



## Polyaza macroligands as potential agents for heavy metal removal from wastewater

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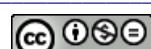
**Abstract:** Two polyaza macroligands *N,N'*-bis(2-aminobenzyl)-1,2-ethanediamine (**L1**) and 3,6,9,12-tetraaza-4(1,2),11(1,2)-dibenzo-1(1,3)-pyridinacyclotridecaphane (**L2**) were characterized and investigated for their metal ion extraction capabilities. The nature of all complexes was established by spectroscopic techniques. The equilibrium constants were determined by spectrophotometric and potentiometric techniques and the residual concentration of metals in the solutions by atomic absorption spectrometry (AAS). The capacity of the ligands to remove heavy metals such as Cu(II), Ni(II), Cd(II), Zn(II) and Pb(II) as insoluble complexes was evaluated in wastewater from industrial effluents. These agents showed high affinity for the studied metals. The values of the equilibrium constants of the isolated complexes (between  $1 \times 10^4$  and  $2 \times 10^7$ ) demonstrated the feasibility of applying these chelating agents as alternatives for the removal of heavy metals from industrial effluents.

**Keywords:** polyaza macroligands; pollutant removal; wastewater; heavy metals.

### INTRODUCTION

The removal of heavy metals from aqueous solutions is an important issue faced by industries discharging wastewater. Due to rapid industrialization, an alarming amount of toxic heavy metals has been released into the environment, endangering natural ecosystems and public health.<sup>1</sup> In recent years, a wide range of treatment technologies, such as chemical precipitation, solvent extraction, adsorption, membrane filtration, and electrodialysis, have been developed for the removal of heavy metals from contaminated wastewater.<sup>2</sup> The use of organic-

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based ligands that produce stable coordination compounds has been proposed as an alternative procedure for the selective extraction and removal of dissolved heavy metals from contaminated water.<sup>3,4</sup>

Some of the main features of a suitable extracting agent are high affinity toward the target metals and their ability to form stable insoluble compounds. In this context, Schiff base macroligands show great potential to act as extracting agents.<sup>5–7</sup> Schiff base condensation reactions have been used to produce a large number of macroligands or receptors that form metal complexes with different stabilities according with the nature of the ligands and the preferences of the metal ions to coordinate.<sup>5,8–14</sup>

The synthesis of new polyaza macrocyclic and their potential applications in areas such as environmental protection for the removal of heavy metals from contaminated effluents are themes of great interest. The synthesis of a polyaza receptor incorporating five nitrogens and a pyridyl unit to obtain the cyclic macroligand 3,6,9,12-tetraaza-4(1,2),11(1,2)-dibenzo-1(1,3)-pyridinacyclotrideca-phane (**L2**) was previously reported. This ligand was capable of binding metal ions such as Ni(II), Pb(II) and Zn(II) to give high yields of fairly stable complexes at room temperature with 1:1 (metal:ligand) stoichiometry that were insoluble in water.<sup>9,10,16</sup>

As part of the ongoing development of new ligands, the goal of this work was to investigate the potential extracting properties of the acyclic and cyclic macroligands **L1** (*N,N'*-bis(2-aminobenzyl)-1,2-diaminoethane) and **L2** toward Cu(II), Ni(II), Cd(II), Zn(II) and Pb(II). These metals are usually reported in wastewater samples from some industries and creeks in Monterrey, Mexico. The capabilities of these ligands to minimize the metal concentration below the allowed limits by the Official Mexican Regulations for treated water discharge<sup>17</sup> were evaluated. The spectral characterization (infrared and MS), elemental analysis and the equilibrium constants determined by UV-vis and potentiometric titration of the complexes of Cu(II), Ni(II), Cd(II), Zn(II) and Pb(II) with **L1** and **L2** are also reported herein.

#### MATERIALS AND METHODS

All reagents of the highest available purity were obtained from Aldrich and used without further purification.

The UV–Vis spectra were recorded on a GBC Scientific Cintra 6 spectrometer and the IR spectra on an IR-FT Nicolet 550 Magna-IR spectrometer or an ATR-FT Perkin Elmer Spectrum 1. The ESI-TOF mass spectra were obtained using a Bruker Daltonics Data Analysis 3.3 instrument. The elemental analysis for C, H and N were performed using a Perkin Elmer 2400 Series II CHNS/O elemental analyzer. The metal ion concentrations were estimated using a GBC Scientific 932 AA atomic absorption spectrometer.

