High liquid-liquid extraction selectivity of Fe(II) and Pb(II) with TD-DFT theoretical calculations of long chain acid pyrazole and triazole based ligands

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High liquid–liquid extraction selectivity of Fe(II) and Pb(II) with TD-DFT theoretical calculations of long chain acid pyrazole- and triazole-based ligands

Morad Lamsayah1,2, Mohamed Khoutoul1, Abdelilah Takfaoui1 and Rachid Touzani1,2*

Abstract: A sensitive and selective liquid–liquid extraction is carried out using four new ligands $L_1$–$L_4$ as chelating agents for extraction of heavy metals from aqueous solution. Their capacities extraction of Fe$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Co$^{2+}$, Zn$^{2+}$, and Ni$^{2+}$ were determined by atomic absorption measurement. The high extractive affinity for Fe(II) is 97.28% ($L_2$) and for Pb(II) is about 91.62% ($L_3$). The effects of pH and ligand concentration upon extraction capability were investigated. The results revealed that the extraction of Fe(II) dependents on the pH with maximum in the pH range of 6–7. A back-extraction of Fe(II) and Pb(II) extracted with $L_3$ leads us to recover for Fe(II) 92.12% (using H$_2$SO$_4$) and for Pb(II) 85.66% (using HNO$_3$). The TD-DFT theoretical calculation has been reported.

Subjects: Ecology - Environment Studies; Environment & Health; Environment & Resources

Keywords: long chain N-ligands; liquid–liquid extraction; metal ions; atomic absorption; TD-DFT theoretical calculations

1. Introduction

As a result of decades of industrial production involving their use, heavy metal contamination of air, water, and soil is becoming widely found in the environment and will eventually enter into the food
chain. Some heavy metals at trace concentrations are essential elements and play important roles in human metabolism. On the other hand, at higher concentrations, most of the heavy metals may be toxic (Khazaeli, Nezamabadi, Rabani, & Panahi, 2013). Water contamination by heavy metals is of great importance from a health point of view because of its high toxicity and susceptible carcinogenic effect (Baraka, Hall, & Heslop, 2007). One of the most crucial properties of these metals which differentiate them from other toxic pollutants is that they are not biodegradable in the environment (Florence, 1982). Heavy metal ions should be accurately evaluated in order to prevent the occurrence of harmful effects (Ghaedi et al., 2008). The cycle of trace metal ions from environment to human is also an important part of environmental studies (Afridi et al., 2007; Jamali et al., 2009; Ramesh, Mohan, Seshaiyah, & Jeyakumar, 2001; Yurtsever Sarica & Türker, 2007). Therefore, accurate determination of trace amounts of heavy metals in the environment is very important. A liquid–liquid extraction (LLE) is a powerful and commonly used sample pretreatment technique for preconcentration and/or separation, which is included in many standard analytical methods especially for determination of metal and metalloids (Mitani & Anthemidis, 2013). Chelating agent or organic extractant is an important part when used in coupling with organic solvent to extract metal ions from water. The extraction efficiency and selectivity can be affected by size of the chelate ring and type of its donor atoms, oxidation state and size of the metal ion, and pH of the solvent system (Bond, Dietz, & Chiarizia, 2000). Many different kinds of functionalities have been studied for their potential to remove metal ions from wastewater. In recent years, intensive research has focused on pyrazole derivatives, which are used in several fields, for example, pharmacology (Cottineau, Toto, Marot, Pipaud, & Chenault, 2002; Park et al., 2005; Rapposelli et al., 2004; Tewari & Mishra, 2001), biology (Calli, Nærøm, Mukhija, & Hjelmencrantz, 2004; Larsen, Zahran, Pedersen, & Nielsen, 1999; Pimerova & Voronina, 2001; Raci, Salhi, & Raci, 2010; Sechi et al., 2005), catalysis (Christenson, Tokar, & Tolman, 1995; Slattery, Bare, Jameson, & Goldsby, 1999), electronics (Estereuelas, Gómez, López, & Orñate, 1998; Marzin, Budde, Steel, & Lerner, 1987), and, particularly, the removal of divalent metal ions from aqueous solutions containing either a single metal species or a mixture of metal ions (Bouabdallah, Touzani, Zidane, & Ramdani, 2007; Harit, Cherfi, Isaoa, Riahi, & Malek, 2012; Malachowski & Davidson, 1989; Tarrago, Zidane, Marzin, & Tep, 1988). The chelating mechanism depends on coordination of the metal ion to active chelating sites present. These active sites characterized by functional groups which are capable of coordination: these would include donor atoms such as O, N, S, and P (Atia, Donia, & Yousif, 2003; Samal, Das, Dey, & Acharya, 2000). Atomic absorption spectrophotometry (AAS) is extensively employed for quantification of metallic species and presents desirable characteristics, such as ease of operational, high selectivity, and low cost (Khazaeli et al., 2013).

