

A Novel Designed Ligands of 4,4,6',6'-Tetramethyl-3'-aryl-3',5',6',7'-tetrahydrospiro[cyclohexane-1,2'-indole]-4',6(1'H)-diones for Metal Cations Removal from Water and Wastewater

Zhian, Hassan; Noroozi Pesyan, Nader*⁺; Rashidnejad, Hamid

Department of Organic Chemistry, Faculty of Chemistry, Urmia University, 57159, Urmia, I.R. IRAN

ABSTRACT: Water is the main pillar of human life, which experiencing widespread pollutions that turn clean waters to a non consumption form gradually. Contaminating resources of the clean waters are the human and industries have been made by the human. Because the available water resources for humans and organisms are limited, we must seek recovery of contaminated waters. Some novel oxime and azo dye-based compounds from spiro dihydrofurans were synthesized. All structures were characterized by IR, ¹H, and ¹³C NMR spectroscopy techniques. Some pollutant metal cations of Ni²⁺, Cu²⁺, Co²⁺, Mn²⁺, and Zn²⁺ in water and industrial wastewater were examined in the presence of novel ligands. The UV-visible spectral data indicated that **4a** selectively absorbed Ni²⁺ at room temperature and natural pH conditions. Instead, **4b** absorbed all cations with exception of Ni²⁺ under the same condition.

KEYWORDS: Pollution; Wastewater; Organic ligand; Metal cation; 2,4-Dinitro phenylhydrazone; Oxime; Thiosemicarbazone.

INTRODUCTION

Because the available water resources for humans and organisms are limited, so the polluted water and sewage should be refined for the consumption of living creatures [1]. These contaminants are generally divided into two categories: a) Sustainable pollutants: including compounds and organic substances which are not removable by natural reactions and the only way is delutioning for decreasing their pollution effect. b) Unsustainable pollution: the material contains bacteria, organic materials, and minerals which are affected by a natural process of decomposition and lose their toxicity over time and their pathogenicity properties. Usually in this type of process chemical and physical factors of the environment will be very effective [2].

Due to the discharge of large amounts of metal-contaminated wastewater, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, and Zn, are the most hazardous among the chemical-intensive industries. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders [3,4]. Therefore, it needs to remove the pollutant metal cations from the water source. One of the most suitable ways is to use absorbent materials that can absorb

* To whom correspondence should be addressed.

+ E-mail: n.noroozi@urmia.ac.ir

1021-9986/2020/1/225-232

8/\$/5.08

any cation or particles of nucleophile and precipitate it [5,6]. The adsorbents may be of mineral, organic or biological origin, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials [7]. Membrane separation has been increasingly used recently for the treatment of inorganic effluent due to its convenient operation. There are different types of membrane filtration such as UltraFiltration (UF), NanoFiltration (NF) and Reverse Osmosis (RO) [7]. Electrotreatments such as electro dialysis [8] has also contributed to environmental protection. Photocatalytic process is an innovative and promising technique for efficient destruction of pollutants in water [9]. Heavy metal removal from wastewater using low cost adsorbents [10], removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents [11]. Even, plants such as *Eichhornia crassipes* have been used for biodegradation of organic pollutants and it also can absorb heavy metals of Zn, Cr, Cu, Pb, Ag, and Cd [12,13].

Several organic and inorganic compounds have been used for the removal of heavy metals from wastewater such as; copper(II) biosorption in the presence of Complexing Agents (CA) onto Orange Peel (OP) [14], polyaza macro ligands [15], organic-inorganic hybrid polymers [16]. Recently, we have reported novel polymeric ligand for the investigation of the some metal absorptions such as Ni, Cu and Cr ions [17].

This article presents synthesis and application of the novel organic ligands of 4,4,6,6'-tetramethyl-3'-aryl-3',5',6',7'- tetrahydrospiro[cyclohexane-1,2'-indole]-4',6(1'H)-diones based on spiro dihydrofurans [18] for the investigation of the chemical treatments for removal of some heavy metal cations from water industrial wastewater.

