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POTENTIOMETRIC STUDIES ON METHYL PYRIDINE DERIVATIVES OF 14-MEMBERED TETRAAZA MACROCYCLES AS SELECTIVE IONOPHORES FOR HEAVY METALS

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Studiul potențiometric al derivaților metal piridinici al compuşilor macrociclici de tip tetraaza, utilizați ca ionofori selectivi pentru cationii metalelor grele, a relevat remarcabile selectivități ale acestora pentru Cd^{2+} şi Pb^{2+}. A fost preparată o nouă membrană electrodică de clorură de poli(vinil) (PVC), bazată pe aceşti ionofori, iar rezultatele preliminare sunt prezentate. Au fost studiate membrane cu diferite compoziții, iar cele optime au continuat să fie utilizate în studii.

The potentiometric study on methyl pyridine derivatives of 4-membered tetraaza macrocycles, used as a selective ionophore for heavy metal cations, showed a remarkable selectivity for Cd^{2+} and Pb^{2+}. A new poly(vinyl)chloride PVC membrane electrode based on these ionophores was prepared and preliminary results are presented. Membranes with different compositions were studied, the optimal ones being further used for the tests.

Keywords: tetraaza macrocycles, sensors, heavy metals

1. Introduction

Complexation of heavy metals is facilitated by soft donor atoms in the structure of macrocyclic ligands. Ligands having 2-pyridylmethyl pendant arms have been studied [1, 2], but values of stability constants have only been determined for very few of them. In general, linear amines with pyridyl substituents show high affinity for heavy metals, such as cadmium, lead or mercury, and very low ones for magnesium and calcium, this property assisting

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the removal from the environment or from living bodies [3] of these toxic metal ions. Costa et al. [4] undertook a detailed study of 2-pyridylmethyl derivatives of L^3 with two (3,11-Bis(2-pyridylmethyl-)3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17)13,15-triene (L^1) and three pendant arms 3,7,11-Tris(2-pyridylmethyl)-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene (L^2), determining their stability constants with several metal ions, such as: Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+} and In^{3+}. L^1 and L^2 present high stability constants for Cd^{2+} and Pb^{2+} in comparison with other ligands and particular selectivities for these metal ions.

It was found that the thermodynamic stability constants of N-(2-pyridylmethyl) derivatives of linear amines with the divalent transition metal ions were higher than expected due to the low overall basicity of these compounds [5].

There are many analytical methods for cadmium determination at low concentrations, mainly developed due to the admissible limits of them [6] in several environmental matrices. Among them, atomic absorption spectrometry (AAS) [7], inductively coupled plasma-optical emission spectroscopy (ICP-MS) [8] and chromatography [9] are the most often used, but all of these allow the detection of total heavy metal and not only of the free metal. Ionophore-based potentiometric sensors for Cd^{2+} were previously reported using as active compounds in the membrane several ionophores such as: crown-ethers and crown-ethers derivatives [10, 11], ETH 5435 [12], thiacalix [4]arene and derivatives [13] and sulphide salts [14]. In this context, a preliminary potentiometric attempt to develop a selective Cd^{2+} electrodic membrane with plasticized poly(vinyl-chloride) PVC membrane containing 3,11-Bis(2-pyridylmethyl)-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene (L^1) is presented here showing convenient characteristics which will be further studied and improved.

