JEE Journal of Ecological Engineering

Journal of Ecological Engineering 2024, 25(3), 120–131
https://doi.org/10.12911/22998993/177627
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Received: 2023.12.22
Accepted: 2024.01.05
Published: 2024.01.22

A New Water-Insoluble β-Ketoimine as a Potential Agent Capable of Water Treatment Applications

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ABSTRACT

This paper describes the synthesis of the new β-ketoimine 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one, and studies its structure, solubility in water and complexation properties in terms of the possibility of its further application for water and wastewater treatment, especially for removing metal ions from aqueous solutions. The synthesis procedure consisted of the addition of 3-ethyl-pentane-2,4-dione to 3-aminopropyltriethoxysilane and subsequent elimination of the water molecules. The structure of the resulting compound was confirmed by nuclear magnetic resonance and Fourier transform infrared spectroscopy-attenuated total reflectance. The affinity of the resulting compound for metal ions binding from aqueous solutions was studied using spectrophotometric methods. Moreover, the stability constants of created in this process complexes of a new β-ketoimine with selected metal ions (Ag^+, Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+} and Zn^{2+}) was determined and it was found that the stability of created complexes of L:M with molar ratios equal 1:1 are changing as follows: $Pd^{2+} > Cr^{6+} > Pt^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Ag^+ > Fe^{3+} > Zn^{2+} > Co^{2+} > Au^{3+} > Mg^{2+}$.

Keywords: β-ketoimine, 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one, removal metal ions, water solutions, complexation agent.

INTRODUCTION

The increase in the level of care of the natural environment is a key issue that will determine its condition in future years. Constantly introducing more stringent legal regulations is one way to minimize the number of threats affecting the lives and health of people and animals [Huang et al. 2023 , Liu et al. 2023]. Metals, especially heavy metals, constitute one of the main threats to the environment, especially when their concentration, e.g. in water, is much higher than the naturally existing level of pollution caused by, among others, the decomposition of parent rocks or volcanic eruptions [Khanzada et al. 2023]. The presence of excessive amounts of heavy metals in the environment is mainly caused by waste from various industries. Dust, sludge and sewage resulting from complex industrial processes often contain toxic metals [Shrestha et al. 2021, Shi et al. 2023]. Considering the importance of the described problem, scientists are currently looking for more effective and environmentally friendly solutions that differ from traditional methods of removing toxic metals. Well-known techniques used to eliminate this contamination include separation techniques such as precipitation [Zhang et al. 2023], solvent extraction [Vieceli et al. 2023], sorption [Fang et al. 2023, Munio et al. 2023] e.g. on the modified ion exchangers [Arslanoğlu et al. 2023] or on the polymer sorbents [Lagiewka et al. 2023, Susmanto et al. 2023], and membrane procedures [Castro-Muñoz et al. 2021, Nasir et al. 2019]. Typically, in those techniques, it is important to select a compound, which is capable of binding metal ions and is called an extractant or ion carrier. There are many substances commercially utilized for this purpose [Zawirucha et al. 2016]. The main disadvantage of the already-known extractants is that they may be partially soluble in water, which may lead to contamination of the aqueous solution previously cleaned of metals. The second drawback can be their relatively high price and not always satisfactory selectivity and separation efficiency in relation to the currently separated material. Due to these facts, in addition to the commercial extractants, the new chemical compounds that are free from the described problems are increasingly being synthesized [Loreti et al. 2021]. In many publications, scientists have repeatedly shown that newly synthesized compounds are more effective than commercial ones [Witt et al. 2016]. The mentioned compounds can bind metal ions from water solutions via precipitate, ion exchange, electrochemical or complexation reactions [Pandey et al. 2023, Laatikainen and Sainio 2019].

For example, a complexation agent (ligand) should be characterized by medium affinity to metal ions, because the high stability of created in this reaction complex may cause problems with the subsequent regeneration of the ligand [Radzymińska-Lenarcik et al. 2018]. The selection of the ligand having a specific type and number of central atoms, as well as the use of mixed ligands, enables the obtaining complexing agents with the desired properties, e.g. desired stability with chosen metal ions. Especially, bidentate or polydentate compounds range in the number of atoms used to bond to a central metal atom or ion and this phenomenon is described by the chelate effect [Yin et al. 2022, Kim et al. 2017]. This effect is associated with an increase in the disorder of the system and thus an increase in entropy. Moreover, other factors that increase the stability of complexes should also be mentioned, such as the number of molecular rings, their size, and the presence of additional substituents [Zhao et al. 2020]. An example of bidentate ligands are β-diketones. It is well known that these compounds form complexes with many metal ions [Ugwu and Conradie 2023]. Silanes, in turn, are a group of polydentate chemical compounds, whose common character is the presence of a central silicon atom in the molecule with four additional substituents. This construction makes these compounds usually more reactive in comparison to the analogous carbon compounds, due to the stronger polarization of silicon-non-metal bonds than carbon-non-metal [Petkowski et al. 2020]. Semenov et al. (2007) proposed a procedure for preparing a silicon-containing imino enol from 3-aminopropyltriethoxysilane (APTES) and acetylacetone. In the next study, the authors synthesized 4-(3-triethoxysilylpropylimino)-pentan-2-one complexes with europium and terbium, which proves the affinity of the obtained compound to metal ions [Semenov et al. 2008]. Moreover, the group of scientists studied the preparation, characterization and application of sorbents, which were synthesized by attaching the chosen metal ions compounds to the silica surface through ketoimine groups. Those groups were obtained in the reaction of APTES with pentane-2,4-dione or its derivatives (benzyl or allyl derivatives) [Rykowska and Wasiak 2009, Wawrzyniak 2009 Wawrzyniak and Wasiak 2004]. Furthermore, Rykowska et al. (2011) dealt also with using prepared sorbents in the solid phase extraction technique for the separation of trace transition metal ions (Cu^{2+}, Cr^{3+} and Zn^{2+}) from water matrices or enrichment of metal ions in real samples (water from a lake adjacent to a power plant). This research clearly confirm the ability of silica-related ketoimine groups to form complexes with metal ions.