In this contribution, we report the synthesis of a series of pyrazolic compounds 11-(((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)undecanoic acid (L1), 11-(((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)undecanoic acid (L2), 11-(((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)undecanoic acid (L3), and 11-(((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)undecanoic acid (L4) in one step by condensation of one equivalent of (3,5-dimethyl-1H-pyrazol-1-yl)methanol, (1H-pyrazol-1-yl)methanol, or (1H-1,2,4-triazol-1-yl)methanol with one equivalent of 11 aminoundecanoic acid in acetonitrile and the mixture was heated under reflux for 4 h. The present study was aimed to report the results of the capacities extraction of our ligands L1–L4 of heavy metals from aqueous solution, to examine their recovery using different aqueous acidic solutions, to study the effect of varying pH and ligand concentrations upon extraction capability, and to investigate the complexation mechanism between the metal and our ligands.

The theoretical investigation using TD-DFT calculation were performed with Gaussian software version 9 for Windows running under Windows 8.1 (64bit) resident in an Intel Core i5 CPU PC workstation.
2. Experimental section

2.1. General methods

NMR spectra were recorded using a Bruker 300 instrument operating at 300.14 MHz for \(^1\)H spectra and 75.47 MHz for \(^13\)C spectra (Pz: pyrazole). Infrared (IR) spectra were recorded on a Shimadzu infrared spectrophotometer using the KBr disc technique. Mass spectra were recorded using a Shimadzu GC-MS 2014 Shimadzu Gas Chromatograph-Mass Spectrometer.

2.1.1. 11-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)undecanoic acid (L1)

Yield: 75%; IR (KBr), \(\nu (\text{cm}^{-1})\): 3536 (NH); 1732 (C=O); 1508 (C=N); 1558 (C=C); 1087 (C–N); \(^1\)H NMR (300 MHz, CDCl3, d (ppm)): 5.82 (s, 1H, H5Pz); 4.87 (s, 2H, N–CH2–N); 2.53 (t, 2H, H16, J = 3 Hz, J = 9 Hz); 2.24 (t, 2H, H7, J = 3 Hz, J = 9 Hz); 2.2.4 (s, 3H, CH3Pz); 1.83 (s, 1H, NH); 1.65–1.09 (m, 16H, H15...H8); 13C NMR (75 MHz, CDCl3, d (ppm)): 178.24 (C=O); 144.12–139.67 (C4Pz, C1Pz); 104.43 (C5Pz); 65.36 (N–CH2–N); 48.63 (C16-NH); 34.80 (C7); 29.46–25.14 (C15...C8); 13.43–12.08 (C21Pz C22Pz); ESI-SM m/z: M = 332.02 ([M + Na]).

2.1.2. 11-(Bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)undecanoic acid (L2)

Yield: 87%; IR (KBr), \(\nu (\text{cm} −1)\): 1717 (C=O); 1538 (C=N); 1636 (C=C); 1131 (C–N); \(^1\)H NMR (300 MHz, CDCl3, d (ppm)): 5.83 (s, 2H, HPz); 4.89 (s, 4H, N–CH2–N); 2.56 (t, 2H, H21, J = 3 Hz, J = 9 Hz); 2.34 (t, 2H, H12, J = 6 Hz, J = 6 Hz); 2.26 (s, 6H, CH3Pz); 1.68–1.10 (m, 16H, H20...H13); 13C NMR (75 MHz, CDCl3, d (ppm)): 178.19 (C=O); 140.03–139.69 (C1Pz C4Pz C6Pz C9pz); 105.69 (C5Pz C10Pz); 65.35 (N–CH2–N); 48.61 (C21-N); 34.77 (C12); 27.36–22.92 (C20...C13); ESI-SM m/z: M = 417 ([M]).