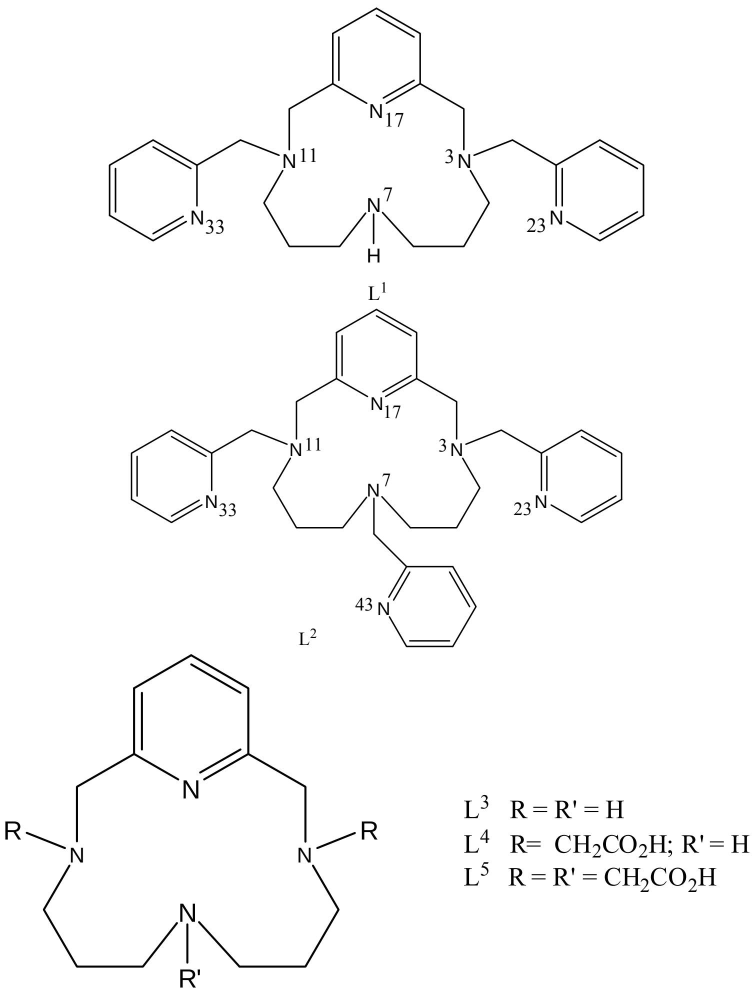

Fig. 1. L^1-(3,11-Bis(2-pyridylmethyl-)3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17)13,15-triene; L^2-3,7,11-Tris(2-pyridylmethyl)-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene

2. Experimental

Reagent L^1 was synthesized by previously reported procedures [4], poly(vinyl chloride) (PVC), bis(2-ethylhexyl)sebacate (DOS), o-nitrophenyl octyl ether (o-NPOE), sodium tetrakis[3,5-bis(trifluoromethyl)]phenylborate (NaTFPB), the lipophylic salt tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) and tetrahydrofuran (THF) were from Fluka AG (Switzerland). Aqueous solutions were prepared with freshly deionized water.

HNO_3, $Cd(NO_3)_2$, $Zn(NO_3)_2$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $Pb(NO_3)_2$, $Cu(NO_3)_2$ were of Suprapur quality from Merck (Germany).

Membrane preparation

The polymeric membranes used for the determination of the stability constants contained ionophore (1 mg) and NaTFPB (50 % vs. ionophore w/w) in PVC/o-NPOE 33 mg/66 mg (total 100 mg). Sodium tetraphenylborate (NaTFB) as anion excluder was added in the appropriate amount (50 % mol vs. the ionophore). The membrane components were dissolved in freshly distilled THF (0.5 mL). The solutions were placed in glass rings mounted on a glass plate and covered with another glass plate to slow down the solvent evaporation. The resulting membrane (thickness 120 μm) was peeled and discs of 7 mm diameter were cut out. The sensors were kept for three hours in ambient conditions for solvent evaporation and conditioned for 24 hours before the experiment in 10^{-4} M $Cd(NO_3)_2$ solution. A reference membrane was elaborated using the same process with no macrocyclic ligand [15].

Potentiometric response to cations and selectivity measurements

Membrane discs of 4 mm active diameter were glued to plasticized PVC tubing with a THF/PVC slurry. The internal filling solutions were 10^{-3} M $Cd(NO_3)_2$ adjusted to pH 7 with HNO_3. All measurements were performed at ambient temperature using a galvanic cell of the following type: Ag/AgCl/3 M KCl/1 M CH_3COOLi/sample/ion-selective membrane/10^{-3} M $Cd(NO_3)_2$ solution/AgCl/Ag. The emf values were measured using a Nicco station, previously described [12].