Based on the described literature data, in the presented paper the main aim was obtaining a new β-ketoimine 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one (L). The characterization of this compound involved the studies of its structure, solubility in water and studies of its complexation properties in terms of the possibility of its further application for water and wastewater treatment, especially for removing metal ions from aqueous solutions. The L was synthesized from APTES, as well as a 3-ethyl-pentane-2,4-dione - previously never used for this purpose. The affinity of the resulting compound for metal ions binding from an aqueous solution was studied using spectrophotometric methods. So far, the stability of complexes of metal ions with ketoimine groups obtained from APTES and derivative of pentane-2,4-dione have never been tested, that is why in this paper, the stability constants of complexes of L with metal ions (Ag^{+}, Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Zn^{2+}) formed in aqueous-methanol solutions were determined. The innovative nature of the described in paper research is evidenced by the fact that the author is the first to apply for a patent in Poland for this solution (Patent Application No. P.442807 [WIPO ST 10/C PL442807]) [Witt 2022]. The new compound may have potential applications in binding metal ions, e.g. from industrial wastewater or pickling solutions, so they may constitute a promising new solution in the field of environmental chemistry, and their use may improve the quality of the environment.

MATERIAL AND METHODS

Synthesis

The new β-ketoimine 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one (L) was synthesized based on the mechanism proposed by Semenov et al. (2007). The synthesis procedure consists of the addition of β-diketone to aminosilane and subsequent elimination of the water molecules. In this synthesis 3-ethyl-pentane-2,4-dione (3 mmol, 0.387 g) and 3-aminopropyltriethoxysilane (APTES) (3 mmol, 0.667 g) were used. The substrates were purchased from Sigma-Aldrich and used without further purification. Stoichiometric quantities of both substrates were added to the round bottom flask. The mixture was magnetically stirred and heated under a reflux condenser at a temperature of 100°C for 2 hours. In the course of this reaction, the molecules of water were released, which were constantly collected azeotropically. The obtained solid product was twice recrystallized from ethanol. The obtained general structure of the new resulting yellow liquid compound 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one was shown in Figure 1.

Structure investigations

The nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 3HD 400 MHz spectrometer working at 400 MHz and 100 MHz for 1H and 13C, respectively. NMR spectra were recorded in a DMSO-d6, 99.8% atom %D solution. The FTIR-ATR spectra were recorded using a Bruker Alpha-PFT-IR device with a diamond attenuated total reflectance (ATR) accessory.

Water solubility tests

The next test was to examine the solubility of the obtained β-ketoimine in water. The tests were carried out at room temperature. For this purpose, 0.1 g of a 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one was placed in a vessel and poured with 10 ml of distilled water. The vessel was closed tightly with a stopper and intensively shaken for a few minutes. After this time, the