*Synthesis of the macroligands and their complexes*

The receptors **L1** and **L2** (Fig. 1) were synthesized according to published procedures.<sup>15</sup> Briefly, **L1** was synthesized by condensation reaction between 2-nitrobenzaldehyde and ethane-1,2-diamine followed by the selective reduction of the imine and nitrate groups using NaBH<sub>4</sub> in methanol and NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O in ethanol, respectively. The **L2** cyclic ligand was produced in the template reaction between **L1** and 2,6-diformyl pyridine (DFP) using Mn(II) ions as the templating agent.

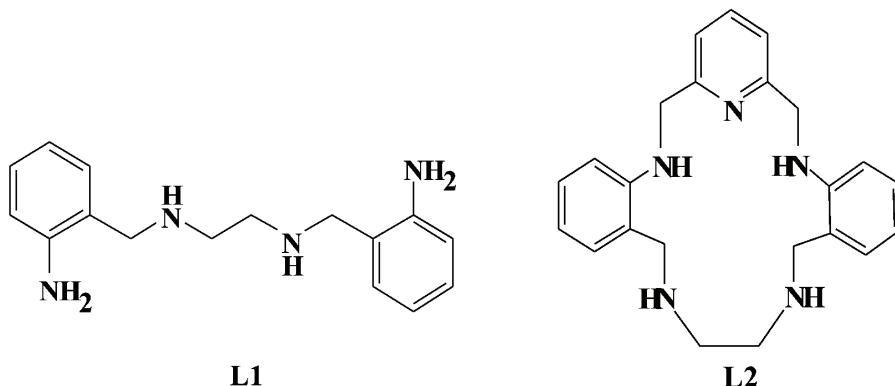


Fig. 1. Polyaza macroligand structures.

The complexes were prepared at room temperature by direct reaction between an ethanolic solution of the required ligand and an ethanolic solution of the appropriate metallic salt (either the nitrate or perchlorate) in a 1:1 mole ratio (M:L) (Eq. (1)):



where L is **L1** or **L2** and M is Cu(II), Ni(II), Zn(II), Cd(II) or Pb(II).

*Ligand 1.* A solution of **L1** (274 mg, 1 mmol) in EtOH (5 mL) was added to 5 mL of an EtOH solution of Ni(II), Cu(II), Zn(II), Cd(II) or Pb(II) (1 mmol) and the mixture was stirred for 30 min. The resulting product was then recrystallized from hot ethanol and finally dried in a vacuum desiccator.

*Ligand 2.* A solution of **L2** (373 mg, 1 mmol) in EtOH (4 mL) was added to 5 mL metal solution of Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) (1 mmol), and this mixture was stirred for 30 min. The resulting product was then recrystallized with hot ethanol and finally dried in a vacuum desiccator.

Elemental analysis, infrared and mass spectrometry studies were used to characterize the compounds. The stability constants of the colored complexes were determined at 25 °C by UV-Vis spectrophotometry with application of the Job Method.<sup>18</sup> Potentiometric titrations were used to characterize the uncolored complexes at 25 °C.<sup>19</sup>

*Affinity studies and equilibrium constants.*

The affinity of **L1** and **L2** toward the metals was determined based on the mole percentage of bound metallic ions.

The obtained complexes were filtered, washed with ethanol and after drying, the solids were weighed and a decimal part of each one was dissolved in the minimum amount of HNO<sub>3</sub> and the sample volume was made up to 50 mL with deionized water. A 1-mL aliquot of the

samples was taken and the volume adjusted to 25 or 100 mL with deionized water. The resulting solutions were analyzed by AAS in order to determine the mole percentage of bound metallic ion. All assays were performed in triplicate and the results are presented as mean values.

*Application to the removal of heavy metals from water samples*

The metals and their concentrations in synthetic water samples were based on previous analysis performed on real water samples.<sup>20</sup> The synthetic samples were a mixture of 0.0001 moles of one or more metal. With respect to the real waters, four samples were selected, two from industry, the third from the Topo Chico Creek, and the fourth from the Boca Lake, which is the main source of drinking water in Monterrey, Mexico. These samples were previously treated by ozonization to eliminate organic matter and, in the cases where this procedure failed, to acid digestion.<sup>21</sup> The pH of the solutions was adjusted to 5.5 before the addition of an excess of the corresponding receptor. The results of the characterization of the water samples are given in Table I. The concentrations of free metal ions were determined by AAS.