The emf measurement

Measurements were done by manual gravimetric additions at pH 7. Separate polyethylene beakers, pretreated with 10^{-1} M HNO_3 for 7 days were used for each concentration. The potential was measured with a custom-made 8-channel electrode monitor at room temperature in stirred solutions. The reference electrode (Metrohm Ag/AgCl in 3 M KCl) had a 1 M LiOAc bridge electrolyte. The pH electrodes were also from Metrohm. All emf values were corrected for liquid junction potential using the Henderson equation and activity coefficients were calculated according to the Debye-Huckel approximation [16]. For selectivity measurements, membranes of the same composition were conditioned in a discriminated ion solution 1 mM $NaNO_3$. This has the effect of avoiding the leaching of the primary ion from the membrane. The nitrate salts of different cations were measured at varying concentrations in the order of increasing preference for the membrane, the emf being determined at three concentrations (10^{-2} to 10^{-4} M). The experimental slopes were used to calculate the selectivity coefficients by using the separate solution method. For the calibration curves the electrodes were sequentially moved from the most to the least dilute sample and the potentials were stabilized before data aquisition for about 20 min as a function of the ion concentration obtained by addition of 10^{-2} M solution of $Cd(NO_3)_2$ in a concentration range of 10^{-7} M up to 10^{-2} M of $Cd(NO_3)_2$. The measurements were done at a constant pH 7 adjusted with 10^{-3} M HNO_3. The response of the sensor was characterized in terms of slope of the curve ΔE(V) vs. pCd, where pCd is the cologarithm of the concentration of the Cd ion.

3. Results and discussion

The promising results of Hancock [17] obtained for N-pyridyl derivatives of macrocyclic ligands with heavy metal ions promted Costa's group to undertake a detailed study of two 2-pyridylmethyl derivatives L^1 (with two pendant arms) and L^2 (with three pendant arms) of L^3. Since the relative selectivity for metal ions depends on the overall basicity of the compounds, the acid-base behavior was potentiometrically studied.

Both ligands L^1 and L^2 show good affinities to copper in the presence of the most tested cations, emphasizing the selectivity for this cation as well. However, the interference of Cu^{2+} was important for L^1 at a fixed concentration of $Cu(NO_3)_2$ of 10^{-2} M. This observation is confirmed by the values of the stability constants of the complexes of L^1 and L^2 with different metal ions presented in Table 1. The pM values determined at physiological pH have shown that L^1 is the most selective compound for cadmium relative to zinc, but from the values of the determined selectivity coefficients, L^1 is selective for Cd^{2+} in the presence of Cu^{2+} ions in solution. We did not obtained selectivity for Cd^{2+} in the presence of Pb^{2+} using fixed interference ion method FIM [18].

Table 1

Protonation (log K) constants of L^1 and L^2 and stability constants ($\log K_{ML}$) of their complexes with some divalent metal ions. T = 25 °C; I = 0.10 M in KNO_3 [4]

Ion	Equilibrium quotient	L^1	L^2
H^+	$[H_4L]/[L]x[H]^4$	21.39	20.56
Ca^{2+}	[ML]/[M]x[L]	3.43	-
Co^{2+}	[ML]/[M]x[L]	13.5	-
Cu^{2+}	[ML]/[M]x[L]	20.13	19.42
Zn^{2+}	[ML]/[M]x[L]	14.65	11.92
Cd^{2+}	[ML]/[M]x[L]	14.85	16.55
Pb^{2+}	[ML]/[M]x[L]	10.69	9.62

As it can be seen from Table 1, the metal complexes of both ligands present different values for L^1 and L^2 with the tested metal ions. The Cd^{2+} complex presents a particularly high stability constant in comparison with the Pb^{2+} complex, the tests in sensors indicating a good selectivity of the sensor for Cd^{2+} in the presence of Pb^{2+} using L^1 in the membrane. L^2 shows good selectivities for Pb^{2+} in the presence of all the other cations from Table 1 tested as interferents.
In the potentiometric studies we have done, the methyl pyridine derivatives of 14-membered tetraaza macrocycles were examined as ionophores in PVC membranes containing lipophilic salts. In order to obtain unbiased $K^{pot}_{I,J}$ values, calibration plots for various cations were done in a concentration range $10^{-2} – 10^{-4}$ M. The electrodes exhibited a Nernstian or near-Nernstian response of pure solutions of highly discriminating cations in the range of $10^{-7} – 10^{-1}$ M.

