Synthesis, Liquid Liquid Extraction of Cu(II) and Pb(II) With DFT Calculation Studies of New Imidazo[1, 2-a]Pyridine Chalcones

M. Koudad[1,2*], M. Lamsayah[1], A. Elaatiaoui[1,2], S. Dadou[1,2], A. Oussaid[1,2], M. Allali[3], R. Touzani[1] and N. Benchat[1]

[1]*Laboratory of Applied Chemistry and Environments (LCAE), Faculty of Sciences, University Mohammed Premier, Oujda.*
[2]*Department of Chemistry, Polydisciplinary Faculty of Nador, UMP.*
[3]*Institute of Nursing Professions and Health Techniques Fez, EL Ghassani Hospital, Fez 30000, Morocco.*

Abstract

New imidazo[1,2-a]pyridine-chalcones derivatives L_2&L_3 were prepared by condensation of one equivalent of 2-(phenyl) Imidazo[1, 2-a]pyridine carbaldehyde and one equivalent of an Acetophenone in the presence of KOH. These compounds were prepared in good yield (L_2:79%; L_3:85%) and fully investigated by ^{1}H and ^{13}C NMR, and Mass spectroscopies, and new imidazo[1,2-a]pyridine (2-phenylimidazo[1,2-a]pyridin-8-ol(L_1)) was prepared by condensation of one equivalent of 2-aminopyridin-3-ol and one equivalent of 2-bromoacetophenonein EtOH.The compounds were used to extract different metal ions. Indeed (Zn^{2+}, Cu^{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. The extractive affinity for Pb(II) is the high and is around 81% (L_3) and for Cu(II) is about 70% (L_1). Interestingly, the competitive extraction and the effect of pH were also investigated. We found a high selectivity towards Pb^{2+} (70%) for L_3, Cu^{2+} (65%) for L_1, respectively for each ligand. A back-extraction of Pb(II) and Cu(II) extracted with L_3 leads us to recover for Pb(II) 95% (using H_2SO_4) and for Cu(II) 96% (using HCl).In addition, geometry optimizations and excited-states of the ligands in order to gain a better insight into the geometry and the electronic structure were carried out by means of DFT calculations.The calculated electronic transitions are in agreement with experimental data.

I. Introduction

The increase in terrible human activities and especially industrial activities cause the contamination of water by heavy metals. Among the anthropogenic sources of heavy metals, we can mention: mining, metallurgical and iron and steel industry, fertilizers and pesticides applied in soil cultivation, waste incineration and ashes, medical waste, waste dumps in cities, emissions from factories and combustion engine, effluent from sewers and sewage sludge. Each source of contamination has its own damaging effects to plants, animals and ultimately to human health, but those that add heavy metals to soils and waters are of serious concern due to their persistence in the environment and carcinogenicity to human beings[1]. They cannot be destroyed biologically but are only transformed from one oxidation state or organic complex to another[2]. Therefore, heavy metal pollution poses a great potential threat to the environment and human health, due to the increased frequency of pollution, we are obliged to develop a program to counter this threat and stop it with one of the methods of treatment to be more environmentally friendly. 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[3].

In recent years, intensive research has focused on imidazopyridinechalcones derivatives, which are used in several fields, for example pharmacology[4], biology[5-6], corrosion[7], and, particularly, removal of divalent metal ions from aqueous solutions containing either a single metal species or a mixture of metal ions.

In this work we report the synthesis of novel imidazopyridine-chalcones derivatives, to study the complexing properties of these derivatives rings in liquid–liquid extraction of bivalent metal ions (Cu(II),Pb(II), Cd(II), Zn(II)).

