FULL PAPER

Solution Complexation Reaction Studies of a Pyrazoloisoindol Derivative Ligand by Some Metal Ions in Acetonitrile Solution

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Abstract:

The complexation reaction between some heavy metal ions such as: Ag^+, Co^{2+}, Hg^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+} and Pb^{2+} with 2,3-dimethyl-1,2-dihydro-8H-pyrazol[5,1-a]isoindol-8-one, ligand in acetonitrile as nonaqueous solvents at 25 ºC were investigated by spectrophotometric and conductometric methods. The formation constants (k_f) of the 1:1 (metal ion to ligand) complexes were calculated by computer fitting of the absorbance-mole ratio data, and molar conductance-mole ratio data at 25 ºC using the KINFIT program, and found that complexes to vary in acetonitrile solvent in the order of Zn^{2+}> Ag^+> Cr^{3+}> Ni^{2+}> Hg^{2+}> Fe^{3+}> Cu^{2+}> Cd^{2+}> Co^{2+}> Mn^{2+}> Pb^{2+}.

Keywords: complexation; spectrophotometry; conductometry; formation constant; pyrazoloisoindol

1. Introduction

During the past two decades, considerable attention has been paid to the chemistry of the metal complexes with nitrogen and oxygen donor atoms ligands [1-3]. This may be attributed to their stability, biological activity and potential applications in many fields such as oxidation catalysis and electrochemistry [4]. Transition metal complexes with O & N donor ligands are one of the most versatile and thoroughly studied systems [5, 6]. Particularly, complexes of divalent transition metal ions involving derivatives of pyrazoloisoindol are important in analytical fields [7, 8]. The study of complexation reaction of O & N donor ligands in non-aqueous matrices could be used as an efficient strategy to design the analytical systems such as potentiometric sensor, bulk and supported liquid membrane transport [9,10], optical sensor [11], solid phase and cloud point extraction [12, 13] and biochemistry fields [14]. Thus, the studies of

complexation reaction of these ligands with metal ions, not only result effective information about complexation, but also lead to a better understanding of the selectivity of these ligands toward different metal cations. It is important for an analytical chemist to know what kind of complexes with what stability may be expected. Knowledge of the composition of a solution in terms of the species formed is of importance in many parts of solution chemistry: in understanding analytical procedures, industrial process, pollution of natural waters and biological fluids. Knowledge of the equilibria is also of importance for interpretation of the kinetics of reactions in solution [15].

To study the formation of complexes between macrocyclic compounds with different metal ions in solution, various physicochemical techniques such as spectrophotometry [16], polarography [17], NMR spectrometry [18], calorimetry [19], potentiometry [20] and conductometry [21, 22] have been used. Among

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these various methods, the conductometric and spectrophotometric techniques offer the advantages for such investigations of sensitive and accurate measurement as well as inexpensive cost with a simple experimental arrangement. Since the nature of solvent may strongly influence the complexation of transition metal complexes in solution, we decided to study the complexation reaction of a recently synthesized pyrazoloisoindol derivative ligand, 2,3-dimethyl-1,2-dihydro-8H-pyrazolo[5,1-a]isoindol-8-one, (Figure 1), with some transition metal ions in acetonitrile solutions.
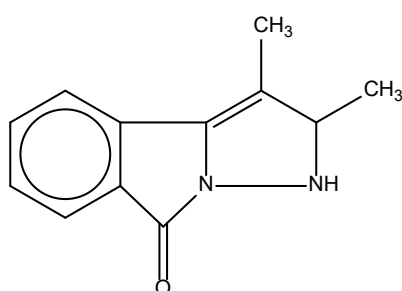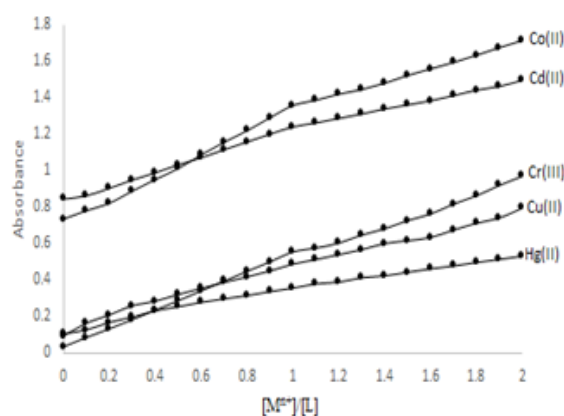

Figure 1. Structure of 2,3-dimethyl-1,2-dihydro-8H-pyrazolo[5,1-a]isoindol-8-one.