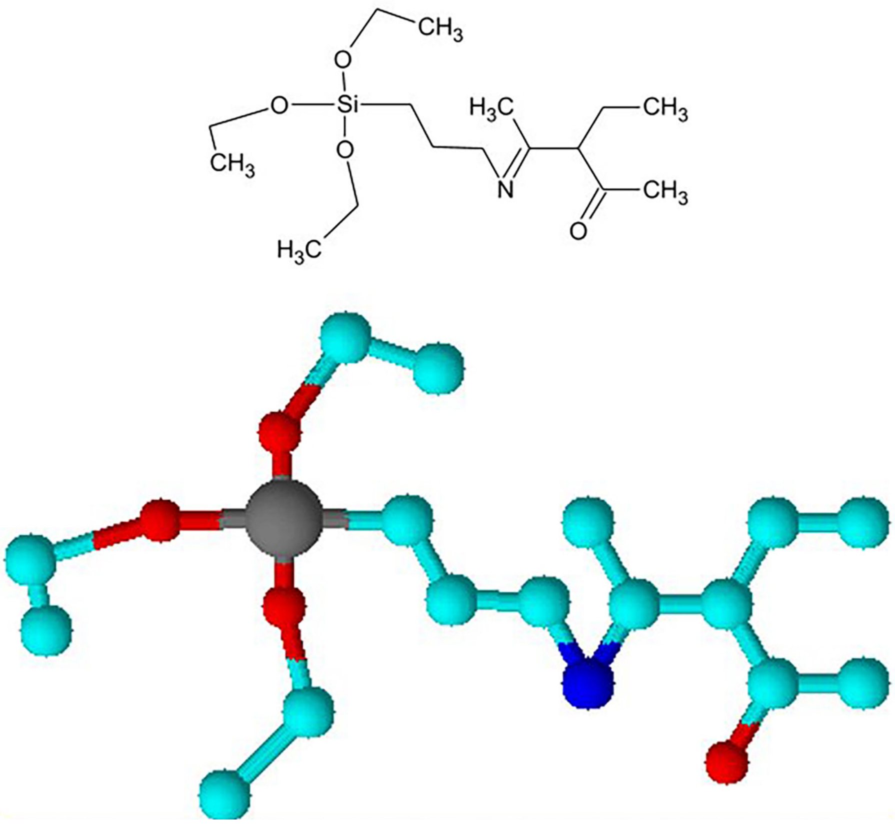

Figure 1. Structure of a new synthesised β-ketoimine 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one (L)

water was poured off and the vessel with L was dried on the air. Further, the vessel was weighed to check if any changes in L mass had occurred.

Affinity of the 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one for chosen metal ions

Stability constants (log K) of the complexes of the synthesized L with the selected metal ions

In the next stage, the affinity of the resulting compound for metal ions present in model aqueous solutions was tested using UV-Vis spectrophotometry. The spectrophotometric titration was made to investigate the complexation reaction between L and a specific metal ion (M). For this purpose, the small amounts of metal ions solution were added constantly to the solution of L and every time, the spectra of obtained samples with various L:M molar ratios were recorded. Titration was made until no changes in spectra shapes were observed. In this study, a methanol solution of L with a constant concentration of 3.82×10^{-5} mol/dm^3 and aqueous stock solutions of metal ions with a concentration of 1000 or 100 mg/dm^3 were used. The spectra were recorded on a Varian Cary 50 spectrophotometer in the range from 200 to 550 nm, with spectral slits at 0.5 nm and 0.2 nm steps using curettes with path lengths of 1 cm. Moreover, the obtained absorption spectra were also used to determine the stability constants (log K) of the formed complexes of the synthesised L with the selected metal ions (Ag^+, Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Zn^{2+}). Calculations were carried out based on the straight-line equation (Eq. 1) [Staniszewski et al. 2011]:

$$y = ax + b \tag{1}$$

where:

$$y = \frac{1}{(\varepsilon - \varepsilon_L)}$$

$$a = \frac{1}{logK(\varepsilon_C - \varepsilon_L)}$$

$$x = \frac{1}{[M]}$$

$$b = \frac{1}{\varepsilon_C - \varepsilon_L}$$

$$\varepsilon = \frac{A}{l\cdot[L]}$$

where: ε_L – the molar absorption coefficient of the ligand (dm^3/mol·cm), ε_C – the molar absorption coefficient of the complex (dm^3/mol·cm), A – the absorbance of the system, l – the thickness of the absorbing layer [cm], L – the molar concentration of the ligand (mol/dm^3), M – the molar concentration of the metal ions (mol/dm^3).

RESULTS AND DISCUSSION

Synthesis

The simplified schema of the probable synthesis of 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one is presented below (Figure 2 and 3). As a result of the reaction between

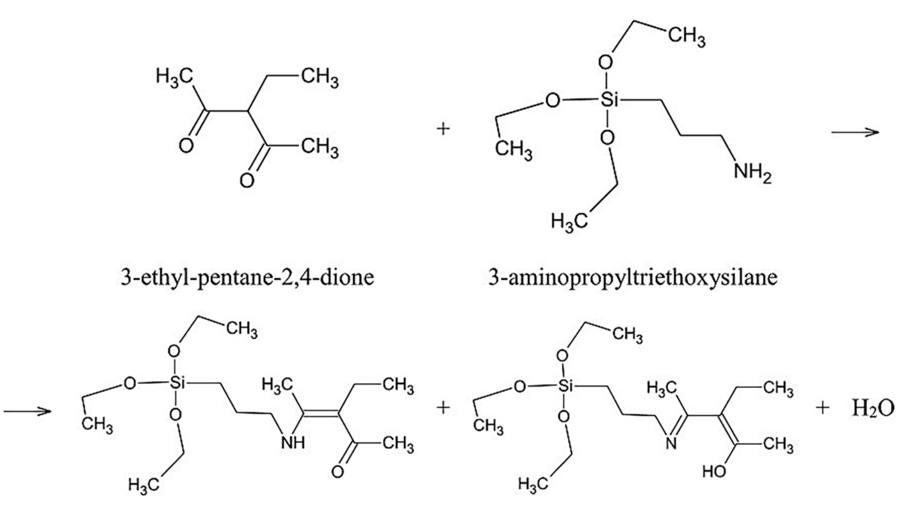

Figure 2. Simplified schema of the synthesis of enamine isomers. Based on [Ashenhurst 2023]

3-ethyl-pentane-2,4-dione and 3-aminopropyltriethoxysilane a mixture of two enamine isomers is probably formed. The progress of this reaction is indicated by the amount of produced water (Figure 2). Then enamine isomers rapidly tautomerase into ketoimine a 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one (Figure 3).