EXPERIMENTAL SECTION

General

The drawing and nomination of compounds were done by ChemDraw Ultra 12 and 8.0 version softwares. Melting points were estimated with a digital melting point apparatus (Electrothermal) and were uncorrected. The IR spectra were determined in the region 4000- 400 cm^{-1} on a Perkin Elmer Spectrum RX1 FT IR spectrometer by KBr pellets (Mahabad Azad University, Mahabad, Iran). The ^1H and ^{13}C NMR spectra were registered on Bruker 300 FT-NMR at 300 and 75 MHz, respectively (Urmia University, Urmia, Iran). The ^1H and ^{13}C NMR spectra were obtained on a solution in $\text{DMSO-}d_6$ and/or CDCl_3 as solvent using TMS as an internal standard. The data were reported as (s = singlet,

d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, bs = broad singlet, coupling constant(s) in Hz, integration). The electronic spectra of the ligands and complexes were recorded on a UV-2450 Shimadzu spectrophotometer in MeOH, chloroform and acetonitrile (Mahabad Azad University, Mahabad, Iran). The ^1H and ^{13}C NMR spectra were opened and analyzed via MestReC software from original spectra files. Compounds **1** were synthesized based on reported references [18,19]. Hydroxylamine hydrochloride, thiosemicarbazide, 2,4-dinitrophenyl hydrazine and used solvents purchased from Merck and Aldrich without further purification.

General procedure for the preparation of the solution of 3-5 for electronic spectra measurements.

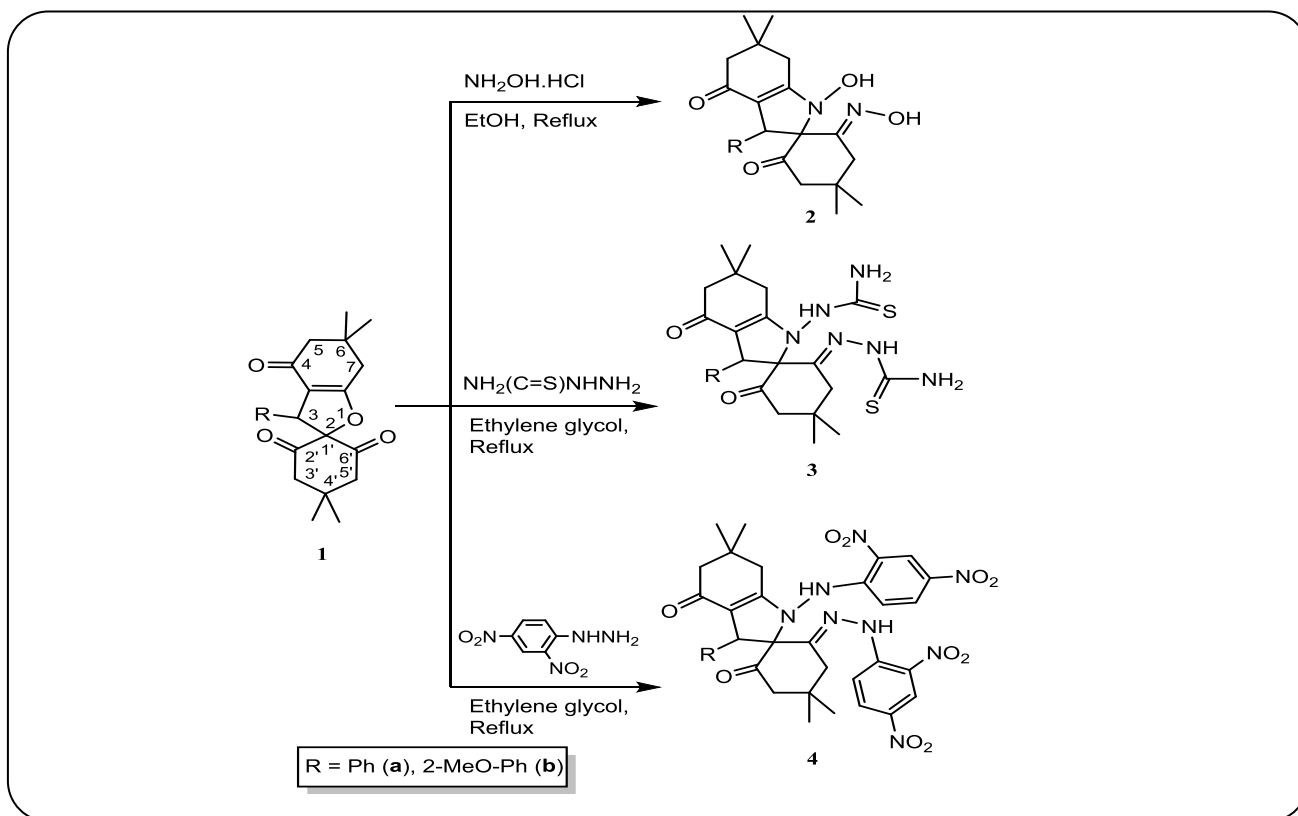
In all stages for the UV-visible spectra measurements, synthesized compounds prepared with 0.1 molar concentrations. We also investigated cations prepared at a concentration of 0.1 molar which are placed in the reaction in reactor with an equimolar ratio. After 10 min stirring UV-visible spectrum of the sample is taken to see the value of removing process. In each curve the synthesized compound spectrum and the spectrum after reaction with cations are shown and determine the status of ligand activity with cation.