2.1.3. 11-(Bis((1H-1,2,4-triazol-1-yl)methyl)amino)undecanoic acid (L3)

Yield: 82%; mp = 52–54°C; IR (KBr), \(\nu (\text{cm} ^{-1})\): 1715 (C=O); 1513 (C=N); 1136–1184 (C–N); \(^1\)H NMR (300 MHz, CDCl3, d (ppm)): 8.28 (d, 2H, H1Pz H9Pz, J = 9 Hz); 7.98 (d, 2H, H4Pz H6Pz, J = 9 Hz); 5.15 (s, 4H, N–CH2–N); 2.67 (t, 2H, H21, J = 6 Hz, J = 3 Hz); 2.34 (t, 2H, H12, J = 6 Hz, J = 6 Hz); 1.65–1.18 (m, 16H, H20...H13); \(^13\)C NMR (75 MHz, CDCl3, d (ppm)): 175.64 (C=O); 149.95 (C4Pz C6Pz); 141.95 (C1Pz C9Pz); 64.05 (N–CH2–N); 48.34 (C21-N); 32.29 (C12); 27.36–22.92 (C20...C13); ESI-SM m/z: M = 349.99 ([2M + Na]).

2.1.4. 11-(Bis((1H-pyrazol-1-yl)methyl)amino)undecanoic acid (L4)

Yield: 69%; mp = 46–48°C; IR (KBr), \(\nu (\text{cm} ^{-1})\): 1707 (C=O); 1470 (C=N); 1541 (C=C); 1089 (C–N); \(^1\)H NMR (300 MHz, CDCl3, d (ppm)): 7.59 (d, 2H, H4Pz H6Pz, J = 3 Hz); 7.53 (d, 2H, H1Pz H9Pz, J = 3 Hz); 6.28 (t, 2H, H5Pz H10Pz, J = 3 Hz, J = 3 Hz); 6.01 (s, 4H, N–CH2–N); 2.61 (t, 2H, H21, J = 6 Hz, J = 6 Hz); 2.34 (t, 2H, H12, J = 6 Hz, J = 6 Hz); 1.67–1.22 (m, 16H, H20...H13); \(^13\)C NMR (75 MHz, CDCl3, d (ppm)): 176.17 (C=O); 137.67 (C4Pz C6Pz); 127.92 (C1Pz C9Pz); 104.03 (C5Pz C10Pz); 65.82 (N–CH2–N); 48.04 (C21-N); 32.50 (C12); 27.48–23.06 (C20...C13).

3. Results and discussion

3.1. Synthesis methodology

The ligands L1–L4 were prepared, in accordance with a literature procedure (Khoutoul et al., 2015; Touzani et al., 2001; Zerrouki, Touzani, & El Kadiri, 2011), by condensation of (3,5-dimethyl-1H-pyrazol-1-yl)methanol, (1H-pyrazol-1-yl)methanol, and (1H-1,2,4-triazol-1-yl)methanol with one equivalent of aminoun decanoic acid in acetonitrile and the mixture was heated under reflux for 4 h, the reaction employed for the synthesis of our ligands is illustrated in Figure 1.

The observed changes in chemical shifts of RMN\(^1\)H and RMN\(^{13}\)C of δ(N–CH₂–N) (Table 1) prove that introduction of the donor groups increases the electron density on the nitrogen atoms, and that the presence of acceptor groups lowers the density. This is ascribed to shielding of the methylene proton in the case of donor groups and deshielding for acceptor groups (Khoutoul et al., 2015).
3.2. Solvent extraction methodology

3.2.1. Liquid–liquid individual extraction (metal–ligand)

A 20 mL solution of Dichloromethane (CH$_2$Cl$_2$) containing (7 × 10$^{-5}$ M) ligand and a 20 mL aqueous solution containing (7 × 10$^{-5}$ M) metal ions (Fe$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Co$^{2+}$, Zn$^{2+}$ or Ni$^{2+}$) were placed in a flask. The mixture was shaken for 2 h. LLE experiments were conducted at room temperature and neutral pH (25°C; pH 7). The aqueous phase was separated and analyzed by atomic absorption spectrometry with an air–acetylene flame. The element standard solutions used for calibration were produced by diluting a Fluka 1,000 mg/L stock solutions. All standards were made acidic, using 2% nitric acid (Tokalioğlu, Kartal, & Elçi, 2000), to avoid metal hydrolysis and to match the sample content.