2. Experimental

2.1 Chemistry
All commercially available chemicals and reagents were purchased from Aldrich and used without further purification. All the solvents were dried and distilled before use. The melting points were measured with a Tottoli apparatus and are uncorrected. The ^{1}H &^{13}C NMR were recorded in CDCl$_3$ using NMR Bruker 500 MHz spectrometer operating at 500 MHz for ^{1}H and 126 MHz for [13]C. Chemical shifts are reported as parts per million (ppm) using tetramethylsilane (TMS) as an internal standard. Mass spectra have been recorded on LC-MS Shimadzu Liquid chromatography–mass spectrometry. Reactions were monitored using thin layer chromatography (TLC) carried out on Merck silica gel 60 F254 precoatedaluminium plates. The visualization was achieved under UV light or staining with I$_2$. Chromatographic separations were achieved on silica gel columns (Merck, 60–120 mesh) using gradient of AcOEt/Hexane as eluent.

2.1.1 Reaction of 2-aminopyridine with α-halogenated carbonyl compounds
This method is the most widely used, and is based on a condensation between 2-aminopyridine and a differently substituted α-halogenated carbonyl compound. It was developed in 1925[8] by Tschitschibabin and appreciated because of its relatively easy implementation, availability of commercially available base reagents and acceptable yields of end products. The reaction of the cyclocondensation between 2-aminopyridine and an α-halogenated carbonyl compound was described in 1982 by Hand and Paudler[9].

2.1.2 Functionalization in position 3:
The Vilsmeier-Haack[10] reaction consists in generating in situ a formaldehyde equivalent from DMF and POCl$_3$. Its application to the 2-substituted imidazole compounds leads to the 2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde derivative.

2.1.3 General procedure for the preparation of Chalcone of Imidazo[1,2-a]Pyridine
Substituted 2-(phenyl) Imidazo[1, 2-a]pyridine carbaldehyde (0.5 mmol) dissolved in 15 ml of ethanol and to this 10 % aqueous KOH (1 ml) solution were added and stirred for 15 to 20 minutes at room temperature. To this mass (0.5 mmol) of p-acetophenone were added. The mixture was stirred for 8 hours at 60 °C. Reaction was monitored by TLC. After completion of reaction, reaction mass was poured in ice cold water and neutralized with sodium hydrogencarbonate, filtered off to obtain the desired product. The resulting product was purified by column chromatography on silica gel (ethyl acetate–hexane, 2:8) to afford pure product.

2.1.4 Spectral data of representative compounds:
*2-phenylimidazo[1,2-a]pyridin-8-ol:*Yield: 70 %; Mp:194-195°C; ^{1}H NMR (500 MHz, Chloroform-d) δ(ppm): 7.91 – 7.85 (m, 2H), 7.83 (s, 1H), 7.77 (dd, J = 6.2, 1.5 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.37 – 7.30 (m, 1H), 6.83 – 6.73 (m, 2H);^{13}C NMR (126 MHz, Chloroform-d) δ 146.35, 144.11, 141.35, 133.05, 128.67, 128.01, 126.47, 117.60, 114.16, 109.39, 107.87; LC-MS : m/z =211.2 (M+1).

*(E)-1-(naphthalen-1-yl)-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)prop-2-en-1-one:*Yield:79 %;Mp:170-171°C; ^{1}H NMR (500 MHz, Chloroform-d) δ(ppm): 8.62 (dd, J = 7.0, 1.5 Hz, 1H), 8.41 (d, J = 1.7 Hz, 1H), 8.31 (dd, J = 15.8, 1.1 Hz, 1H), 8.09 (dd, J = 8.5, 1.7 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.99 – 7.87 (m, 3H), 7.87 (s, 1H), 7.82 (dd, J = 9.0, 1.2 Hz, 1H), 7.72 – 7.61 (m, 2H), 7.65 – 7.57 (m,3H), 7.59 – 7.52 (m, 1H), 7.46 (ddd, J = 8.8, 6.9, 1.4 Hz, 1H), 7.13 (tt, J = 6.9, 1.6 Hz, 1H); ^{13}C NMR (126 MHz, Chloroform-d) δ 189.45, 151.71, 147.41, 135.67, 135.47, 134.19, 132.61, 129.70, 129.68, 129.61, 129.52, 129.06, 128.89, 128.61, 128.41, 127.86, 127.01, 126.82, 125.26, 124.39, 118.38, 117.83, 114.20; LC-MS : m/z =375.2 (M+1).