Identification of 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one

Nuclear magnetic resonance

The structure of obtained compound L was confirmed by 1H and 13C NMR. The yield was 83% (0.8305 g). Boiling point: 170.5−172.9 °C, light yellow liquid. 1H NMR (400 MHz, DMSO-d6): δ 0.58–0.62 (m, 1H), 0.94 (t, 1H), 1.05 (m, 7H), 1.15 (m, 5H), 1.53 (t, 1H), 1.84 (s, 1H), 1.95 (s, 3H), 2.17–2.23 (q, 1H), 3.19–3.24 (q, 1H), 3.34–3.46 (q, 5H), 3.71–3.77 (m, 4H), 4.36 (s, 2H), 12.05 (s, 1H). 13C NMR (101 MHz, DMSO-d6): δ 193.29, 162.63, 104.82, 94.97, 58.21, 58.15, 58.10, 56.49, 45.33, 40.64, 40.43, 40.22, 40.01, 39.80, 39.59, 39.38, 27.69, 23.91, 22.04, 19.01, 18.65, 16.19, 14.51, 7.61.

Fourier transform infrared spectroscopy-attenuated total reflectance

The FTIR-ATR spectrum of obtained compound L is shown in Figure 4. The interpretation of the infrared spectrum was made using the IRPal 2.0 Tabledriven Infrared Application. All bands identified on the FTIR-ATR spectrum were summarized in Table 1. The presence of characteristic bands on the above FTIR-ATR spectrum confirms that the intended compound was obtained. Moreover, the presence of N-H, C-O and C=C bonds suggests that the enamine isomers can also exist in the product.

Water insoluble β-ketoimine

The mass of β-ketoimine after the solubility test did not change. Solubility test confirmed the insolubility in water and non-polar character of the studied compound L, which is very important for their further use as active agents, e.g. metal ion carriers in separation materials such as polymer membranes or immobilized ion exchangers, or as extractants in classic solvent extraction.

The affinity of the 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one for chosen metal ions. The stability constants of created complexes of L with selected metal ions

In this chapter the results of spectrophotometric titration studies were described. UV-Vis spectrophotometry is a method which allows for the observation of equilibria of reaction of binding metal ions from water solutions by investigated ligand (L). In this process complex compound is formatted between those two molecules. The experiments were conducted to investigate the affinity of 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one to bind following metal ions: Ag^{+}, Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Zn^{2+}. Studies were carried out in aqueous-methanol solutions. Cations in an aqueous solution exist in a hydrated form (aqua cations) [Fedel et al. 2020]. The substitution of water molecules with new ligand (L) molecules takes place gradually. During this reaction, several equilibria

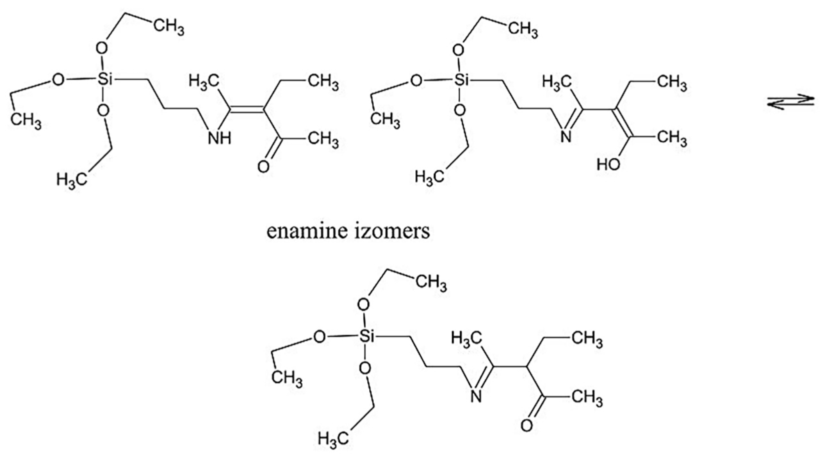

Figure 3. Transformation of enamine isomers to the final product. Based on [Ashenhurst 2023]

