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The Preparation and the Structure of Cobalt(III) Complexes Containing a *cis*-2-Butene-1,4-diamine Chelate Ring

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Synopsis. New cobalt(III) complexes containing a seven-membered chelate ring, $[Co(en)_2(dcb)]^{3+}$, $[Co(acac)_2(dcb)]^{+}$ and $[Co(dcbta)]^{-}$, were synthesized and resolved into optical isomers, and their structures were determined; dcb=*cis*-2-butene-1,4-diamine, dcbta=*cis*-2-butene-1,4-diamine-*N,N,N',N'*-tetraacetate ion.

cis-2-Butene-1,4-diamine (dcb) can coordinate to a metal ion as a bidentate or terdentate ligand because dcb has two amino groups and one double bond. However, there have been no reports on the metal complex of dcb. This Note will deal with the preparation and the structure of complexes in which dcb coordinates to a trivalent cobalt ion with two amino groups.

Experimental

cis-*2-Butene-1,4-diamine (dcb).* This was prepared *via* 1,4-diphthalimido-*cis*-2-butene from *cis*-2-butene-1,4-diol according to the usual method;[1,2] yield, 45%. The ^1H NMR spectrum of the diamine gave the following signals: $-NH_2$, δ 1.27 singlet; $-CH_2-$, δ 3.33 doublet; $-CH=$, δ 5.53 double triplets. The diamine was converted to the picrate for analysis. Found: C, 35.35; H, 3.22; N, 20.29%. Calcd for $C_{16}H_{16}N_8O_{14}$: C, 35.30; H, 2.96; N, 20.59%.

Sodium cis-*2-Butene-1,4-diamine*-N,N,N',N'-*tetraacetate (dcbta-Na_4).* This was synthesized by a method similar to that used for trimethylenediaminetetraacetate.[3] Chloroacetic acid (10.5 g) in 30 cm^3 of water was neutralized with 4 g of NaOH in 30 cm^3 of water below 20 °C. To the solution we added 2.2 g of dcb, after which the solution was heated at 80 °C for 3 h. During the heating, the pH of the solution was kept at 8 by adding 3 g of NaOH in 30 cm^3 of water in small portions. This solution itself was used for the synthesis of the dcbta complex.

$[Co(en)_2(dcb)]Br_3$. This was synthesized by a method similar to that used for $[Co(en)_2(tmd^{***})]Br_3$.[4] To 200 cm^3 of DMSO containing 3 g of *cis*-$[CoCl_2(en)_2]Cl$ we added 0.9 g of dcb in 50 cm^3 of DMSO. The solution was kept at 20—30 °C for two days. The remainder of the procedure used to obtain the complex was identical with the method used for $[Co(en)_2(tmd)]Br_3$. Yield, 0.5 g. Found: C, 19.04; H, 5.32; N, 16.46%. Calcd for $C_8H_{26}N_6CoBr_3$: C, 19.03; H, 5.20; N, 16.65%.

$(-)_{405}$-$[Co(en)_2(dcb)]Cl_3\cdot H_2O\cdot HCl$. The racemate was resolved according to a method similar to that used for $[Co(amb^{****})(en)_2]^{2+}$.[5] The racemate (0.28 g), adsorbed on an SP-Sephadex column ($\phi 4\times 150$ cm), was eluted with a solution of 0.15 M potassium $(+)_{589}$-tartratoantimonate. The eluate containing the $(-)_{405}$-isomer was again passed through an SP-Sephadex column ($\phi 1.8\times 20$ cm), and the adsorbed band was eluted with a 0.36 M HCl solution. The eluate was evaporated to dryness in a vacuum desiccator over KOH. Found: C, 22.74; H, 7.00; N, 19.19%. Calcd for $C_8H_{29}N_6Cl_4Co$: C, 22.54; H, 6.87; N, 19.72%.

$[Co(acac)_2(dcb)]ClO_4$. The procedure used here is identical with the method used for $[Co(acac)_2(en)]ClO_4$,[6] except for using dcb instead of ethylenediamine. The dcb complex was prepared by mixing $Na[Co(acac)_2(NO_2)_2]\cdot 5H_2O$ and dcb (1:1) in aqueous methanol in the presence of charcol and by then adding $NaClO_4$. Found: C, 38.23; H, 5.41; N, 6.47%. Calcd for $C_{14}H_{26}N_2O_8ClCo$: C, 37.81; H, 5.89; N, 6.30%.