TABLE I. Characterization of crude water samples. Average value of the three determinations; “ $\pm$  confidence interval ( $P = 0.05$ ;  $n = 3$ ); Cd concentrations were below  $< 0.10 \text{ mg L}^{-1}$ ; ND: not detected

Sample	pH	Concentration, $\text{mg L}^{-1}$			
		Cu(II)	Ni (II)	Zn(II)	Pb(II)
Topo Chico	5.9	3.01 $\pm$ 0.19	3.35 $\pm$ 0.21	3.49 $\pm$ 0.22	ND
San Juan River	6.1	2.96 $\pm$ 0.23	2.20 $\pm$ 0.18	2.65 $\pm$ 0.21	ND
Industrial water 1	5.1	6.63 $\pm$ 0.39	12.5 $\pm$ 0.66	2.02 $\pm$ 0.17	5.37 $\pm$ 0.31
Industrial water 2	5.2	ND	24.0 $\pm$ 1.20	72.0 $\pm$ 3.6	ND

## RESULTS AND DISCUSSION

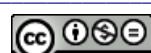
All products were characterized by UV–Vis, IR and MS spectroscopy. The yields, colors, elemental analyses and mass spectrometry data of the ligands and their complexes are given in Table II. The receptors formed stable complexes with Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) at room temperature. The complexes were isolated in high yield (71–96 %) as colored crystalline mononuclear solids. The complexes of Cd(II) and Pb(II) with **L1** and **L2** were found to be soluble in methanol. The complexes of Cu(II), Ni(II) and Zn(II) with **L1** were soluble in acetonitrile and methanol while the complexes of Cu(II), Ni(II) and Zn(II) with **L2** were soluble in acetonitrile. Mass spectroscopy was used for the structural characterization of the solid products (Table II). The mass spectral data indicated complex formation since all the products showed a characteristic molecular ion ( $M^+$ ) that represented the molecular ion peak of the complex. The mass spectra of **L1** and **L2** also showed a parent peak at  $m/z$  271.4 and 374, respectively, corresponding to protonated **L1** and **L2**. Each of the complexes had a 1:1 (ligand:metal) stoichiometry. The formula is in agreement with the mass spectral data.



TABLE II. Physical properties, elemental analysis and mass spectrometry data of the ligands and their complexes

