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Preparation and Properties of Metal Complexes in Non-aqueous Solutions. I. Preparation of the *trans*-Dicyano-bis(ethylenediamine)cobalt(III) Complex by the Use of Dimethylsulfoxide as Solvent[1]

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An isomeric form of the hitherto known *cis*-$[Co(CN)_2\ en_2]^+$ was prepared from *cis*- or *trans*-$[CoCl_2\ en_2]^+$ and potassium cyanide in dimethylsulfoxide solution. The new complex was characterized by UV, IR and NMR spectra, and its trans configuration was established.

Two peculiarities may be noticed about the preparation of $[Co(CN)_2en_2]^+$. One is the fact that only the cis form is known. The other is the way of its preparation. Usually, diacido-bis-ethylenediamine complexes, $[CoX_2en_2]^+$ can be prepared from *trans*-$[CoCl_2en_2]^+$ by substitution of X for Cl. However, the cyano mixed complex is obtained only via *trans*-$[Co(S_2O_3)_2en_2]^-$. When the dichloro complex is treated with potassium cyanide in an aqueous solution, disproportionation occurs to produce $[Co\ en_3]^{3+}$ and $[Co(CN)_6]^{3-}$. This fact indicates that the incoming cyano groups expel the other kind of ligands from the coordination sphere. On the other hand, it is generally known that cobalt(III) ammines were quite labile in an alkaline solution. In the preparation of the cyano mixed complex, the reaction mixture is fairly alkaline due to hydrolysis of the added cyanide. This alkalinity of the solution might make

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3) H. Yoneda, This Bulletin, **31**, 74 (1958).

the complex labile and lead it to disproportionation.

In our previous report[3] on the decomposition of cobalt(III) ammines, the proton dissociation mechanism was proposed. In that mechanism, it was assumed that, in the decomposition process, proton dissociation from the coordinated NH_3 takes place first, and that then the NH_2^- thus produced came out of the coordination sphere. A similar proton dissociation may be considered in the present case. Therefore, it was felt necessary to work under conditions where proton dissociation can not occur. To fulfill these conditions, we tried to use dimethylsulfoxide as a solvent and succeeded in obtaining the cyano diamine mixed complex which proved to be isomeric to the hitherto known *cis*-$[Co(CN)_2en_2]^+$ complex, directly from the dichloro complex.[4,5]

Experimental

Method of Preparation. One gram (0.016 mol) of powdered potassium cyanide was dissolved in 150 m*l* of dimethylsulfoxide heated at 60°C. To this solution was added in small portions 1.5 g (0.05 mol) of *trans*-$[CoCl_2en_2]NO_3$ under constant stirring. The added complex reacted gradually with the cyanide and, after a while, yellow precipitate of greenish tint was formed. At about 60°C, the reaction was complete in 15—20 min. When *cis*-$[CoCl_2en_2]Cl$ was used as a starting material, the reaction proceeded much more smoothly to form an orange yellow precipitate in one or two minutes. (Both reactions gave the same final product). The greenish tint probably originated from unreacted green *trans*-$[CoCl_2en_2]NO_3$. The precipitate thus formed was filtered and washed with warm dimethylsulfoxide and then with acetone. Through this procedure the precipitate became light yellow. This product was supposed to be $[Co(CN)_2en_2]Cl$ with some contamination. This was not soluble in dimethylsulfoxide nor in ethanol. In water it was too much soluble to obtain good crystals. Therefore, purification was attempted by converting it to the perchlorate salt. The crude product was dissolved in a small volume of water and, after filtration, was added with the saturated solution of sodium perchlorate. An orange yellow crystalline powder came out. This was washed with small amount of water and ethanol, and dried in air.

Found: C, 21.79; H, 5.06; N, 24.88%. Calcd for $[Co(CN)_2en_2]ClO_4$: C, 21.80; H, 4.88; N, 25.42%.

Spectral Measurements. The UV spectra were measured with a Shimadzu QR 50 spectrophotometer. The IR spectra were recorded with a Hitachi EPI S2 spectrophotometer equipped with NaCl optics. The KBr disc method was adopted in the IR measurement. The NMR spectra were run on a Varian A60 NMR spectrometer. Deuterium oxide was used as solvent, and the sodium salt of trimethylsilylpropane sulfonic acid was used as an internal reference.

Results and Disucssion

The Ligand Field Absorption Bands. The UV absorption curve of the new $[Co(CN)_2en_2]$-ClO_4 is shown in Fig. 1 with that of the known *cis*-$[Co(CN)_2en_2]ClO_4$. The absorption data are summarized in Table 1. The main difference between the absorption curves of both isomers appears in their first absorption bands: While the first band of the cis isomer shows no clear split, that of the new one seems to split into two components. A similar kind of difference is observed in the first bands of *cis*- and *trans*-$[CoCl_2en_2]^+$ too.[6] In this case also, the cis isomer has no

