LITERATURE CITED


OPTICALLY ACTIVE MIXED CHELATE COMPLEXES.

6. MIXED CHELATES OF Co(II) AND Co(III) WITH ACETYLACETONE

AND AROMATIC AMINO ACIDS

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We have attempted to clarify the stereochemistry of the intermediate ternary catalyst—modifier—substrate complexes in enantioselective hydrogenation catalysts [1] in work on models of these ternary complexes — mixed chelates of Cu and Ni with acetylacetone (acac) and aromatic amino acids (AA) in solution and in the solid state — by circular dichroism (CD), optical rotatory dispersion (ORD), magnetooptical rotatory dispersion (MORD), IR and UV spectroscopy, and x-ray diffraction [2-6].

Here we have used CD, MORD, and UV spectroscopy to examine the Co(acac)₂—Co(AA)₂ system, where AA is D-phenylalanine (D-Phe), D-tyrosine (D-Tyr), and D-tryptophan (D-Trp), in DMF solution.

EXPERIMENTAL

The amino acid complexes of Co(II), Co(acac)₂, and Co(acac)₂(AA) were prepared by the methods of [7-9]. The CD spectra were measured with a Jobin-Yvon III dichrograph in the 250-750 nm region with solution concentrations of 0.652-3.73 mmole/liter. The UV spectra were recorded on a Specord UV-VIS spectrophotometer in the 200-800 nm region in the concentration range 0.1-1.55 mmole/liter. The MORD curves were measured in DMF solution on a Spectropol-1 spectropolarimeter in a magnetic field of 7490 ± 30 Oe in the 320-580 nm region in a cell with layer thickness 2 mm in the concentration range 1-12 mmole/liter.

RESULTS AND DISCUSSION

Unstable mixed chelate complexes of Co(II) with acetylacetone and aromatic AA's can be formed in solution by ligand exchange between the simple chelates in the same way as the Ni complexes [6]

Co(acac)₂ + Co(AA)₂ ⇔ 2 Co(acac)(AA)  \( (1) \)

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TABLE 1. Absorption Spectra of Same-Ligand and Mixed Chelates of Co(II) in DMF

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}}, \text{nm} ) (lg ( \varepsilon ) *)</th>
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<tbody>
<tr>
<td>Co(acac)₂</td>
<td>287 (4,06) 325 sh (3,52) 385 sh (2,37) 540 (1,61)</td>
</tr>
<tr>
<td>Co(D-Phe)₂</td>
<td>&lt;265 sh (&gt;3,80) 385 sh (2,32) 540 (1,79)</td>
</tr>
<tr>
<td>Co(D-Tyr)₂</td>
<td>277 (3,97) 390 sh (3,28) 590 (1,97)</td>
</tr>
<tr>
<td>Co(D-Trp)₂</td>
<td>208 sh (3,99) 283 sh (3,95) 293 sh (3,89) 530 (2,06)</td>
</tr>
<tr>
<td>Co(acac)(D-Phe)</td>
<td>&lt;265 sh (&gt;3,87) 280 sh (3,8) 335 sh (3,08) 390 sh (3,36) 540 (1,86)</td>
</tr>
<tr>
<td>Co(acac)(D-Tyr)</td>
<td>274 (3,86) 330 sh (3,1) 360 sh (2,33) 533 (1,88)</td>
</tr>
<tr>
<td>Co(acac)(D-Trp)</td>
<td>272 sh (4,14) 282 sh (4,12) 292 sh (4,08) 330 sh (3,36) 520 (2,16)</td>
</tr>
<tr>
<td>Co(acac)(D-Phe)</td>
<td>260 (4,46) 282 sh (4,12) 292 sh (4,08) 330 sh (3,36) 520 (2,16)</td>
</tr>
<tr>
<td>in CHCl₃</td>
<td>285 (3,47) 327 sh (3,03) 390 sh (2,19) 580 (2,57)</td>
</tr>
</tbody>
</table>

*The values of \( \varepsilon \) were calculated for the Co(acac)₂:Co(AA)₂ (1:1) systems with allowance for the complete disproportionation into the mixed chelates.

