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Liquid-liquid extraction of metal ions, DFT and TD-DFT analysis of some

1,2,4-triazole Schiff Bases with high selectivity for Pb(II) and Fe(II)

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Abstract

Liquid-liquid extraction of metal ions using some 1,2,4-triazole Schiff base derivatives as new extractants was studied. Fe^{2+} , Zn^{2+} , Cu^{2+} , Co^{2+} , Cd^{2+} and Pb^{2+} were extracted from the aqueous phase into the organic phase and the extractability for each metal ion was determined by atomic absorption. Interestingly, a competitive extraction was also investigated and then examined at different pH in order to explore the effect of the different substituent groups on metal extraction. Accordingly, high selectivity towards Fe^{2+} (90.1%) and Pb^{2+} (94.3%) provided respectively by the presence of electron withdrawing group and electron donor group was attained. In addition, geometry optimizations of the ground and excited-states of the ligands in order to get better insight into the geometry and the electronic structure were carried out by means of DFT and TD-DFT calculations.

Keywords: 1,2,4-triazoles; Schiff base; DFT; Liquid-Liquid extraction; metal cations.

1. Introduction

1,2,4-Triazoles are class of nitrogen heterocyclic compounds which attract considerable attention in organic chemistry owing to their pharmacological and medicinal properties such as anticonvulsant, [1] antimicrobial, [2] antihypertensive, [3] analgesic, [4] antiviral, [5] antioxidant, [6] anti-inflammatory, [7] and anticancer [8,9] properties. Moreover, Schiff bases incorporating 1,2,4-triazole scaffold are well established in the literature as important active compounds in medicinal [10] and coordination chemistry [11]. Liquid-liquid extraction which is one of the most important and promising techniques for metals separation has recently attracted a great deal of attention for selective recovery of metal ions from industrial wastes [12-14]. However, the success of this recovery process is still limited by the extraction selectivity for the targeted metal using a specific extractant. Actually, despite the large number of extractants that have been investigated and developed to efficiently separate metal ions, such as phosphoric acid, α -hydroxy oximes, β -diketones, amines and substituted pyridines [15-21], the design of selective extractants for the separation of heavy metals particularly bivalent metal cations has remained a great challenge in wastewater treatment. Recently, researches have been directed towards Schiff-base derivatives as the main extractant candidates. In this context, we have previously investigated the liquid-liquid extraction of metals using nitrogen-donor pyrazole ligands and studied their ability to extract metals from aqueous solutions [22-26].

In view of these above, we report herein the synthesis of some Schiff base derived from 4amino-5-methyl-1,2,4-triazol-3-thione, the study of their liquid-liquid extraction of metals ions and experimental (UV-Vis) and theoretical calculations DFT and TD-DFT at B3LYP level [27] have been carried out aiming to investigate the structure geometries and to determine the nature of electronic transitions and their dependences.

2. Experimental section

2.1. Synthesis of 4-amino-5-methyl-2,4-dihydro-1,2,4-triazole-3-thione (1)

The starting material 4-amino-5-methyl-2,4-dihydro-1,2,4-triazole-3-thione (1) was prepared according to the reported literature [28]. A mixture of thiocarbohydrazide (5 g) in glacial acetic acid (15 mL) was refluxed in ethanol for 4 hr. The solution was cooled and a white solid appeared. The obtained precipitate was filtered and recrystallized from water to afford the desired product. Yield 85%, m.p. 153 °C, IR (KBr, v, cm⁻¹): 3213-3367 (NH, NH₂), 1687 (C=N), 1299 (C=S); ¹H NMR (DMSO- d_6 , δ ppm):2.36 (3H, s, CH₃), 5.65 (2H, s, NH₂),14.34 (1H, s, SH triazole); ¹³C NMR (DMSO- d_6 , δ ppm): 10.56 (CH₃), 161.83, 167.06 (C=N).

2.2. General procedure for the synthesis of ligands $L_{I-}L_{II}$

A mixture of 4-amino-5-methyl-2,4-dihydro-1,2,4-triazole-3-thione (1) (10 mmol) and the appropriate benzaldehyde derivatives 2-12 (10 mmol) was refluxed in ethanol for 6 hours with the presence of catalytic amount of hydrochloric acid (conc. HCl). After cooling, the resulting precipitate was filtered, and recrystallized from ethanol to obtain the desired Schiff Bases (ligands) L_1-L_{11} in good yield (80-90%) (Figure1).

Fig. 1. Chemical structures of studied ligands L_1 - L_{11}

2.3. Characterization of ligands L_1 - L_{11}

All synthesized ligands have been characterized using IR, ¹H NMR techniques (Table. 1).

