Preparation and Circular Dichroism of L(+)-Alaninol Cobalt(III) Complex

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So far no report has been published on the stereospecific coordination of optically active aminoalcohols to metal ions. Using the method described for ethanolamine cobalt(III) complex,[1] we have prepared a new crystalline diastereoisomer of tris-L(+)-alaninol-tris-L(+)-alaninolato-dicobalt(III) perchlorate dihydrate, $(-)_D$-$[Co_2\{NH_2CH(CH_3)CH_2OH\}_3\{NH_2CH(CH_3)CH_2O\}_3](ClO_4)_3\cdot 2H_2O$ by the reaction of $[Co(OH_2)(NH_3)_5](ClO_4)_3$ and L(+)-alaninol (L(+)-2-amino-1-propanol[2]).

Found: C, 24.00; H, 6.21; N, 9.46%. Calcd for $C_{18}H_{55}O_{20}N_6Cl_3Co_2$: C, 24.02; H, 6.16; N, 9.33%.

Nearly symmetrical absorption curves of the first band in the three kinds of solvent indicate that the complex ion always has the *fac* geometrical configuration.[1,3] The circular dichroism (CD) spectrum of this complex in acid exhibits one strong positive and one weak negative peak in the first band region, and is very similar to that of Δ-*fac*-[Co(L-alanine$^-$)$_3$].[4] The complex ion in acid solution will exist as a monomeric protonated tris-alaninol complex, and we conclude that the complex ion is of *fac*-Δ type around the cobalt(III) ion. It is reasonable that L(+)-alaninol, which has a similar skeletal structure to that of *d*-propylenediamine, forms stereospecifically a tris-metal complex of Δ configuration (*lel* form).[5] A strong negative CD peak at 41650 cm^{-1} (in acid) suggests that the ligand is in a δ gauche form.[6]

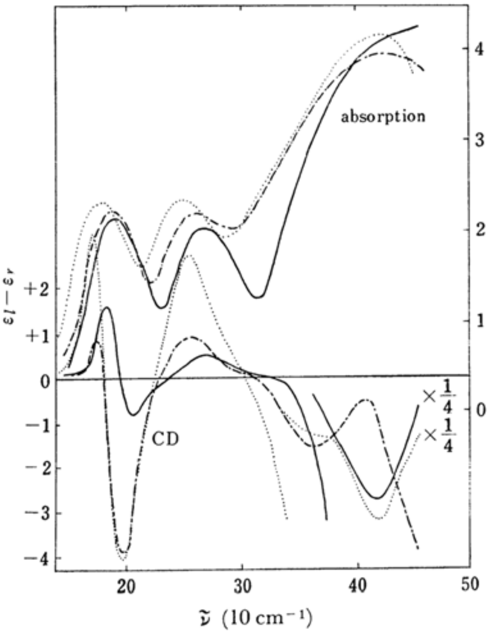

Fig. 1. Absorption and circular dichroism curves of $(-)_D-[Co_2\{NH_2CH(CH_3)CH_2OH\}_3\{NH_2CH(CH_3)CH_2O\}_3]^{3+}$

—— in 4 N $HClO_4$
—-— in absolute methanol
······ in 0.05 N NaOH in 50%(vol) methanol
log ε and $\Delta\varepsilon$ are converted into per one mole of cobalt.

The CD curves in methanol and in alkaline solution are very different from that in acid solution. Such a big change might be caused by an association between mutually oriented complex ions or molecules in these solvents. A most probable structure of the aggregate in methanol will be a dimeric form with face-to-face O···H···O hydrogen bonding between three OH groups of the triprotonated $[Co\{NH_2CH(CH_3)CH_2OH\}_3]^{3+}$ and three oxygen atoms of the deprotonated $[Co\{NH_2CH(CH_3)CH_2O\}_3]$. A similar but less remarkable effect was observed by Mason and Norman[7] in a system involving the tris-ethylenediaminecobalt(III) and the phosphate ion in water. The dimeric structure would also hold in the solid state as indicated by the chemical analysis.

In alkaline solutions, all alcoholic protons would be removed and the dimeric form would have O···H···N hydrogen bonding between three oxygen atoms of a complex molecule and three amino groups of another molecule.

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