Potentiometric determination of the stability constants

The selectivity of polymeric membranes is provided by the ion-ionophore interactions, expressed by affinity constants of the complexes. The complex formation constants were determined using the segmented sandwich method [19]. Experiments were carried out according to the procedure described in [20]. Two sets of membranes were prepared with and without a ionophore. A series of 7 mm i.d. membrane discs were cut from the parent membrane and the disks were conditioned for 24 h in appropriate salt solutions 10^{-4} M ($Cu(NO_3)_2$, $Pb(NO_3)_2$, $Cd(NO_3)_2$, $Ca(NO_3)_2$, $Mg(NO_3)_2$). Two measurements were carried out for a sandwich membrane with and without ionophore and these for a for every given membrane and given cation. The sandwich membrane was obtained after drying the individual membranes with ionophore and without ionophore, which were immediately immersed into the appropriate salt solution in the same concentration as the one for conditioning. The potential was recorded as the mean of the last minute of a 10 min measurement period in the test solution. The membrane potential values Δ emf were calculated by subtracting the cell potential for a membrane without ionophore from that of the sandwich membrane, the formation constant being calculated using the following equation:

$$\beta_{IL_n} = (L_T - n \cdot R_T / z_I)^{-n} \exp(\Delta emf \cdot z_I \cdot F / RT) \qquad (1)$$

where n is the complex stoichiometry, L_T and R_T are the concentrations of ionophore and ionic site additives in the membrane, respectively.

The values of the formal constants (Table 2) show that for L^1 with heavy metals are particularly high showing that this ligand can selectively bind these metal cations, especially Cd^{2+} and Cu^{2+}.

Table 2

Formal complex formation $\log\beta_{\mathrm{ILn}}$ obtained with ionophore L^1 in PVC membranes using the segmented sandwich method

Cation	Log β_{ILn}, membrane
Ca^{2+}	2.50
Mg^{2+}	3.20
Pb^{2+}	8.25
Cu^{2+}	20.52
Cd^{2+}	17.40

Standard deviations were lower than 1.5 from three replicate measurements. All measurements were realized at a constant pH of 7.

Sensors with ionophore L^1 exhibited a Nernstian response towards Cd^{2+} in the presence of K^+, Ca^{2+} and subNernstian in the presence of Pb^{2+} (log $K_{Cd,Pb}$=-1.2). The value of the stability constant of this ligand with Cd^{2+} has a particularly high value of 14.85 (T = 25 ^{0}C, I = 0.1M) being particularly high. From the X-ray structure determination of the complex [4] it was found that it bonds all the donor atoms of the ligand, in comparison with the other metal ions studied. The fact that the value of the stability constant of this ligand with Cu^{2+} is very high, 20.13 (T = 25 ^{0}C, I = 0.1 M), while the potentiometric membrane does not have a Nernstian response vs. this cation is questionable.

The values of the selectivity coefficients (Table 3) show a good selectivity for Cd^{2+}, and it was also observed that the type of plasticizer is not quite significant, slightly differences appearing between the values of ($\log K^{\mathrm{pot}}_{\mathrm{Cd,J}}$) for the same interferents at the same concentrations, and with different plasticizers in the membrane.

Table 3

Potentiometric selectivity coefficients ($\log K^{\mathrm{pot}}_{\mathrm{Cd,J}}$) of membranes containing 1 mg of L^1 - (3,11-Bis(2-pyridylmethyl-)3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17)13,15-triene and two plasticizers, a polar one o-nitrophenyl octylether (o-NPOE) and a less polar one bis(2-ethylhexyl)sebacate DOS

Plasticizer	$\log K^{\mathrm{pot}}_{\mathrm{Cd,J}}$								
	K^+	Ca^{2+}	Pb^{2+}	Mn^{2+}	Co^{2+}	Cu^{2+}	Fe^{3+}	Cr^{3+}	Al^{3+}
o-NPOE	- 3.2	- 2.5	- 3.0	- 3.5	- 1.9	- 0.3	- 4.0	- 4.5	- 4.8
DOS	- 3.5	- 2.5	- 2.2	- 3.5	- 2.0	- 0.5	- 3.9	- 4.5	- 5.0

The logarithmic values of the selectivity coefficients ($\log K^{pot}_{Cd,J}$) indicated that the ionophores are capable to interact selectively with cations in the polymeric membrane phase.