Table. 1. Spectroscopic data of ligandsL₁-L₁₁

2.4. Liquid-liquid extraction tests

A solution of 7.10^{-5} M of ligand in CH₂Cl₂ (20 mL) was stirred for 2h with 20 mL of an aqueous solution of metal salt (7.10^{-5} M). Liquid-liquid extraction experiments were carried out at room temperature and pH neutral [26]. All experiments were carried out in an atmosphere of dry argon using schlenck techniques. Solvents were distilled and degassed.

The aqueous phase was separated and analysed by atomic absorption spectrometry with an air-acetylene flame. Single element standards were prepared for these metals from Fluka 1000 mg/L stock solutions. The measurements are carried out using standard conditions for calibration. All standards were made acidic to avoid metal hydrolysis and to match content in the sample using nitric acid 2%.

The organic phase was back-extracted with HCl, H₂SO₄ and HNO₃ solution (1M).

The metal ion concentrations in the organic phases were calculated from the mass balance between the aqueous and organic phases.

The extractability or the extraction efficiency (E%) and distribution ratio (D) of the metal were calculated from Equation (1) and (2), respectively.

$$\boldsymbol{E(\%)} = \frac{[M]_{arg,eq}}{[M]_{aq,init}} \times 100 = \frac{[M]_{aq,init} - [M]_{aq,eq}}{[M]_{aq,init}} \times 100(1)$$

$$\boldsymbol{D} = \frac{[\boldsymbol{M}]_{org,eq}}{[\boldsymbol{M}]_{aq,eq}} = \frac{[\boldsymbol{M}]_{aq,init} - [\boldsymbol{M}]_{aq,eq}}{[\boldsymbol{M}]_{aq,eq}} (2)$$

Where $[M]_{aq,init}$ represents the initial concentration of metal ion in the aqueous phase. $[M]_{aq,eq}$ and $[M]_{org,eq}$ are the total concentrations of metal ion in the aqueous and organic phases, respectively, at equilibrium.

Moreover, the complexation mechanism between metals and ligands was investigated by slope analysis.

2.5. Theoretical calculations

All calculations were performed using the GAUSSIAN 09 program package [29] with the aid of the GaussView visualization program [30]. The ground state geometries of L_1 and L_{11} were fully optimized using the hybrid B3LYP functional methods [27] in combination with the 6-

31G (d,p) basis set. The excited state properties of the optimized ground state geometries were calculated in both the gas phase and with dichloromethane solvent by using the timedependent density functional formalism (TD-DFT) and the pople 6-31G+(d,p) basis set. Solvent effects were included by employing the Polarizable Continuum Model (PCM)[31], as implemented in Gaussian09. The fractional contributions of various groups to each molecular orbital were calculated by using Gauss Sum [32] and Chemissian was used for spectrum analysis [33].

3. Results and discussions

The resulting spectroscopic data were in agreement with that previously reported in the literature [34-39] (see **Table. 1**). Thus, the IR spectra of all Schiff BasesL₁-L₁₁showed characteristic absorption bands at 1630-1660 and 3200-3356 cm⁻¹ assigned for the C=N and N–H groups, respectively. Moreover, the¹HNMR spectral results, obtained for all Schiff Bases in DMSO- d_6 , together with the hydrogen assignments are presented in the **Table. 1**. All ligands showedtwo characteristic singlets at δ_H 14.40–14.60 and 9.60-10.20 ppm assigned to the NH and CH=N imine protons, respectively.

3.1. Individual extraction of metal ions with the ligands L_{1-11}

To examine the coordination capacity of these ligands against each metal, we proceeded to extract the metals individually from aqueous media. Obtained extractabilities are presented in **Table. 2**.

Table. 2. Extraction efficiencies of metal cations using L_1 - L_{11} .

The **Table.2** display a remarkable and high extraction efficiency for both Fe^{2+} and Pb^{2+} , while this ligands L_1-L_{11} shown a medium and low efficiencies with Cu^{2+} , Cd^{2+} , Zn^{2+} and Co^{2+} .

The extractabilities of Fe²⁺ by these ligands vary between 7.5% (\mathbf{L}_7) and 96.3% (\mathbf{L}_4). In fact, the presence of a methoxyormethyl group in *para* position of the phenyl gives a high value of extraction efficiency; 92.6% (\mathbf{L}_1) and 91.7% (\mathbf{L}_2) respectively. Interestingly, the displacement of the chloro group from the *ortho* position (\mathbf{L}_3) to the *meta* position (\mathbf{L}_4) has allowed higher extractability to be reached; 96.3% instead of 42.1%, whilst 85.3% can be attained when the substitution in the *para* position (\mathbf{L}_5). Ligands bearing a bromo group display a low extractability in the case of *meta* position (7.5% for \mathbf{L}_7), a medium efficiency in the case of *ortho* position (53.7% for \mathbf{L}_6). The extraction efficiency reach 92.9% when the presence of fluoro group in *para* position (\mathbf{L}_8). Interestingly, the existence of nitro group has significantly improved the extraction of Fe²⁺. Actually, the extraction efficiency has not ceased increasing by passing from the position *para* (91.6%) for \mathbf{L}_{10} to the *meta* position (93.6%) for \mathbf{L}_9 to finally reachits maximum value of 95.7% with the ligand \mathbf{L}_{11} bi-substituted in *ortho* position by a nitro group and a chloro group in *meta* position.