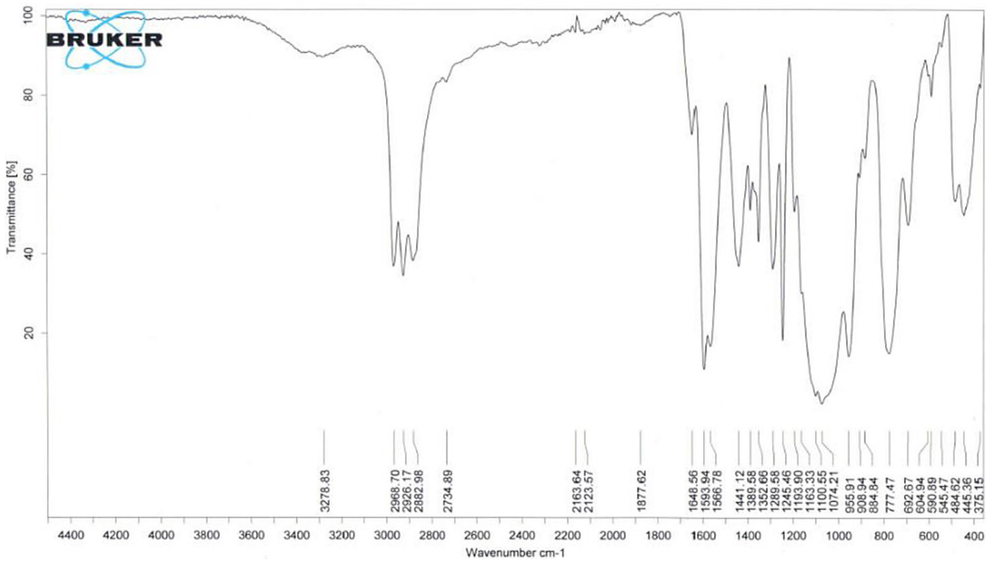

Figure 4. FTIR-ATR spectrum of obtained compound L

Table 1. Interpretation of FTIR-ATR spectrum

Bond	Wavenumber [cm^{-1}]	Typical absorption range [cm^{-1}]*
N-H	692.67, 777.47	665–910
=NOH	955.91	930–960
Si-OR	1074.21	1000–1110
C-O	1100.55	1100
Si-CH$_2$	1245.46, 1289.58	1250
C-H	1352.66	1360
C=C	908.94, 1566.78, 1648.56	910, 1566, 1650
-CH$_2$-	2926.17	2925

Note: * data source: IRPal 2.0 Tabledriven Infrared Application.

are established, and a number of complexes with different molar ratios of metal ion to ligand M:L are formed. The total complex formation reaction is shown below.

$$M(H_2O)_m{}^{n+} + mL \leftrightarrows [ML_m]^{n+} + mH_2O \quad (2)$$

where: M – central atom, n – the valence of the central ion, m – the coordination number (amount of the ligand in the coordination compound).

The above equation contains the concentrations. This means that the activity coefficients of all ions participating in the formation of the complex are equal to one. This state only takes place in highly diluted solutions, which were applied in these experiments [Pitzer 2017].

The general structure of created complex compounds, which are probably formed between L and metal ion is shown in Figure 5. The obtained absorption spectra of complexes of 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one with selected metal ions (M = Ag$^+$, Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Zn^{2+}) are presented below (Figure 6).

The differences between the shapes of the curves of the above absorption spectra during the addition of a metal ion solution to the solution of free ligand L confirm binding metal ions by 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one, which lead to decrease in its concentration in favor of an increase in the concentration of the resulting complex formed between L and M.. Moreover, the equilibrium which exists between a free ligand form and the created complex (with

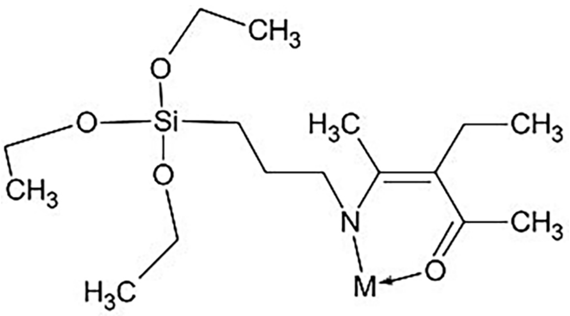

Figure 5. The probable structure of complex of new synthesised β-ketoimine 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one (L) with chosen metal ion (M)