General procedure for the synthesis of novel ligands 4. [20]

In a 25 mL round bottom flask equipped with the magnetically stirrer, dissolved 2 mmol 2,4-dinitrophenyl hydrazine in 5 mL ethylene glycol and stand 2 hrs then added 1 mmol spiro dihydrofuran (**1**) into the flask at room temperature. Afterward, added 5 drops of concentrated HCl. The red solid precipitated, filtered off and the recrystallized in few mL EtOH.

(E)-1'-((2,4-dinitrophenyl)amino)-2-(2-(2,4-dinitrophenyl)hydrazono)-4,4,6,6'-tetramethyl-3'-phenyl-3',5',6',7'-tetrahydrospiro[cyclohexane-1,2'-indole]-4',6(1'H)-dione (4a):

Red solid, FT-IR (KBr) 3400, 3312, 3050, 2963, 2366, 1726, 1661, 1613, 1592, 1518, 1501, 1429, 1333, 1308, 1138, 1060, 919, 833, 743, 582 cm^{-1} ; ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 0.70 (s, 3H, **Me**), 1.14 (s, 6H, **2Me**), 1.20 (s, 3H, **Me**), 1.99-3.74 (m, 8H, 4 $-\text{CH}_2-$), 4.65, 4.86, 4.90 (3s, 1H, benzylic **CH**, mixture of diastereomers), 7.25 (d, 2H, $J = 8.4$ Hz, **Ph-H**), 7.36 (d, 2H, $J = 3.6$ Hz, **Ph-H**), 7.83 (t, 1H, $J = 9.3$ Hz, **Ph-H**), 8.52 (m, 1H, 8.76



(m, 1H, NO₂-Ph-H), 8.85 (m, 1H, NO₂-Ph-H), 10.82 (s, 1H, NH), 11.00, 11.02 (2s, NH).

(*E*)-1'-((2,4-dinitrophenyl)amino)-2-(2-(2,4-dinitrophenyl)hydrazono)-3'-(2-methoxyphenyl)-4,4,6,6'-tetramethyl-3',5',6',7'-tetrahydrospiro[cyclohexane-1,2'-indole]-4',6(1'*H*)-dione (**4b**):

Red solid, FT-IR (KBr) 3313, 3108, 2951, 2871, 2366, 1665, 1628, 1612, 1588, 1519, 1493, 1429, 1366, 1331, 1311, 1205, 1141, 1101, 989, 919, 759, 742, 567 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 0.84 (s, 3H, Me), 0.88 (s, 3H, Me), 1.03 (s, 3H, Me), 1.12 (s, 3H, Me), 1.98-2.41 (m, 8H, 4-CH₂-), 3.77 (s, 3H, OMe), 5.02 (s, 1H, benzylic CH), 6.86 (m, 2H, MeO-Ph-H), 7.06 (t, 1H, *J* = 7.8 Hz), 7.34 (d, 1H, *J* = 6.6 Hz, MeO-Ph-H), 8.02 (d, 1H, *J* = 9.6 Hz, NO₂-Ph-H), 8.53 (d, 1H, *J* = 9 Hz, NO₂-Ph-H), 8.84 (s, 1H, NO₂-Ph-H), 10.95 (s, 1H, NH).

General procedure for the synthesis of novel ligands 2.