Compound	Yield %	Color	Elemental analysis			Mass spectrometry	
			Found (Calcd.), %			Molecular mass	Ion molecular fragment
			C	H	N		
<b>L1</b>	54	Pale yellow	70.9 (70.1)	8.2 (8.2)	20.5 (20.7)	270.1	[L1+H] <sup>+</sup> (271)
C <sub>16</sub> H <sub>22</sub> N <sub>4</sub>							
[CuL1](NO <sub>3</sub> ) <sub>2</sub>	95	Dark blue	42.01 (41.92)	4.93 (4.84)	18.15 (18.30)	457.5	[CuL1-2H] <sup>+</sup> (332)
C <sub>16</sub> H <sub>22</sub> N <sub>6</sub> CuO <sub>6</sub>							
[NiL1](NO <sub>3</sub> ) <sub>2</sub>	90	Lilac	41.86 (42.42)	4.81 (4.89)	18.28 (18.44)	453.1	[NiL1-2H] <sup>+</sup> (327)
C <sub>16</sub> H <sub>22</sub> N <sub>6</sub> NiO <sub>6</sub>							
[ZnL1](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	93	Creamy	34.41 (34.77)	4.62 (4.38)	10.23 (10.14)	[ZnL1](ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O (335)	[ZnL1] <sup>+</sup> (335)
C <sub>16</sub> H <sub>22</sub> N <sub>4</sub> ZnO <sub>8</sub> Cl <sub>2</sub>						(552.7)	[ZnL1ClO <sub>4</sub> -H] <sup>+</sup> (433)
[CdL1](NO <sub>3</sub> ) <sub>2</sub>	75	Creamy	38.20 (37.92)	4.38 (4.30)	16.43 (16.58)	–	–
C <sub>16</sub> H <sub>22</sub> N <sub>6</sub> CdO <sub>6</sub>							
[PbL1](NO <sub>3</sub> ) <sub>2</sub>	90	White	31.40 (31.94)	3.62 (3.69)	13.83 (13.97)	601.6	[PbL1-H] <sup>+</sup> (477)
C <sub>16</sub> H <sub>22</sub> N <sub>6</sub> PbO <sub>6</sub>							
<b>L2</b>	57	White	73.5 (73.6)	7.4 (7.9)	19.1 (18.6)	373.0	[L2+H] <sup>+</sup> (374)
C <sub>23</sub> H <sub>27</sub> N <sub>5</sub>							
[CuL2](NO <sub>3</sub> ) <sub>2</sub> ·EtOH	94	Green	49.43 (49.46)	5.50 (5.48)	16.49 (16.15)	607.1	[CuL2-H] <sup>+</sup> (435)
C <sub>25</sub> H <sub>33</sub> CuN <sub>7</sub> O <sub>7</sub>							
[NiL2](NO <sub>3</sub> ) <sub>2</sub> ·EtOH	88	Purple	49.43 (49.86)	5.50 (5.52)	16.49 (16.28)	602.3	[ZnL2-H] <sup>+</sup> (436)
C <sub>25</sub> H <sub>33</sub> NiN <sub>7</sub> O <sub>7</sub>							
[ZnL2](ClO <sub>4</sub> ) <sub>2</sub>	96	White	43.54 (43.31)	3.72 (4.27)	10.47 (10.98)	637.9	[CdL2-H] <sup>+</sup> (484)
C <sub>23</sub> H <sub>27</sub> ZnN <sub>5</sub> O <sub>8</sub> Cl <sub>2</sub>							
[PbL2](NO <sub>3</sub> ) <sub>2</sub>	77	White	39.40 (39.20)	3.10 (3.86)	13.76 (13.91)	704.7	[PbL2-H] <sup>+</sup> (579)
C <sub>23</sub> H <sub>27</sub> PbN <sub>7</sub> O <sub>6</sub>							
[CdL2](NO <sub>3</sub> ) <sub>2</sub> ·EtOH	71	Creamy	45.40 (45.77)	4.78 (5.07)	14.36 (14.95)	[CdL2](NO <sub>3</sub> ) <sub>2</sub> ·EtOH (639.9)	[CdL2-H] <sup>+</sup> (484)
C <sub>25</sub> H <sub>33</sub> CdN <sub>7</sub> O <sub>7</sub>							

Elemental analysis data were also obtained. The results were in good agreement with the formula. The structures of the ligands (**L1** and **L2**) and their complexes were also determined from their FT-IR spectra (Table III). The IR spectra of the free ligands were compared with those of the metal complexes to determine the bonding mode of the ligands to the metal in the complexes. In the IR spectral data of the ligands, strong bands for **L1** (3398 and 3316 cm<sup>-1</sup>) and for **L2** (3420 and 3249 cm<sup>-1</sup>) belong to the ν(N–H) vibration of the aromatic amine groups. In the spectra of complexes, these bands were shifted to lower frequencies. The IR spectra confirmed the existence of cyclic ligands in the complexes, by the presence of strong absorption bands at ca. 1600–1608 cm<sup>-1</sup> and 1412–1510 cm<sup>-1</sup>, expected for the two highest-energy pyridine or benzene ring vibrations.<sup>22</sup> All complexes showed weak to medium intensity bands in the region 710–1380 cm<sup>-1</sup>, which were absent in the spectra of the free ligands; these can be attributed to (M–N). The absorptions of the counter ions (NO<sub>3</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup>) pro-



vided some useful structural information. The IR spectra of the nitrate complexes showed bands at 1342–1322 cm<sup>-1</sup> and *ca.* 1034 cm<sup>-1</sup>, suggesting the presence of coordinated nitrate groups, as well as a band at *ca.* 1384 cm<sup>-1</sup> attributable to NO<sub>3</sub><sup>-</sup>. Thus, the IR spectra gave evidence that that the nitrate groups are involved in the coordination sphere of the metal ion. The IR spectra of the perchlorate complexes exhibited bands attributable to the asymmetric Cl–O stretching mode at 1088 cm<sup>-1</sup> and the asymmetric Cl–O bending mode at 627 cm<sup>-1</sup>.<sup>23</sup> The bands of the perchlorate complexes did not suggest interaction of perchlorate anions with the metal.<sup>23</sup> Therefore, it could be concluded that the **L1** and **L2** ligands bound to the metal ions through nitrate N groups. Spectroscopic studies and elemental analysis suggested a 1:1 metal–ligand ratio for all the formed complexes.

