Stereoselective Formation of [Cr(edda or eddp)(N-N)]-Type Complexes with 1,10-Phenanthroline (edda = ethylenediamine-*N*,*N*'-diacetate; eddp = ethylenediamine-*N*,*N*'-dipropionate)

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The [Cr(edda or eddp)(N-N)]-type complexes (edda= ethylenediamine-*N*,*N*'-diacetate; eddp=ethylenediamine-*N*,*N*'-dipropionate), *trans*(O)-[Cr(edda)(phen)]Cl and *cis*(O)-[Cr(eddp)(phen)]Cl, were first prepared stereoselectively and characterized by UV-Vis absorption and IR spectra and X-ray crystal analysis. The optically active $(-)^{CD}_{510}$-[Cr(edda)(phen)]$^+$ was readily racemized even in an acidic aqueous solution within a period of several hours.

Stereochemistry of transition-metal complexes with the edda-type (edda=ethylenediamine-*N*,*N*'-diacetate) ligands has been extensively studied, and it has been reported that the edda as a tetradentate ligand in the octahedral complexes took both trans(O) and cis(O) geometries.[1,2] For the octahedral cases the [M(edda)(N-N)]-type complexes have been prepared for M=Co(III) and Ni(II).[2-4] Although for chromium(III) a number of [Cr(edda)(O-O)]-type complexes have been reported, the [Cr(edda)(N-N)]-type complexes have not been isolated yet due to the synthetic difficulty.[1] It is worthwhile to synthesize that kind of complexes and then to investigate the molecular structures and spectroscopic properties by comparison of the differences between the Cr(III) and Co(III) complexes. Moreover, it is interesting to study about the formation and stability of the chromium(III) complex with a five-membered edda or a six-membered eddp (eddp=ethylenediamine-*N*,*N*'-dipropionate). We wish to report here the first results of the preparation and characterization of the [Cr(N)$_4$(O)$_2$]-type, [Cr(edda or eddp)(phen)]$^+$, complex.

[Cr(edda)(phen)]Cl was prepared as follows: A mixed solution of $CrCl_3 \cdot 6H_2O$ (1.33 g, 5.0 mmol) and H$_2$edda (0.88 g, 5.0 mmol) in 50 cm^3 of H_2O was adjusted to pH 7 and stirred at room temperature for 5 min. To this solution a methanolic solution (20 cm^3) of 1,10-phenanthroline monohydrate (0.99 g, 5.0 mmol) was added, adjusted to pH 4, and refluxed for 2 h. The color of the solution turned from violet to red. The reaction solution was evaporated to remove methanol and poured onto an SP-Sephadex C-25 column. Only red band was eluted by 0.2 mol dm^{-3} KCl solution. The eluate was concentrated and desalted by adding methanol. Red crystals were obtained by standing the solution at room temperature for a few days.[5]

[Cr(eddp)(phen)]Cl complex cannot be obtained by the above method. Then, the synthesis was carried out by the use of [CrCl$_2$(H$_2$O)$_2$(phen)]Cl as a precursor[6]: A mixed solution of [CrCl$_2$(H$_2$O)$_2$(phen)]Cl (1.87 g, 5.0 mmol) and H$_2$eddp·2HCl (2.08 g, 7.5 mmol) in MeOH-H$_2$O solution (7 : 2) was adjusted to pH 6 and refluxed for 4 h. The desired red complex was purified and crystallized by the similar procedure described above.[7]

The edda ligand may adopt two geometrical configurations (trans(O) and cis(O)) concerning [Cr(edda)(N-N)]-type octahedral complexes. Both edda and eddp complexes provided only one isomer in the column chromatographic separation. The UV-Vis absorption spectra of these complexes exhibit a similar spectral pattern in the region of 350 - 200 nm to each other. However, the peak position of the first d-d absorption band of the eddp complex is observed at 500 nm with a shoulder in the lower energy side (ca. 549 nm), in contrast to 505 nm with a shoulder in the higher energy side (ca. 403 nm) for the edda complex. It is thought that these two complexes have different

