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CONFORMATION OF COORDINATED AMINO ACIDS. I. TETRAMMINE(L-PHENYLALANINATO)-COBALT(III) ION

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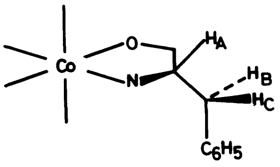
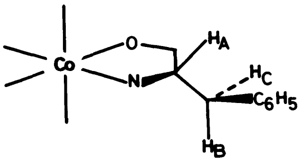
The ABX type spectrum of three CH protons of L-phenylalanine in tetrammine(L-phenylalaninato)cobalt(III) ion was analysed and it was found that fractional populations of three rotational isomers of the amino acidato ligand are significantly different from those in the free amino acid.

Cobalt(III) complexes of amino acids have been prepared and studied by many workers.1) These investigators have used mainly absorption and circular dichroism spectra to establish the geometrical disposition of coordinating ions or molecules around the central cobalt(III) ion. Little attention has been paid, however, to the conformation of coordinated amino acids. It is hoped, therefore, that utilization of proton magnetic resonance spectra yields conformational information of amino acid or amino acidato ligands. This letter reports the preliminary result of the conformational analysis of the L-phenylalaninato ligand in the titled complex ion, $[Co(NH_3)_4(L\text{-phe})]^{2+}$, in D_2O. The results for other cobalt(III) amino acid compounds will be published elsewhere.

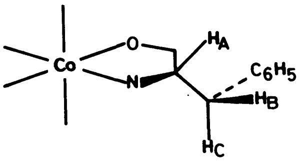
The complex was prepared after Shimura2) and the desired product was obtained by passing the reaction mixture through a chromatographic column packed with SP-Sephadex C-25. Spectra were recorded at 35°C on a Hitachi R-22 spectrometer operating at 90 MHz. Fractional populations of rotational isomers I to III were obtained by $p_I = 1 - p_{II} - p_{III}$, $p_{II} = (J_{AB}-J_g)/(J_t-J_g)$, and $p_{III} = (J_{AC}-J_g)/(J_t-J_g)$, in which J_t = 13.56 Hz and J_g = 2.60 Hz.3,4) The observed and calculated spectra are compared in Fig. 1. Least squares analysis yielded the spectral parameters given in Table 1, where parameters of the free amino acid at various pD are also cited. It is noted that the rotational isomer I increases significantly upon coordination at the expense of the isomer III . The steric hindrance between the phenyl group and one of the oxygen atoms of the carboxylate group(not shown in



I



II



III

Table 1. The fractional population of L-phenylalanine. Spin-spin coupling constants are given in Hz. Complex means the $[Co(NH_3)_4(L\text{-}phe)]^{2+}$ ion.

	free amino acid[4]			complex
pD	0.4	7.1	12.5	
p_I	26	28	29	37
p_{II}	46	48	45	51
p_{III}	28	24	26	12
J_{AB}	7.65	7.90	7.53	8.19
J_{AC}	5.65	5.20	5.42	3.97

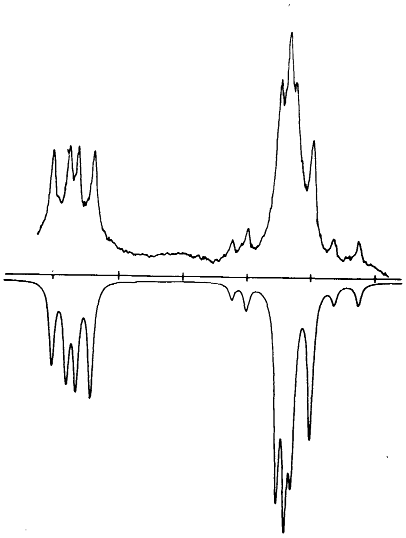


Fig. 1. The observed (upper) and calculated (below) spectra of $[Co(NH_3)_4(L\text{-}phe)]^{2+}$ at 90 MHz and 35°C after complete deuteration of the ammine and amino groups. The absorption due to the phenyl group is omitted. One division of the abscissa is 20 Hz and the magnetic field increases from left to right.

the inset) can be seen to be greater in III than in I, which will make the rotamer III least stable. In the isomer II, the carboxylate and phenyl groups are trans to each other and the population of this isomer will not be so different in both free and chelated forms. In conclusion, the chelation has been found to affect greatly the rotamer distribution of L-phenylalanine and the effect of chelation is greater in determining the rotamer stabilities than that of pD.

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