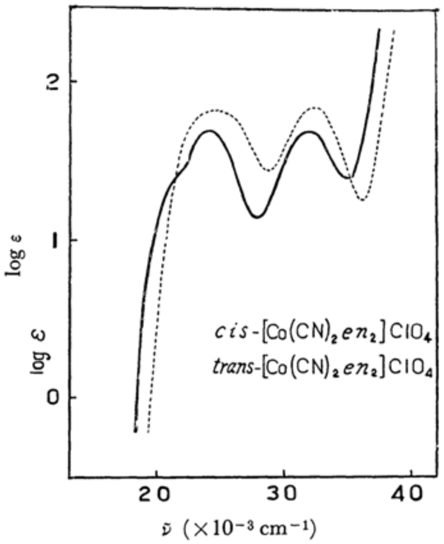

Fig. 1. UV Absorption spectra of *cis*-$[Co(CN)_2en_2]$·ClO_4 and its new isomer (aqueous solution).
…… *cis*-$[Co(CN)_2en_2]ClO_4$
—— new isomer

TABLE 1. THE ABSORPTION DATA OF *cis*-$[Co(CN)_2en_2]ClO_4$ AND ITS NEW ISOMER

	1st Band		2nd Band	
	$\tilde{\nu}_{max}$ (cm^{-1})	log ε_{max}	$\tilde{\nu}_{max}$ (cm^{-1})	log ε_{max}
cis form	24.6	1.82	32.4	1.83
new isomer	19.3(shoulder) 24.0	 1.69	32.0	1.68

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[4] Two works concerning the preparation of $[Co(CN)_2en_2]^+$ in an aqueous solution were reported at the 21st Annual Meeting of the Chemical Society of Japan (April, 1968): K. Kuroda prepared *cis*-$[Co(CN)_2en_2]^+$ by treating $[CoCO_3en_2]^+$ with CN^- in an aqueous solution. M. Shibata *et al.* prepared *cis* and *trans*-$[Co(CN_2)en_2]^+$ from $[Co\ en_3]^{3+}$ and CN^- in an aqueous solution.

[5] Previously we reported the preparation of *cis*-$[Co(CN)_2en_2]Cl$ by the use of dimethylsulfoxide as solvent. H. Yoneda, T. Baba and M. Muto. This Bulletin, **40**, 1736 (1967). However, no attempts were successful to reproduce the result. The interconversion between the cis and trans forms is now being studied.

[6] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **271**, 101 (1952).

split band, and the trans isomer has a markedly split first band. Therefore, if we assume the trans configuration for the new $[\mathrm{Co(CN)_2en_2}]^+$, the present situation can reasonably be understood. However, this can not be a decisive proof for the trans configuration, because we know that the first band of *trans*-$[\mathrm{CoCl(CN)en_2}]^+$ shows no split, while that of the cis isomer split markedly into two components.7) In addition, there are several possible structures which are isomeric to the known *cis*-$[\mathrm{Co(CN)_2en_2}]^+$.

Corey and Bailar8) classified two possible conformations of the ethylenediamine molecules in $[\mathrm{Co\ en_3}]^{3+}$ into the "lel" and "ob" forms. The "lel" form represents the conformation in which the C-C axis is nearly parallel to the threefold axis of $[\mathrm{Co\ en_3}]^{3+}$, and the "ob" form to the conformation in which the C-C axis is almost perpendicular to the threefold axis of the complex (In the actual $[\mathrm{Co\ en_3}]^{3+}$, all three ethylenediamine molecules take the "lel" form). Such kinds of conformation can be considered in the *cis* bisethylenediamine complex too. In this case, there are three possible combinations of two ethylenediamine molecules, lel-lel, lel-ob and ob-ob form. The active chloride9) of *cis*-$[(\mathrm{Co(CN)_2en_2}]^+$ proved to have an ob-ob conformation, while the racemic chloride10) of *cis*-$[\mathrm{CoCl_2en_2}]^+$ a lel-ob conformation. Thus our new complex can be considered to have the following several possible structures.

1) The two cyano groups are linked to the metal ion with the nitrogen atom.11)

2) The two ethylenediamine molecules take a lel-lel or lel-ob conformation.

3) The two cyano groups are coordinated to the metal ion in trans positions.

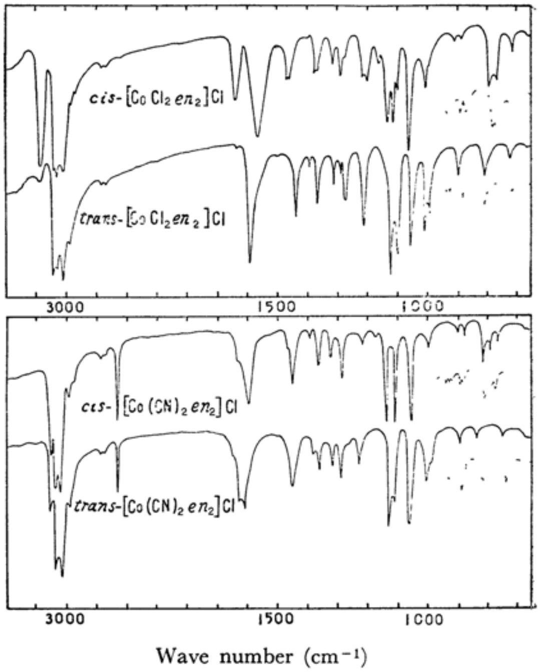
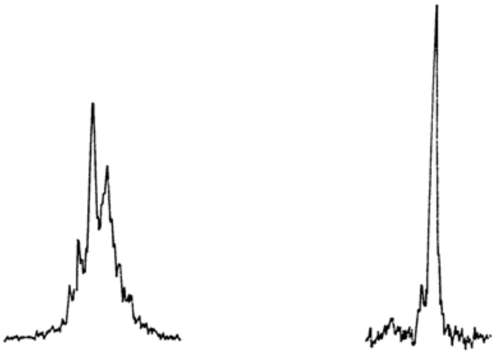