TABLE III. Frequencies of significant bands in the IR spectra of the ligands and their complexes; ν<sub>s</sub> – symmetric stretching and ν<sub>as</sub> – asymmetric stretching

Compound	ν <sub>s</sub> (N–H) and ν <sub>as</sub> cm <sup>-1</sup>	ν <sub>s</sub> (C–N) cm <sup>-1</sup>	ν <sub>s</sub> (ArC=C) cm <sup>-1</sup>	ν(free or coordinate anion) cm <sup>-1</sup>
L1	3398, 3316	1627, 1502	1496, 1459	–
[CuL1](NO <sub>3</sub> ) <sub>2</sub>	3266, 3195	1620, 1581	1498, 1464	1381, 1334, 1094, 851, 826, 765 ν(NO <sub>3</sub> <sup>-</sup> )
[NiL1](NO <sub>3</sub> ) <sub>2</sub>	3311, 3260	1615, 1574	1497, 1412	1308, 1088, 1034, 852, 819 ν(NO <sub>3</sub> <sup>-</sup> )
[ZnL1](ClO <sub>4</sub> ) <sub>2</sub>	3333, 3295	1620, 1585	1499, 1460	1091, 624 ν(ClO <sub>4</sub> <sup>-</sup> )
[CdL1](NO <sub>3</sub> ) <sub>2</sub>	3430, 3293	1618	1498, 1458	1384, 1272, 1037, 843, 820 ν(NO <sub>3</sub> <sup>-</sup> )
[PbL1](NO <sub>3</sub> ) <sub>2</sub>	3350, 3264	1608	1496, 1456	1330, 1052, 825, 752 ν(NO <sub>3</sub> <sup>-</sup> )
L2	3420, 3249	1604	1510, 1433	–
[CuL2](NO <sub>3</sub> ) <sub>2</sub> ·EtO	3150	1612	1500, 1475	1359, 1332, 826, 740 ν(NO <sub>3</sub> <sup>-</sup> )
H				
[CuL2](ClO <sub>4</sub> ) <sub>2</sub>	3262, 3251	1600	1501, 1456	1090, 622 ν(ClO <sub>4</sub> <sup>-</sup> )
[NiL2](NO <sub>3</sub> ) <sub>2</sub> ·EtOH	3278, 3230	1605	1471, 1451	1388, 1322, 839, 732 ν(NO <sub>3</sub> <sup>-</sup> )
[ZnL2](ClO <sub>4</sub> ) <sub>2</sub>	3290, 3250	1609	1497, 1460	1094 ν(ClO <sub>4</sub> <sup>-1</sup> )
[CdL2](NO <sub>3</sub> ) <sub>2</sub> ·EtO	3254, 3235	1603	1505, 1470	1387, 1324, 1287, 828, 736 ν(NO <sub>3</sub> <sup>-</sup> )
H				
[PbL2](NO <sub>3</sub> ) <sub>2</sub>	3283, 3215	1600	1504, 1460	1372, 1342, 1035, 740, 710 ν(NO <sub>3</sub> <sup>-</sup> )

#### Affinity of **L1** and **L2** toward Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II)

The interactions of **L1** and **L2** and the metal ions were studied by AAS (Table IV). The results suggested that these complexing agents have high affinity for the analyzed metals.

The order of affinity of **L1** toward the metals follows the Irving Williams series.<sup>24</sup> The affinity series took the following order: Cu(II) > Ni(II) > Zn(II) > Cd(II) > Pb(II). With respect to the cyclic ligand **L2**, its selectivity and the



stability of its complexes could be related to the ionic radius of the metal<sup>25</sup> and the size of the ligand cavity. The highest stability of complexes was previously described as being when the ionic radius best fitted into the ligand cavity.<sup>26</sup> The affinity series took the following order for **L2**: Cd(II) > Cu(II) > Zn(II) > Ni(II) > Pb(II).