In the present work, we decided to investigate conductometric and spectrophotometric studies and the effect of the ligands structure on the stability constants of the complexation of the some metal ions with a pyrazoloisoindol derivative ligand. Based on this data, one can focus to synthesize new ligands with proper stability constant toward metallic ions for the selective and sensitive determination of special metal ion.

2. Results and Discussion

The electronic absorption spectra of pyrazoloisoindol derivative ligand and its Ag^+, Co^{2+}, Hg^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+} and Pb^{2+} complexes in acetonitrile are shown in Figure 2. The resulting complexes are distinguished by a strong spectral shift of about 70 nm for Cr^{3+}, Fe^{3+}, Cu^{2+} and about 20 nm for Hg^{2+}, Ag^+ toward longer wavelength, in comparison to the free ligand.
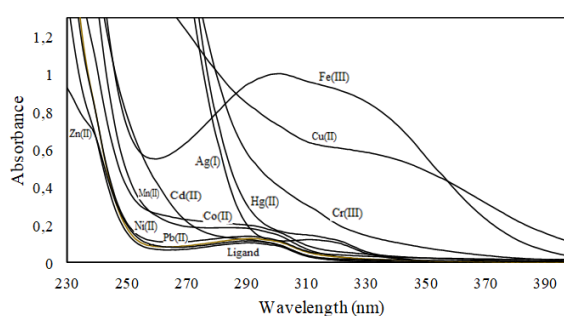

Figure 2. Spectra of pyrazoloisoindol derivative ligand and its complexes with Ag^+, Co^{2+}, Hg^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+} and Pb^{2+} ions.

The stoichiometry of the metal complexes was examined by the mole ratio method at λ_{max} of its complexes. A sample of the resulting plots is shown in Figure 3 and it is evident that 1:1 (metal ion to ligand) complexes are formed in solution.
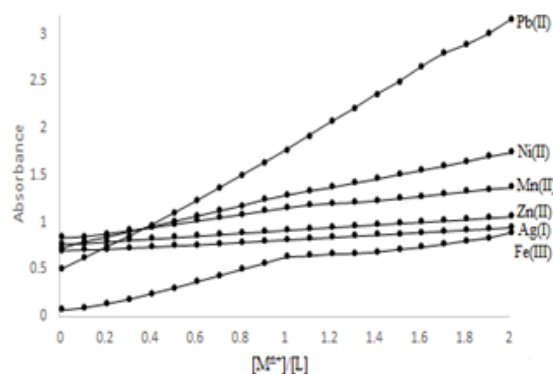

Figure 3. Mole ratio plots of pyrazoloisoindol derivative ligand (5.0×10^{-5} mol.L^{-1}) with metals ions at λ_{max} of its complexes at 25 °C.

431

Orbital: Electron. J. Chem. 10 (6): 430-434, 2018

The formation constants of the resulting complexes were obtained at 25 °C by absorbance measurements of solutions in which varying concentrations of metal ions were added to fixed amounts (5.0×10^{-5} mol.L^{-1}) of pyrazoloisoindol derivative ligand solution, at λ_{max} of complexes. All the resulting absorbance-mole ratio data were best fitted to Equation 1 [23], which further supports the formation of ML complexes in solution.

$$K_f [L]^2 + (1 + K_f C_M - K_f C_L) [L] - C_L = 0 \quad (1)$$

For evaluation of the formation constants and molar absorptivity coefficients from absorbance vs. [M^{n+}]/[L] mole ratio data, a non-linear least squares curve fitting program KINFIT was used. A sample computer fit of the absorbance-mole ratio data for Cu^{2+} ion and pyrazoloisoindol derivative ligand at 25 °C is shown in Figure 4.
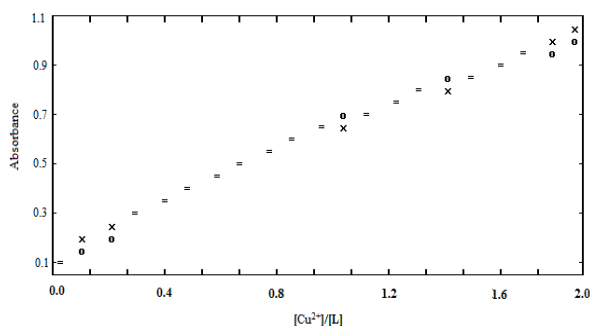

Figure 4. Computer fit of absorbance vs [Cu^{2+}]/[L] mole ratio plot in acetonitrile at 25 °C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot.