Fig. 2. IR absorption spectra of diacido-bis-ethylenediamine cobalt(III) complexes.
—— chlorides ······ perchlorates



cis-$[\mathrm{Co(CN)_2en_2}]\mathrm{ClO_4}$ *trans*-$[\mathrm{Co(CN)_2en_2}]\mathrm{ClO_4}$

Fig. 3. NMR spectra of *cis*-$[\mathrm{Co(CN)_2en_2}]\mathrm{ClO_4}$ and its new isomer ($\mathrm{D_2O}$ solution).

IR Spectra. In order to obtain informations concerning the structure of the new complex, the IR spectra of the new and the *cis*-$[\mathrm{Co(CN)_2en_2}]^+$ were measured.12) For comparison, the spectra of *cis*- and *trans*-$[\mathrm{CoCl_2en_2}]^+$ were also measured. The results are shown in Fig. 2. Usually $\mathrm{CN^-}$ is linked to the metal ion with the C atom. In the case of *cis*-$[\mathrm{Co(CN)_2en_2}]^+$, this was confirmed by X-ray analysis.9) If $\mathrm{CN^-}$ were linked to the metal ion through the N atom in the new complex, the CN bond nature in the new isomer should be different from that of the *cis* isomer. While in the C coordination, $\mathrm{CN^-}$ should have a triple bond character ($\mathrm{Co^{3+}} \leftarrow {}^{-}\mathrm{C{\equiv}N}$), in the N coordination it should have a triple bond character ($\mathrm{Co^{3+}} \leftarrow {}^{-}\mathrm{N{=}C}$). Therefore, the absorption band due to the CN stretching in the new isomer should appear in longer wavelength region than that in the cis

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7) K. Ohkawa, J. Hidaka and Y. Shimura, This Bulletin, **39**, 1715 (1966).

8) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

9) K. Matsumoto, Y. Kushi, S. Ooi and H. Kuroya, This Bulletin, **40**, 2988 (1967).

10) K. Matsumoto, S. Ooi and H. Kuroya, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect)*, **89**, 167 (1968).

11) K. Kuroda and P. S. Gentile, Proceedings of 10th ICCC, p. 280 (1967).

12) The pure chloride of the new $[\mathrm{Co(CN)_2en_2}]^+$ for IR measurement was obtained as follows. The crude chloride was dissolved in a small volume of water, and, after filtration, ethanol was added in small portions until a slight turbidity appeared. The solution was filtered and the filtrate was evaporated to dryness under reduced pressure without heating. The dried residue was dissolved in water, and the procedure was repeated.

13) Baldwin also reported that the spectrum pattern in these regions is more complicated in the *cis*-$[\mathrm{CoX_2en_2}]^+$ than in the trans isomer. M. E. Baldwin, *J. Chem. Soc.*, **1960**, 4369.

isomer. However, this is not the case. The CN stretching absorption band appears just at the same wave number (2130 cm^{-1}). Therefore, the N coordination can not be considered. If the new complex had the lel-ob conformation, the spectrum pattern of the new complex should be similar to that of *cis*-$[CoCl_2en_2]^+$. This is not the case. The IR spectra of the new $[Co(CN)_2 en_2]^+$ and the *cis*-$[CoCl_2en_2]^+$ are fairly different in appearance. Rather, the spectrum pattern of the new complex shows a similarity to that of *trans*-$[CoCl_2en_2]^+$, especially in the CH_2 twisting and NH_2 rocking regions (see Fig. 2, 900—700 cm^{-1}). On the other hand, *cis*-$[CoCl_2en_2]^+$ and *cis*-$[Co(CN)_2en_2]$ show quite a unique splitting of bands in the CH_2 twisting and the NH_2 rocking region.[13] This fact makes a marked contrast to the trans isomer. This situation holds not only in the chlorides but also in the perchlorates. These findings seem to support the trans configuration of the new isomer, although they can not exclude the possibility of the lel-lel conformation.

NMR Spectra. To obtain the decisive conclusion concerning the structure of the new complex, the NMR spectra of the new and the known *cis*-$[Co(CN)_2en_2]^+$ dissolved in deuterium oxide were recorded. Figure 3 shows the CH_2 signals of both isomers (The NH_2 signals disappeared soon after dissolution due to deuteration). As expected, the CH_2 signal of the cis isomer shows a complicated pattern. On the contrary, the new isomer shows a sharp singlet which corresponds to the single species of the CH_2 protons. Thus the trans configuration of the new isomer was established.

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