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Utilization of Steric Hindrance at the Metal Site in Separation of Copper(ll) Chelates

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NOTE

Utilization of Steric Hindrance at the Metal Site in Separation of Copper(II) Chelates

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Abstract

The chromatographic behavior of copper(II) chelates differing in the arrangement of their alkyl chains is influenced by the steric hindrance at the copper(II) site. This hindrance prevents the solvent molecules from coordinating on the remaining coordination positions, and thus R_F values of chelates decrease with increasing compression at the copper(II) site.

Much work has been devoted to the application of chromatography in coordination chemistry (for reviews, see Refs. *1* and *2*). The most significant among these is the separation of geometrical and optical isomers. However, little attention has been paid to the study of factors which influence chromatographic behavior of metal complexes.

In this note we describe the separation of copper(II) chelates of isomeric ligands containing the same number of carbon atoms in the molecule but differing from each other in the arrangement of their alkyl chains. These include complexes of (*S*)-α-amino-*n*-caproic (nleu), (*S*)-α-aminoisocaproic (leu), and (2*S*, 3*S*)-α-amino-β-methylvaleric (ileu) acids.

All these chelates, which were prepared by dissolving basic copper(II) carbonate in a hot solution of the proper ligand, have the same trans-

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planar geometry (*3*), corresponding to $Cu(N)_2(O)_2$ chromophore as can be concluded from their electronic absorption spectra (λ_{max} = 620 nm). The chelates described are not soluble in common solvents, and their separation was possible only by using a solvent capable of coordination. Of a wide variety of the solvent systems tested, pyridine–water 93:7 gave the most satisfactory results, even though some tailing occurred in all cases. The use of acetic acid (one drop) in the developing solvent prevented formation of tails; however, it depressed separation. R_F values (Lucefol, ready-made cellulose plates, Kavalier, CSR. Distance of start line: 1 cm; detection by spray with $K_4[Fe(CN)_6]$ solution) were as follows: $Cu(nleu)_2$ = 0.11; $Cu(leu)_2$ = 0.67; $Cu(ileu)_2$ = 0.83.

The chromatographic behavior of metal chelates depends both on the character of the central atom (*4*) and on the ligand. While the latter contributes to the total polarity of the molecule, the former can act as a Lewis acid. To decide which of these factors predominates, free ligands were chromatographed under the same conditions as described above. However, in all cases we observed $R_F = 0$. Thus we consider that R_F differences, as can be also demonstrated by the study of molecular models, are due to the steric hindrances imposed by the side alkyl chains of ligands which prevent, in different degrees, the solvent molecules from coordinating on the remaining coordination site of copper(II) (Fig. 1).

A study of the models shows that the degree of possible interactions decreases in the series: nleu $\gg$ leu > ileu, which is the reverse order of the R_F values observed. Our assumption concerning the mechanism of separation can be supported by chromatography of these chelates in the 2, 6-dimethylpyridine–water 93:7 solvent system, in which all chelates studied showed $R_F = 0$. The presence of $-CH_3$ groups in the 2 and 6 positions of the pyridine ring leads to several steric clashes, which make the coordination of this solvent practically impossible.

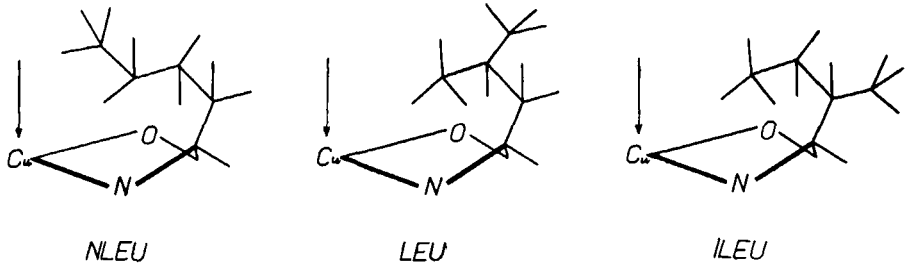

FIG. 1. Arrangement of side alkyl chains in copper(II) chelates.

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