The extractability (Ex %) was determined from the decrease in the metal concentration in the aqueous phase (Equation (1)):

$$
\text{EX} \% = \left( \frac{[\text{metal}]_{\text{blank}} - [\text{metal}]_{\text{water}}}{[\text{metal}]_{\text{blank}}} \right) \times 100
$$

Table 1. Comparison of $^1$H NMR and $^{13}$C NMR chemical shifts for the different ligands

| Ligand | RMN$^1$H ppm | RMN$^{13}$C ppm |
|--------|--------------|----------------|
|        | $\delta$(N–CH$_2$–N) | $\delta$(N–CH$_2$–N) |
| L1     | 4.87         | 65.36          |
| L2     | 4.89         | 65.35          |
| L3     | 5.15         | 64.05          |
| L4     | 5.01         | 65.82          |

The extractability (Ex %) was determined from the decrease in the metal concentration in the aqueous phase (Equation (1)).

Figure 1. General structure of the ligands (L1–L4).
For the extraction of Fe\textsuperscript{2+} and Pb\textsuperscript{2+} ligands, L\textsubscript{2}–L\textsubscript{4} are very efficient (Fe\textsuperscript{2+}: 97, 90 and 90%, respectively), (Pb\textsuperscript{2+}: 86, 91 and 81%, respectively). For L\textsubscript{1}, the efficiency of extraction is low (48% for Fe\textsuperscript{2+} and 23% for Pb\textsuperscript{2+}) (Table 2). This may due to the presence of proton attached to the nitrogen atom, this protonation decreases the extractability of L\textsubscript{1} of all the metal ions, the presence of two pyrazolic or triazolic rings in each structure of L\textsubscript{2}–L\textsubscript{4} increases the efficiency of extraction of Fe\textsuperscript{2+} and Pb\textsuperscript{2+}. The methyl group linked to the pyrazol ring of L\textsubscript{2} increases the affinity to Fe\textsuperscript{2+}. For extraction of Cu\textsuperscript{2+}, the ligand L\textsubscript{3} is relatively efficient, with percentage extraction 65%. L\textsubscript{3} gave a good extractability compared to other ligands and this may due to the presence of two sp\textsubscript{2} nitrogen atoms in each triazole ring. The complexation mechanism between the metal ions (Fe\textsuperscript{2+}, Pb\textsuperscript{2+} and Cu\textsuperscript{2+}) and our ligands was investigated in details in the current work. For extraction of Cd\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, and Zn\textsuperscript{2+}, the efficiency of extraction is low, between 0.05 and 43%. Based on these results, it seems that our ligands do not have good affinity for these metals.

3.2.2. Liquid–liquid extraction selectivity study (Mixture of metals-ligand)

A solution (7 × 10\textsuperscript{−5} M) of mixture of metals (Fe\textsuperscript{2+}, Pb\textsuperscript{2+}, Cu\textsuperscript{2+} and Cd\textsuperscript{2+}) is used. This aqueous solution (20 mL) was stirred for 2 h with 20 mL of an organic solution of the ligand (in CH\textsubscript{2}Cl\textsubscript{2}) (7 × 10\textsuperscript{−5} M). LLE experiments were conducted at room temperature and neutral pH (25°C; pH 7). Diluted standard solutions were prepared from the stock standard solutions. All standards were made acidic, using 2% nitric acid [1]; the aqueous phase was separated and analyzed by atomic absorption spectrometry with an air-acetylene flame measurement. The extractability of the metal cations is expressed by means of Equation (1):

\[
\text{Iron metal is selectively extracted by ligands L2 and L4 (79 and 75%, respectively) and we noticed that these two ligands have high efficiency of extraction in individual extraction test of Pb\textsuperscript{2+} and Fe\textsuperscript{2+}. However, through a competitive extraction, these two ligands are selective to Fe\textsuperscript{2+} more than Pb\textsuperscript{2+} (Table 3). The absence of any selectivity to Cu\textsuperscript{2+} and Cd\textsuperscript{2+} confirm the previous results obtained with individual liquid–liquid extraction.}