TABLE IV. Percentage of metallic ion bounded to **L1** and **L2** receptors

Metallic ion	Ionic radii <sup>24</sup> , Å	Ion to <b>L1</b> , %	Ion to <b>L2</b> , %
Cu(II)	0.73	99.2	98.6
Ni(II)	0.69	98.7	94.8
Zn(II)	0.78	97.9	97.1
Cd(II)	0.95	96.3	99.1
Pb(II)	1.55	92.7	85.4

#### *Equilibrium constants*

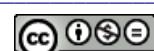
The equilibrium constants of the colored complexes were determined at 25 °C and pH 6.5 by UV–Vis spectrometry applying the Job method, and by potentiometric titration for the uncolored complexes under the same conditions. The constants reported in Table V (coefficient of variation (CV) < 5 %) indicated high stability for all complexes, so the receptors show potential usefulness as extracting agents for Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II). Metal–ligand ratio was confirmed to be 1:1 in all cases, as shown in Fig. 2 for CuL1 and CdL1.

TABLE V. Equilibrium constants of complexes with L1 and L2; average value of the three determinations

Complex	$K_{fML} \times 10^{-5}$	CV
[CuL1]	166	4.0
[NiL1]	158	4.43
[ZnL1]	11.5	3.63
[CdL1]	1.76	4.44
[PbL1]	0.291	4.47
[CuL2]	226	4.2
[NiL2]	15.4	4.26
[ZnL2]	73.7	4.07
[CdL2]	97.0	4.03
[PbL2]	1.66	4.00

#### **L1** and **L2** as extracting agents

The study of macroligands **L1** and **L2** as extracting agents was performed on synthetic and real water samples based on triplicate analyses. Synthetic water samples with a mixture of two, three or four heavy metals were prepared according to the concentration reported in a previous analysis performed on real waters (data not shown). The initial metal concentrations were 29.0, 23.4, 36.5, 22.2 and 39.0 mg L<sup>-1</sup> for Cu(II), Ni(II), Cd(II), Zn(II) and Pb(II), respectively; the pH of



the solutions was in the range of 4.9–6.5. The complexing agents were added in excess. On increasing the metal ions concentration, the ligands functioned efficiently over a wide range of concentrations up to 100 mg L<sup>-1</sup> for Cu(II), Ni(II), Cd(II), Zn(II) and Pb(II) ions (data not shown). The free metal ion concentrations in solution after treatment with the macroligands **L1** and **L2** were determined by AAS ( $CV < 5\%$ ). The receptor tendencies to bind each metal ion are shown in Figs. 3a–3d. In all cases, the ligands were able to minimize the metal concentration to below the limit allowed by the Official Mexican Regulation for treated water discharge (daily averages, in mg L<sup>-1</sup> are: Cu, 1.5; Ni, 6; Zn, 9; Cd, 0.75 and Pb, 1.5).<sup>17</sup>

