

Complexation of Pb^{2+} by Macrocyclic Benzo- and Pyridinophanes

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Abstract

Eleven macrocyclic compounds containing benzene and/or pyridine moieties are synthesized and their application for lead(II) cation binding processes is investigated using cyclic voltammetry and UV–VIS techniques.

Introduction

The inclusion properties of macrocyclic compounds constitute a very interesting subject of studies. A search for selectively complexing receptors is meaningful in the aspects of chemistry and biology as well as medicine. Therefore, shortly after the publication of the pioneering report concerning the complexation of alkali metal ions by crown ethers [1], papers covering the synthesis and properties of modified crown ethers started to appear in the literature [2]. In the seventies of the previous century, the aromatic systems (e.g., benzene) and/or heteroaromatic systems (e.g., pyridine) have been introduced into the crown structure [3].

In the recent years, the synthesis [4–11] of macrocyclic diamides was intensively studied at our laboratory. The complex formation of heavy metal cations, including Pb^{2+} , with diazacoronands [12–15] as well as with crown ethers [16], polyazamacrocycles [17], and calixarenes [18] has also been studied. On the basis of our own investigations, we introduced a general method for the preparation of macrocyclic diamides, including compounds containing aromatic and heteroaromatic systems (Scheme 1), using α,ω -diamines and methyl α,ω -dicarboxylates as starting materials.

Here we present the set of macrocyclic ligands (Figure 1) containing benzene and/or pyridine moieties, obtained *via* the methodology above-mentioned, as well as their complexation properties towards lead(II) cation, determined using cyclic voltammetry and UV–VIS techniques.

Experimental

Materials

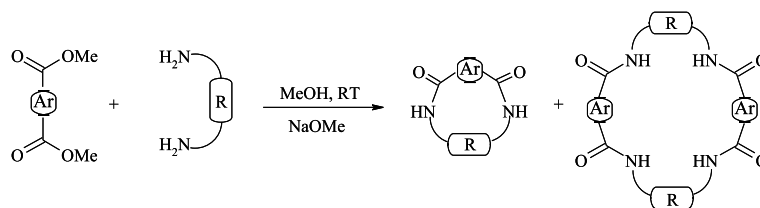
All ligands **1–11** were prepared according to the known procedure [12, 13, 15] and have spectral and analytical data identical to those given in the literature. Commercially available lead perchlorate (a concentrated stock solution) from SERVA, Germany, tetrabutylammonium perchlorate from Fluka, Switzerland, acetonitrile from POCH, Poland, and propylene carbonate from Aldrich, Germany, were used.

Methods

Voltammetric investigations

The voltammetric measurements were carried out using a hanging mercury drop electrode (663 VA, Metrohm, Autolab) and an Autolab electrochemical instrument. As the reference electrode, an Ag/AgCl electrode filled with 0.1 M solution of tetraethylammonium chloride in methanol, connected to the cell with an electrolytic bridge containing 0.1 M solution of tetrabutylammonium perchlorate in acetonitrile (or in propylene carbonate) was used. In all experiments, 0.1 M solution of tetrabutylammonium perchlorate in acetonitrile or in propylene carbonate was used as supporting electrolyte. All solutions were deaerated with argon before the measurement. The concentrations of lead(II) cation, typically at the level of 10^{-4} M, were obtained by addition of small volume of a $\text{Pb}(\text{ClO}_4)_2$ concentrated stock solution directly to the cell. For a given concentration of metal cation, a series of measurements was made for various metal/ligand concentration ratios. For each metal/ligand ratio the voltammograms were measured twice and averaged, at scan rates of 0.05, 0.1 and 0.2 V/s.

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Scheme 1. A general route to macrocyclic bisamides and tetraamides.

