Studies on Separation and Determination of Metal Ions Using Crown Compounds.

- Application of Novel Acyclic Bis(hydrazone) Derivatives, Forming Pseudo-Crown Ether Structures, as Chromogenic Extractants for Metal Ions. -

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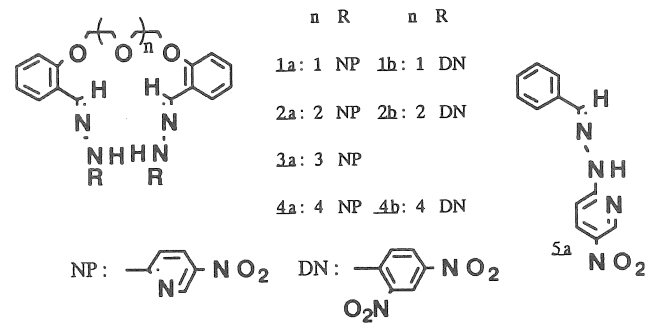
Summary

Hydrazone derivatives bearing some heterocyclic groups have been utilized for colorimetric determination of some transition metal ions because they form stable complexes with the metal ions and their absorption spectra are remarkably changed upon complexation with the metal ions. Especially, the hydrazones form predominantly 2:1 (hydrazone:metal ion) complexes with some kinds of divalent metal ions, such as Cu^{2+}, to extract them into organic phase. It is well-known that an oligoethylene glycol forms the pseudo-cyclic structure, like a crown ether, to give complex with an appropriate alkali metal ions when the donor atoms of the ethylene glycol chain participate in coodination with the metal ion. It occured to us that a bis(hydrazone) derivative bearing two hydrazone moieties linked with oligoethylene glycol can form binuclear metallic complex with an alkali metal and a transition metal ions to enhance the complexability and selectivity for the transition metal ion.

In this study, novel bis(hydrazone)s were synthesized and the complexabilities and the extractabilities of the bis(hydrazone)s for metal ions were evaluated spectrophotometrically. It was realized that the complexabilities of bis(hydrazone)s for alkali metal ions in H_2O - 1,4-dioxane (72/28 vol%) solution varied with the length of the oligoethylene glycol units. Especially, 3a, and 4a and 4b exhibited high selectivities for Na^+ and K^+, respectively.

On the solvent extraction of alkali, alkaline earth and some transition metal ions using the hydrazones with nitropyridyl group, Cu^{2+} was selectively extracted from aqueous solution at pH 6.2 into 1,2-dichloroethane while no extraction of the other metal ions were shown. The co-extraction between a particular alkali metal ion and Cu^{2+} with 3a and 4a were also realized. Determination of Cu^{2+} in the seawater using 3a was attained by spectrophotometry.



Structural formulas of hydrazone derivatives.