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A SELECTIVE ESTER-EXCHANGE REACTION IN THE COPPER(II) CHELATE OF THE SCHIFF BASE DERIVED FROM SALICYLALDEHYDE AND DIBENZYLASPARTATE

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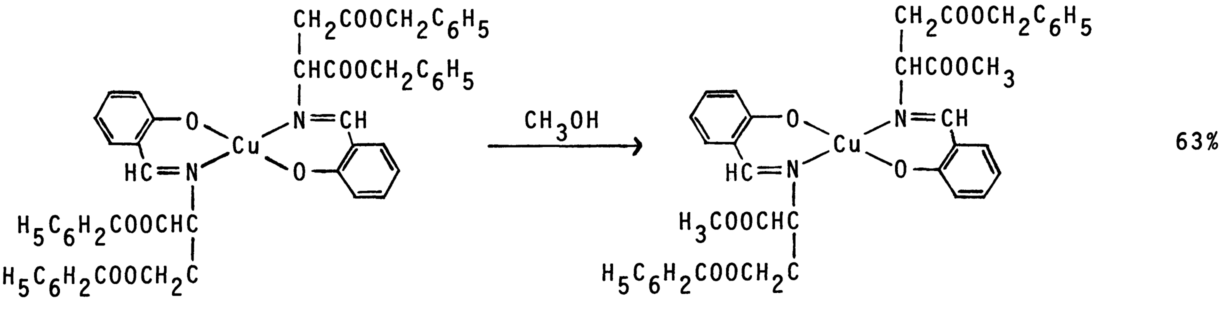
Upon refluxing a solution of bis(N-salicylidenedibenzyl-DL-aspartato)-copper(II), 1, in methanol, bis(N-salicylidene-α-methyl-β-benzyl-DL-aspartato)copper(II) 2, was obtained in a 63% yield, suggesting that an ester-exchange reaction occurred preferably at the α-position of the aspartate.

There have been reported a number of investigations which aimed at elucidation of the mechanism of ester-exchange reactions of bis(salicylaldiminato)copper(II) derived from various amino acid esters.[1-5] However, most of them have been confined to the reactions of bis(salicylaldiminato)copper(II) chelates with neutral amino acid esters.

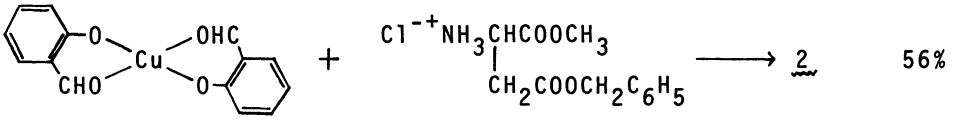
In this letter we report on a selective ester-exchange reaction in the copper(II) chelate of the Schiff base derived from salicylaldehyde and dibenzyl-DL-aspartate, 1, which was prepared by heating a mixture of bis(salicylaldehydato)copper(II) and benzenesulfonate of dibenzyl-DL-aspartate. The chelate 1 melted at 138-140°C, Found: C, 67.30; H, 5.12; N, 3.17%. Calcd for $C_{50}H_{44}O_{10}N_2Cu$: C, 66.98; H, 4.96; N, 3.13%. Heating of chelate 1 (1 g) in methanol(200 ml)-chloroform(50 ml) mixture under reflux for 30 min gave olive-green crystals (mp. 130-131°C) (Scheme 1). Found: C, 61.00; H, 5.03; N, 3.98%. Calcd for $C_{38}H_{36}O_{10}N_2Cu$: C, 61.32; H, 4.89; N, 3.76%. In order to confirm the structure of the product, bis(salicylaldiminato)copper(II) as illustrated in 2 was separately prepared by a reaction of bis(salicylaldehydato)copper(II) 3 with α-methyl-β-benzyl-DL-aspartate hydrochloride 4 (mp. 120-121°C), which had been synthesized by a



1 2

Scheme 1

similar way[6] as described for α-methyl-β-benzyl-L-aspartate hydrochloride (Scheme 2).

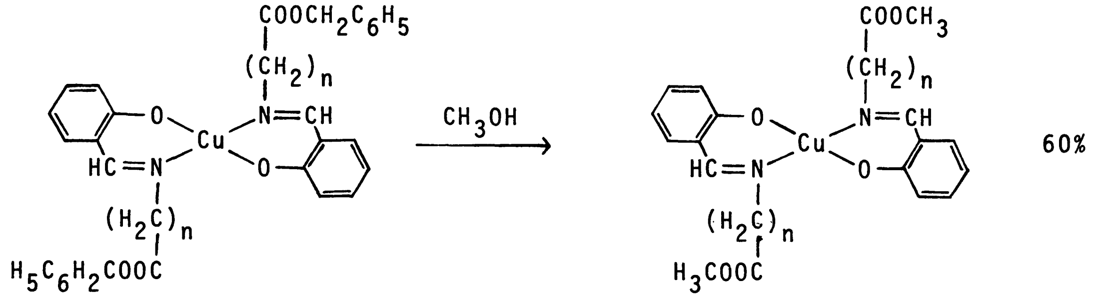


3 4

Scheme 2

mp. 131-133°C. The two crystals obtained by the reactions indicated in Schemes 1 and 2 revealed that there was no difference in their melting points, infrared spectra as well as the results of elemental analysis. The identity of the compound was also confirmed by a mixed-melting point test of the two crystals. Thus it has been concluded that the ester-exchange reaction occurs preferably at the α-position in the chelate 1.

On the other hand, the benzyl ester group at α- or β-position in benzyl-glycinate or -β-alaninate, respectively are exchangeable by methyl ester group as illustrated in Scheme 3. In the light of these experimental results, it is of interest to note that only the ester group at α-position of the chelate 1 were exchanged and that at β-position were not.



n = 1 or 2

5 6

Scheme 3

Further investigations are now in progress.

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