3.2.3. Effect of pH on the extraction of metal ion Fe\textsuperscript{2+}

Solution pH is an important factor affecting the efficiency of extraction of metal ions by ligands, especially those containing such functional groups as amino, carboxy, and hydroxy, which can be easily protonated or deprotonated in solutions at different pHs (Khoutoul et al., 2015). The effect of pH on the extraction of Fe\textsuperscript{2+} by the ligands L\textsubscript{2}–L\textsubscript{4} was investigated in the equilibrium pH range (3–8) at a phase ratio of 1:1. It was observed that extraction of metal ions increased with pH in the pH range (3–7), and Fe\textsuperscript{2+} was highly extracted into the organic phase at equilibrium pH of 7 by our ligands L\textsubscript{1}–L\textsubscript{3} (97, 89 and 90%, respectively) (Figure 2). A low extraction values of Fe\textsuperscript{2+} by the ligands L\textsubscript{2}–L\textsubscript{4} is 39%.
were observed in pH 3 (37, 29 and 42%, respectively) and this can be explained by a rapid and total protonation of coordination sites. At pH values greater than 7.0, the extraction of Fe$^{2+}$ may decreased because of hydrolysis of Fe$^{2+}$ (leading to the hydroxide of Fe(III): Fe(OH)$^{+}$ and Fe(OH)$_2$). There is an increase in Fe$^{2+}$ during extraction to organic phase as pH increases. When log $D$-pH graph is examined, there are two pH ranges (3–5 and 5–7), which can be attributed to a different form of protonation or deprotonation. It can be said that there is two structural conformations when forming metal complex at different pHs.

3.2.4. Effect of extractant concentration
To study the effect of extractant concentration on the extractability of Fe$^{2+}$ and Pb$^{2+}$, the concentration of the ligands was varied in the range of (2 × 10$^{-5}$ M–7 × 10$^{-5}$ M) and the concentration of the aqueous solution containing metal ions Fe$^{2+}$ and Pb$^{2+}$ was fixed to (7 × 10$^{-5}$ M). The experimental results show that the extraction of Fe$^{2+}$ increases with an increase in the extractant concentration. As it has been perceived, iron metal extraction increases from 4 to 47% for L1, 38–97% for L2, 43–89% for L3, and 29–90 for L4 (Figure 3); whereas, extraction of Pb$^{2+}$ increases in the range 28–86% for L2, 18–91% for L3, and 10–81% for L3 (Figure 4).

Figure 2. The effect of pH on the liquid–liquid extraction of Fe$^{2+}$.

Figure 3. The effect of ligands concentration on the liquid–liquid extraction of Fe$^{2+}$.

Figure 4. The effect of ligands concentration on the liquid–liquid extraction of Pb$^{2+}$.
The distribution ratio ($D$) is the ratio of the concentration of the metal ion $M$ in the two ionic liquid phases, at equilibrium, is measured most conveniently by measuring the concentration of the metal ion in the aqueous phase after extraction and by comparing it with the initial concentration (Equations 2 and 3) (Rout & Binnemans, 2014):

$$D = \frac{C_i - C_f}{C_f} \times \frac{V_{IL1}}{V_{IL2}}$$  \hspace{1cm} (2)

where $C_i$ and $C_f$ are the concentrations of the metal ions in the feed phase before (initial concentration) and after extraction (final concentration), respectively. $V_{IL1}$ is the volume of the aqueous phase and $V_{IL2}$ is the volume of the organic phase [1]. In general, a phase volume ratio of 1:1 was used

$$D = \frac{C_i - C_f}{C_f}$$ \hspace{1cm} (3)

3.2.5. Log–log plot analysis

The complexation mechanism between the metal and our ligands was investigated by slope analysis. The logarithm of the distribution ratio increased with increasing concentration of ligand. The slope of the relationship between the logarithm of the distribution ratio of metals and the logarithm of ligand concentration indicates the number of molecules involved in the extraction of a metal ion.

To characterize the extraction ability, the dependence of the distribution coefficient $D$ of the cation between the two phases upon the ligand concentration was examined. In order to establish the number of moles of ligand participating in the extraction system, a plot of log $D$ vs. log [L] was made as shown in Figures 5 and 6.

A plot of log $D$ vs. log [L] should be linear ($\log D = a \cdot \log [L] + b$) and its slope should be equal to the number of ligand molecules per metal cation in the extracted species (Gup, Alpoguz, & Beduk, 2002). The solvent extracted Fe$^{2+}$ and Pb$^{2+}$ metal cation from CH$_2$Cl$_2$ at different concentrations of L1–L4 as shown in Figures 3 and 4.

Figure 5. log $D$ vs. log [L] for the extraction of Fe$^{2+}$ using L1–L4.

