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# PREPARATION AND CIRCULAR DICHROISM OF OPTICAL ACTIVE COBALT(III) COMPLEX CONTAINING 3,3'-DIMETHYL-2,2'-BIPYRIDINE

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Cobalt(III) complex of a bulky ligand 3,3'-dimethyl-2,2'-bipyridine (dmbpy), $[\mathrm{Coen_2dmbpy}]\mathrm{Cl(ClO_4)_2 \cdot H_2O}$ was synthesized and resolved. Stereospecific coordination was found. The effects of non-coplanarity of coordinated dmbpy were observed in the absorption (AB) and circular dichroism (CD) spectra of the resolved complex.

2,2'-Bipyridine (bpy) is a bidentate ligand which forms stable chelates with many kinds of metal ions,[1)] and the chelate ring has an almost planar structure.

When the two hydrogen atoms at 3- and 3'- positions are replaced by bulky substituents such as methyl or phenyl, two pyridine moieties are no longer coplanar. 3,3'-Dimethyl-2,2'-bipyridine (dmbpy) (Fig. 1) is one of these compounds, and a pair of optical isomers can be produced. Whenever a dmbpy molecule coordinates to a metal ion to form an inert complex, the conformation of the ligand can be fixed to give right or left handed chiral structure.

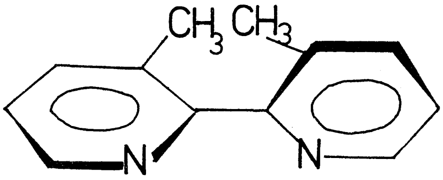

Fig. 1. 3,3'-Dimethyl-2,2'-bipyridine

The present author synthesized dmbpy cobalt(III) complex $[\mathrm{Coen_2dmbpy}]\mathrm{Cl(ClO_4)_2 \cdot H_2O}$ by treating trans-$[\mathrm{CoCl_2en_2}]\mathrm{Cl}$ in an aqueous solution with dmbpy [2)] in the presence of activated charcoal. This complex was resolved into a pair of optical isomers by use of $(+)_D\mathrm{K_3[Co(L\text{-}cysu)_3]}$ [3)] (cysu = cysteinsulphinato). Anal. Calcd for $[\mathrm{Coen_2dmbpy}]\mathrm{Cl(ClO_4) \cdot H_2O}$: C,31.17; H,4.87; N,13.64%. Found C,31.24; H,4.98; N,13.77%. This complex has two kinds of dissymmetric sources; one is the dissymmetric conformation of ligand (R and S) and the other is the dissymmetry around the central metal ion ( $\Delta$ and $\Lambda$ ). Only two of the four possible isomers have been obtained. This result was also verified by the chromatographic study using a SP-SEPHADEX C-25 resin with 0.15 mol. potassium (+)$_D$-tartrateantimonate(III) solution as eluent. Proton magnetic resonance spectrum (60 MHz) of the racemate complex (Fig. 2) also showed that it contains only one pair of enantiomers. The CD spectra of the isolated isomers were enantiomeric to each other over all the wave length region, indicating that they are a pair of enantiomers. The AB and CD spectra of resolved (+)$_D$-[Coen$_2$dmbpy]$^{3+}$ and (+)$_D$-[Coen$_2$bpy]$^{3+}$[3] are shown in Fig. 3. Both AB and CD peaks in d-d region of the resolved dmbpy complex are at a longer wave length and their intensities are bigger than those of the bpy complex. The rotatory strength in the d-d transition region of the dmbpy complex is greater than that of bpy, presumably owing to the puckered comformation of dmbpy. The dmbpy complex gives two negative Cotton effects at about 29 and 34 kK. They may correspond to the electronic transitions of the coordinated dmbpy. The observed splitting also seems to be related to the non-coplanarity of the ligand.

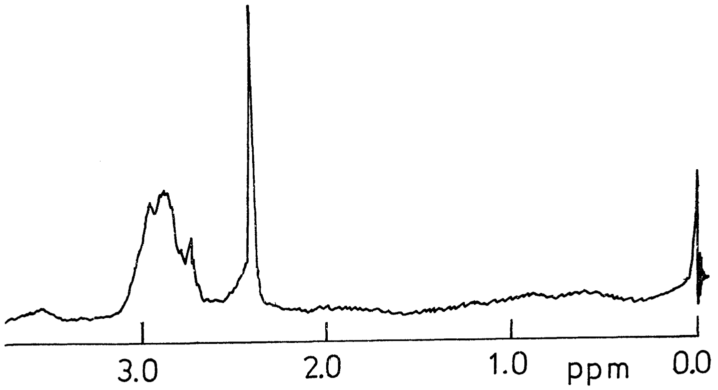

Fig. 2
The 60 MHz PMR spectrum of racemic [Coen$_2$dmbpy]$^{3+}$ in $D_2O$.

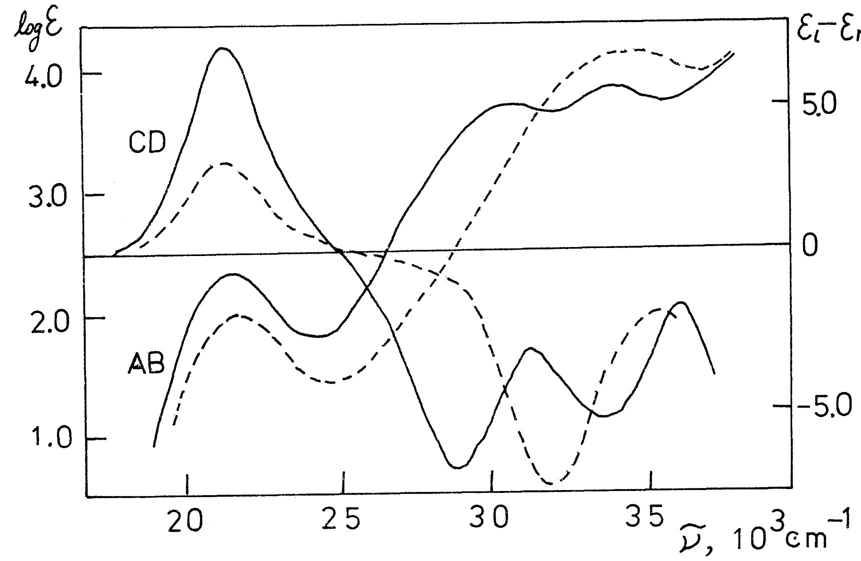

Fig. 3
The AB and CD spectra of (+)$_D$[Coen$_2$dmbpy]$^{3+}$(————) and (+)$_D$[Coen$_2$bpy]$^{3+}$ (- - - - - - -).

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