Neutral Diamide Ionophores — Phenylendioxydiacetamides

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The preparation of a series of neutral ligands containing ether and amide groups is described. These ligands as well as related ones bearing other diamide groups are shown to selectively chelate Group II A cations by picrate extraction from water to methylene dichloride. This result was also confirmed by atomic absorption measurement. The changes in UV absorption of aromatic rings and amide groups in the ligands upon titration with metal salts in methanol allow the estimation of the ordering of cation binding.

(Keywords: Acyclic ionophores; Neutral ionophores; Phenylendioxydiacetamide, complexation studies)

Neutral Diamide Ionophore — Phenylendioxyacetamide


Introduction

Naturally occurring macrocyclic and acyclic ionophores are involved in the selective transport of essential metal cations across biological membranes\textsuperscript{2a,b}. Synthetic ionophores are of interest in that they provide model systems which can be varied greatly in structure. They can solubilize metal cations in lipid-like solvents and are useful in applications such as cation analysis, catalysis, organic synthesis and the study of the mechanisms of ion transport across membranes.
Previously, an acyclic 1,2-ethylenedioxydiacetamide system was found to show selective Group II A cation complexation. It was also reported that aromatic and acyclic analogues of this system display a wider range of selective binding properties in ion sensitive electrodes. We would like to report the synthesis of a series of phenylenedioxydiacetamides together with the studies of their complexation properties using picrate extraction, atomic absorption and UV spectroscopy.

**Results and Discussion**

Phenylene dioxydiacetic acid (1) is known. Improved yields were obtained by reaction of catechol with ethyl bromoacetate in the presence of excess base (10% excess) in water. The reaction of acid chloride (2) with the amines in question gives the amides (3).

\[
\begin{align*}
\text{OH} & \\
\text{OH} & \\
\text{BzCEHCOOEt} & \\
\text{NaOH-H}_2\text{O} & \\
\rightarrow & \\
\text{OCH}_2\text{COOH} & \\
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\end{align*}
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Qualitative UV Studies

The complexation of various cations with ligands 3 was studied in methanol, a solvent for which there is much data on the complexation of crown ethers and other molecules. The single broad absorption of 3 at around 270 nm changes to either a doublet or higher absorbance upon its complexation.