Figure 6. log $D$ vs. log [L] for the extraction of Fe$^{2+}$ using L2–L4.
The obtained log D vs. log [L] plot displayed in Figure 5 is shown as 1:1 ratio of metal–ligand for Fe$^{2+}$ with $L_2$–$L_4$ and 1:2 ratio of metal: ligand for Fe$^{2+}$ with $L_1$.

The structures of $L_2$–$L_4$ have an active chelating site, which may indicated that one ligand participated in the extraction process to form iron complex in the organic phase.

As for $L_1$, log D vs. log [L] plot is shown as 1:2 ratio of metal: ligand for Fe$^{2+}$ which indicated that two ligands participated in the extraction process to form iron complex in the organic phase. $L_1$ is obtained from a monoalkylation of pyrazol cycle that may implied that two molecules of ligand $L_1$ were needed to form an active chelating site.

As it can be seen in Figure 6, for Pb$^{2+}$ a slope of about 2 was obtained for $L_2$–$L_4$ which signified that two molecules of ligand participated in the extraction process to form lead complexes in the organic phase.

3.2.6. Back-extraction of Fe$^{2+}$ and Pb$^{2+}$

Most metals can be back-extracted from an organic solution into an aqueous solution; this is achieved by acid decomposition of the metal complexes or the complexing agent. The recovery of Fe$^{2+}$ and Pb$^{2+}$ from organic solution of ligands $L_1$, $L_3$, and $L_4$, using hydrochloric acid solution, nitric acid solution, and sulfuric acid solution at the same concentration (1 M) was studied.

Based on the obtained results, the recovery was between 73 and 92% for the iron metal, HCl gave a good yield for $L_1$ an $L_4$ (92 and 91, respectively). For $L_3$, the iron metal was recovered with a good yield (92%) in sulfuric acid solution and lead with 86% in nitric acid solution. 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 (Table 4).

### Table 4. Back-extraction of metal ions extracted with using $L_1$–$L_4$

|       | Fe$^{2+}$ (%) | Pb$^{2+}$ (%) |
|-------|--------------|---------------|
|       | $L_2$ | $L_3$ | $L_4$ | $L_3$ |
| HCl 1 M | 91.90 | 87.82 | 90.81 | 63.50 |
| HNO$_3$ 1 M | 77.79 | 72.95 | 79.26 | 85.66 |
| H$_2$SO$_4$ 1 M | 82.27 | 92.12 | 85.13 | 57.08 |

4. Theoretical calculations

4.1. Computational details

We have utilized DFT theory for the computation of molecular structure, vibrational frequencies, and energies of optimized structures. A considerable effort has been directed to the understanding of organic molecule of theoretical calculations with the DFT (Hohenberg & Kohn, 1964), with the Becke’s three-parameter hybrid functional (B3) (Becke, 1993) for the exchange part and the Lee–Yang–Parr (LYP) correlation function (Lee, Yang, & Parr, 1988). The molecules were first optimized using the B3LYP with 6–31G (d, p) basis set in Gaussian 09. Thereafter, a molecular visualization program, Gaussview 5 was used to study the electronic properties, such as HOMO–LUMO energies and HOMO–LUMO energy visualization contours.

4.2. Quantum chemical parameters

The HOMO and LUMO energy values are related to the ionization potential (IP) and electron affinities (EA): (IP = $-E_{\text{HOMO}}$) (EA = $-E_{\text{LUMO}}$) (Wolinski, Hinton, & Pulay, 1990). The difference between HOMO and LUMO energy values gives the HOMO–LUMO energy gap. By using these HOMO–LUMO energy values,
The important properties like global hardness ($\eta$), global softness ($\sigma$), electronegativity ($\chi$), chemical potential ($\mu$), and electrophilicity index ($\omega$) were calculated.

The hardness ($\eta$) of a species (atom, ion, or molecule): $\eta = (\text{IP}−\text{EA})/2 = -(E_{\text{LUMO}} - E_{\text{HOMO}})/2$ is a qualitative indication of how polarizable it is, in another way how much its electron cloud is distorted in an electric field.

The softness ($\sigma$) is simply the reciprocal of the hardness:

$$\sigma = 1/\eta$$

(Gázquez, Martinez, & Méndez, 1993; Pearson, 1963, 1966).