In general, the extractability of Pb^{2+} by these ligands is good and varies from 37.9% (L₉) to 98.9% (L₄),the substitution of a methyl group by a methoxy group in *para* position on the phenyl ring has improved the extraction efficiency, from 93.6% for L₂ to 97.3% for L₁respectively.The existence of a chloro group in *meta* (L₄; 98.9%) or in *para* (L₅; 98.1%) position has perfectly improved the efficiency when comparing with *ortho* (L₃; 90.1%) position. With the bromo substituent groups, a notable amelioration in extraction efficiency was observed when passing from *ortho*(65.7% for L₆) to *meta*(79.3% for L₇) position. Ligand L₈ which has bearing a fluoro group in *para* position show a very good extractability against Pb²⁺ (96.7%). In the case of nitro substituent group, the extraction was improved while changing position on the phenyl ring from *meta* (37.9% for L₉) to *para* (72.4% for L₁₀) and reached 87.2% (L₁₁) with *ortho* position in presence of chloro group in *meta* position. For the extraction of Cu^{2+} , the tested ligands do not show a good efficiency and the values remain between 25% and 63.1%(L₉).

In general, the liquid-liquid extraction of Zn^{2+} , Co^{2+} and Cd^{2+} remains low. For Zn^{2+} and Co^{2+} these ligands show an identical behavior but the extraction efficiencies remain very low and do not exceed 7.2% in the best case. The ligands do not show an important efficiencytoward Cd^{2+} and the maximum value is 49.8% for L_{10} .

According to the results obtained by these ligands, it seems that some molecules have trend to coordinate with Fe^{2+} , other with Pb^{2+} and most of cases with both of metals. This can be attributed to the different nature of each ligand as well asits capacity to complex the various metals, the nature of metal may also be animportant factor. The phenyl ring which is directly attached to an imine function which involvea sp^2 nitrogen and which forms with the sulphur a coordination site to receive metals is strongly influenced by the nature of the substituent group and its position. For these ligands, there are various substituents into different positions. Therefore, the extraction efficiencyisaffected by electronic effects of substituents at *ortho*, *meta* and *para*positions on the phenyl ring, each substituent group has a specificeffect on the coordination site in way that may increase or decrease the coordination capacity of the ligands.

3.2. Selective extraction of divalent metal cations

To understand the behavior of these ligands toward metal cations, we proceeded to investigate the selectivity of these ligands through a competitive extraction. For this purpose, we have extracted metal cations from a solution containing the four metals that have previously shown certain affinity vis-a-vis these ligands (Fe^{2+} , Pb^{2+} , Cu^{2+} and Cd^{2+}). The obtained results of this study are displayed in **Fig. 2**.

Fig. 2.Competitive extraction E(%) of metal ions using L_1 - L_{11}

From the obtained results of the competitive extraction, the ligands unveil good efficiencies to extract selectively Fe^{2+} and Pb^{2+} . The ligands L_1 and L_2 show an excellent selectivity towards Pb^{2+} while L_3 and L_7 display a remarkable efficiency but some interference was shown with Fe^{2+} and Cu^{2+} . So at equilibrium these ligands complex the lead (II) after a competitive liquid-liquid extraction. The most efficient ligands that extract selectively Pb^{2+} with efficiencies higher than 90% are L_1 (94.3%) and L_2 (91.2%). Iron (II) is selectively extracted by L_9 , L_{10} , and L_{11} , the best one is L_{11} with reported efficiency of 90.1%.

When extracting from a mixture of metals L_4 , L_5 , L_6 , and L_8 do not show any trend to complex selectively one cation, so a competition between Fe²⁺ and Pb²⁺ has displayed.

Certain ligands present an important affinity towards Pb^{2+} , especially with the molecules bearing an electron-donor substituent, others with the electron-withdrawing group show a good affinity towards Fe^{2+} . Therefore, the electronic effect of substituent does not only affect the extraction efficiency of the ligand, but also its selectivity by the fact that molecules with electron-donor group extract Pb^{2+} selectively and molecules with electron-withdrawing group extract Fe^{2+} selectively. The substitution on the phenyl by a halogen group (Br, Cl and F) and the changing of the position do not improve sufficiently the selectivity

3.3. Determination of complexation mechanism

To characterize the extraction ability, the dependence of the distribution ratio*D* of the cation between the two phases on the ligand concentrationwas examined.

