Novel Isomers of the *trans*-(O–CN)-Cyanoaminoacidatodiethylenetriamine Cobalt(III) Complex Ion

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Recently we prepared many complexes containing the *trans*-(O–X)-[Co·X·am·dien]$^+$ type ions, (X=CN^-, Cl^-, NO_2^-, am=α-aminoacidato ion and dien=$NH_2CH_2CH_2NHCH_2CH_2NH_2$), and confirmed the geometrical structure of these ions from an analysis of their ultraviolet absorption spectra.1) In these new complex ions, dien occupies the cis-trans (mer) position, and their NMR spectra (60 Mc) give the methylene signal of meridional dien ring in the same region as reported before.2)

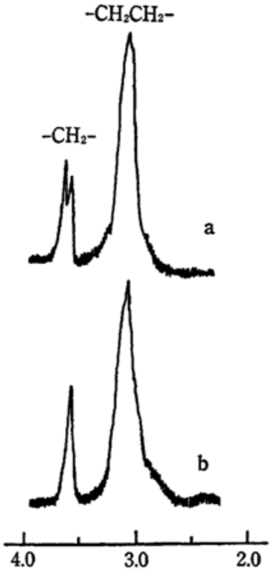

Fig. 1. The NMR spectra (60 Mc) of *trans*-(O-CN)-[Co(CN)gly·dien]$^+$ in D_2O.
a) Sample prepared from [Co(CN)(SO_3)(NH_3)$_4$]
b) Sample prepared from *trans*-(O-Cl)-[Co·Cl·gly·dien]$^+$
NaTMS was used as an internal reference.

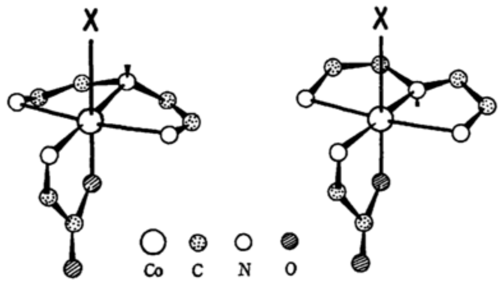

Fig. 2. Two isomers of *trans*-(O–X)-[Co·X·gly·dien]$^+$.

As Fig. 1-a shows, however, the NMR spectrum of the *trans*-(O–CN)-[Co(CN)gly·dien]$^+$ ion (gly=glycine), which was prepared from [Co(CN)(SO_3)(NH_3)$_4$] *via* Co(CN)dien(OH_2)Br_2, shows two kinds of methylene signal due to glycine ring at 210.5 and 213.5 cps. On the other hand, the corresponding chloro or nitro complex exhibits only one methylene signal at 216.3 and 213.4 cps, respectively. Such a difference was also observed in L-alaninate and α-aminoisobutyrate complexes.

The appearance of the two kinds of methylene signal in the cyanoglycinato complex would be due to existence of the two isomers shown in Fig. 2, or to any other reason coming from the coordination of CN^-. The latter reason, however, will be ruled out by the evidence that another sample of *trans*-(O–CN)-[Co(CN)gly·dien]$^+$, derived from the corresponding chloro complex by reaction of CN^- in DMSO, exhibits the same absorption spectrum with that prepared from [Co(CN)(SO_3)(NH_3)$_4$], but its NMR gives only one methylene signal (Fig. 1-b). This singlet signal coincides with one of the two signals mentioned above to support the existence of such an isomerism.

This isomerism would be attributed to the coordination of CN^- on either of the non-equivalent sides of the N_4 plane involving the puckered rings of dien. Hence such an isomerism cannot be substantiated in such complexes as [Co(NO_2)$_3$-dien],3) in which both sides of the N_4 plane are occupied by two NO_2^- ions.

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