 24,000 and 26,900 cm^{-1}, respectively. These three positions coincide nearly with the predicted positions, although no absorption is observed at lower-energy-side of the first band region contrary to the prediction. In this connection, it has been reported that related iminodiacetato and L-aspartato complexes, trans(N)-[Co(ida)$_2$]$^-$ 2) and trans(N)-[Co(L-asp)$_2$]$^-$ 9) exhibit marked splittings of the first bands into Ia and Ib and that the intensities of their Ia bands are considerably lower than those of the Ib. Thus, the present spectrum is understood as that of the trans complex. A similar shoulder in the second absorption band region has been reported with the mer(trans-diammine) isomer of a carbonato(α-aminoacidato)diamminecobalt(III) complex.10) Viewed in the light of Yamatera's predictions, this shoulder also is regarded as a split component of the second band. In the spectrum of the red-violet complex, so-called pyridine band8) having the components of the vibrational structure can still be observed at ca. 39,000 cm^{-1} in the charge transfer region.

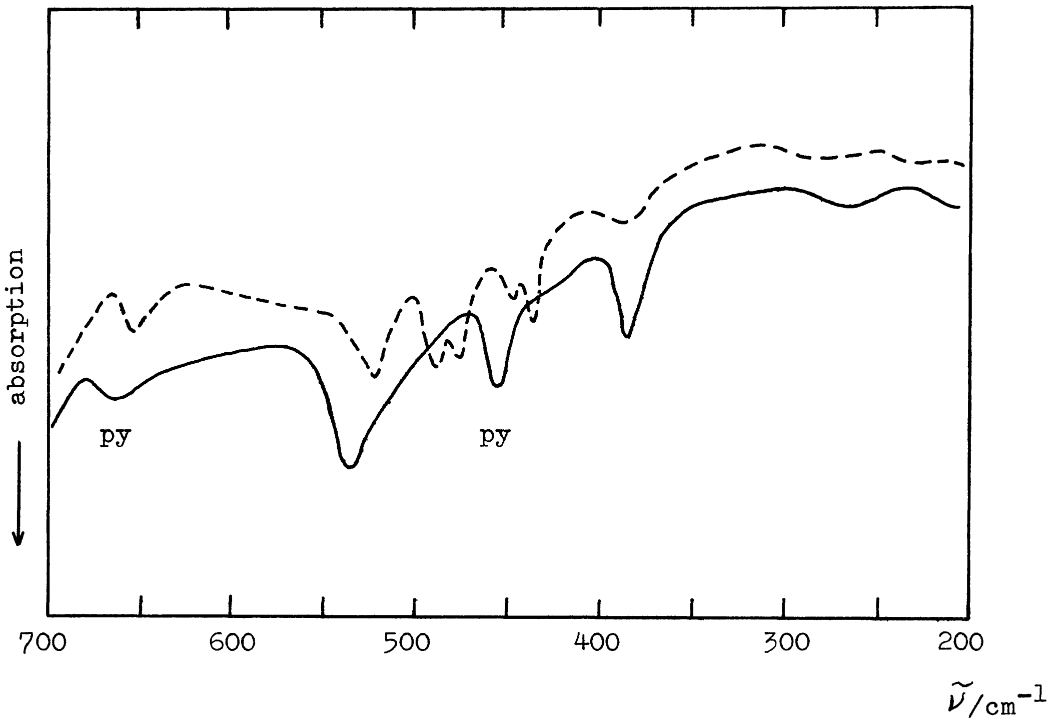

Fig.2 Far-infrared spectra of the red-violet (———) and violet (-----) complexes

It was ascertained that the carbonate ions in each complex act as the bidentates by the IR spectral data — that is, by the observation of the bands near

1600, 1270, 1020, and 770 cm^{-1}.11) Figure 2 shows the far-infrared spectra of the two complexes. In general, it is known that the py vibrations at 604 and 405 cm^{-1} are shifted to higher frequencies upon coordination.11) In view of this fact, two peaks at ca. 650 cm^{-1} and ca. 450 cm^{-1} observed in common with both isomers can be assigned to these vibrations. The remaining peaks — two for the red-violet complex and five for the violet one — should be due to Co-N and Co-O stretchings. Group theory predicts one Co-N and one Co-O stretching for the trans-structure of the $[Co\ N_2\ O_4]^-$-type complex, while corresponding cis-form has two Co-N and four Co-O stretchings.11) Based on these, trans-structure is certainly assigned to the red-violet complex. The cis-structure for the violet complex is also verified by this complex spectrum.

The trans complex anion was safely eluted with 0.1 M sodium chloride on a column of Dowex 1 X 8 region in chloride-form, but in the co-existence of the cis complex the trans species isomerized to cis ones, and no chromatographic separation was attained. Corresponding to this fact, it was found that the prolonged reaction of the tricarbonatocobaltate(III) species and pyridine decreased the yield of the trans complex. By means of measurements of spectra in solutions it was found that the acid-hydrolysis of each isomer took place with full retention of configuration.

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