$(-)_{405}$-$[Co(acac)_2(dcb)]^+$. The racemate was resolved according to a method similar to that used for $[Co(acac)_2(RS\text{-}2,4\text{-ptn}^{\dagger})]ClO_4$.[7] The racemate and sodium hydrogen dibenzoyltartrate were dissolved in water at 65 °C. A violet powder was precipitated by cooling the solution to 20 °C and then filtered off. The powder was recrystallized from water fractionally until the ratio of the $\Delta\varepsilon$ and ε values of the powder became constant. The pure powder was converted into perchlorate by treating it with aqueous methanol containing $AgClO_4$. The perchlorate of the $(-)_{405}$-isomer was hygroscopic and was obtained in only a slight amount. The quantitative CD curve of this isomer was determined with the aid of the ε values of the racemate.

$Na[Co(dcbta)]\cdot 2H_2O$. The procedure used here is almost identical with the method used for $[Co(RR\text{- and }SS\text{-}2,4\text{-ptnta}^{\dagger\dagger})]^-$.[8] To a solution containing 26 mmol of $dcbtaNa_4$ we added 8.1 g of $Na_3[Co(NO_2)_6]$[9], after which the solution was warmed at 55 °C for 40 h. Crystals were obtained by gradually evaporating the solution at 30 °C. Found: C, 33.26; H, 4.07; N, 6.42%. Calcd for $C_{12}H_{18}N_2O_{10}NaCo$: C, 33.35; H, 4.20; N, 6.48%.

$K(+)_{589}$-$[Co(dcbta)]\cdot 2H_2O$. The silver salt of the racemate was dissolved in 30 cm^3 of water. To the solution we then added 0.9 g of $(+)_{589}$-$[Co(NO_2)_2(en)_2]Br$[10] in 20 cm^3 of water. The solution was then warmed at 50 °C, and the AgBr was filtered off. The filtrate was evaporated to dryness, and the residue was suspended in a small amount of water. The undissolved powder was filtered off and dissolved in a large amount of hot water. Crystals were obtained fractionally from the solution by evaporation in a vacuum desiccator over P_2O_5. Each fraction was checked by means of its CD, and pure crystals were obtained by repeating such fractional recrystallizations. The pure crystals were suspended in water and converted into potassium salt by stirring with a cation exchanger, Dowex 50W-X8. Found: C, 32.44; H, 3.97; N, 6.44%. Calcd for $C_{12}H_{18}N_2O_{10}KCo$: C, 32.15; H, 4.06; N, 6.25%.

Measurements. The visible and ultraviolet absorption spectra were recorded with a Hitachi 323 spectrophotometer.

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*** 1,4-Butanediamine.

**** 4-Aminobutanoate ion.

† (2*R*,4*S*)-2,4-Pentanediamine.

†† 2,4-Pentanediamine-*N,N,N',N'*-tetraacetate ion.

The CD curves were obtained on a JASCO Model ORD/UV-5 spectrophotometer with a CD attachment. The ^1H NMR spectra in D_2O were obtained on Varian T-60 and HA-100 spectrometers, using Na–TMS as the internal standard.

Results and Discussion

The ^1H NMR spectrum of $(-)_{405}$-[Co(en)$_2$(dcb)]$^{3+}$ (**1**) exhibits only two kinds of broad signals (δ 2.84 and 3.40) and a multiplet signal (δ 5.98). The ^1H NMR spectrum of $(-)_{405}$-[Co(acac)$_2$(dcb)]$^+$ (**2**) gives only two kinds of singlet signals (δ 1.20 and 1.28) on the methyl groups. These facts suggest that **1** and **2** have a symmetry element other than C_1 and, so the dcb in the