In a 25 mL round bottom flask equipped with the magnetically stirrer, dissolved 1 mmol spiro dihydrofuran (**1**) and 2 mmol of hydroxylamine hydrochloride in a mixture of 5 mL pyridine and 5 mL of EtOH,

refluxed for 3 h. Yellow solid precipitated, filtered off, evaporated and then recrystallized in few mL EtOH.

(*E*)-1'-hydroxy-2-(hydroxyimino)-4,4,6,6'-tetramethyl-3'-phenyl-3',5',6',7'-tetrahydrospiro[cyclohexane-1,2'-indole]-4',6(1'*H*)-dione (**2a**)

Yellow solid, FT-IR (KBr) 3407, 3068, 2959, 2368, 1727, 1612, 1485, 1390, 1246, 1040, 750, 679 cm⁻¹; ¹H NMR (300 MHz, DMSO-*d*₆) δ 0.62 (s, 3H, Me), 0.99 (s, 3H, Me), 1.05 (s, 6H, 2Me), 1.70-1.85 (m, 2H), 2.06-2.12 (m, 2H, -CH₂-), 2.32-2.67 (m, 2H), 3.21 (d, 2H, *J* = 14.7 Hz, -CH₂-), 4.50 (s, 1H, benzylic CH), 5.13 (bs, 4H, stucked H₂O), 7.19 (m, 2H, ph-H), 8.10 (m, 1H, ph-H), 8.62 (t, 1H, *J* = 7.5 Hz, ph-H), 8.94 (d, 1H, *J* = 3.9 Hz, ph-H), 10.45, 11.31 (bs, 1H, NOH); ¹³C NMR (75 MHz, DMSO-*d*₆) 201.09, 193.09, 176.88, 153.58, 146.99, 141.89, 137.92, 129.28, 128.63, 128.13, 127.87, 113.44, 98.59, 54.53, 53.98, 51.10, 36.95, 34.32, 34.24, 33.26, 30.18, 28.94, 28.25, 25.93.

RESULTS AND DISCUSSION

New designed ligands **3**, **4** and **5** were synthesized under simple condition as are shown in Scheme 1. In this research, first, our aim was design and synthesis of

bidendate ligands of **2-4**. (Scheme 1). The structures of **2-4** were characterized by spectroscopic data. For the characterization of compounds **3-5**, the IR spectra showed the OH and/or NH stretching frequency at 3430 (NH), 3312 (NH) and 3407 cm^{-1} (OH), respectively. In the FT-IR spectra of compounds **1**, the carbonyl stretching frequencies ($\text{C2}'=\text{O}$ and $\text{C6}'=\text{O}$) were shown at 1737 and 1713 cm^{-1} for **1a** and 1742 and 1715 cm^{-1} for **1b**, respectively [18]. These stretching frequencies were disappeared in the reaction products that supported the conversion of **1** to the **2-4**. The measurement of NMR spectra of new compound **3** was unsuccessful due to the problem in the solving. The new compounds **4** were analyzed by means of FT-IR and NMR spectroscopy and X-ray technique (See later) [20]. Representatively, FT-IR spectrum of **4a** showed a broadened at ≈ 3400 and a sharp NH stretching frequency at 3312 cm^{-1} that indicated the existence of both intra- and intermolecular hydrogen bonds. The ^1H NMR spectrums data were good agreement with the formula structure (see experimental data).

Representatively, FT-IR spectrum of **2a** showed a broad hydroxyl frequency stretching at 3407 cm^{-1} corresponded to oxime and hydroxylamine groups. A moderate peak at 1727 cm^{-1} corresponded to mono carbonyl absorption. In the ^{13}C NMR spectrum of this compound, a peak at δ 201.09 ppm corresponded to carbonyl group in spiro cyclohexanone moiety. Two peaks at δ 193.09 and at 176.88 ppm corresponded to α,β -unsaturated carbonyl and β -carbon atom, respectively (Fig. 1 (B)). In the ^{13}C NMR spectrum of **1a**, it has been shown that two peaks at δ 199.30 and 198.84 ppm corresponded to the carbonyl groups in cyclohexanedione ring moiety (Fig. 1 (C)) [18]. These data confirmed the mono oximation of **1a**.