The potentiometric selectivity coefficients (3) given by the Eisenman's equation (below) were evaluated by the fixed interference method, where a_i is the activity of the primary ion, a_j is the activity of the interferent and Z_i, Z_j are the respective charges.

$$E = E_0 + \frac{2.303RT}{Fz_i}\log(a_i + \sum K_{ij}^{pot} a_j^{(z_i/z_j)}) \tag{2}$$

$$K_{ij}^{pot} = \frac{a_i}{a_j^{(z_i/z_j)}} \tag{3}$$

Potentiometric selectivity coefficients were determined by the separate solution method (SSM) [21]. Selectivity coefficients ($K_{i,j}^{pot}$) were obtained from adequate unbiased E^0 measurements for each cation, based on the equation:

$$K_{i,j}^{pot} = \exp[z_I F / RT(E_J^0 - E_I^0)] \tag{4}$$

where R, T and F are the gas constant, absolute temperature and the Faraday constant, respectively. The charge of the primary ion I is indicated as z_I and the potentials obtained by the extrapolation of the linear part of calibration curve to log a = 0 for primary and interfering ions are put as E_J^0 and E_I^0, respectively. Activity coefficients were calculated according to the Debye-Huckel approximation [16].

The values of the potentiometric selectivity coefficients reported in Table 3 show good selectivities of the sensor to cadmium in the presence of most tested cations for L^1, emphasizing the remarkable selectivity for this cation in the presence of Pb^{2+}. However, the interference of Cu^{2+} is important at a fixed concentration of $Cu(NO_3)_2$ of 10^{-3} M. Indeed, electrodes with membranes based on L^1-(3,11-Bis(2-pyridylmethyl-)3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17)13,15-triene ionophore showed an enhanced selectivity towards Cu^{2+}. It must be pointed that the value of ($K_{i,j}^{pot}$) for Cu^{2+} is roughly estimated because in copper nitrate solutions the electrodes responded to Cu^{2+} ion in a super Nernstian way. From single crystal X-ray structure of the complex it was concluded that in the case of L^1 with copper, in the presence of three bulky pyridylmethyl groups constraining the geometric arrangement of the nitrogen atoms around the metal, but the influence of the steric effects on the structural preferences is still studied

Taking into account that the selectivity coefficients were investigated only in PVC membranes, other polymers as polysiloxanes will be tested, being well-known that the plasticized PVC membranes can detach from the transducing part of the sensor and that the plasticizer and the ionophore can leach out from the membrane.

The effect of the pH on the electrode potential at various cadmium concentrations was studied by adding diluted solutions of 0.1 M HCl or 0.1 M NaOH and adjusting the pH using a pH-meter in the range 2.0-9.0 with an electrode containing an internal filling solution of $1.0\text{x}10^{-3}$ M $Cd(NO_3)_2$. It was observed that the response does not vary significantly in the range of pH values from 4 to 8. At higher values of the pH, hydroxi complexes of Cd^{2+} can be formed and at lower values the H_3O^+ ions interfere. The results are presented in Table 4.

Table 4

Influence of the pH on the potential response of Cd^{2+}-ISE

pH value	emf, mV
2	360
3	335
4	320
5	321
6	319
7	320
8	321
9	340

In order to investigate the effect of the anions, the electrode potentials were measured using sulphate salts and nitrate salts, no significant changes in the characteristics of the electrode being observed, so nitrate salts have been used in further studies.

In the study of the response of electrodes, the Cd^{2+} concentration was changed by adding known amounts of prepared stock solutions under constant stirring in the range 10^{-7} – 10^{-1} M. The measurement time between two concentrations was 10 min, the response time being of about 10 s.

The calibration curve was obtained in the presence of 10^{-4} M $Cu(NO_3)_2$. The linear range of the sensor response was up to $10^{-6.5}$ M of cadmium with a slope of 27.5 mV/dec for DOS used as plasticizer and approximately 26.5 mV/dec for o-NPOE. It must be emphasized that the lower detection limit reached about 10^{-6} M, which leads us to the possibility of improvement for the future studies.

