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Separation of Nickel(II) Amino Acid Complexes on Silica Gel

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NOTE

Separation of Nickel(II) Amino Acid Complexes on Silica Gel

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Summary

Chromatography of 25 nickel(II) amino acid chelates on silica gel using phenol–water 75:25 (w/w) as solvent system was described. In general, it was found that adsorbability of complexes formed with terdentate ligands is greater than that of complexes formed with bidentate ligands. In other cases R_F values increased with the increasing number of carbon atoms present in the chelate molecule. Steric effects of side chains of amino acids, which influenced the degree of solvation of nickel ion, were also considered.

Separation of metal amino acid complexes has been the subject of a number of recent studies. However, little is known about the chromatographic behavior of mentioned complexes. In an earlier work (*1*) dealing with the paper chromatography of Cd, Cu, Ni, and Zn bis(glycinate) complexes, it was stated that R_F values are influenced by the ionic radii of central atoms. In addition the effect of geometrical arrangement of the chelate cycle was also studied (2). Besides this, other characteristics such as polar or steric interactions must be also considered.

Since much interest is given to complexes of metal ions with amino acids because of their biochemical significance, this work deals with the application of thin-layer chromatography to the separation of nickel(II) amino acid complexes. The results obtained are considered with some generalizations correlating R_F value and structure.

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EXPERIMENTAL

Nickel(II) amino acid complexes were prepared as 0.01 *M* solution (with respect to the amino acid used) by the method described by Lang (3). Ten microliters of these solutions was applied on the starting line (1 cm from the edge) of the chromatogram. Thin-layer chromatograms were prepared in the usual manner. They consisted of a 250-μ layer of silica gel G (Macherey-Nagel) on 100 × 200 mm glass plates. The plates were activated by heating at 115°C for 2 hr and developed with phenol–water 75:25 (w/w) as solvent until the solvent front had migrated 10 cm from the origin. After drying, the plates were sprayed with a 0.2% solution of dimethylglyoxime for the detection of Ni^{2+}.

RESULTS AND DISCUSSION

All chelates studied are characterized by the presence of two five-membered chelate rings. They differ from one another in their side chain. The R_F values given in Table 1 are in agreement with the polarity as demanded by the structure of the complexes investigated. Thus the following conclusions can be drawn from the data given in Table 1.

Insofar as complexes of aliphatic amino acids are concerned, the R_F values increase with an increase in the side chain of the chelate rings. This shows that silica gel surfaces act as a polar sorbent. Chelates formed with the amino acids containing an *n*-alkyl chain give higher R_F values in comparison with those containing a branch side chain. Higher R_F values observed are caused by the steric hindrance of hydration in the sense of Irving and Pettit's theory (*4*) and thus a transfer to the mobile phase is favored. With the increase of the side-chain length, the degree of steric hindrance increases. Some tailing was observed with the lower member of chelates of aliphatic amino acids. The tailing was somewhat independent on the load. Activation of plates prevents tailing probably because of the reduction of the number of active silanole centers to dehydration.

Results further indicated that chelates formed with terdentate ligands (except histidine) yield low R_F values, suggesting that the energy of formation of the hydrogen bond between the silanole- or silandiole-active silica gel sites and the solute exceeded the energy of solvation. In the case of nickel(II) α,β-diaminopropionate and

TABLE 1

R_F Values of Nickel(II) Amino Acid Chelates

Nickel(II), chelate of	R_F
1. Glycine	0.17[a]
2. L-α-alanine	0.24[a]
3. L-α-aminobutyric acid	0.33
4. L-α-aminoisobutyric acid	0.32
5. L-norvaline	0.43
6. L-valine	0.38
7. L-leucine	0.47
8. L-isoleucine	0.44
9. Sarcosine	0.33[a]
10. Serine	0.15
11. L-threonine	0.28
12. L-methionine	0.76
13. L-tyrosine	0.49
14. L-proline	Tails
15. L-hydroxyproline	Tails
16. L-tryptophane	0.61
17. L-α,β-diaminopropionic acid	0.08, 0.44
18. L-α,γ-diaminobutyric acid	0.08, 0.41
19. L-ornithine	0.08
20. L-lysine	0.08
21. L-arginine	0.26
22. L-histidine	0.73
23. L-aspartic acid	0.05
24. L-glutamic acid	0.05
25. L-α-aminoadipic acid	0.05

[a] Some tails.

α,γ-diaminobutyrate, two spots were found on the chromatogram [both ligands can act in the presence of Ni^{2+} as bidentate or terdentate ones (5)]. Increased R_F values of α,β-diaminopropionate and α,γ-diaminobutyrate may be explained by a dual nature of interactions, i.e., by the presence of intramolecular bonding, which generally reduces the energy of adsorption, or by the changes in the basicity of ω-amino groups. The behavior of nickel(II) prolinate and hydroxyprolinate is unusual and can be considered as a result of the low stability of these complexes.

Considering the mechanism of adsorption of metal complexes, several of the plates (containing applied complexes) were developed after having stood for 24 hr. In all cases tailing was ob-

served due to the adsorption. This can be explained by the fact that the siloxy anions may enter the coordination sphere of labile complexes (6).

Owing to the fact that labile complexes may be bonded by weak coordination of siloxy anions (6), chromatography of nickel(II) amino acid chelates on silica gel with simple organic solvents usually used in the separation of amino acids was unsuccessful. It suggested that an eluent system capable of hydrogen bonding with active sites was necessary. In this respect the use of phenol was favored.

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