The equilibrium can be displaced toward the mixed chelate at constant Co(AA)₂ concentration by adding a large excess of Co(acac)₂.

Complexes of Co(II) with L-alanine have three bands at 530, 620, and 1338 nm in the d-d region; they are assigned respectively to the \( ^4T_g + ^4T_{1g}(F), ^4T_g + ^4T_{2g}(A), \) and \( ^4T_g + ^4T_{2g}(F) \) transitions of the octahedral complex [10]. Only the first band appears in the absorption spectra; the other two bands were located by calculation [10]. The long-wavelength region of the absorption spectra of the AA complexes of Co(II) also have only one broad maximum at 520-540 nm (Table 1). However, the CD spectra (Fig. 1) of the chelates of all three AA's contain two maxima in the long-wavelength region at 485-490 and 585-590 nm. We have observed discrepancies between the absorption and CD spectra of the equivalent Ni complexes [6]. This suggests that the shallow maximum at 520-540 nm observed in the absorption spectra actually involves contributions from two transitions that are not resolved experimentally and appear only in the CD spectra. Consequently, the symmetry of the AA complexes of Co(II) may well be lower than was supposed in [10].

The CD spectra of the Co(D-Phe)₂—Co(acac)₂ and Co(D-Trp)₂—Co(acac)₂ systems with excess Co(acac)₂ (Fig. 1a, d) contain four maxima in the d-d region. The appearance of the new maxima in the CD spectra of these systems by comparison with the spectra of the AA chelates, as in the case of the Ni(II) complexes [6], may be due to reduction in the symmetry of the complex and may be considered as experimental evidence for the formation of the mixed chelate complex Co(acac)(AA) in solution. In the case of the Co(D-Tyr)₂—Co(acac)₂ system with excess Co(acac)₂ (Fig. 1c) this is indicated by the substantial bathochromic shift of the two CD maxima relative to the corresponding maxima of the tyrosine chelate. We got similar results for the D-Phe and D-Trp chelates. The other CD maxima may not be visible because of the weakness of the CD. Equilibrium (1) for two optically active compounds should correspond to a set of CD curves with distinct isodichroic points where the magnitudes of the CD at other wavelengths vary in the same sense, which is not consistent with experiment (Fig. 1a). This suggests that Eq. (1) does not fully describe the entire set of optically active complexes present in the solution.

The dichroic absorption \( \Delta \varepsilon \) for the three maxima due to the formation of the mixed chelate in the Co(D-Phe)₂—Co(acac)₂ system (Fig. 2) reaches a maximum at a Co(D-Phe)₂:Co(acac)₂ ratio of 1:13.5 and falls rapidly with increase in this ratio. This feature apparently reflects the occurrence in the solution of another reaction, apart from reaction (1), that competes with the first in the presence of a certain excess of Co(acac)₂. This reaction could for example be the formation of the Co(acac)₂ trimer, like the trimerization of Ni(acac)₂ [11].

The charge-transfer (CT) region of the CD spectra of the Co(AA)₂—Co(acac)₂ systems for all three AA's contains a very intense maximum at 330 nm, whose intensity increases with Co(acac)₂ concentration, as is exemplified by the system with D-Phe (Fig. 1a). The absorption spectra of Co(AA)₂—Co(acac)₂ (1:1) contain in this region a very weak band in the form of a shoulder, which is also present in the spectrum of Co(acac)₂. The dichroism of the transition of the acetylacetonate ligand in Co(acac)(AA) can be attributed to the conformational effect caused by the folding of the acetylacetonate ligand induced by the asymmetrical influence of the chiral AA ligand, as was described earlier in the equivalent Cu and Ni complexes [3, 6].