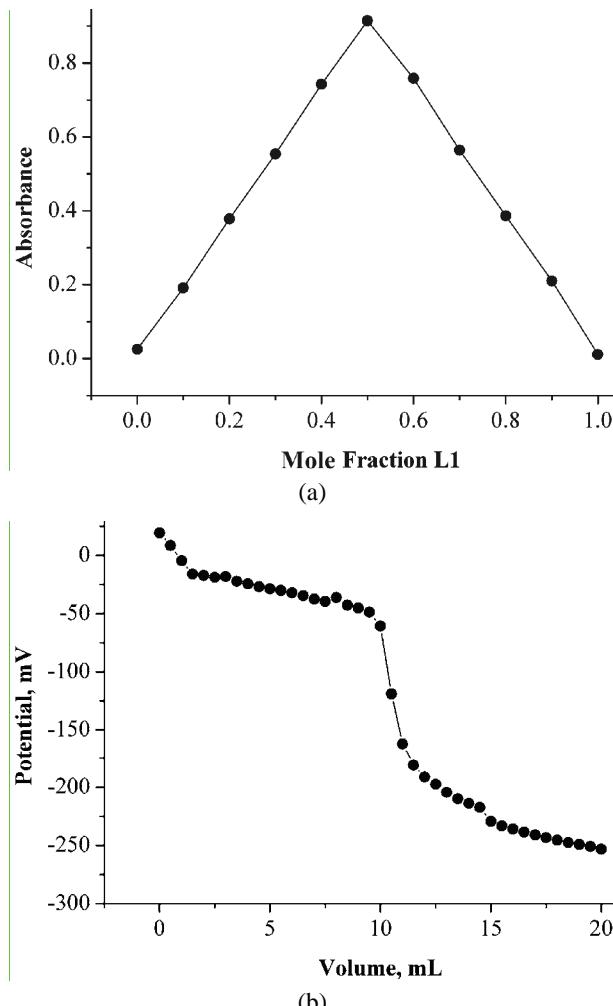


Fig. 2. a) Job's method for CuL1 complex and b) potentiometric titration for CdL1.

**L1** and **L2** were essentially similar in the efficiency of metals affinity to bond complexes in both single and multiple metal solutions. Ligand **L1** was associated with a higher effectiveness for the removal of the evaluated metal ions compared with ligand **L2**, especially for Ni(II) and Pb(II) (Fig. 3). Thus, even without direct evidence, it could be suggested that one ion is too large and the other is too small for the cavity of ligand **L2**, reducing slightly the stability of such complexes.

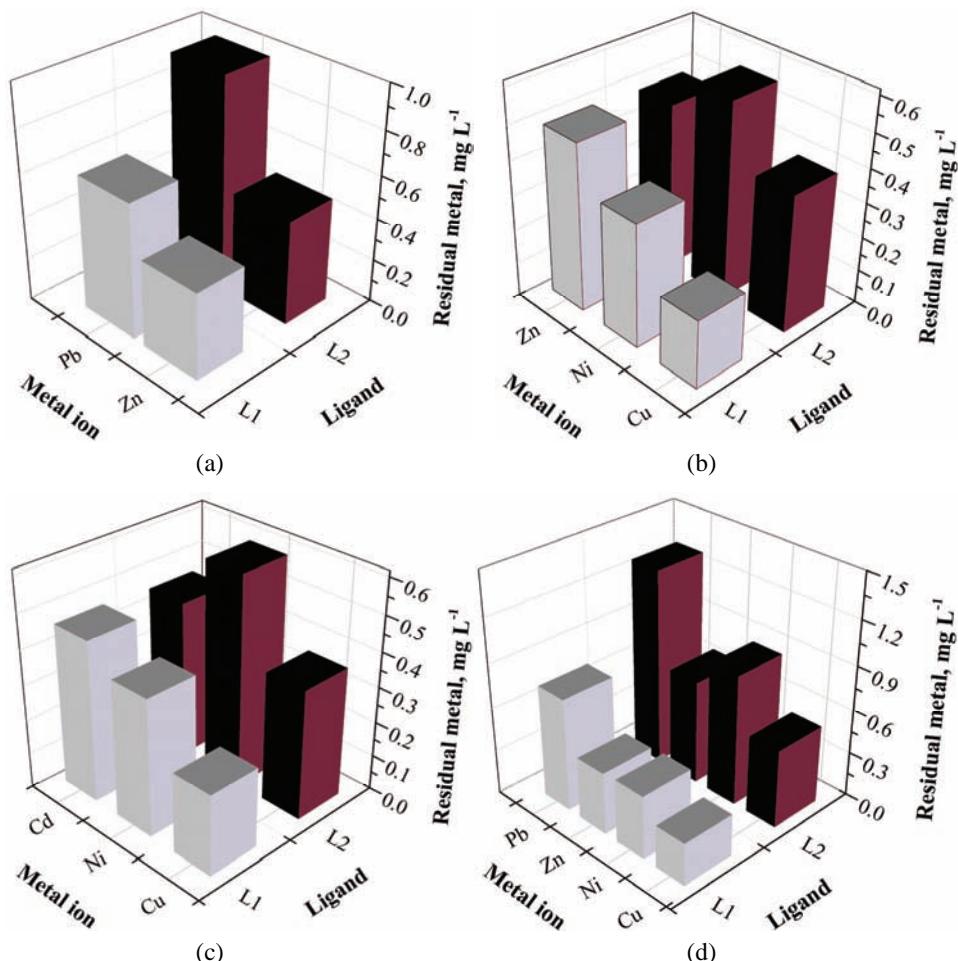


Fig. 3. Residual metal concentration in the synthetic water samples containing mixture of metals treated with receptors **L1** and **L2**: a) two metals, b–c) three metals and d) four metals.