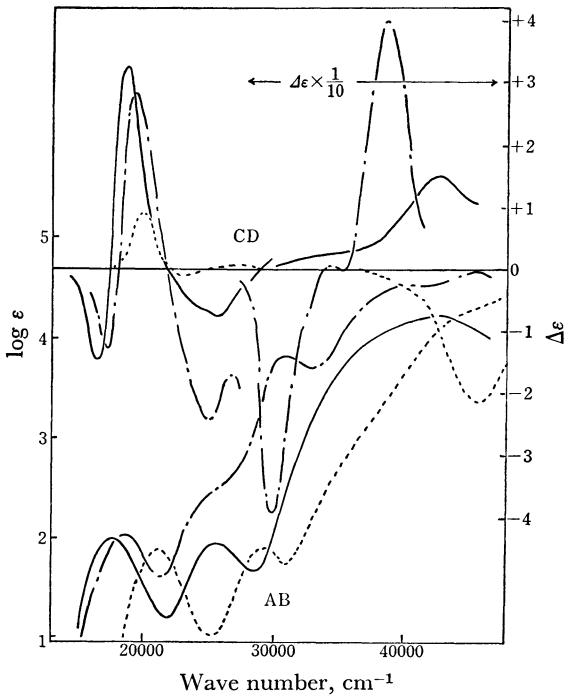

Fig. 1. Absorption (AB) and CD spectra of (----) $(-)_{405}$-[Co(en)$_2$(dcb)]$^{3+}$, (-·-): $(-)_{405}$-[Co(acac)$_2$-(dcb)]$^+$, (——): $(+)_{589}$-[Co(dcbta)]$^-$ in water.

complexes acts as a bidentate ligand. As Fig. 1 shows, the absorption spectra of **1** and **2** are similar to those of the analogous complexes, [Co(en)$_2$(tmd)]$^{3+}$,[4] and [Co(acac)$_2$(2,4-ptn)]$^+$,[7] respectively. The CD curve of **1** is very similar to that of $\Lambda(+)_{589}$-[Co(en)$_3$]$^{3+}$.[11] In the region from 15000 to 40000 cm^{-1}, the CD curve of **2** is almost enantiomeric with that of $\Lambda(-)_{546}$-[Co(acac)$_2$(*RR*-2,4-ptn)]$^+$.[7] It is thus clear that **1** and **2** have a *cis*-2-butene-1,4-diamine chelate ring (seven-membered ring). In addition, **1** and **2** seem to be assignable to the Λ- and Δ-configurations respectively.

In the region from 15000 to 40000 cm^{-1}, the absorption and CD spectra of $(+)_{589}$-[Co(dcbta)]$^-$ (**3**) are very similar to those of $\Delta(+)_{589}$-[Co(*RR*-2,4-ptnta)]$^-$,[8] respectively. This suggests that the dcbta coordinates to the cobalt(III) ion as a sexadentate ligand such as 2,4-ptnta and that **3** has the $\Delta(\lambda)$ structure (C_2 symmetry), as is shown in Fig. 2. This $\Delta(\lambda)$ structure seems also to be supported by the ^1H NMR spectrum of **3**

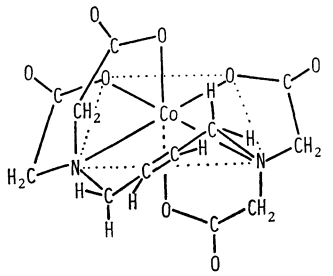

Fig. 2. Schematic structure of $\Delta(\lambda)$-[Co(dcbta)]$^-$.

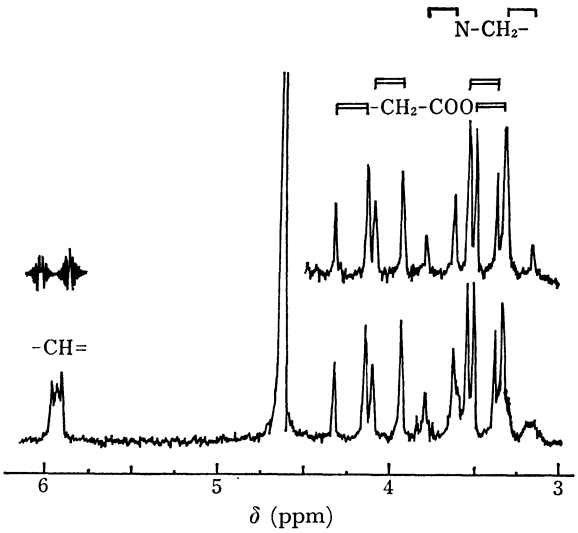

Fig. 3. ^1H NMR spectrum (100 MHz) of $(+)_{589}$-[Co-(dcbta)]$^-$ in D_2O.

shown in Fig. 3. The spectrum exhibits a kind of –CH= signal, two kinds of –CH$_2$–COO signals (two kinds of double doublets), and a kind of N–CH$_2$– signal. The assignment of the N–CH$_2$– signal is confirmed by the fact that the complicated signal becomes double doublets (axial H and equatorial H) upon irradiation at δ 5.95.

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