*(E)-1-mesityl-3-(2-phenylimidazo[1,2-a]pyridin-3-yl)prop-2-en-1-one:*Yield: 85 %; Mp:154-155°C; ^{1}H NMR (500 MHz, Chloroform-d) δ(ppm): 8.55 (dt, J = 6.9, 1.2 Hz, 1H), 7.80 (dt, J = 8.9, 1.2 Hz, 1H), 7.72 (d, J = 16.6 Hz, 1H), 7.72 – 7.61 (m, 2H), 7.51 – 7.39 (m, 4H), 7.10 (td, J = 6.9, 1.3 Hz, 1H), 6.92 (dd, J = 8.8, 7.7 Hz, 3H), 2.31 (d, J = 32.7 Hz, 9H); ^{13}C NMR (126 MHz, Chloroform-d) δ 200.87, 152.48, 147.92, 138.44, 136.96, 133.94, 133.30, 132.54, 129.36, 128.98, 128.65, 128.45, 127.36, 125.92, 122.98, 118.35, 117.29, 114.37, 21.15, 19.39; LC-MS : m/z =367.2 (M+1).

2.2 Liquid–liquid individual extraction :

A 7.10^{-5} M solution of the ligand in 20 ml of CH_2Cl_2has been stirred for 2h with 20 ml of a 7.10^{-5}M aqueous solution of metal salt. Liquid-liquid extraction experiments were carried out at room temperature and neutral pH[11]. For the experiment with Pb(II) ions, we used a closed system with no air, and a non-aggressive magnetic agitation. The aqueous solution of Pb(II) was prepared and agitated in closed system. The aqueous phase has been isolated and analyzed 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 have been carried out using standard conditions for calibration. All standards were made acidic by using nitric acid 2% to avoid metal hydrolysis and to match content in the sample[12]. The extractability (Ex %) has been determined by considering the decrease in the metal concentration in the aqueous phase (equation) :

EX % = (([metal] blank - [metal] water)/ [metal] blank) X 100, where [metal] blank and [metal] water are the metal concentrations in the aqueous phase after extraction with a dichloromethane solution containing extractants.

2.3 Liquid–liquid extraction selectivity study:

A 7.10^{-5} M solution of mixture of metals (Zn^{2+}, Pb^{2+}, Cu^{2+} and Cd^{2+}) has been used. The 20 ml of aqueous solution was stirred for 2 h with 20 ml of an organic solution of the ligand (in a 7.10^{-5} M CH_2Cl_2 solution). LLE experiments were conducted at room temperature and with neutral solutions (25°C; pH 7). Diluted standard solutions were prepared from the stock standard solutions by making them acidic, using 2% nitric acid; the aqueous phase was isolated and analyzed by atomic absorption spectrometry with an air–acetylene flame measurement.

2.4 Theoretical Calculations

Density functional theory has developed the concept of chemical potential (μ) and absolute electronegativity (χ)[13] :

$$\mu = (\delta E / \delta N)v(r) = -\chi \quad (1)$$

Where, E is the total energy, N is the number of electrons, and v(r) is the external potential of the system.
Hardness (η) is defined[14] as the corresponding second derivative.

$$\eta = (\delta 2 E / \delta N2)v(r) = (\delta\mu / \delta N)v(r) \quad (2)$$

ionization energy (IE) and electron affinity (A), the electronegativity (χ), global hardness (η) and softness (S), may be defined in terms of the energy of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) according to Koopman's theorem[15].
Softness (σ) is the inverse of hardness and is given as follows:

$$\sigma = 1/\eta \quad (3)$$

ionization energy (IE) is defined as the amount of energy required to remove an electron from a molecule[16].It is related to the energy of the E_{HOMO} :

$$IE = -E_{HOMO} \quad (4)$$

Electron affinity (A) is defined as the energy released when a proton is added to a system[17]. It is related to E_{LUMO} :

$$A = -E_{LUMO} \quad (5)$$

Using a finite difference method working equations for the calculations of χ and η may be given as:

$$\chi = (IE + A) / 2 \quad (6)$$
$$\eta = (IE - A)/2 \quad (7)$$

If ε_{HOMO} and ε_{LUMO} are the energies of the HOMO and LUMO, respectively, the previous Eqs can rewritten using Koopman's theorem[16] :

$$\chi = -(\varepsilon_{LUMO} + \varepsilon_{HOMO}) / 2 \quad (8)$$
$$\eta = -(\varepsilon_{LUMO} - \varepsilon_{HOMO}) /2 \quad (9)$$