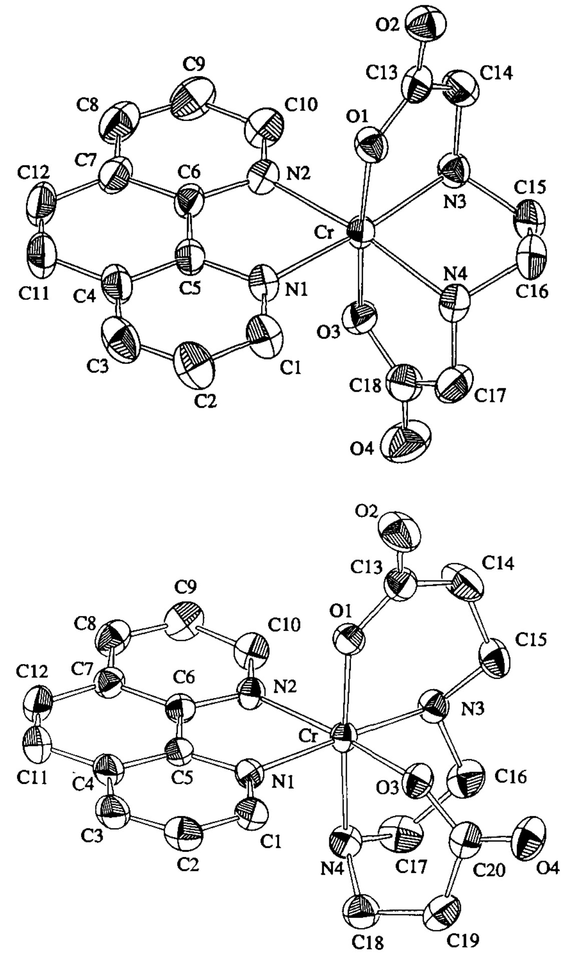

Figure 1. Molecular structures of the cations of *trans*(O)-[Cr(edda)(phen)]Cl (top) and *cis*(O)-[Cr(eddp)(phen)]Cl (bottom).

structures from each other, so the X-ray diffraction studies were carried out in order to determine the geometrical structures and elucidate the cause of such stereoselective formation of each complex.[8,9]

The molecular structures of the edda and eddp complexes are shown in Figure 1. It is interesting to clear that the edda complex takes a trans(O) structure and the eddp complex does a cis(O) one. The bond distances and angles in the edda moiety are similar to those of the [Cr(edda)(gly)] and [Cr(edta)]$^-$ complexes.[10,11] The bond distances in the present complexes are resemble to each other, whereas the N-Cr-O angles at β-alaninate (six-membered) ring in the eddp ligand are larger than those at glycinate (five-membered) one in the edda ligand. The N-Cr-O angles for the *trans*(O)-Cr(III) complex are slightly smaller than the N-Co-O angles for the *trans*(O)-Co(III) one, whereas those are nearly the same for cis(O) complexes.[4] The formation of only cis(O) isomer in the eddp complex is attributable to the analogous bond distances and angles around Cr(III) center between the *trans*(O)-edda and *cis*(O)-eddp complexes because of the relaxation of the strain on the β-alaninate ring. The ethylenediamine chelates in the edda and eddp take δ and λ conformations in the Δ isomer, respectively. These behaviors are similar to those of the [Co(edda)(N-N)]-type complexes.[4]

The IR spectra of the present complexes exhibited different spectral patterns and intensities in the 2800 - 3200 cm^{-1} region derived from a C(aliphatic)-H stretching band. By comparison, the ν(C-H) vibration bands of trans(O) isomer ($\nu_{\rm max}$ = 2919, 2878 cm^{-1}) were stronger than the corresponding band of cis(O) one ($\nu_{\rm max}$ = 2907 cm^{-1}). A similar tendency was also found for the corresponding ethylenediamine and 2,2'-bipyridine complexes.[12]

These edda and eddp complexes are stable in an aqueous solution. Although the attempted optical resolution of edda complex using the method of a column chromatographic technique was unsuccessful, the fractional resolution using [Sb_2(d-tart)$_2$]$^{2-}$ anion was successful. It is noteworthy that only $(-)^{\rm CD}_{510}$ isomer of edda complex was obtained as precipitates and this isomer was readily racemized (not accompanied by isomerization) in an aqueous solution as shown in Figure 2. The racemization occurred not only in the basic solution but in the acidic solution. Such a rapid racemization has not been observed so far in the other Cr(III)-edda complexes.[1,10]

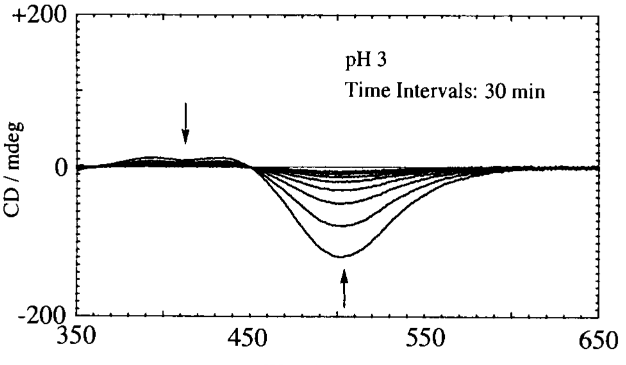

Figure 2. CD spectral change of $(-)^{\rm CD}_{510}$-[Cr(edda)(phen)]$^+$.

Further study on the cause of this racemization and the magnetic properties is now in progress.