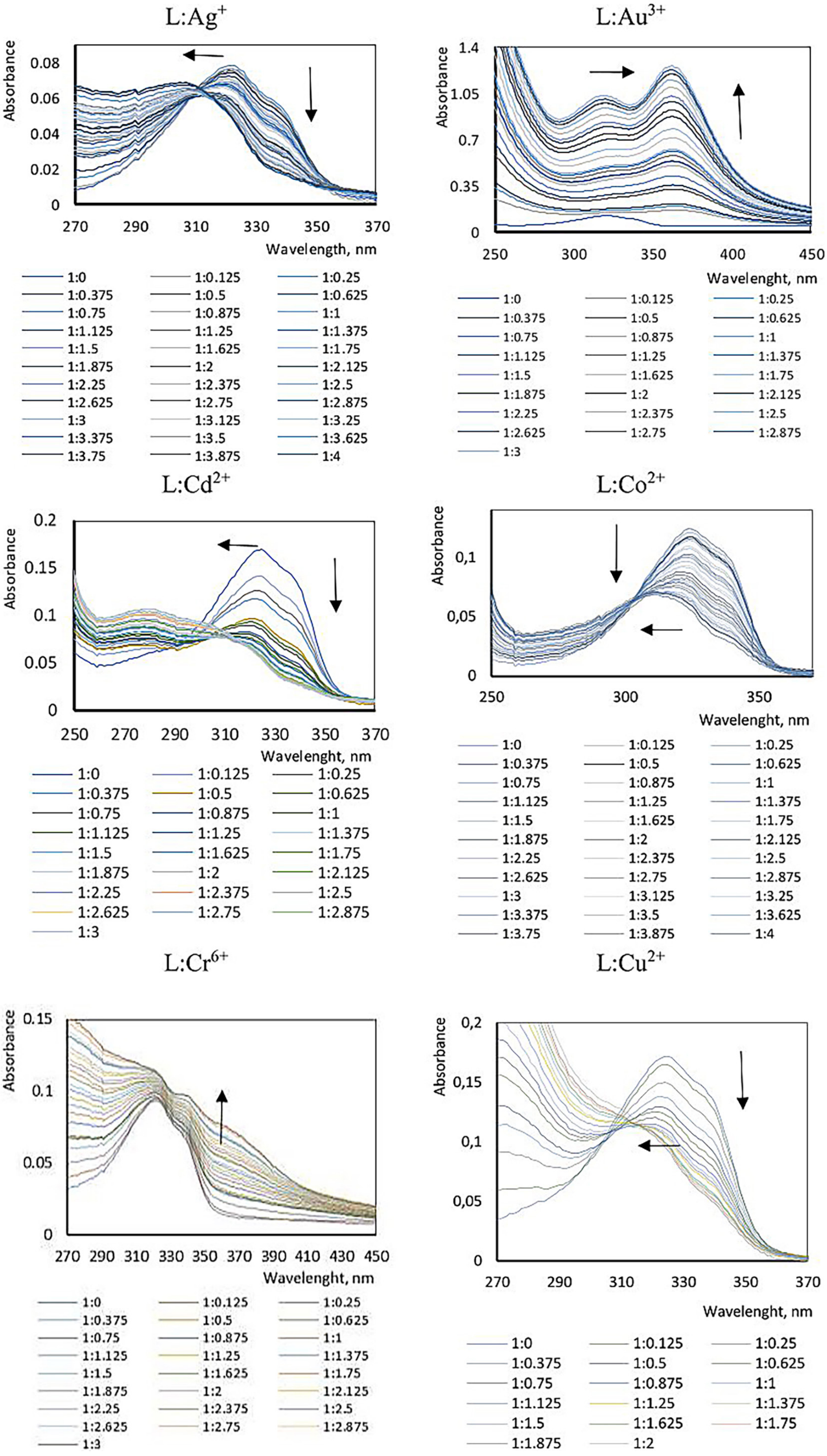

Figure 6. Absorption spectra of 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one with metal ions (M = Ag^{+}, Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Zn^{2+})