If the general extraction equilibrium is given by Eq.(3)

 $M^{2+}_{(aq)} + x[L]_{(org)} \leftrightarrow [ML_x]_{(org)}(3)$

The extraction equilibrium constant K_{ex} is given by Eq. (4)

$$Kex = \frac{[MLx]}{[M] [L]^{x}} (4)$$

Moreover, the distribution ratio of the metal cation between the organic and aqueousphases is defined as

$$D = \frac{[M]_{org,gq}}{[M]_{aq,gq}}(2)$$

By introducing D into (4) and taking logarithm of both sides, (5) isobtained:

$$\log D = \log K_{ex} + x \log [L]$$

(5)

Under these assumptions, a plot of log*D* versus log [L]should be linear and its slope should be equal to the number of ligand molecules per metal cation in the extracted species (**Figure. 3**).

Fig. 3. Plot of log *D* versus log L for
$$Pb^{2+}$$
 of ligand L_1

The obtained log*D* versus logL plot displayed in Figures 3 and 4 are displayed as 1:1 in ratio of metal-ligand for Fe^{2+} with L_{11} and for Pb^{2+} with L_1 .

$$Fe^{2+}, x = 1.10078 (L_{11})$$
; $Pb^{2+}, x = 0.96257 (L_1)$

The logarithmic extraction constant log K_{ex} corresponding to (5) is calculated:

$$\log K_{ex} = 5.90273$$
 for Fe²⁺ with L₁₁ , $\log K_{ex} = 5.5503$ for Pb²⁺ with L₁

3.4. Effect of the pH medium on metal extraction

The aqueous phase pH is one of the determining factors for metals extraction by ligands. To examine the behavior of these ligands in different pH values and to determine the optimum pH, we have carried out a competitive liquid-liquid extraction of four metals (Fe^{2+} , Pb^{2+} , Cu^{2+} and Cd^{2+}) at different pH.The extraction properties of Fe^{2+} by L_{11} and of Pb^{2+} by the ligand L_1 were investigated over the pH range 1 to 8.

For the both ligands L_1 with Pb^{2+} and L_{11} with Fe^{2+} , an identical behavior has been shown. In 4-8 pH range, the efficiency decreased slowly with pH decreasing, which can be explained by a stable coordination. Under pH 4 the efficiencies decreases seriously and become neglected when the pH attained a value of pH 1, this can be explained by a rapid and total protonation of coordination sites. Above pH 8 and because of hydrolysis of Fe²⁺ and Pb²⁺, we cannot distinguish between hydrolyzed or extracted cation. It seems that these ligands resist acidic to the protonation and remain effective in medium. There is an increase in Fe²⁺ and Pb²⁺ during extraction to organic phase as pHincreases. When log D-pHgraph is examined, there are two pH range (1-4 and 4-8), which can be attributed to different formof protonation or deprotonation. It can be said that there is two structural conformations when forming metal complex at different pH.

3.5. Back extraction of metal ions extracted with L_1 and L_{11}

In back-extraction, metal ions are extracted from the metal ligand complex using a stripping liquid immiscible with the organic solvent used. As the extraction of Fe^{2+} and Pb^{2+} by L_{11} and L_1 respectively decreases at acidic pH, we chose aqueous acid as stripping solution for the back-extraction. All back-extraction tests were carried out in 10 minutes; the results are summarized in **Table. 3**.

Table. 3. Back-extraction of metal ions extracted with L_{11} and L_1 .

According to the results presented in **Table 3**, a complete stripping of Fe^{2+} from the organic phase containing Fe-L₁₁ complex was observed using 1 M HNO₃ (97%) while a recovery percentage of 95% and 91% were respectively achieved in the presence of 1 M H₂SO₄ and 1 M HCl. Pb²⁺ was effectively stripped from the organic phase, a maximum back-extraction percentage of metal may be achieved using 1 M HNO₃ (99%) and 1 M H₂SO₄ (94%), high recovery percentage of 89% was also obtained with 1 M HCl. It was found that the used

acids as back-extraction reagents were extremely effective; the ligands could be recycled and reused after stripping the metal ions from the organic phase and the kinetic of back-extraction was found to be fast.

3.6. DFT analysis

To investigate the structure geometries, we performed full geometry optimization of L_1 and L_{11} in the gas phase using DFT/B3LYP level calculations. As illustrated in Fig. 4, the optimized structures are planar and the imine function constitutes a bridge between the two rings of the molecule. We also notice that the cavities formed between C=S and sp² Nitrogen in both molecules have similar size and the arrangement of the triazole and the phenyl ring minimizes the steric hindrance and thus enabling the ligands structures to have stable geometries.

