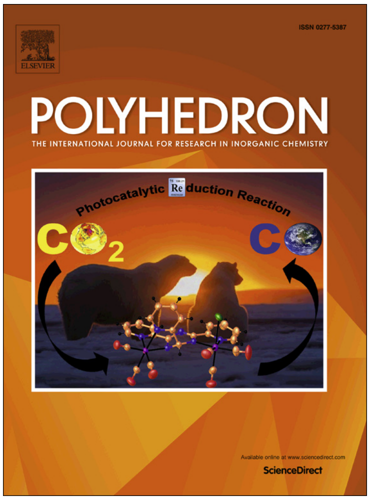

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PII: S0277-5387(16)30688-X
DOI: http://dx.doi.org/10.1016/j.poly.2016.12.037
Reference: POLY 12395

To appear in: *Polyhedron*

Received Date: 16 November 2016
Revised Date: 22 December 2016
Accepted Date: 23 December 2016

Please cite this article as: Yu.V. Fedorov, O.A. Fedorova, S.N. Kalmykov, M.S. Oshchepkov, Yu.V. Nelubina, D.E. Arkhipov, B.V. Egorova, A.D. Zubenko, Potentiometric studies of complex formation of amidopyridine macrocycles bearing pendant arms with proton and heavy metal ions in aqueous solution, *Polyhedron* (2016), doi: http://dx.doi.org/10.1016/j.poly.2016.12.037

Potentiometric studies of complex formation of amidopyridine macrocycles bearing pendant arms with proton and heavy metal ions in aqueous solution

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ABSTRACT

A novel pyridine-azacrown ether amide macrocycles comprising pyridine or carboxylic pendant arms were synthesized. The protonation constants of the compounds and the stability constants of their complexes with a wide range of metal ions (Ag^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Y^{3+}, Eu^{3+}, Lu^{3+}) were determined by potentiometric method. The different complexes of macrocycles with cations, including HML, ML and $ML(OH)_n$ were found to form. The increase of the stability of the complexes provides the presence of carboxyl substituents in pyridine-azacrown ether amide macrocycles; the values for the Cu^{2+}, Ni^{2+} and Pb^{2+} complexes of ligand containing three carboxylic arms are exceptionally high. Single crystal structures of a few complexes with Cu^{2+} and Pb^{2+} were determined. In all complexes, the metal centre exhibit a strong coordination with amine N-atoms and arm's ligand groups. The rigid structure of pyridine-2,6-dicarbamide fragment and an open macrocyclic cavity provide a possibility to fast kinetics of complex formation.

1. Introduction

Macrocyclic ligands have wide applications in catalysis, metal separation, molecular recognition, sensoring due to their ability to form complexes with different metal ions or anionic species [1-9]. The binding properties of ligands are determined by the nature and arrangement of donor atoms, the ring size and configurational rigidity of the molecule. It is well known that crown ethers have affinity to alkali and alkaline earth metal ions whereas azacrown ethers show high affinity towards softer metal ions [2]. Polyazacompounds are able to interact with both metal cations and inorganic anions [10–11]. Attachment of various substituents to the nitrogen heteroatoms can further influence the coordination properties of the polyazacrown ligands introducing the possibility for a different interactions with guests [12,13]. The addition of the amide group to macrocyclic ligands results in amide-based macrocycles which characteristics are higher negative charge on oxygen than for ether and ester groups, and geometrical rigidity. Amide-based macrocycles typically adopt preorganization of their binding sites through hydrogen bonding or configurational rigidity around the amide carbon-nitrogen bond [14].

In our previous studies we have synthesized and investigated the coordination properties of some azacrown, pyridine-azacrown ethers and pyridine-azacrown ether amide macrocycles with heavy metal cations [15-18]. It was demonstrated that both the size of the cavity and its heteroatom composition were important factors influencing on complex formation with the heavy metal ions (Ag^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}) [15]. Also it was shown that benzo-diaza-crown ether with carboxylic pendant arms is attractive ligand for binding of trivalent cationic radionuclides (Y^{3+}, Lu^{3+}, Bi^{3+}, Ac^{3+}) applicable for synthesis of radiopharmaceuticals due to fast complex formation [18]. Pyridine-azacrown ether amide macrocycles