The crystal structure of **4a** is shown in Fig. 2. This structure indicated that the both fused five and six membered rings in tetrahydrospiro[cyclohexane-1,2'-indole]-4',6(1'*H*)-dione moiety were distorted and the spiro cyclohexanone ring has chair conformation. Crystal structure of **4a** revealed dimeric self-assembly of the molecule. Four $\text{NH}\cdots\text{O}_2\text{N}-o$, two $\text{NH}\cdots\text{N}=\text{C}$ intramolecular H-bonds and two $o\text{-NO}_2\cdots\text{O}_2\text{N}-o$ intermolecular interactions creates cohesive forces between two molecules of the dimer (Fig. 3) [20].

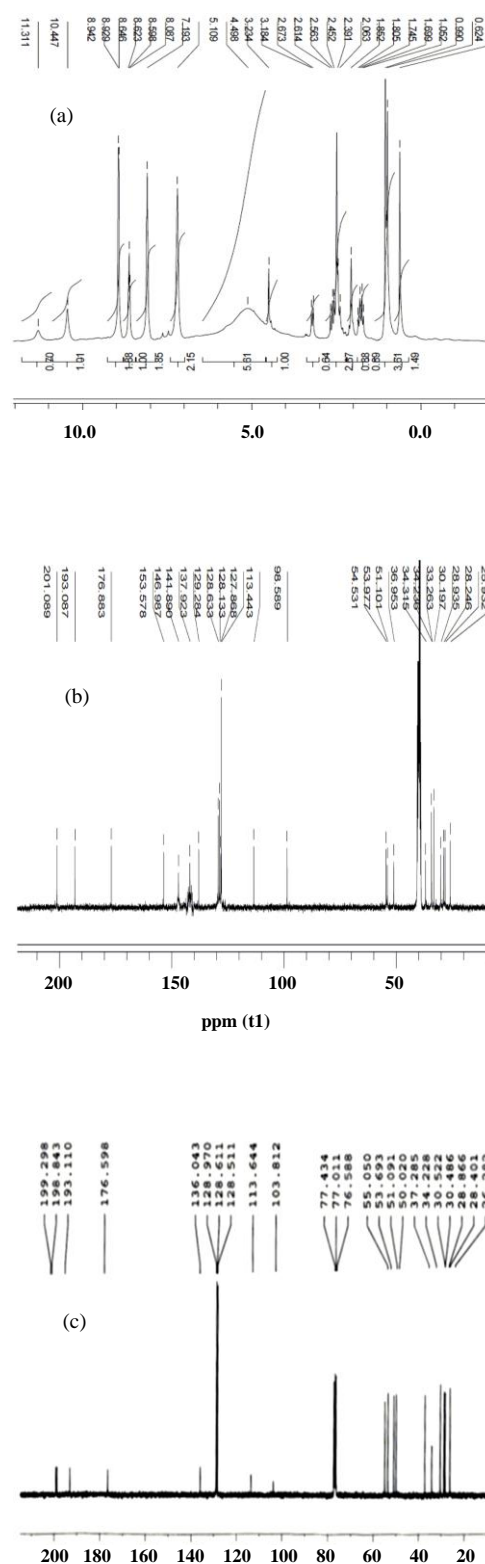


Fig. 1: ^1H NMR (A), ^{13}C NMR spectra of **2a** (B) and **1a** (C) [18].