Additionally to the geometry optimization, density functional theory has been found to be successful in providing insights into the chemical reactivity and stability, the analysis of the frontier molecular orbitals is a crucial way to obtain information on reactivity of molecules and to study electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The LUMO represents the ability of the molecule to capture an electron while the HOMO represents the ability to donate an electron. The difference between the HOMO and the LUMO energy values is the HOMO–LUMO energy gap, which explains the eventual charge transfer interaction taking within the molecule.

Molecules with a small energy gap are generally associated with a high chemical reactivity, low kinetic stability and are also considered as soft molecules [40, 41] while those with large energy gap have higher stability and are termed as hard molecules because they oppose charge transfer and changes in their electron density and distribution.

In addition, the energy of HOMO is directly related to the ionization potential ($IP = -E_{HOMO}$) and the energy of LUMO is related to the electron affinity ($EA = -E_{LUMO}$) [42]. By using these values, interesting properties such as global hardness (η), global softness (σ),electronegativity (χ), chemical potential (μ) and electrophilicity index (ω) may be calculated.

The hardness of a species is a qualitative indication of how polarizable it is, in another wayhow much its electron cloud is distorted in an electric field. The hardness and softness were suggested in literature [43-45]. Electronegativity is the tendency of molecules to attract electrons [46]. Chemical potential denotes the affinity of an electron to flee and is defined as the first derivative of the total energy with respect to thenumber of electrons in a molecule [40], chemical potential is simply the negative of electronegativity value; $\mu = -\chi$. The capability of a substance to acceptelectrons is quantified as electrophilicity index and it was proposed as ameasure of the electrophilic power of a molecule [47]. The calculated energy values and some properties of $L_1 - L_{11}$ are presented in **Table. 4**.

Table. 4. Quantum chemical parameters forL₁-L₁₁ obtained by using B3LYP/6-31G(d,p).

Based on the results reported in **Table. 4**, a comparison between L_1 and L_{11} , show a marked difference in their HOMO, LUMO and gap energies. The presence of the nitro function on the phenyl ring in L_{11} , which reduce the value of the HOMO conversely to L_1 that contains the methoxy group. Therefore, the withdrawing group on the phenyl ring decreases the donor character of the molecule while the donor group increases this character. Furthermore, the reported energies gap of L_1 and L_{11} are respectively, 3.9603 eV and 2.9435eV, which meansthat L_1 is more stable than L_{11} . Thus, the presence of themethoxy improves the stability of the molecule while the presence of the nitro group allows the molecule to be more reactive.

The values of the electronegativity, chemical potential and electrophilicity index confirm the electron donor character of L_1 whilst the values of chemical hardness and softness explain the reactivity and the easier excitation of L_{11} compared to L_1 that displays higher stability and opposes charge transfer.

In **Fig. 4**, we also presented the MOs frontiers shapes of the studied ligands. In all molecules, the occupied orbitals are mainly localized on the triazole fragment and the imine function while the unoccupied orbitals have their major contribution from the phenyl ring. These results suggest that the transitions involve charge transfer from the triazole moiety to the phenyl ring.

Fig. 4. Shapes of MOs frontiers of L_1 - L_{11} obtained by DFT (B3LYP/6-31G(d,p)) method.

3.7. Experimental and theoretical investigation of the electronic properties

According to the results reported in **Table. 5.** We can notice that the third transition is the most important electronic transition for L_1 owing to its oscillator strength (0.485 and 0.453 (DCM)). This transition corresponds to the raise of an electron from the occupied molecular orbital (HOMO-2) to the lowest unoccupied molecular orbital (LUMO) (HOMO-2 \rightarrow LUMO). The second electronic transition has also an important oscillator strength in the gas phase (0.241) and greater value in DCM (0.426). This transition presents a $\pi \rightarrow \pi^*$ character and correspond to the transition from the high occupied molecular orbital (HOMO) to the lowest uncopied molecular orbital (LUMO). The other transitions display a weak value of oscillator strength and has also a $\pi \rightarrow \pi^*$ character. Using the same analysis, one can notice that the most interesting transitions for L_{11} in the gas phase is the second, the fourth and the sixth owing to their high f values. The second transition corresponds to the raise of an electron from HOMO to LUMO in gas phase as well as in DCM with respectively an oscillator strength of 0.082 and 0.09. The fourth corresponds to the transition from HOMO to

L+1 with an oscillator strength in the gas phase of 0.062 and in DCM (0.087). The sixth transition is the most important transition with an oscillator strengthof 0.146 and 0.162 respectively for gas phase and DCM. The last transition mainly corresponds to a transition from H-2toLUMO (88%). The other transitions have negligible oscillator strength and are considered as weakly allowed transitions.

Table. 5. Experimental (λ_{Exp}) and calculated (λ_{Th}) wavelengths, energy in eV (E), oscillator strength multiplied by 100 (*f* * 100) and their percentage contributions for L₁ and L₁₁.