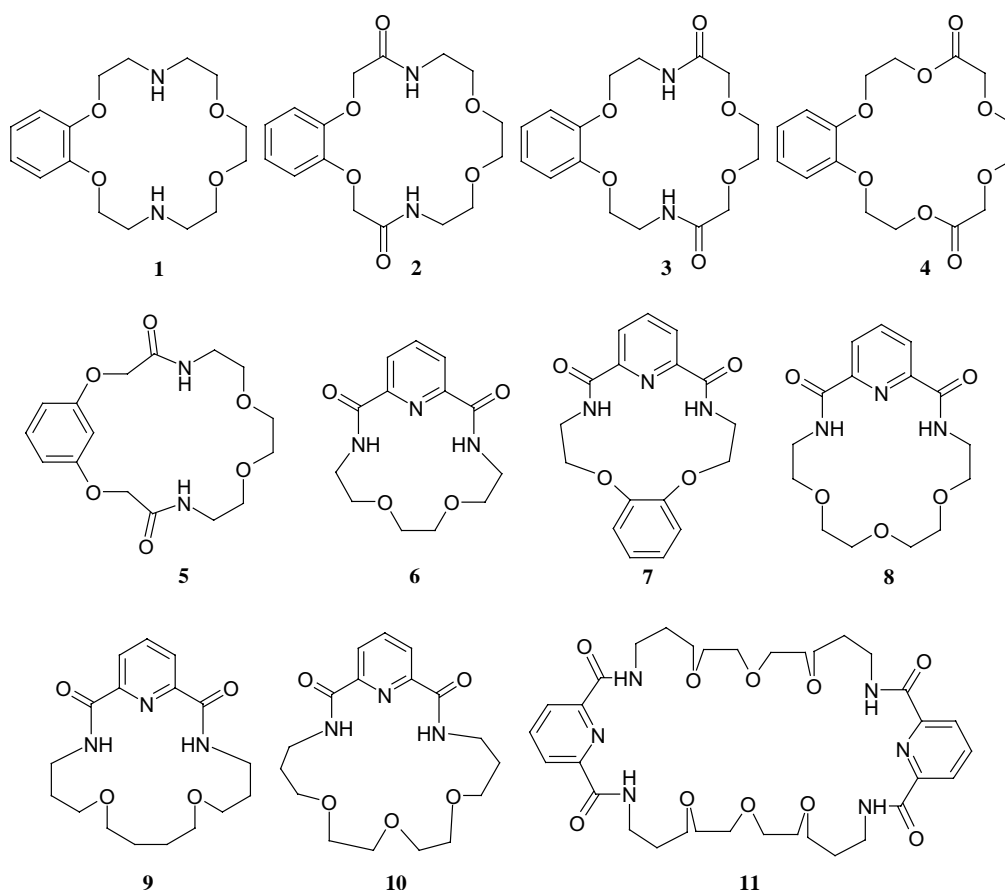


Figure 1. Structure of the substrates used.

UV–VIS measurements

UV–VIS measurements were carried out with a Thermo Spectronic UV 500 spectrophotometer equipped with a Thermo Neslab dual channel temperature controller, precision $\pm 0.1^\circ$. All experiments were performed in a quartz cuvette with a volume of 3 mL and a path length of 1 cm in an acetonitrile solution (5×10^{-4} M) over the range 190–900 nm. The spectra were analyzed using the Vision32 program.

Results and discussion

In this paper, we describe an extension of our investigations of binding behavior to macrocyclic benzo- and pyridinophanes including different functional groups. In

our research, diamine **1**, eight diamides (**2–3** and **5–10**), diester **4** and tetraamide **11** were the host molecules, and Pb^{2+} cation was a guest (Figure 1). We started cyclic voltammetry measurements using acetonitrile as a solvent. The stability constants of labile complexes of said ligands with Pb^{2+} cation were determined using DeFord–Hume method [19]. Although Pb^{2+} did not show perfectly reversible reaction, the peak separation was very close to the theoretical value for two-electron reduction process. The potentials used for calculations were taken as averages between the cathodic and anodic voltammetric peak. Alternatively, the voltammograms were semi-differentiated [20] and average values of cathodic and anodic semi-derivative peaks were used in calculations to minimize the impact of small changes of peak potentials caused by the addition of ligands. The

Table 1. The stability constants ($\log \beta$) of complexes of Pb^{2+} with benzo- and pyridinophanes **1–11** calculated from voltammetric measurements

Ligand	Log β		Type of complex
	In acetonitrile	In propylene carbonate	
1	~20	–	Labile 1:1
2	5.0	–	Labile 1:1
3	3.7	–	Labile 1:1
4	4.2	–	Labile 1:1
5	3.3	–	Labile 1:1
6	1.6	Observed but not measurable ^a	Labile 1:1
7	2.75	–	Labile 1:1
8	3.4	–	Labile 1:1
9	3.6	Observed but not measurable ^a	Labile 1:1
10	5.1–5.2	Observed but not measurable ^a	Labile 1:1
11	^b	–	Inert 1:1

^aThe potential shift is noticeable and systematically increasing, however, too small for quantitative interpretation.

^bThe value exceeded the measurement limit ($>10^4$).

results of both approaches were very similar and the $\log \beta$ values obtained in both ways were practically the same. The stability constants for inert complex with lead cation were determined from the decrease of the peak height of free Pb^{2+} ions upon addition of the ligand. The data were fitted to the models for ML , ML_2 and M_2L complex formation, and only the models giving non-negative values for stability constants were taken into consideration. Since the stability constants of complexes **6**, **8** and **10** were determined earlier [13], we also decided to carry out these measurements in propylene carbonate as a solvent for comparison. The calculated stability constants are collected in Table 1.

Furthermore, we decided to apply UV–VIS spectroscopy in our studies of complexation properties of one macrocyclic diamine **1** and four macrocyclic diamides **2–5**. For better correspondence, we carried out the measurements in acetonitrile. As a main technique of measurement, we chose the spectrophotometric titration. For ligands **1–5**, both stability constants and stoichiometry of complexes were determined. In the case of pyridinophanes, the analysis of results was difficult. Ligand **6** revealed an affinity to lead cation, but quantitative interpretation of that phenomenon was impossible. Results of UV–VIS spectroscopy measurements are presented in Table 2.

Table 2. The stability constants ($\log \beta$) of complexes Pb^{2+} with benzophanes **1–5** calculated from UV measurements

Ligand	Log β	Type of complex
1	$\gg 20$	1:1
2	4.8	1:1
3	5.6	1:1
4	3.4	1:1
5	3.8	1:1

Conclusions

In conclusion we have shown that determination of the stability constants using both voltammetric and UV–VIS methods lead to basically similar results, with only one exception of compound **3**. It should be additionally noted that the electrochemical method is better for distinction between labile and inert complexes, whereas the UV–VIS one is superior for establishing stoichiometry of complexes. Further, more detailed studies are in progress.

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