The resulting K_f of the pyrazoloisoindol derivative ligand complexes at 25 °C are listed in Table 1. The data given in Table 1 revealed that, at 25 °C, the stability of the complexes of the pyrazoloisoindol derivative ligand with different cations decrease in the order Zn^{2+}> Ag^{+}> Cr^{3+}> Ni^{2+}> Fe^{3+}> Hg^{2+}> Cu^{2+}> Cd^{2+}> Co^{2+}> Mn^{2+}> Pb^{2+}.

The molar conductance of the nitrate salts of Ag^{+}, Co^{2+}, Hg^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+} and Pb^{2+} in acetonitrile solvent was monitored as a function of the pyrazoloisoindol

derivative ligand to metal ion mole ratio, and the stoichiometry of the complexes in acetonitrile was examined by the mole ratio method at 25 °C temperature. A sample of the resulting plots for Cr^{3+} and Ag^{+} ions complexes is shown in Figure 5, and it is evident that ML complexes are formed in solution.
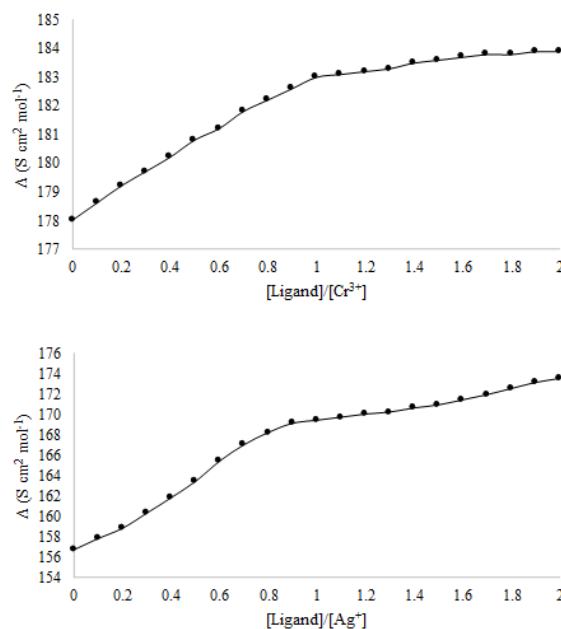

Figure 5. Mole ratio plots of pyrazoloisoindol derivative ligand and its complexes with Cr^{3+} and Ag^{+} ions at 25°C temperature.

Table 1. Formation constant at 25 °C.

Cation	Spectrophotometric Log k_1 ± SD	Conductometric Log k_1 ± SD
Ag^{+}	4.96 ± 0.01	5.13 ± 0.01
Co^{2+}	3.81 ± 0.01	2.80 ± 0.01
Hg^{2+}	3.91 ± 0.01	3.36 ± 0.01
Zn^{2+}	5.12 ± 0.01	5.18 ± 0.01
Ni^{2+}	4.35 ± 0.01	3.96 ± 0.01
Cu^{2+}	3.89 ± 0.01	3.15 ± 0.01
Cd^{2+}	3.83 ± 0.01	3.13 ± 0.01
Mn^{2+}	3.73 ± 0.01	2.69 ± 0.01
Cr^{3+}	4.37 ± 0.01	4.39 ± 0.01
Fe^{3+}	3.92 ± 0.01	3.34 ± 0.01
Pb^{2+}	2.55 ± 0.01	1.84 ± 0.01

Note: SD= Standard deviation

As can be seen in acetonitrile solvent, addition of the ligand to the metal ions solutions cause a continuous increase in molar conductance of the solutions. This might indicate that the complexes formed are more mobile than the solvated metals ions. It is well known that

432

Orbital: Electron. J. Chem. 10 (6): 430-434, 2018

transition metals ions strongly are complexed with acetonitrile [24] and such a solvated ions will be highly ordered and sluggish [25].

The first addition of pyrazoloisoindol derivative ligand will complex with metals ions resulting in a more mobile system with relatively high conductivity. Further additions of ligand to the relatively mobile system will cause a gradual increase in conductivity. However, the slope of the corresponding molar conductance-mole ratio plots change at the point where the ligand to ions ratio are one, and further additions of the ligand cause no or very slight changes in the molar conductance. Such a conductance behavior is indicative of the formation of ML complexes in solutions.