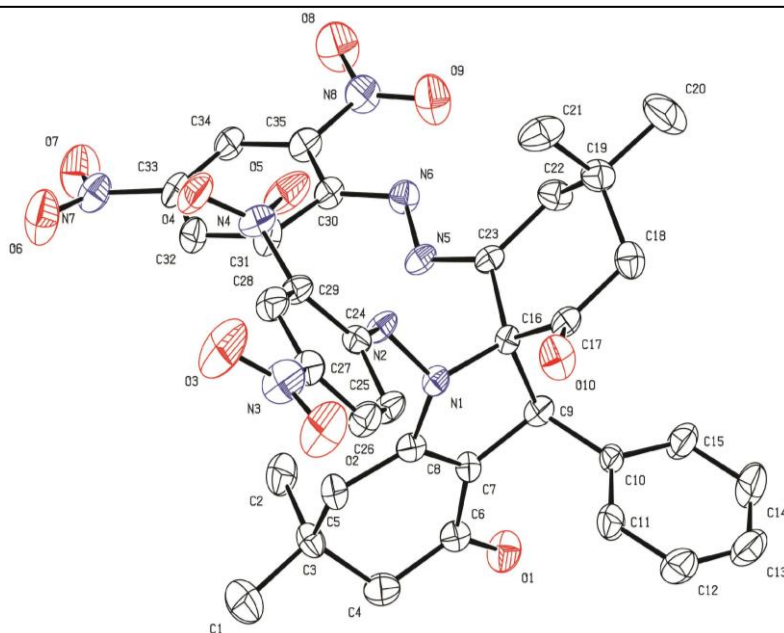


Fig. 2: ORTEP diagram of **4a** (Hydrogen atoms are omitted for clarity).

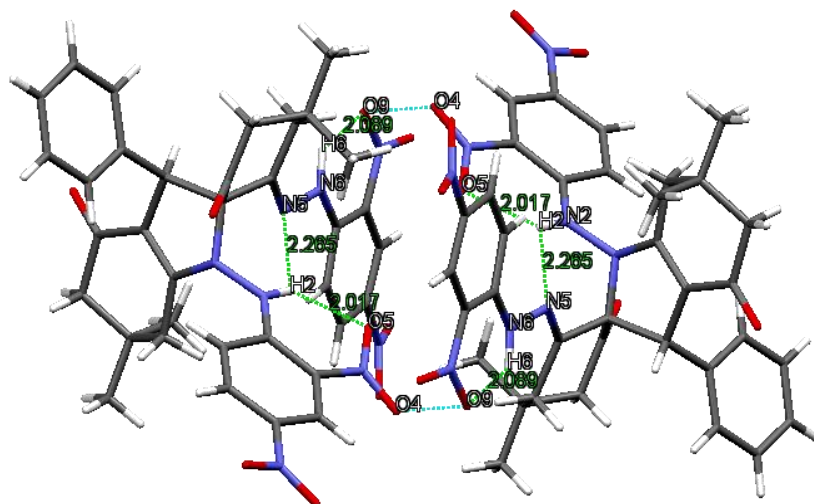


Fig. 3: Dimeric form of crystal structure **4a** (Intramolecular H-bond in green (---) and intermolecular interaction in blue dashed-lines (----)).

The electronic spectral results of compounds **3-5** are shown in Table 1. According to the obtained graphs synthesized compounds can remove dissolved cations but, to achieve optimal conditions and best conditions for each cation and ligand, further examination should be taken into account [21].

Representatively, the UV-visible spectra of **4a** and Ni-**4a** complex are shown in Fig. 4. The λ_{\max} of pure ligand and complex are 394 and 415 nm, respectively.

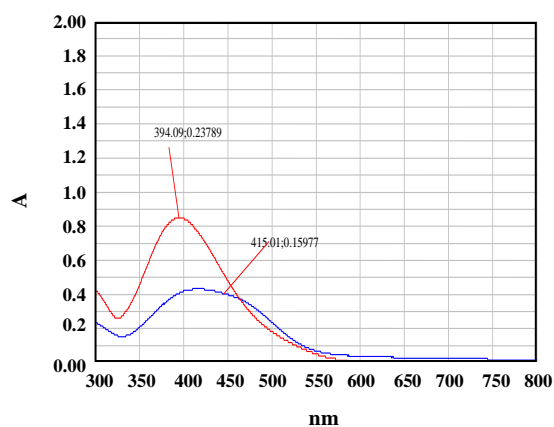
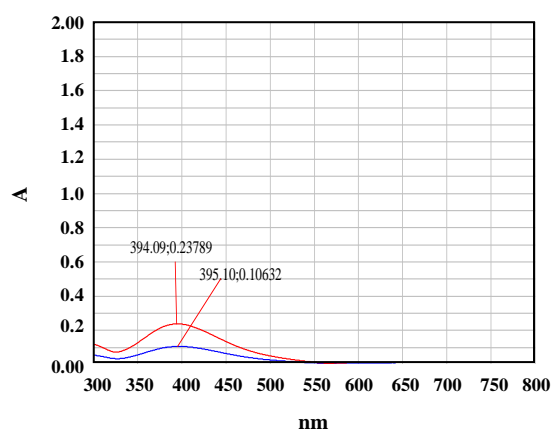
The λ_{\max} of complex bathochromically shifted and indicated the formation of complex Ni-**4a** (Fig. 4 and Table 1). Instead, for instance, in the reaction mixture of copper nitrate with **4a**, no reaction was occurred due to no any change the λ_{\max} of the reaction mixture (Fig. 5 and Table 1). The UV-visible results indicated that the ligand **4a** is selectively absorbed the Ni²⁺ cation. Instead, **4b** absorbed all cations with exception of Ni²⁺. All Absorption data were summarized in Table 2. It can be

Table 1: The λ_{\max} of ligands and possible complexes.

