CHEMISTRY LETTERS, pp. 57- 58, 1974. Published by the Chemical Society of Japan

# PREPARATION AND OPTICAL RESOLUTION OF TRIS(TETRAMETHYLENEDIAMINE) COBALT(III) COMPLEX

Junnosuke FUJITA and Hiroshi OGINO
Department of Chemistry, Faculty of Science, Tohoku University,
Aoba, Aramaki, Sendai, 980

A new red complex of the luteo type $[Co(tmd)_3]Br_3$, where tmd denotes tetramethylenediamine, has been prepared from Co(II) nitrate and tmd in dimethylsulfoxide(DMSO) by air oxidation. The complex has been resolved into optical isomers. The $(-)_D$-isomer shows a weak positive and a strong negative circular dichroism band in the first absorption band region.

Attempts to prepare cobalt(III) complexes containing chelated diamines which have more methylene groups than trimethylenediamine have not all been successful since Werner's age.$^{1)}$ Recently we have obtained $[Co(en)_2NH_2(CH_2)_nNH_2]Br_3$(en:ethylenediamine, n=4,10,12) by the reaction of cis-$[CoCl_2(en)_2]Cl$ with the diamines in DMSO.$^{2,3)}$ In this letter, we report the preparation and optical resolution of $[Co(tmd)_3]Br_3$ as well as its absorption and circular dichroism(CD) spectra.

To a DMSO(500 g) solution containing $Co(NO_3)_2 \cdot 6H_2O$(8.7 g, 0.03 mol) and tmd-dihydrochloride(4.8 g, 0.03 mol) was added a DMSO(500 g) solution of tmd(7.8 g, 0.09 mol) and 1 g of activated charcoal. The cobalt ions were oxidized by bubbling a stream of air through the solution for 48 hr. The dark red solution resulted was diluted with water to 3$\ell$ and the pH of the solution was adjusted to be about 3 with conc. HCl. This was passed through a SP-Sephadex C-25 ion-exchange column($\phi$ 5 x 50cm). After washing the column with water, the adsobed band was eluted with a 0.3M aqueous solution of KBr adjusted to pH 3 with HBr. Pink(very small amount), reddish violet (very small amount) and red(small amount) eluates were obtained in this order. Other products remained on the Sephadex column and they would be polymeric high charged complexes.$^{2)}$ The first pink eluate was cobalt(II) species. The second reddish violet eluate was reloaded on SP-Sephadex column and adsorbed band was eluted with 0.2M HCl. By evaporating the eluate, green trans-$[CoCl_2(tmd)_2]Cl \cdot H_2O$ was obtained.(Anal. Found: C,26.93; H,7.25; N,15.87 %.) The desired complex $[Co(tmd)_3]Br_3$ was obtained by evaporating the third red eluate under reduced pressure at 50°C and recrystallized from warm water adjusted to pH 3 with HBr. Yield: about 1 g. Anal. Calcd for $[Co(tmd)_3]Br_3$: C,25.60; H,6.44; N,14.92 %. Found: C,26.02; H,6.39; N,14.65 %. The racemic $[Co(tmd)_3]Br_3$ was resolved into optical isomers as follows: To a 150 ml of aqueous solution of $[Co(tmd)_3]Br_3$(0.001 mol) was added silver$(+)_D$-tartaratoantimonate (III)(0.002 mol) with stirring. After 2 hr, silver bromide was filtered off and the filtrate was evaporated under reduced pressure at 50°C to about 80 ml. Pink crystals of diastereoisomer were filtered off, washed with cold water and recrystallized from water repeatedly until the CD showed a constant curve. This diastereoisomer was converted into bromide, $(-)_D$-[Co(tmd)$_3$]Br$_3$, by treating with SP-Sephadex and KBr. The resolution was also achieved by SP-Sephadex column chromatography (ϕ 3 x 100 cm) using a 0.15M potassium $(+)_D$- tartaratoantimonate(III) solution as an eluent.$^{4)}$ The separation of the band was incomplete, but the first fraction of the eluate showed a CD curve corresponding to an optically pure $(+)_D$-[Co(tmd)$_3$]$^{3+}$.