3. Results and Discussion

3.1 Chemistry:

The ligand2-(phenyl) Imidazo[1,2-a]pyridine and L_1 was synthesized by condensation between 2-aminopyridine (2-aminopyridine-3-olfor L_1) and 2-Bromo-1-phenylethanoneas shown in Scheme 1. The Vilsmeier-Haack reaction was applied to 2-(phenyl) Imidazo[1, 2-a]pyridinetogive the 2-phenylimidazo[1,2-a]pyridine-3-carbaldehyde derivative.Imidazo[1,2-a]PyridineL_2 and L_3were prepared by reacting2-(phenyl) Imidazo[1,2-a]pyridine carbaldehyde and *p*-acetophenone. The resulting productswere purified by column chromatography

on silica gel (ethylacetate–hexane, 2:8) to afford pure products to give satisfactory yield (65%). The structures was unambiguously ascertained by ^{1}H &^{13}C NMR and ES[+]-MS. ^{1}H NMR spectra of these compounds exhibit the expected characteristic protons at the NMR time scale (CDCl$_3$, 298 K). Further information about the isolation and full characterization ofthese compoundswereprovided in the experimental section.
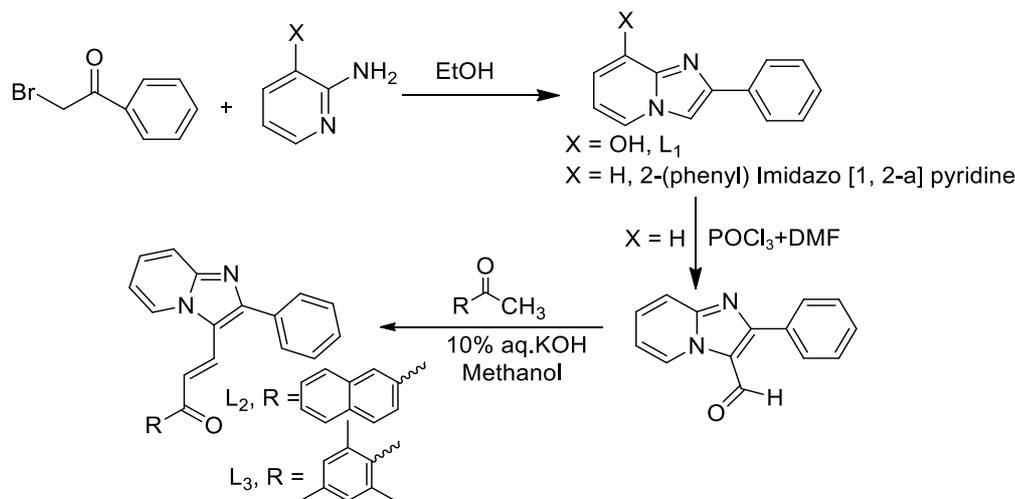
Scheme 1: Route synthesis of the ligands (L$_1$–L$_3$).

3.2 Liquid–liquid individual extraction:

The Table 1 display a remarkable and high extraction efficiency for both Pb^{2+} and Cu^{2+}.The extractability of Pb^{2+}by these ligands is good and varies from 31 % (L$_1$) to 81 % (L$_3$), the presence of the methyl group in *para*, *meta* and *ortho* position of the phenyl gives a high value of extraction efficiency; 81 % (L$_3$), this may be due to the presence of the hydrophobic methyl groups electron donor by inductive effect.