Entry	Complex	λ_{\max} (nm)	Ligand	λ_{\max} (nm)
1	Ni-4a	415.01	4a	394.09
2	Cu-4a	395.10		
3	Co-4a	395.41		
4	Mn-4a	396.09		
5	Zn-4a	397.17		
6	Ni-4b	404.03	4b	398.76
7	Cu-4b	414.98		
8	Co-4b	430.05		
9	Mn-4b	430.13		
10	Zn-4b	440.97		
11	Ni-2a	256.79	2a	255.98
12	Cu-2a	256.75		
13	Co-2a	256.73		
14	Mn-2a	256.75		
15	Zn-2a	256.78		
16	Ni-3a	234.70	3a	235.18
17	Cu-3a	234.85		
18	Co-3a	234.53		
19	Mn-3a	234.52		
20	Zn-3a	233.97		

Table 2: Summary of absorption data for 2-4.

Entry	Compound	Absorbed cation
1	3a	None
2	4a	Ni ²⁺
3	4b	Cu ²⁺ , Co ²⁺ , Mn ²⁺ , Zn ²⁺
4	2a	None

**Fig. 4: UV-visible spectra of 4a (red) and possible Ni-4a complex (blue).****Fig. 5: UV-visible spectra of 4a (red) and Cu-4a mixture (blue).**

shown that among of compounds, **4a** acted as a selective ligand for absorption. On the other words, **4a** is a selective ligand for the detection of Ni²⁺ as a sensor. No absorption was observed by compounds **3** and **5** under the same condition.

CONCLUSIONS

In this research, new compounds **2-4** were synthesized and their structures were characterized. The UV-Visible spectral data indicated that **4a** selectively absorbed Ni²⁺ at room temperature and natural pH condition. No absorption was observed by compounds **2** and **3** under the same condition. Instead, **4b** absorbed all cations with exception of Ni²⁺. We conclude that the **4a** can be as a sensor for the detection of Ni²⁺ cation in water and wastewater process.

SUPPLEMENTARY DATA

Some spectra of compounds and UV-visible spectral data are available.

Acknowledgments

We gratefully acknowledge financial support by the Research Council of Urmia University.