The absorption and CD spectra of [Co(tmd)$_3$]$^{3+}$ are shown in the Figure, in which those of [Co(en)$_3$]$^{3+}$ and [Co(tn)$_3$]$^{3+}$(tn:trimethylenediamine) are given for comparison. The [Co(tmd)$_3$]$^{3+}$ gives the first and the second absorption bands at 19,900 cm$^{-1}$($\varepsilon$= 77.8) and 27,900 cm$^{-1}$($\varepsilon$=70.4), respectively. The $(-)_D$-[Co(tmd)$_3$]$^{3+}$ shows a weak positive($\Delta\varepsilon$= + 0.17, 18,200 cm$^{-1}$) and a strong negative($\Delta\varepsilon$= - 1.83, 20,500 cm$^{-1}$) CD band in the first absorption band region. This isomer was assigned to Λ-configuration by the following reasons; 1) The appearance of the positive and the negative CD bands from longer to shorter wavelength in this region is the same as those of Λ-[Co(en)$_3$]$^{3+}$ and Λ-[Co(tn)$_3$]$^{3+}$. 2) The weak positive band disappears completely in a 0.1M Na$_2$SeO$_3$ aqueous solution by an ion-pair formation between the complex and SeO$_3$$^{2-}$ions.$^{5)}$ 3) The sign of the CD in the charge-transfer region($\Delta\varepsilon$= - 26.2, 43,500 cm$^{-1}$) is negative. In general, a Λ-tris(diamine)cobalt(III) complex gives a CD band with minus sign at longer wavelength side in this region.$^{6)}$ Further studies including an X-ray analysis are now in progress.

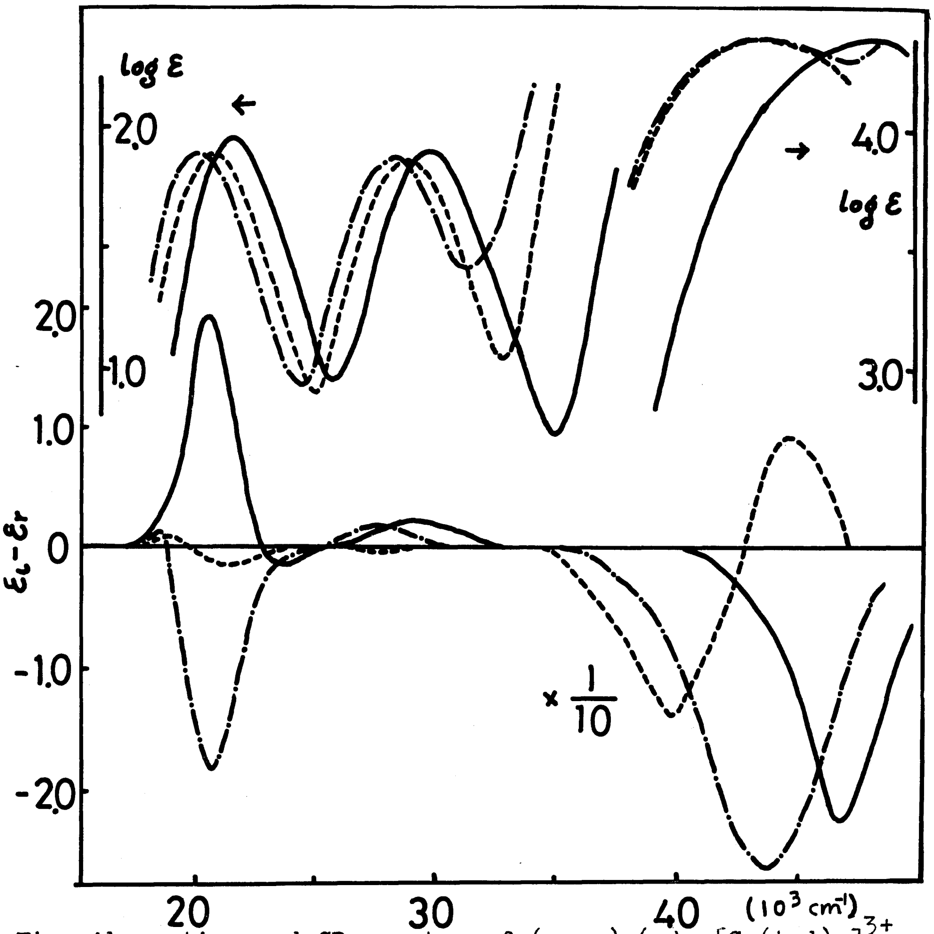

Fig. Absorption and CD spectra of (—·—·):$(-)_D$-[Co(tmd)$_3$]$^{3+}$, (-----):Λ-[Co(tn)$_3$]$^{3+}$ $^{7)}$ and (——):Λ-[Co(en)$_3$]$^{3+}$.

References

1) A.Werner, Ber.,40,15 (1907); Ann., 386,1 (1911): J.C.Bailar, Jr. and J.B.Work, J. Am.Chem.Soc.,68,232 (1946).
2) H.Ogino and J.Fujita, Chem.Lett.,1973,517.
3) H.Ogino and J.Fujita, Presented at the 23rd Symposium on Coordination Chemistry, Fukuoka, (1973).
4) Y.Yoshikawa and K. Yamasaki, Inorg.Nucl. Chem.Lett.,6,523(1970).
5) S.F.Mason and B.J. Norman, Chem.Commun., 1965,73.
6) K.Ogino,K.Murano and J.Fujita,Inorg.Nucl. Chem.Lett.,4,351(1968).
7) P.G.Beddoe and S.F. Mason,ibid.,4,433 (1968).

(Received November 16, 1973)