Electronegativity is the tendency of molecules to attract electrons:

$$\chi = (\text{IP} + \text{EA})/2 = -(E_{\text{LUMO}} + E_{\text{HOMO}})/2.$$

Chemical potential denotes the affinity of an electron to flee and is defined as the first derivative of the total energy with respect to the number of electrons in a molecule (Kavitha, Sundaraganesan, & Sebastian, 2010), chemical potential is simply the negative of electronegativity value: $\mu = -\chi$.

Electrophilicity index is the capability of a substance to accept electrons, it was proposed as a measure of the electrophilic power of a molecule and it can be measured through the equation:

$$\omega = (\mu^2/2\eta)$$ (Parr, Szentpály, & Liu, 1999).

Molecules with large energy gap are hard which implies higher stability and opposing charge transfer, since they oppose changes in their electron density and distribution. On the contrary, molecules, which require a small energy gap for its excitation, are also termed as soft molecules. Hence, they are highly polarizable in nature. In terms of chemical change, soft molecules are more reactive than hard molecules. (Pilli, Banerjee, & Mohanty, 2015).

4.3. HOMO–LUMO analysis

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. We can determine the way the molecule interacts with other species; hence, they are called the frontier orbitals. HOMO, which can be thought the outermost orbital containing electrons, tends to act as electron donor. On the other hand, LUMO can be thought the innermost orbital containing free places to accept electrons (Gece, 2008). The HOMO and LUMO energies are calculated (Table 5). This electronic transition absorption corresponds to the transition from the ground to the first excited state and is mainly described by an electron excitation from the HOMO to the LUMO.

### Table 5. Quantum chemical parameters for L1–L4 obtained by using B3LYP/6-31G(d, p)

| Property (eV) | L1                        | L2                        | L3                        | L4                        |
|--------------|---------------------------|---------------------------|---------------------------|---------------------------|
| $E_{\text{HOMO}}$ | -6.066508624              | -6.073583587              | -6.715772533              | -6.309778504              |
| $E_{\text{LUMO}}$ | 0.316740649               | 0.340414564               | -0.15026906               | 0.312114712               |
| $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ | 6.383249274               | 6.413998151               | 6.56565627                | 6.621893217               |
| Electronegativity ($\chi$) | 2.874883987               | 2.866584512               | 3.432989719               | 2.998831896               |
| Chemical hardness ($\eta$) | -3.191624637              | -3.206999076              | -3.282782813              | -3.310946608              |
| Softness ($\sigma$) | -0.313320053              | -0.311817988              | -0.304619604              | -0.302028428              |
| Chemical potential ($\mu$) | -2.874883987              | -2.866584512              | -3.432989719              | -2.998831896              |
| Electrophilicity index ($\omega$) | -1.29478853               | -1.281152032              | -1.795034744              | -1.358069731              |
The HOMO is located over the pyrazole ring. For $L_1$, $L_2$, and $L_4$, the HOMO→LUMO transition implies an electron density transfer to the carboxylic group from pyrazole ring. For $L_3$, the LUMO is located over the triazole ring and it can be explained by the presence of two sp2-hybridized nitrogen atoms, which increases the acceptor character of the ring cycle, and the HOMO→LUMO transition in this situation implies an electron density transfer in the same triazole ring. The atomic compositions of the frontier molecular orbital are shown in Figure 7.

4.4. Vibrational spectral analysis

IR spectra were performed by a comparison of experimental data with those calculated by Gaussian using B3LYP/6-31G. The experimental and calculated IR spectra are shown in Table 6. The vibrational bands assignments have been made using Gauss-View molecular visualization program. Table 6 presents the calculated vibrational frequencies and their experimentally measured values. We have compared our calculation with the experimental results. To make comparison with experiment, we present correlation graphics in Figure 8 based on the calculations. As it seen from calculation graphic Figure 8, good agreement is seen between calculated and experimental IR spectra.