The formation constants of the resulting complexes were obtained by molar conductance measurements of solutions in which varying concentrations of ligand (5.0×10^{-3} mol.L^{-1}) were added to fixed amounts (5.0×10^{-5} mol.L^{-1}) of metals ions solution. The entire resulting molar conductance-mole ratio data were best fitted to Equation 1, which further supports the formation of mixed complexes in solution. For evaluation of the formation constants from molar conductance vs. [L]/[M^{n+}] mole ratio data, a non-linear squares curve fitting program KINFIT was used. A sample computer fit of the absorbance-mole ratio data for Cr^{3+} ion and pyrazoloisoindol derivative ligand at 25ºC is shown in Figure 6.
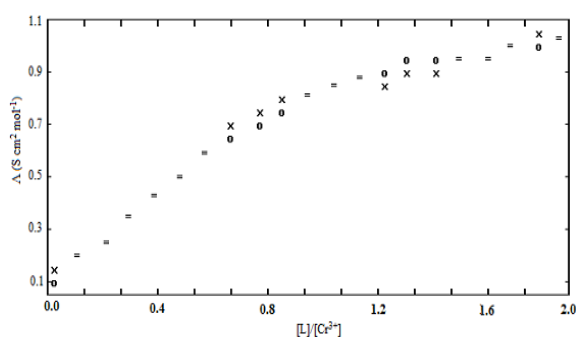

Figure 6. Computer fit of molar conductance *vs*. [L]/[Cr^{3+}] mole ratio plot in acetonitrile at 25°C, (X) experimental point, (O) calculated point, (=) experimental and calculated points are the same within the resolution of the plot.

The resulting K_f of the pyrazoloisoindol derivative ligand complexes at 25 °C are listed in Table 1. The data given in Table 1 revealed that,

at 25 °C, the stability of the complexes of the pyrazoloisoindol derivative ligand with different cations decrease in the order Zn^{2+}> Ag$^+$> Cr^{3+}> Ni^{2+}> Hg^{2+}> Fe^{3+}> Cu^{2+}> Cd^{2+}> Co^{2+}> Mn^{2+}> Pb^{2+}.

3. Material and Methods

Reagent grade nitrate salts of silver, cadmium, zinc, chrome, cobalt, mercury, copper, manganese, nickel, iron, Lead and dried acetonitrile (H$_2$O < 0.005%) (All from Merck) were of the highest purity available and used as received. The pyrazoloisoindol derivative ligand was synthesized using the literature with highest purity [26] and was used without any further purification.

All UV-Vis spectra recorded on a computerized double-beam GBC cintra 2020 spectrophotometer, using two matched 10 mm quartz cell. In a typical experiment, 2.0 mL of ligand solution (5.0×10^{-5} mol.L^{-1}) in acetonitrile was placed in the spectrophotometer cell and the absorbance of solution was measured. Then a known amount of the concentrated solution of metal ions in an (5×10^{-3} mol.L^{-1}) was added in a stepwise manner using an l0 μL Hamilton syringe. The absorbance of the solution was measured after each addition. The metal ions solution was continually added until the desired metal to ligand mole ratio was achieved.

Conductometric measurements were carried out by Jenway 4510 conductometer equipped with a Julabo ED circulator. In a typical experiment, 10.0 mL of metal ion solution (5.0×10^{-5} mol.L^{-1}) in acetonitrile was placed in the two wall conductometer glass cell and the conductance of solution was measured. Then a known amount of the concentrated solution of pyrazoloisoindol derivative ligand in an (5.0×10^{-3} mol.L^{-1}) was added in a stepwise manner using an l0 μL Hamilton syringe. The conductance of the solution was measured after each addition. The pyrazoloisoindol derivative ligand solution was continually added until the desired ligand to metal ion mole ratio was achieved.

The formation constant and the molar absorptivity (ε) of the resulting 1:1 (metal ion to ligand) complexes between the pyrazoloisoindol derivative ligand and different cations at 25 °C were calculated by fitting the observed

433

Orbital: Electron. J. Chem. 10 (6): 430-434, 2018

absorbance, A$_{obs}$, at various metal ion/ligand mole ratios to the previously derived equations [27, 28] which express the A$_{obs}$ as a function of the free and complexed metal ions and the formation constant evaluated from a non-linear least-squares program KINFIT [29]. For evaluation of the formation constant from molar conductance (Λ) vs C$_L$/C$_M$ mole ratio data, the KINFIT program was also used. Adjustable parameters are the K_f, molar conductance of free metal ion, and molar conductance of complex. The free metal ion concentration, [M] was calculated by a Newton-Raphson procedure. When the value of [M] had been obtained, the concentration of all other species involved are calculated from the mass balance equations by using the estimated value of the formation constant at the current interaction step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed molar conductance for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum of squares and the standards deviation of the data [**30**].

4. Conclusions

The conductometric and spectrophotometric techniques offer the advantages for such investigations of sensitive and accurate measurement as well as inexpensive cost with a simple experimental arrangement .The ligand can be used for solid phase extraction and determination of trace amounts of these metallic ions in aqueous samples.

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434

Orbital: Electron. J. Chem. 10 (6): 430-434, 2018