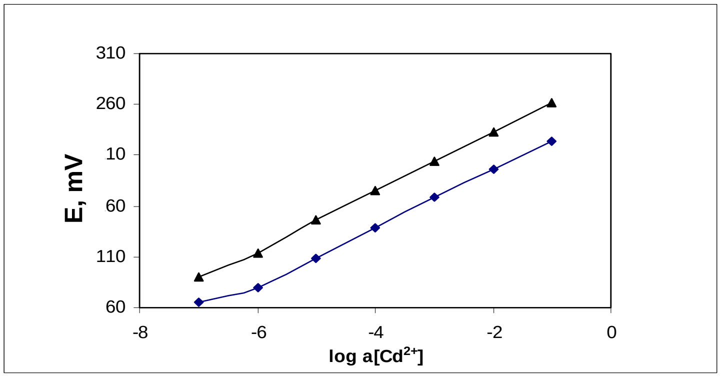

Fig. 2. Average calibration plots of the Cd-selective electrode with L^1 - 3,11-Bis(2-pyridylmethyl)-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene and two plasticizers, o-nitrophenyl octylether (o-NPOE) (■) and bis(2-ethylhexyl)sebacate DOS (▲)

Linear curve fitting using IUPAC method was used for the determination of ISEs characteristics. A linear response was shown by the electrode (with a correlation coefficient of 0.9989) to the activity of the Cd^{2+} ions. Response characteristics of the Cd-ISEs are presented in Table 5.

Table 5

Response characteristics of the studied Cd^{2+}-ISE

Parameter	Value
Slope, mV /dec	27.5
Linear range, mol / L	$10^{-6.5}$-10^{-1}
Limit of detection, mol / l	10^{-6}
Repeatability, s.d.	+ 0.3 mV
Stability	3 months
Working pH range	3-7

It was interesting to find that the calibration curve was deteriorated in the presence of 10^{-4} M Pb^{2+}, meaning that it is not possible to determine Cd^{2+} in the presence of Pb^{2+} in solution at this concentration level. Only trace amounts of Cu^{2+} in tested solutions allowed Cd^{2+} determination, but only in the concentration range of cadmium of 10^{-1} – $10^{-5.5}$ M. Until now, it was possible to obtain a calibration curve for Cu^{2+} only in solutions without any interferents, at a fixed pH of 7.

Eight electrodes were simultaneously measured, having the same compositions of the membranes. The potential generated across the membranes was reproducible and repeated monitoring of the potential on the same solution gave a standard deviation s.d. ± 0.3 mV.

Application of the method

The electrode was used for the determination of cadmium in samples with phosphate matrices as fertilizers using Chelex 100-an iminodiacetate type of chelating resin for the preconcentration of cadmium. The samples were dissolved as in [22]. Both potentiometric Cd^{2+}-ISEs and atomic absorption spectrometry AAS were used in order to compare the results [23]. The samples of fertilizers are pretreated with the resin using the batch procedure, with 0.5 g of Chelex 100, a contact time of 60 min and an elution volume of 20 mL 1.5 M HNO_3. The results are indicated in Table 6.

Table 6

Cadmium content (ppm) in different fertilizers with phosphate matrix determined by AAS with graphite furnace and Cd^{2+}-ISEs (batch procedure)

Fertilizer	Method		Recovery %	RSD %*
	AAS	Cd^{2+}-ISE		
NPK 10-30-10	21.1	22.5	98.2	0.8
NPK 10-40-20	20.6	21.0	97.7	0.9
NPK 10-40-10	17.27	18.5	97.0	1.4

*Relative standard deviation RSD% was calculated for an average of 6 determinations.

4. Conclusions

In summary, novel methyl pyridine derivatives of 14-membered tetraaza macrocycles, L^1 - 3,11-Bis(2-pyridylmethyl-)3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17)13,15-triene and L^2 - 3,7,11-Tris(2-pyridylmethyl)-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),13,15-triene have been synthesized and preliminary applied for electrodes in PVC membranes. L^1 showed a remarkable selectivity for Cd^{2+} in the presence of Cu^{2+}, but not for Cd^{2+} in the presence of Pb^{2+}.

The present work will serve as a basis for future Cd^{2+}- sensor selective for cadmium, having the possibility to be directly used in certain matrices. Several influences such as: type of polymer, amount and type of plasticizer, amount and type of ion-exchanger and sensor fabrication will be studied, as well as possible contamination and fouling. It must be emphasized that compound L^2 exhibits selectivity for Pb^{2+} in the presence of other interferents and this will be further studied in membranes of ion selective minielectrodes.

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