For extraction of Cu^{2+}, L$_1$ gave a good efficiency of 70% relative to the other ligands, this may be due to the presence of a hydroxyl group, such that copper will forms a strong coordination bond with the oxygen atom.

For the extraction of Cd^{2+}and Zn^{2+}, the tested ligands show the very low efficiency not exceeding 12 % for Zn^{2+} and 35 % for Cd^{2+}.

Table 1: Efficiency of individual extraction of metal ions E (%) using L$_1$–L$_3$

	L$_1$(%)	L$_2$(%)	L$_3$(%)
Zn^{2+}	12.6	10.36	9.65
Cd^{2+}	22.52	35.40	26.20
Cu^{2+}	**70.6**	38.85	28.5
Pb^{2+}	30.1	**50.3**	**81.2**

3.3 Liquid–liquid extraction selectivity study:

Lead metal is selectively extracted by L$_3$ with reported efficiency of 65 %, and L$_1$ shows good selectivity to Cu^{2+} 65 %, confirming the previous results obtained with individual liquid-liquid extraction. L$_2$ do not show any selectivity (Table 2).

Table 2: Competitive extraction E(%) of metal ions using L$_1$-L$_3$

	Zn^{2+}(%)	Cd^{2+}(%)	Cu^{2+}(%)	Pb^{2+}(%)
L$_1$	09.47	08.56	**65.30**	*15.20*
L$_2$	15.2	20.36	23.60	*40.61*
L$_3$	7.89	9.21	13.23	***70.36***

3.4 Effect of pH on extraction of Pb^{2+} by the ligands L$_2$ and L$_3$

The pH of a solution is an important factor affecting the efficiency of extraction of metal ions by ligands, especially for those containing functional groups which can be easily protonated or deprotonated (such as amino, carboxy, and hydroxyl) in solutions at different pH. The extraction properties of Pb2+ by the ligand L2 and L3 were investigated in the pH range of 1–7 as it is shown on Figure 1, the efficiency decreased slowly with pH decreasing, which can be explained by a stable coordination. Under pH 3 the efficiencies decreases seriously

and become negligible when the pH attained a value of pH 1, this can be explained by a rapid and total protonation of coordination sites, Moreover, by increasing pH from 7, the extractant efficiency increased slowly and this can be explained by a stable coordination.
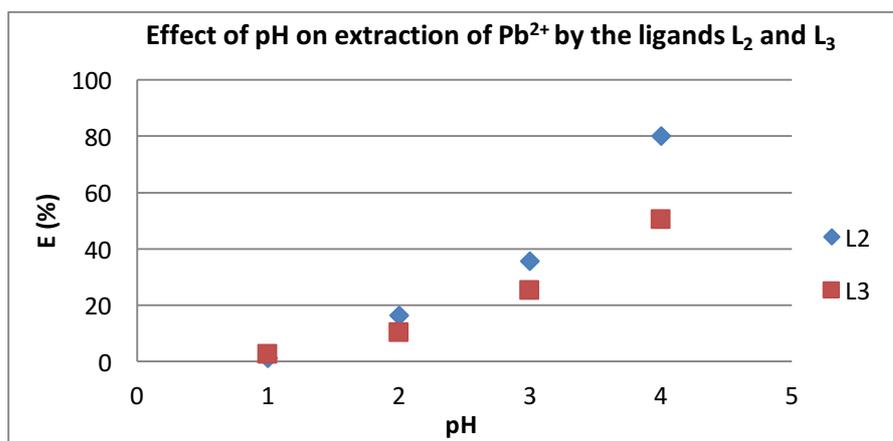

Figure1. The effect of pH on extraction of Pb^{2+} by the ligands L_2 and L_3.

3.5 Back-extraction of Cd^{2+} Cu^{2+} and Pb^{2+} with L_3:

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 Pb^{2+} by L_3 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_3

	Pb^{2+}(%)	Cu^{2+}(%)	Cd^{2+}(%)
HNO_3 1M	34.65	19.67	40.81
HCl 1M	92.50	96.85	09.41
H_2SO_4 1M	95.65	96.12	38.25

Based on the obtained results, HCl and H_2SO_4 gave a good yield for Pb^{2+} and Cu^{2+}, the recovery was between 92 and 96%.