References and Notes

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5 Anal. Found: C, 42.90; H, 4.56; N, 11.04%. Calcd for [Cr(edda)(phen)]Cl·2.8H_2O ($C_{18}H_{23.6}ClCrN_4O_{6.8}$): C, 43.92; H, 4.83; N, 11.38%. UV-Vis [H_2O; $\lambda_{\rm max}$, nm (log ε, mol^{-1} dm^3 cm^{-1})]: 505 (1.94), 403 (2.0sh), 348 (2.88), 336 (3.1sh), 317 (3.6sh), 303 (3.9sh), 277 (4.37), 224 (4.51), 204 (4.68). The sh denotes a shoulder. IR (KBr disk; $\nu_{\rm max}$): 3050 {C-H(phen)}, 2919, 2878 {C-H(edda)}, 1644, 1429 {C=O}, 1524 {C=N, C=C}, 1071 {C-NH}, 855 cm^{-1}{C=N}.

6 Unpublished data: The preparation was carried out by the reaction of chromium(VI) oxide with phen. Anal. Found: C, 34.88; H, 3.92; N, 6.69%. Calcd for [$CrCl_2(H_2O)_2$-(phen)]Cl·2H_2O ($C_{12}H_{16}Cl_3CrN_2O_4$): C, 35.10; H, 3.93; N, 6.82%. IR (KBr disk; $\nu_{\rm max}$): 3083 {C-H(phen)}, 1520 {C=N, C=C}, 851 cm^{-1} {C=N}.

7 Anal. Found: C, 44.68; H, 5.28; N, 10.27%. Calcd for [Cr(eddp)(phen)]Cl·3.5H_2O ($C_{20}H_{29}ClCrN_4O_{7.5}$): C, 45.07; H, 5.49; N, 10.52%. UV-Vis [H_2O; $\lambda_{\rm max}$, nm (log ε, mol^{-1} dm^3 cm^{-1})]: 549 (2.0sh), 500 (2.19), 351 (2.85), 333 (3.1sh), 321 (3.5sh), 303 (3.9sh), 278 (4.37), 225 (4.53), 205 (4.68). The sh denotes a shoulder. IR (KBr disk; $\nu_{\rm max}$): 3083 {C-H(phen)}, 2907 {C-H(eddp)}, 1644, 1624, 1429 {C=O}, 1524 {C=N, C=C}, 1088 {C-NH}, 855 cm^{-1}{C=N}.

8 Crystal data for [Cr(edda)(phen)]Cl·2.8H_2O: M_W = 492.26, triclinic, $P\bar{1}$, (No. 2), a = 11.104(1), b = 11.602(2), c = 8.797(1) Å, α = 100.47(1), β = 104.57(1), γ = 76.181(9)°, V = 1057.7(3) Å^3, Z = 2, D_C = 1.545 g cm^{-3}, $R(R_W)$ = 0.043(0.041) for 4147 reflections ($I > 3\sigma(I)$). Selected bond distances (Å) and angles (°): Cr-N1 = 2.081(3), Cr-N2 = 2.081(2), Cr-N3 = 2.085(3), Cr-N4 = 2.056(3), Cr-O1 = 1.924(2), Cr-O3 = 1.957(2), N1-Cr-N2 = 80.18(10), N3-Cr-N4 = 84.3(1), N3-Cr-O1 = 82.96(10), N4-Cr-O3 = 82.87(10), O1-Cr-O3 = 175.63(9).

9 Crystal data for [Cr(eddp)(phen)]Cl·3H_2O: M_W = 523.91, triclinic, $P\bar{1}$, (No. 2), a = 10.692(2), b = 15.834(2), c = 7.571(1) Å, α = 100.51(1), β = 110.05(1), γ = 100.64(1)°, V = 1140.6(3) Å^3, Z = 2, D_C = 1.525 g cm^{-3}, $R(R_W)$ = 0.038(0.039) for 5227 reflections ($I > 3\sigma(I)$). Selected bond distances (Å) and angles (°): Cr-N1 = 2.075(2), Cr-N2 = 2.110(2), Cr-N3 = 2.065(2), Cr-N4 = 2.068(3), Cr-O1 = 1.936(2), Cr-O3 = 1.934(2), N1-Cr-N2 = 79.58(9), N3-Cr-N4 = 84.1(1), N3-Cr-O1 = 91.33(9), N4-Cr-O3 = 89.36(9), O1-Cr-O3 = 89.94(8).

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12 The private data of these authors. *trans*(O)-[Cr(edda)(en or bpy)]$^+$ ($\nu_{\rm max}$ = 2924 cm^{-1} or 3036, 2882 cm^{-1}), *cis*(O)-[Cr(eddp)(bpy)]$^+$ ($\nu_{\rm max}$ = 3135 cm^{-1}).