To obtain information about the nature of the electronic transitions, the absorption spectra of the ligands L_1 and L_{11} were recorded in dichloromethane solution of a concentration about 7.10⁻⁵ M at room temperature. As it can be seen an example for L_{11} in Fig. 5, the ligands display three principal peaks at 345 nm, 283 nm and 262 nm for L_1 , at 357 nm, 283 nm and 250 nm for L_{11} . For L_1 , The transition which corresponds to the raise of an electron from HOMO to LUMO orbital appears in the gas phase at 359 nm and a shift to 348 nm in DCM was observed. This blue shift may be ascribed to the solvent effect and the pure transition $\pi \rightarrow \pi^*$. The experimental maximum absorption at this range was observed at 345 nm and may be attributed to the π -conjugation in the triazol system.On the other hand, we notice a red shift from 293 nm (gas phase) to 301 nm (DCM), these transitions correspond to HOMO-2 \rightarrow LUMO whilst the experimental maximum absorption at this range was observed at 283 nm and may be attributed to π -conjugation in phenyl system.

Fig. 5. Experimental and theoretical electronic spectra of L_{11}

In the case of L_{11} , a blue shift was observed due to the solvent effect and the pure transition HOMO \rightarrow LUMO which corresponds to $\pi \rightarrow \pi^*$, this transition appears at 520 nm in gas phase and is shifted to 510 nm in DCM while the experimental absorption appears at 357 nm.Additionally, we remark two transitions (HOMO \rightarrow L+1 and H-2 \rightarrow LUMO) at higher

energies in the case of gas phase which correspond to 379 nm and 326 nm respectively. These transitions was combined in the case of DCM, the higher in terms of oscillator strength was H-2 \rightarrow LUMO which appears at 346 nm, from HOMO toL+1 correspond to 360 nm. The experimental values was obtained at 283 nm and 250 nm, may be ascribed to the effect of the nitro group on the π -conjugation in phenyl system.

For complex Fe-L₁₁, an increase in absorption intensity was observed in the short wavelength region that can be attributed to the hyperchromic effect in which the metal may participate. For complex Pb-L₁, unless a week perturbation in the transitions at short wavelength region, no clear effect was observed. After the analysis of electronic transitions, we can conclude that the maximum absorption for both ligands (L₁and L₁₁) at the longest wavelength region corresponds to the HOMO \rightarrow LUMO transition which has a $\pi \rightarrow \pi^*$ nature and primarily caused by the intramolecular charge transfer from the triazole to the phenyl ring. Whilst the maximum absorption in the short wavelength region represent the effect of substituent group on the phenyl.

4. Conclusion

The studiedligands were found to be efficient for the liquid-liquid extraction of metal cations. Fe^{2+} and Pb^{2+} were selectively extracted with these triazole derivatives and the studies of pH effect confirm the performance of such type of ligands in selective extraction as well as in protonation resistance. These results have conclusively shown that the formation of coordination complexes for these ligands is highly dependent on the substituent nature; high selectivity towards Fe^{2+} is provided by electron withdrawing group whilst high selectivity against Pb^{2+} is ensured by the presence of electron donor group. Interestingly, it was found that the back-extraction was extremely effective by using acidic solutions. The present work has also investigated the ground and excited state geometries using DFT and TDDFT method. From the results of our calculation, we suggest that the presence of the methoxy

group improves the stability of the molecule while the presence of the nitro group allows the molecule to be more reactive. On the other hand, The electronic transitions at the longest wavelengths region correspond to HOMO \rightarrow LUMO transition which has a $\pi \rightarrow \pi^*$ and are primarily related to the intramolecular charge transfer from the triazole to the phenyl ring.Moreover, the maximum absorption in the short wavelength region is represented by different transitions which elucidate the effect of substituent group. It was also shown that the calculated electronic transitions resulted from TD-DFT (B3LYP/6-31+G(d,p)) calculations are in an acceptable agreement with experimental data.

