

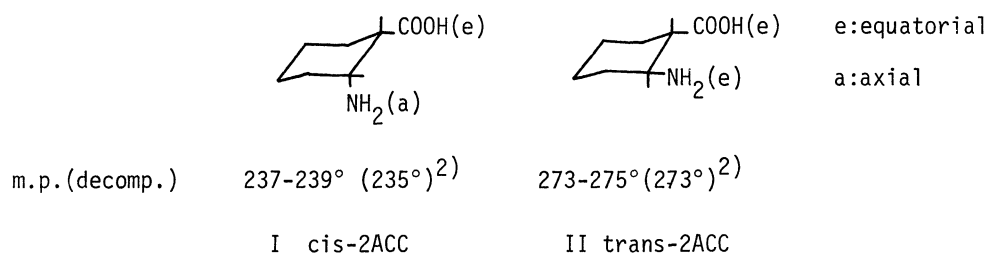
STUDIES ON THE METAL CHELATES OF cis- AND trans-2-AMINOCYCLOHEXANECARBOXYLIC ACIDS

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Metal chelates of cis- and trans-2-aminocyclohexanecarboxylic acids with divalent metals were newly synthesized and the binding ratios were found to be 2:1. Measurements of pK_a of cis- and trans-ligands, as well as the stability constants of Cu and Ni chelates were performed and the stability constants of cis chelates were found to be larger than those of the corresponding trans chelates.

It has been reported¹⁾ that cis- and trans-2-aminocyclohexanecarboxylic acids (cis-2ACC and trans-2ACC) exist dominantly in the following conformations, such as I and II.



Hünig et al.²⁾ observed the reactions of these ligands with Cu ion qualitatively, and Nikolasev et al.³⁾ reported on the stabilities of cis-2ACC chelates with divalent ions.

The authors this time attempted the syntheses of metal chelates with cis- and trans-2ACC, and simultaneously the measurements of pK_a of cis- and trans-2ACC, as well as of the stability constants of Cu and Ni chelates in aqueous solution, in order to investigate the stabilities and the physical properties, depending on the differences of the structural configuration.

cis- and trans-2ACC were synthesized in our laboratory, referring to the method of Armitage et al.⁴⁾ IR analysis of cis- and trans-2ACC indicated that any γ_{NH_2} and γ_{COOH} bands have not been observed in their IR spectra of both cis- and trans-2ACC, and therefore, they are considered

to be in the zwitterion structure, similarly to amino acids.

Metal chelates of Cu, Ni, Co, Zn and Cd have been synthesized successfully in aqueous solution and identified by the elementary analyses. Binding ratios of cis- and trans-2ACC with Cu, Ni and Co were 2:1, containing 2 moles of water of crystallization, while the ratios of both Zn and Cd chelates of cis- and trans-2ACC were 2:1, without possessing water of crystallization.

Dissociation constants of cis- and trans-2ACC in aqueous solution were measured, according to the method of Schwarzenbach⁵⁾ and the pK_{a_1} and pK_{a_2} values are 3.38 and 10.82 for cis-2ACC, and 3.31 and 10.19 for trans-2ACC, respectively.

Stepwise stability constants of Cu and Ni chelates of cis- and trans-2ACC, obtained by potentiometric measurement, according to Bjerrum method⁶⁾, are shown in Table I. The stability constants of cis chelates are found to be almost as same as those of β -alanine⁷⁾.

Table I Stability constants of cis- and trans-2ACC chelates ($\mu=0.1$, 25°)

	cis-2ACC		trans-2ACC		β -alanine ⁷⁾	
	Cu-chelate	Ni-chelate	Cu-chelate	Ni-chelate	Cu-chelate	Ni-chelate
$\log k_1$	7.39	4.41	6.53	3.74	7.13	4.63
$\log k_2$	5.74	3.31	4.84	2.71	5.47	3.40

It was found that the stability constants of cis chelates of both Cu and Ni were much stable than those of trans chelates in aqueous solution. It may be caused of the steric factors, though the reason has not been clarified yet.

The detailed studies with regard to the physico-chemical properties, as well as the detailed discussions on the relationship between stabilities and configurations will be reported.

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