Chromatographic Separation of Optically Active Neutral Tris-chelated Cobalt(III) Complexes

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Summary Four diastereomeric pairs of complexes of the type [Co(*S*-amino-acid)(acetylacetone)$_2$] were separated by column chromatography on alumina, and the $(+)_D$ isomers were assigned the Λ absolute configuration by ^{1}H n.m.r. spectroscopy.

SEPARATION of diastereomeric neutral tris-chelated cobalt(III) complexes can be accomplished by column chromatography using non optically-active substrates. The system [Co(*S*-amino-acid) (acetylacetone)$_2$] (with *S*-amino-acid = *S*-alanine, *S*-valine, *N*-methyl-*S*-alanine, and *N*-methyl-*S*-valine) was prepared using a procedure similar to the one published by Laurie.[1] Separation into optically-active Δ and Λ diastereomers was accomplished by column chromatography on aluminium oxide and elution with ethyl acetate–ethanol mixtures. The optically-active diastereomers are soluble in acetone and water and have finite solubilities in methanol, ethanol, chloroform, and Me$_2$SO.

The Table gives specific rotations and n.m.r. data on each of the diastereomers isolated. The n.m.r. signal in D_2O for the methine proton of the co-ordinated amino-acid is deshielded (*i.e.* downfield) in all of the $(+)_D$ isomers compared to the corresponding $(-)_D$ isomers. Arguments developed by Berends and Brushmiller to assign the absolute configurations of tris-chelated cobalt(III) complexes ($CoNO_5$) from chemical-shift data have been applied to this system,[2] and all the $(+)_D$ diastereomers with a deshielded methine proton are assigned the Λ configuration.

TABLE

Specific rotations and n.m.r. data on some [Co(*S*-amino-acid)(acac)$_2$] *complexes*

	$[\alpha]_D$ in H_2O	N.m.r. data[a] D_2O C–H	D_2O N–Me	$[^2H_6]$Acetone N–Me
$(+)_D$-[Co(*S*-ala)(acac)$_2$]	+2208	3·75	—	—
$(-)_D$-[Co(*S*-ala)(acac)$_2$]	−2016	3·55	—	—
$(+)_D$-[Co(*S*-val)(acac)$_2$]	+2439	3·57	—	—
$(-)_D$-[Co(*S*-val)(acac)$_2$]	−2607	3·40	—	—
$(+)_D$-[Co(*N*-Me-*S*-ala)(acac)$_2$]	+2472	3·58	2·24	2·32
$(-)_D$-[Co(*N*-Me-*S*-ala)(acac)$_2$]	−1567	3·42	2·10	2·10
$(+)_D$-[Co(*N*-Me-*S*-val)(acac)$_2$]	+1986	3·45	2·72	2·40
$(-)_D$-[Co(*N*-Me-*S*-val)(acac)$_2$]	−1833	3·36	2·46	2·04

[a] Chemical shifts are measured relative to DSS in D_2O and Me_4Si in $[^2H_6]$acetone, both references being internal.

The chemical shift of the co-ordinated *N*-methyl group of [Co(*N*-methyl-*S*-amino-acid)(acetylacetone)$_2$] can also be used to assign the absolute configuration of the complexes. For tris-chelated complexes of this type, the methylated nitrogen atoms have the *R* configuration forced upon them by the adjacent bulky *S* carbon atom in the co-ordinated amino-acid. The n.m.r. signal in both D_2O and $[^2H_6]$-acetone of the *N*-methyl group is deshielded in the $(+)_D$ isomer compared to its position in the $(-)_D$ isomer. Again applying the Berends–Brushmiller model $(+)_D$-[Co(*N*-methyl-*S*-alanine)(acetylacetone)$_2$] and $(+)_D$-[Co(*N*-methyl-*S*-valine)(acetylacetone)$_2$] have the Λ configurations.

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