Synthesis, Separation, and Identification of Optically Active Bis(pentane-2,4-dionato)(*S*-amino-acidato)chromium(III) Complexes

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Summary The synthesis of [Cr(*S*-amino-acid)(acac)$_2$] complexes (where *S*-amino-acid = *S*-alanine, *S*-valine, *S*-proline and acac = pentane-2,4-dione) is described along with techniques for separating the diastereoisomers into their optically active chiral forms.

Although a number of optically active, mixed ligand, amino-acid cobalt(III) complexes have been synthesized and studied, no analogous chromium(III) complexes have been prepared. This is surprising in the light of the important physiological role attributed to Cr^{III} and Cr^{III}–amino-acid complexes in glucose utilization.[1] We now report the synthesis of [Cr(*S*-amac)(acac)$_2$] complexes and a method for separating the complexes into their Δ and Λ chiral, optically active configurations.

The complexes were prepared by ligand exchange reactions starting with [Cr(acac)$_3$]. [Cr(acac)$_3$] was dissolved in a large volume of MeOH and the *S*-amino-acid dissolved in a small amount of water containing KOH was added. The reaction mixture was irradiated with a visible light source of wide wavelength range (Sylvania Sun Gun) for several hours to give [Cr(*S*-amac)(acac)$_2$] in about 20% yield. Heating the reaction mixture without irradiation with light does not produce the desired product. The solvent was removed, and unchanged [Cr(acac)$_3$] was separated by column chromatography on alumina. Separation into diastereoisomeric Δ and Λ chiral forms was accomplished for [Cr(*S*-alanine)(acac)$_2$] and [Cr(*S*-valine)(acac)$_2$] by column chromatography on alumina using CCl_4, $CHCl_3$, and C_6H_{14} mixtures. Separation of [Cr(*S*-proline)(acac)$_2$] into its Δ and Λ chiral forms was accomplished by fractional crystallization from a C_6H_{14}–$CHCl_3$ mixture. The specific rotations in $CHCl_3$ at 589 nm are: [Cr(*S*-alanine)(acac)$_2$] + 242° and −480°; [Cr(*S*-valine)(acac)$_2$] + 460° and −882°; and [Cr(*S*-proline)(acac)$_2$] + 1570° and −640°.

The major reaction products were identified as [Cr(*S*-amac)(acac)$_2$] rather than [Cr(*S*-amac)$_2$(acac)] by i.r. spectroscopy. The i.r. spectra of the analogous cobalt(III) complexes, [Co(*S*-amac)(acac)$_2$],[2] whose structures are known from ^{1}H n.m.r. spectroscopy were obtained in $CHCl_3$ between 600 and 2000 cm^{-1}. In addition to the intense characteristic frequencies of co-ordinated acac[3] at 1576, 1520, and 1384 cm^{-1}, a band at 1660 cm^{-1} appears which is characteristic of a co-ordinated amino-acid ligand. The spectra of the [Co(*S*-amac)(acac)$_2$] complexes and the [Cr(*S*-amac)(acac)$_2$] products are almost identical and quite different from the spectra of [Co(*S*-amac)$_2$(acac)] complexes.

The visible absorption spectra of the Cr^{III} complexes shows a band at 547 nm in $CHCl_3$ which is at a considerably shorter wavelength than for [Cr(acac)$_3$] itself (560 nm).[4] This is in agreement with the crystal field model which says that replacement of an acac ligand by an amac ligand should cause the band to move to shorter wavelengths. The Cr^{II} complexes have a high solubility in water and a wide range of organic solvents including $CHCl_3$, EtOH, and MeOH.

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