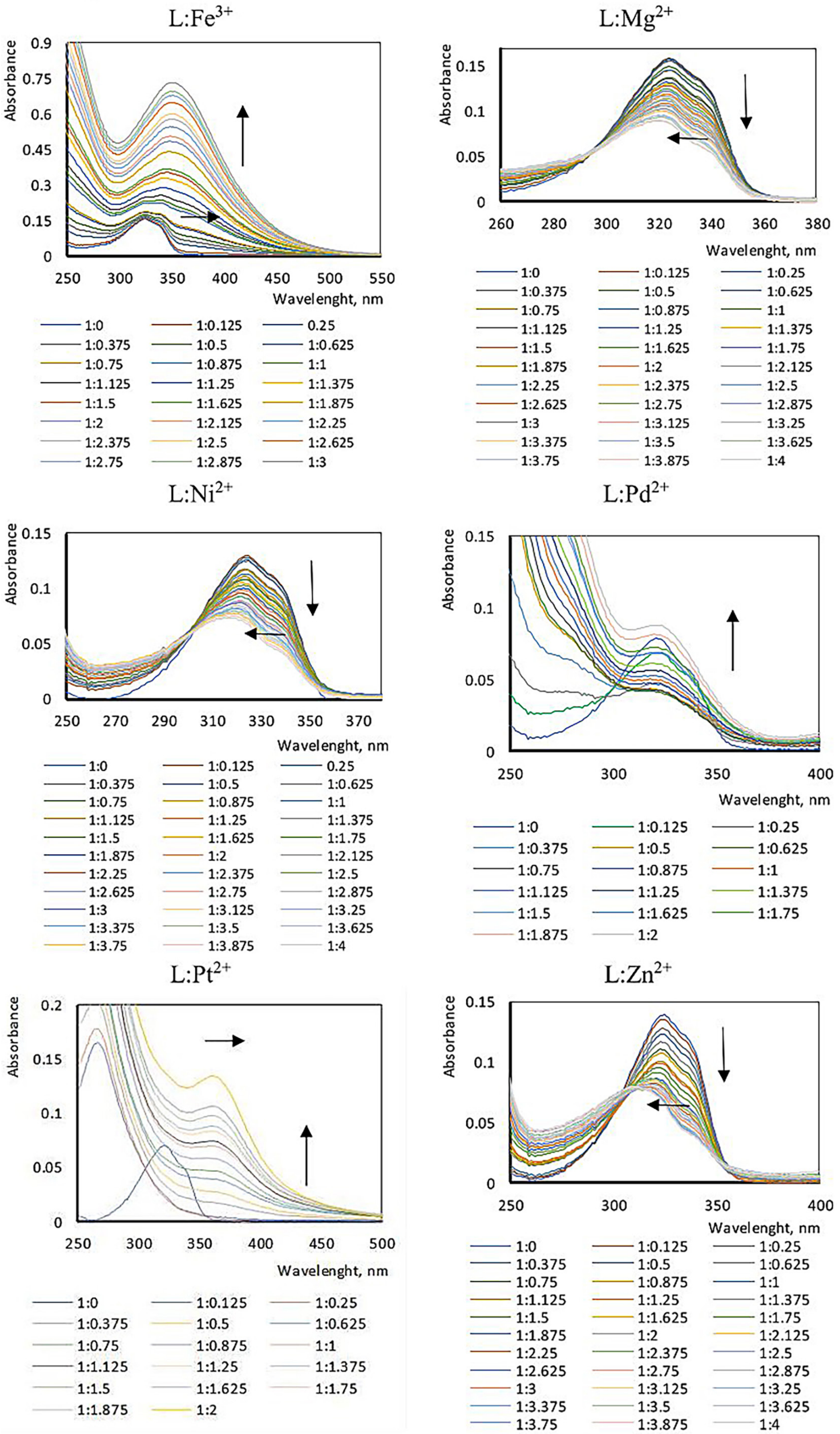

Figure 6. Cont. Absorption spectra of 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one with metal ions (M = Ag^+, Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Zn^{2+})

Ag^+, Co^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+} ions, as shown in Figure 6) is confirmed by the presence of isosbestic points. This phenomenon corresponds to a specific wavelength at which all curves on the spectra cross each other. The requirement for an isosbestic point to occur is that two species involved in complexation reaction are related linearly by stoichiometry. When one mole of reagent gives one mole of product, the absorbance of the reaction mixture at this wavelength remains invariant, regardless of the extent of the reaction. The isosbestic point occurs because two substances absorb light of that specific wavelength to the same extent, and the analytical concentration remains constant. Also, other ratios than 1:1 between involved substances are possible. But sometimes, in this situation, the spectra can typically intersect at varying wavelengths, creating the impression that the isosbestic point is not clearly visible (spectra of L:Cd^{2+}, L:Cu^{2+}, L:Pd^{2+}). The reason can be that it is unlikely for three compounds to have their extinction coefficients linked in a linear relationship by chance for one particular wavelength [Mohamed et al. 2017].

In the case of complexes of L with Ag^+, Cd^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, and Zn^{2+} ions, a hypsochromatic together with hypochromic effect is observed. The effect occurs when certain substituents are introduced into the molecule of a compound, which are characterized by the absence of double bonds or free electron pairs [Biedulska et al. 2020]. A high increase in band intensity can be observed for the spectra of L with Au^{3+}, Cr^{6+}, Fe^{3+}, Pd^{2+}, Pt^{2+} (a hyperchromic effect). Moreover, in the case of complexes with Au^{3+}, Fe^{3+}, and Pd^{2+}, the bathochromic shift occurs, and this can be related to the high electronegativity of mentioned metal ions [Biedulska et al. 2020].

Furthermore, based on the above spectra and using Equation 1, the stability constants of complexes formed between 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one and metal ions were calculated and summarized in Table 2. The obtained values of stability constants for complexes of L:M molar ratios equal 1:1 are changing in the following order: $Pd^{2+} > Cr^{6+} > Pt^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Ag^+ > Fe^{3+} > Zn^{2+} > Co^{2+} > Au^{3+} > Mg^{2+}$. As a complexation reaction occurs, i.e., as more and more molecules are attached to the complex, the values of their gradual stability constants (*log K*) apparently decrease. It is usually explained as an effect of steric difficulties that occurs when ligands have larger sizes than water molecules attached to the central atom [Dalton and Rovis 2013]. That phenomenon can be observed for created complexes of L with most studied metal ions, except Cd(II), Cu(II) and Zn(II) ions (Table 2). Three metal ions mentioned are structurally different from the other tested metal ions, and that can cause differences in the values of stability constants. The copper atom configuration [Ar] $4s^1 3d^{10}$ is related to so-called electron promotion, i.e., when one electron moves from the 4s to 3d orbital, in which the copper is more energetically favourable. In turn, the