3.6 Theoretical Calculations

3.6.1 Geometry optimization

All calculations were performed using the Gaussian 09W series of program[16]. The geometry optimization of the three ligands (Figure 2) was optimized by the density functional theory DFT[18] with the Becke's three parameter exchange functional and the Lee Yang Parr correlation functional (B3LYP)[14] .

3.6.2 Molecular orbital energies

Highest Occupied Molecular Orbital Energy (E_{HOMO}) and Lowest Unoccupied Molecular Orbital Energy (E_{LUMO}) are very popular quantum chemical parameters. These orbitals, also called the frontier orbitals, determine the way the molecule interacts with other species. The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that has room to accept electrons. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbitals (HOMO and LUMO) of reactants[19]. The energy of the HOMO is directly related to the ionization energy and the energy of the LUMO is directly related to the electron affinity. The HOMO–LUMO gap, i.e. the difference in energy between the HOMO and LUMO, is an important stability index[20]. A large HOMO–LUMO gap implies high stability for the molecule in chemical reactions[21]. The concept of ''activation hardness" has been also defined on the basis of the HOMO–LUMO energy gap. The qualitative definition of hardness is closely related to the polarizability, since a decrease of the energy gap usually leads to easier polarization of the molecule [22].

L_1 L_2 L_3

Figure 2: Optimized structures of ligands L_1, L_2 and L_3 calculated by B3LYP/6-31G(d).

LIGAND	HOMO	LUMO	MEP
L_1			
L_2			
L_3			

Figure3: The highest occupied (HOMO), lowest unoccupied (LUMO) molecular orbitals and molecular electrostatic potential (MEP) of ligands L_1-L_3.

The 3D plots of the frontier orbitals HOMO and LUMO and the molecular electrostatic potential map (MEP) figures for three molecules are shown in Figure 3. MEP is directly related to electron density and a very useful descriptor in site detection for electrophilic and nucleophilic attack reactions, as well as hydrogen bonding interactions[23-24]. The electrostatic molecular potential was evaluated using the method B3LYP / 6-31G (d). The red region: the site is rich in electrons, blue region: the site is deficient in electrons, Yellow region: the site is poor in electrons, Green region: neutral.

Table 4 : HOMO and LUMO energies, ionization energy (IE), electron affinities (A), energy gap , Electronegativity (χ), Chemical hardness (η), Softness (σ), Chemical potential (μ), Electrophilicity index (ω)

Ligand	E_{HOMO} (ev)	E_{LUMO} (ev)	ΔE (ev)	IE (ev)	A (ev)	Energy gap (ev)	M (d)	χ (ev)	η (ev)	σ (ev)	μ (ev)	ω (ev)
L_1	-0.20	-0.03	0.17	0.20	0.03	-0.17	3.86	0.12	-0.085	-11.76	-0.19	-0.21
L_2	-0.21	-0.08	0.13	0.21	0.08	-0.13	4.10	0.15	-0.065	-15.38	-0.15	-0.17
L_3	-0.21	-0.07	0.14	0.21	0.07	-0.14	4.13	0.14	-0.07	-14.28	-0.14	-0.21

On the basis of the results reported in Table 4, the GAP value for L_1 ligand is low which means that L_1 has the highest nucleophilic power, hence the molecule remains more reactive,the 3D plots of molecular electrostatic potential map (MEP) clearly show the nucleophilic attack site of L_1.

The values of electronegativity, chemical potential and ionization energy confirm the electron donor character and the reactivity of L_1.

Conclusion

In conclusion, we tested the effect of substitution of a new series of imidazopyridine-chalcones on the extraction efficiency of different metal ions Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} from aqueous solutions, our results show a significant affinity for Lead (II) and copper (II).

Interestingly, it was found that the back-extraction was extremely effective by using acidic solutions. It was also shown that the calculated electronic transitions resulted from DFT calculations are in an acceptable agreement with experimental data.

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