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Tables

L _n	R	IR (KBr, v, cm ⁻¹)	¹ H NMR (DMSO- d_6 , $\delta_{\rm H}$ ppm)
L ₁	4-MeO	3276 (NH), 1698 (C=N), 1306 (C=S)	2.37 (s, 3H, CH ₃),3.82 (s, 3H, OCH ₃), 7.14 (d, 2H, $J = 8$ Hz, arH), 7.82(d, 2H, $J = 8$ Hz, arH), 9.70 (s, 1H, H-C=N), 13.74 (s, 1H, NH)
L_2	4-Me	3280 (NH), 1688 (C=N), 1306 (C=S)	2.39 (s, 3H, CH ₃), 2.45 (s, 3H, arCH ₃), 7.30 (d, 2H, $J = 8$ Hz, arH), 7.77 (d, 2H, $J = 8$ Hz, arH), 9.98 (s, 1H, H-C=N), 13.70 (s, 1H, NH)
L ₃	2-C1	3356 (NH), 1711 (C=N), 1302 (C=S);	2.36 (s, 3H, CH ₃), 7.59 (dd, 2H, <i>J</i> = 4 Hz, <i>J</i> = 8 Hz, arH), 7.79-7.85 (m, 1H, arH), 8.07-8.12 (m, 1H, arH), 10.74 (s, 1H, H-C=N), 13.71 (s, 1H, NH)
L_4	3-Cl	3262 (NH), 1690 (C=N), 1274 (C=S)	2.34 (s, 3H, CH ₃), 7.44-7.49 (m, 2H, arH), 7.80 (d, 1H, $J = 8$ Hz, arH), 8.14 (s, 1H, arH), 10.16 (s, 1H, H-C=N), 13.77 (s, 1H, NH)
L ₅	4-Cl	3258 (NH), 1630 (C=N), 1301 (C=S)	2.32 (s, 3H, CH ₃), 7.61 (d, 2H, <i>J</i> = 8 Hz, arH), 7.90 (d, 2H, <i>J</i> = 8 Hz, arH), 10.09 (s, 1H, H-C=N), 13.72 (s, 1H, NH)
L ₆	2-Br	3305 (NH), 1712 (C=N), 1244 (C=S)	2.38 (s, 3H, CH ₃), 7.56 (dd, 2H, <i>J</i> = 4 Hz, <i>J</i> = 8 Hz, arH), 7.77-7.82 (m, 1H, arH), 8.10-8.15 (m, 1H, arH), 10.79 (s, 1H, H-C=N), 13.76 (s, 1H, NH)
L ₇	3-Br	3362 (NH), 1745 (C=N), 1309 (C=S)	2.39 (s, 3H, CH ₃), 7.50 (dd, 2H, <i>J</i> = 4 Hz, <i>J</i> = 8 Hz, arH), 7.84 (d, 1H, <i>J</i> = 8 Hz, arH), 8.12 (s, 1H, arH), 10.10 (s, 1H, H-C=N), 13.80 (s, 1H, NH)
L ₈	4-F	3262 (NH), 1690 (C=N), 1294 (C=S)	2.34 (s, 3H, CH ₃), 7.40 (dd, 2H, arH), 7.99 (dd, 2H, arH), 9.96 (s, 1H, H- C=N), 14.22 (s, 1H, NH triazole)
L9	3-NO ₂	3277 (NH), 1723 (C=N), 1324 (C=S)	2.41 (s, 3H, CH ₃), 7.52-7.59 (m, 2H, arH), 7.87 (d, 1H, $J = 8$ Hz, arH), 8.16 (s, 1H, arH), 10.17 (s, 1H, H-C=N), 13.89 (s, 1H, NH)
L ₁₀	4-NO ₂	3262 (NH), 1660 (C=N), 1294 (C=S)	2.37 (s, 3H, CH ₃), 7.67 (d, 2H, <i>J</i> = 8 Hz, arH), 7.98 (d, 2H, <i>J</i> = 8 Hz, arH), 10.14 (s, 1H, H-C=N), 13.76 (s, 1H, NH)
L ₁₁	2-NO ₂ -	3200 (NH), 1690 (C=N), 1264 (C=S)	2.43 (s, 3H, CH ₃), 7.67-7.74 (m, 2H, arH), 8.13 (s, 1H, arH), 10.79 (s, 1H,

Table. 1. Spectroscopic data of ligands L_1 - L_{11}

		Extractability (E%)				
Ligands	Fe(II)	Cu(II)	Zn(II)	Pb(II)	Co(II)	Cd(II)
L_1	92.6	24.9	1.2	97.3	1.0	40.2
\mathbf{L}_2	91.7	25.0	2.5	93.6	0.0	37.9
L_3	42.1	34.8	0.5	90.1	3.0	28.4
L_4	96.3	51.3	3.1	98.9	5.5	13.3
L_5	85.3	43.6	2.5	98.1	0.0	10.0
L_6	53.7	53.7	0.9	65.7	4.1	8.9
L_7	7.5	30.5	1.7	79.3	7.2	0.0
L_8	92.9	33.6	2.0	96.7	2.7	1.9
L9	93.6	63.1	6.7	37.9	4.9	18.6
L_{10}	91.6	29.5	3.5	72.4	6.6	49.8
L ₁₁	95.7	53.4	2.0	87.2	6.5	24.0

Table. 2. Extraction efficiencies of metal cations using L_1 - L_2	11.
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Table. 3.Back-extraction of metal ions extracted with L_{11} and L_1 .