Received : Jul. 28, 2018 ; Accepted : Oct. 22, 2018

REFERENCES

- [1] Shen X.J., Pei X.Q., Fu S.Y., Friedrich K., Significantly Modified Tribological Performance of Epoxy Nanocomposites at Very Low Graphene Oxide Content, *Polymer.*, **54**(3): 1234-1242 (2013).
- [2] Skinner K., Wright N., Porter-Goff E., Mercury Uptake and Accumulation by Four Species of Aquatic plants, *Environ. Pollut.*, **145**(1): 234-237 (2007).
- [3] Babel S., Kurniawan T.A., Cr (VI) Removal from Synthetic Wastewater Using Coconut Shell Charcoal and Commercial Activated Carbon Modified with Oxidizing Agents and/or Chitosan, *Chemosphere.*, **54**(7): 951-967 (2004).
- [4] Barakat M.A., New Trends in Removing Heavy Metals from Industrial Wastewater, *Arab. J. Chem.*, **4**: 361-377 (2011).
- [5] Eccles H., Treatment of Metal-Contaminated Wastes: Why Select a Biological Process?, *Trends Biotechnol.*, **17**(12): 462-465 (1999).
- [6] Leung W.C., Wong M.F., Chua H., Lo W., Yu P.H., Leung C.K., Removal and Recovery of Heavy Metals by Bacteria Isolated from Activated Sludge Treating Industrial Effluents and Municipal Wastewater, *Water Sci. Technol.*, **41**(12): 233-240 (2000).
- [7] Kurniawan T.A., Chan G.Y., Lo W.H., Babel S., Physico-Chemical Treatment Techniques for Wastewater Laden with Heavy Metals, *Chem. Eng. J.*, **118**(1-2): 83-98 (2006).
- [8] Pedersen A.J., Characterization and Electrodialytic Treatment of Wood Combustion Fly Ash for the Removal of Cadmium, *Biomass and Bioenergy.*, **25**(4): 447-458 (2003).
- [9] Skubal L.R., Meshkov N.K., Rajh T., Thurnauer M., Cadmium Removal from Water Using Thiolactic Acid-Modified Titanium Dioxide Nanoparticles, *J. Photochem. Photobiol., A.*, **148**(1-3): 393-397 (2002).
- [10] Tripathi A., Ranjan M.R., Heavy Metal Removal from Wastewater Using Low Cost Adsorbents, *J. Bioremed Biodeg.*, **6**(1000315): 5 (2015).
- [11] Hegazi H.A., Removal of Heavy Metals from Wastewater Using Agricultural and Industrial Wastes as Adsorbents, *HBRC J.*, **9**: 276-282 (2013).
- [12] Odjegba V.J., Fasidi I.O., Phytoremediation of Heavy Metals by *Eichhornia crassipes*, *The Environmentalist.*, **27**(3): 349-355 (2007).
- [13] Yapoga S., Ossey Y.B., Kouame V., Phytoremediation of Zinc Cadmium, Copper and Chrome from Industrial Wastewater by *Eichhornia crassipes*, *Int. J. Conservation Sci.*, **4**(1): 81-86 (2013).
- [14] Izquierdo M., Marzal P., Lens P.N., Effect of Organic Ligands on Copper (II) Removal from Metal Plating Wastewater by Orange Peel-Based Biosorbents, *Water Air Soil Pollut.*, **224**(4): 1507-1522 (2013).
- [15] Elizondo M.P., Nájera M.B., Pérez R.N., Reyes H.L., Río DG., Polyaza Macroligands as Potential Agents for Heavy Metal Removal from Wastewater, *J. Serb. Chem. Soc.*, **78**(4): 591-602 (2013).
- [16] Samiey B., Cheng C.H., Wu J., Organic-Inorganic Hybrid Polymers as Adsorbents for Removal of Heavy Metal Ions from Solutions: A Review, *Materials.*, **7**(2): 673-726 (2014).

- [17] Hosseinzadeh M., Noroozi Pesyan N., Moghadam P.N., [Synthesis and Characterization of Polymer Metal Chelates Derived from Poly \(2, 2, 3, 3-tetra methyleneaminecyclopropyl\) phenyl Acrylate](#), *Adv. Polym. Tech.*, **37**(2): 461-467 (2018).
- [18] Noroozi Pesyan N., Shokr A., Behroozi M., Şahin E., [Selective Formation of Spiro Dihydrofurans from One-Pot Reaction of Dimedone with BrCN and Aldehydes in the Presence of Et₃N](#), *J. Iran. Chem. Soc.*, **10**(3): 565-575 (2013).
- [19] Wang G.W., Gao J., [Selective Formation of Spiro Dihydrofurans and Cyclopropanes Through Unexpected Reaction of Aldehydes with 1, 3-Dicarbonyl Compounds](#), *Org. Lett.*, **11**(11): 2385-2388 (2009).
- [20] Zhian H., Noroozi Pesyan N., Aalinejad M., Rashidnejad H., Notash B., [Unexpected Simple and Catalyst-Free Condensation Reaction of Spiro Dihydrofurans with 2,4-Dinitrophenylhydrazine, Thiosemicarbazide, and Hydroxylamine for the Synthesis of Novel Corresponding 4,4,6',6' Tetramethyl-3'-aryl-3',5',6',7'-tetrahydrospiro \[cyclohexane-1,2'-indole\]4',6\(1'H\)-diones: Crystal Structure](#), *J. Heterocycl. Chem.*, in press (2018).
- [21] Urgun-Demirtas M., Benda P.L., Gillenwater P.S., Negri M.C., Xiong H., Snyder S.W., [Achieving Very Low Mercury Levels in Refinery Wastewater by Membrane Filtration](#), *J. Hazard. Mater.*, **215**: 98-107 (2012).