NH theoretical stretching mode was observed at 3,589 cm⁻¹, C=N at 1,501 cm⁻¹. For $L_1$, OH stretching modes are observed in the region 3,412–3,649 cm⁻¹, CH ring stretching vibrations are observed in the region 3,284–3,333 cm⁻¹; experimental C=O stretching modes are observed at 1,732, 1,717,
Table 6. Some experimental and theoretical wavenumbers for \( L1 \)–\( L4 \) obtained by using B3LYP/6-31G (\( \nu \): Stretching)

| L1 | L2 | L3 | L4 | Streching bond |
|----|----|----|----|----------------|
| Theoretical wavenumbers (cm\(^{-1}\)) | Experimental wavenumbers (cm\(^{-1}\)) | Theoretical wavenumbers (cm\(^{-1}\)) | Experimental wavenumbers (cm\(^{-1}\)) | Theoretical wavenumbers (cm\(^{-1}\)) | Experimental wavenumbers (cm\(^{-1}\)) | Theoretical wavenumbers (cm\(^{-1}\)) | Experimental wavenumbers (cm\(^{-1}\)) |
| 1501 | 1508 | 1502 | 1538 | 1500 | 1508 | 1478 | 1470 |
| 1610 | 1558 | 1609 | 1636 | – | – | 1507 | – |
| 1792 | 1732 | 1751 | 1717 | 1751 | 1715 | 1550 | 1541 |
| 3034 | 3047 | 3017 | 3038 | 3069 | 2918 | 3063 | 2922 |
| 3100 | 3134 | 3134 | 3132 | 3137 | 3117 | 3132 | 3119 |
| 3284 | 3202 | 3204 | 3202 | 3319 | 3254 | 3295 | 3213 |
| 3632 | 3649 | 3608 | 3647 | 3607 | 3412 | 3607 | 3447 |
| 3589 | 3536 | – | – | – | – | – | – |

\( \nu \) C=\( \text{N} \)  
\( \nu \) C=\( \text{C} \)  
\( \nu \) C=O  
\( \nu_{\text{sym}} \text{CH}_2 \) (NCN)  
\( \nu_{\text{asym}} \text{CH}_2 \) (NCN)  
\( \nu \) CH Ring  
\( \nu \) OH  
\( \nu \) NH
1,715, and 1,707 cm\(^{-1}\) for \(L_1-L_4\), respectively, and are in better agreement with theoretical wave-numbers 1,792, 1,751, 1,751, and 1,751 cm\(^{-1}\) respectively.

Other essential characteristic vibrations of our compounds are CH\(_2\) (in N–C–N) symmetric and asymmetric stretching. These modes have been calculated at 3,017–3,074 cm\(^{-1}\) for symmetric stretching and at 3,100–3,143 cm\(^{-1}\) for asymmetric stretching; these results are in correlation with experimental wavenumbers. The other modes are shown in Table 6.

To see correlation between the experimental and calculated wavenumbers were plotted correlation graphics and given in Figure 8. The relation between experimental and calculated wavenumbers is usually linear and described for \(L_1-L_4\) by the following equations:

\[
\begin{align*}
L_1: & \quad v_{\text{Theo}} = 0.9818 \, v_{\text{Exp}} + 48.392 \quad (R^2 = 0.9919) \\
L_2: & \quad v_{\text{Theo}} = 0.9956 \, v_{\text{Exp}} + 14.026 \quad (R^2 = 0.9932) \\
L_3: & \quad v_{\text{Theo}} = 0.9904 \, v_{\text{Exp}} + 12.694 \quad (R^2 = 0.9994) \\
L_4: & \quad v_{\text{Theo}} = 1.0004 \, v_{\text{Exp}} - 7.4713 \quad (R^2 = 0.9986)
\end{align*}
\]

The IR calculations gave a slightly better coefficient and lower standard error \(R^2\) (Figure 8). However, the small deviation between the experimental and computed wavenumbers may be due to the difference between the molecular geometry in the gas phase and in its solid phase.

5. Conclusion

Some conclusive remarks can be tentatively derived from the results mentioned above:

(1) Extraction of heavy metals with pyrazole and triazole N-ligand \(L_1-L_4\) shows high extractability of Fe(II) and Pb(II) for \(L_2-L_4\) and a significant extractability of Copper (II), while lowest extraction efficiency was found for Ni(II), Cd(II), Co(II), and Zn(II).
(2) pH is one of the determining factors for metals extraction by ligands. The extractability of Fe$^{2+}$ and Pb$^{2+}$ increased with pH values, it becomes more and more important while approaching the neutral pH.

(3) The effect of varying ligand concentrations upon extraction capability of Fe(II) and Pb(II) was investigated for establishing the number of moles of ligand participating in each extraction system.

(4) Very good agreement has been noticed between experimental and calculated IR spectra using TD-DFT (B3LYP/6-31G) and the structural geometries of ligands were investigated.

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