	Back-extraction (%) of :				
Back-extraction reagent	Fe(II) extracted by L_{11}	Pb(II) extracted by L ₁			
1 M HC1	91	89			
1 M HNO ₃	97	99			
$1 \text{ M H}_2 \text{SO}_4$	95	94			

Licondo	Property (eV)									
Ligands	E _{HOMO}	$E_{\rm LUMO}$	ΔE	χ	η	σ	μ	ω		
L_1	-5.5231	-1.5628	3.9603	3.5429	-1.9802	-0.5050	-3.5429	-3.1695		
L_2	-5.6219	-1.7116	3.9103	3.6667	-1.9551	-0.5115	-3.6667	-3.4384		
L_3	-5.7394	-2.0139	3.7255	3.8767	-1.8628	-0.5368	-3.8767	-4.0340		
L_4	-5.8290	-2.0471	3.7818	3.9380	-1.8909	-0.5288	-3.9380	-4.1007		
L_5	-5.8042	-2.0204	3.7837	3.9123	-1.8919	-0.5286	-3.9123	-4.0453		
L_6	-5.7438	-1.9766	3.7671	3.8602	-1.8836	-0.5309	-3.8602	-3.9556		
L_7	-5.8232	-2.0417	3.7816	3.9325	-1.8908	-0.5289	-3.9325	-4.0894		
L_8	-5.7356	-1.8460	3.8896	3.7908	-1.9448	-0.5142	-3.7908	-3.6946		
L9	-5.9871	-2.6409	3.3462	4.3140	-1.6731	-0.5977	-4.3140	-5.5616		
L_{10}	-6.0684	-2.9603	3.1081	4.5144	-1.5540	-0.6435	-4.5144	-6.5569		
L ₁₁	-5.9596	-3.0161	2.9435	4.4878	-1.4717	-0.6795	-4.4878	-6.8425		

Table. 4. Quantum chemical parameters for L_1 - L_{11} obtained by using B3LYP/6-31G(d,p).

		E (eV)	$\lambda_{Exp}(nm)$	λ _{τh} (nm)	f *100	Major contribs
	Gas	3.225		385	0.03	H-1->LUMO (97%)
		3.454	345	359	24.17	HOMO->LUMO (98%)
		4.228	283	293	48.53	H-2->LUMO (92%)
		4.456	262	278	1.25	H-3->LUMO (18%), HOMO->L+1 (75%)
		4.587		270	0.02	H-1->L+1 (12%), H-1->L+2 (80%)
		4.714		263	0.03	H-1->L+1 (87%), H-1->L+2 (12%)
Г						
		3.461		358	0.04	H-1->LUMO (97%)
		3.565	345	348	42.59	HOMO->LUMO (98%)
	Σ	4.125	283	301	45.32	H-2->LUMO (94%)
	Da	4.539	262	273	0.27	H-3->LUMO (48%), HOMO->L+1 (42%)
		4.764		260	0.03	H-1->L+2 (87%)
		4.955		250	0.15	H-3->LUMO (30%), H-2->L+1 (10%), HOMO->L+1 (53%)
		2.213		560	0.01	H-1->LUMO (98%)
		2.385	357	520	8.18	HOMO->LUMO (100%)
	Gas	3.139	283	395	0.01	H-1->L+1 (96%)
		3.271	250	379	6.20	HOMO->L+1 (99%)
		3.542		350	0.00	H-4->LUMO (87%)
		3.808		326	14.64	H-3->LUMO (14%), H-2->LUMO (79%)
L ₁₁						
		2.384		520	0.01	H-1->LUMO (98%)
	DCM	2.430	357	510	9.01	HOMO->LUMO (100%)
		3.368	283	368	0.02	H-1->L+1 (95%)
		3.449	250	360	8.74	HOMO->L+1 (98%)
		3.583		346	16.20	H-2->LUMO (88%)
		3.648		340	0.00	H-4->LUMO (82%)

Table. 5. Experimental (λ_{Exp}) and calculated (λ_{Th}) wavelengths, energy in eV (E), oscillator strength multiplied by 100 (f * 100) and their percentage contributions for L₁ and L₁₁.

Figures



Fig. 1. Chemical structures of studied ligands L_1 - L_{11}



Fig. 2.Competitive extraction E(%) of metal ions using L_1 - L_{11}



Fig. 3. Plot of log *D* versus log L for Pb^{2+} of ligand L_1



Fig. 4.Shapes of MOs frontiers of L_1 - L_{11} obtained by DFT (B3LYP/6-31G(d,p)) method.



Fig. 5. Experimental and theoretical electronic spectra of L_{11}

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Highlights

- Liquid-liquid extraction of metal ions using eleven ligands 1,2,4-triazole Schiff base.
- Determination of the extractability for each metal ions.
- Investigation of competitive extraction at different pH values.
- High selectivity towards Fe^{2+} (90.1%) and Pb^{2+} (94.3%).
- Use of DFT and TD-DFT for electronic structure elucidations.