Table 2. The stability constants of complexes of various molar ratios 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one to metal ions (M = Ag^+, Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Zn^{2+})

Central ion	ion radius [pm]	L:M			
		1:1	1:2	1:3	1:4
		log K			
Ag(I)	115	4.156	3.544	3.699	3.699
Au(III)	85	4.000	3.523	3.301	
Cd(II)	95	4.456	4.875	5.176	
Co(II)	70	4.041	3.602	3.602	
Cr(VI)	44	5.477	5.176	4.875	
Cu(II)	73	4.301	4.757		
Fe(III)	60	4.146	3.824	3.699	
Mg(II)	72	3.845	3.398	3.155	3.058
Ni(II)	70	4.475	3.310	2.813	3.301
Pd(II)	86	5.512	4.427		
Pt(II)	80	5.262	4.230		
Zn(II)	74	4.125	4.007	4.176	4.301

Note: the given values of the stability constants carry ± 0.001% tolerance.

electronic configuration of copper(II) ions is [Ar] $3d^9$, which means that only one electron is necessary to create a bond in copper compounds [Kaur et al. 2016]. For this reason, copper(II) ions create two types of stable complexes L:M and L:2M. In these studies, the one more stable is that with two metal ions bonded to the one ligand. In turn, the Zn(II) and Cd(II) ions have following configuration [Ar] $3d^{10}$ and [Kr] $4d^{10}$, respectively. The completely filled 3d or 4d subshells mean that these ions do not have free electrons that can be promoted to a higher level on 3d or 4d split subshells during the reaction with ligands [Ghorbani et al. 2021]. The bond nature for Zn(II) and Cd(II) ions is more ionic in comparison to other transition metal ions with the presence of unfilled d orbitals, which bind to ligands with a higher proportion of covalent bonds and make it possible to form Π bonds with a ligand.

Furthermore, the value of stability constants depends on the properties of the components that form the coordination compound and on the interactions between them. The stability of the complex increases with decreasing ionic radius. These relationships were found by Calvin and Melchior [Gupta et al. 2013], and Irving and Williams [Miličević et al. 2011]. For example, the stability of complexes for elements of the third period of the periodic table should be changed with the changes of ionic radius in the following order: $Cr^{6+} > Fe^{3+} > Ni^{2+} = Co^{2+} > Cu^{2+} > Zn^{2+}$. In these studies, that order is maintained, except for Fe(III) and Co(II) ions. The position of a central atom in the periodic table, in turn, is the main factor that determines the coordination number of the obtained complex. A central atom exhibits a certain maximum number of ligands that can be attached to this atom. The electron structure of the metal - the number of orbitals that can accept electrons of ligands - is relevant. Besides, the literature data analysis provides information concerning the possibility of metal ions accepting more than one coordination number [Sreenivasulu and Subramaniam 2019]. The type of ligand has also an impact on this; most importantly is, its basicity, predisposition to form Π bonds, and structure also have a significant effect on the complexing parameters [Sreenivasulu and Subramaniam 2019, Celik et al. 2023, Kowalik et al. 2022]. When a coordination reaction takes place, the energy level of central atom orbitals becomes split, and its magnitude depends on the strength of the generated field. This magnitude also corresponds to the wavelength of absorbed light that is specific to itself [Wolters and Bickelhaupt 2015]. For the reasons described above, in conducted studies, the creation of complex compounds with various molar ratios M:L can be observed (Table 2).

CONCLUSIONS

In the studies presented in this paper, the new β-ketoimine 4-(3-triethoxysilylpropylimino)-3-ethyl-pentan-2-one (L) was successfully synthesized using 3-ethyl-pentane-2,4-dione and 3-aminopropyltriethoxysilane, which was confirmed by NMR and FTIR-ATR methods. Moreover, solubility tests improved the insolubility of the obtained compound in water and its non-polar character, which is very important for the possibility of further use as complexation agents for separation metal ions from aqueous solutions. Complexation studies proved that for the tested metal ions ($M = Ag^{+}$, Au^{3+}, Cd^{2+}, Co^{2+}, Cr^{6+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Zn^{2+}) the complex compounds with obtained β-ketoimine L in various molar ratios L:M were created, and it was confirmed by the changes of the shape occurring on absorption spectra. The calculated stability constants of complexes of a new β-ketoimine strictly depend on the properties of a ligand and a metal ion, especially the size of its ionic radius. The order of obtained values of stability constants for complexes of L:M with molar ratios equal 1:1 are changing as follows: $Pd^{2+} > Cr^{6+} > Pt^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Ag^{+} > Fe^{3+} > Zn^{2+} > Co^{2+} > Au^{3+} > Mg^{2+}$.

Acknowledgments

The work was created as a result of the grant „Synthesis of new water-insoluble β-ketoimines, obtained from β-diketone derivatives and aminosilanes, capable of binding metal ions from aqueous solutions", no. 2023/07/X/ST4/00361 financed by National Science Centre (NCN)

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