The ligands **L1** and **L2** were evaluated for their ability as extracting agents to remove Cu(II), Ni(II), Zn(II) and Pb(II) from real water samples. Cadmium was not considered in this study since the initial concentration of Cd(II) in the

real water samples was below the detection limit. There were no significant differences in the results obtained for the real water samples (Table VI) compared to synthetic water samples (Table IV).

TABLE VI. Residual concentration of metals in crude water samples after adding **L1** and **L2**; the receptor was added in excess; confidence interval ( $P = 0.05$ ;  $n = 3$ ); ND: not detected

Sample	Concentration, mg L <sup>-1</sup>			
	Cu(II)	Ni (II)	Zn(II)	Pb(II)
L1–Topo Chico	0.38±0.04	0.46±0.04	0.50±0.05	ND
L1–San Juan River	0.38±0.03	0.42±0.04	0.44±0.04	ND
L1–Industrial water 1	0.33±0.03	0.43±0.04	0.59±0.05	0.91±0.09
L1–Industrial water 2	ND	0.42±0.04	0.42±0.04	ND
L2–Topo Chico	0.39±0.03	0.41±0.04	0.47±0.04	ND
L2–San Juan River	0.39±0.04	0.45±0.04	0.43±0.04	ND
L2–Industrial water 1	0.40±0.04	0.60±0.05	0.54±0.05	1.54±0.12
L2–Industrial water 2	ND	0.42±0.04	0.44±0.04	ND

These findings indicated that **L1** is a better extracting agent than **L2**. In addition, ligand **L1** was efficiently synthesized in a relatively simple procedure compared to **L2** since **L1** was the precursor of **L2**.

#### CONCLUSIONS

Elemental analyses, and spectroscopic data of the metal complexes confirmed that the metal:ligand ratio of the complexes with **L1** and **L2** were 1:1. The IR data of both the Schiff bases and their metal complexes showed that the **L1** and **L2** were coordinated to the metal ion through the nitrogen atom of the nitrate group. The complexing agents **L1** and **L2** were demonstrated to be efficient extraction agents for lowering metal ion concentrations of Cu(II), Ni(II), Cd(II), Zn(II) and Pb(II) in real water samples. The results demonstrated that the receptors minimized the concentrations of the metals to below the allowed limits of the Official Mexican Regulations<sup>17</sup> for treated water discharge. **L1** seemed to be better agent because it minimized the concentration of all metals to lower values than **L2** did. The results showed that a high removal efficiency of heavy metals from wastewaters could be achieved by receptors **L1** and **L2**. These extraction experiments will serve as an initial evaluation of the capabilities of polyaza receptors for the removal of heavy metals from environmental water samples.

И З В О Д

ПОЛИАЗНИ МАКРОЛИГАНДИ КАО ПОТЕНЦИЈАЛНИ АГЕНСИ ЗА УКЛАЊАЊЕ  
ТЕШКИХ МЕТАЛА ИЗ ОТПАДНИХ ВОДА

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Два полиазна макролиганда *N,N*-бис(2-амиnobензил)-1,2-етандиамин (L1) и 3,6,9,12-тетрааза-4(1,2),11(1,2)-дibenзо-1(1,3)-пиридинациклотридекафено (L2) карактерисани су и испитивани на способности екстракције металног јона. Природа свих комплекса установљена је спектроскопским техникама. Константе равнотеже су одређене спектрофотометријски и потенциометријски, а концентрација остатка метала у раствору атомском апсорпционом спектрометријом (AAC). Капацитет лиганада да уклоне тешке метале као што су Cu(II), Ni(II), Cd(II), Zn(II) и Pb(II) као нерастворне комплексе испитан је у отпадној води индустријских ефлуената. Ови агенси су показали висок афинитет према испитиваним металима. Вредности константи равнотеже изолованих комплекса (од  $1\times10^4$  до  $2\times10^7$ ) показали су употребљивост ових хелатних агенаса као једну од алтернатива за уклањање тешких метала из индустријских ефлуената.

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