

Determination of the Ratios of Ligands to Metal Ion of some Metal Complexes of Triazoles by Using Electronic Spectra in Organic Solvents

Ali A.H. Saeed *

Ayad. H. Jassim **

Mahasin F. Ahmed ***

Date of acceptance 18/1/2004

Abstract

We found that 4,5- diphenyl- 3(2- propynyl) thio- 1,2,4- triazole [I] forms a complex with Pd (II) ion of ratio 1:1 which absorbs light in CH_2Cl_2 at 400 nm, and 4,5- diphenyl- 3(2- propenyl) thio- 1,2,4- triazole [II] forms complexes with Pd (II) ion of ratio 1:1 which absorbs light at 390 nm, and of ratio 2:1 which absorbs light at 435 nm. On the other hand, we found that the new derivative 4- phenyl- 5(p- amino phenyl) -3- mercapto- 1,2,4- triazole [III] forms complexes with Cu (II) ion of the ratio 1:1 which absorbs light at 380 nm, with Ni (II) ion of the ratio 3:1 which absorbs light at 358 nm; and with Co (II) ion of the ratio 3.2:1 which absorbs light at 588 nm. The ratio of the complexes were determined by measuring the electronic spectra of the complexes in CH_2Cl_2 and $(\text{CH}_3)_2\text{NCHO}$ at different concentrations of the ligands and fixed concentrations of the metal ion in every case, then applying the molar ratio plots on the data. Our results were confirmed by precipitating most of the above complexes in solid state, and then each complex was analyzed elementally.

Introduction

Many metal complexes have been studied by determination of ligand: metal ion ratio spectrophotometrically in the uv-visible region by measuring the electronic spectra in a suitable solvent

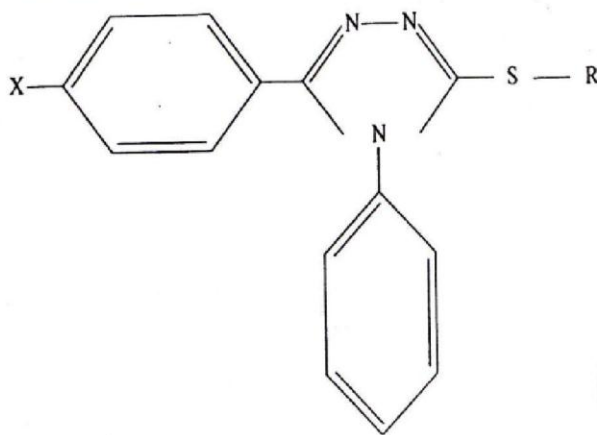
(1-4). From these studies and others (5-7) the spectrophotometric method becomes very important in this respect. It was found that 2,2'- dipyridyl ketoxime is a specific reagent to Fe (II)

* Dr. -prof- Chemistry, Dept. -college of science- University of Baghdad.

** Dr. -Assistant prof.- Chemistry, Dept. - college of science- AL-Nahrain University.

*** Dr. -Assistant prof- Chemistry, Dept. -college of Science for Women- University of Baghdad

⁽⁶⁾, 2,2'-dipyridyl ketene azine is specific for Cu (II) ⁽⁷⁾, 2,2'-dipyridyl ketenylidene aromatic amines is specific for Fe (II) and Fe (III) ⁽¹⁾, and 2,2'-dipyridyl ketenylidene-N-1,3-diamino-2-propanol is specific for Cu (II) ⁽²⁾. In the present work, the complexes of Cu (II), Co (II), Ni (II) and Pd (II) with 4,5-diphenyl-3(2-propynyl)thio-1,2,4-triazole [I], 4,5-diphenyl-3(2-propenyl)thio-1,2,4-triazole [II], and 4-phenyl-5-(p-amino)-3-mercapto-1,2,4-triazole [III] (Scheme 1) were investigated spectrophotometrically in methylene chloride and dimethylformamide.



- [I] ; X = H, R = -CH₂C≡CH
 [II] ; X = H, R = -CH₂C=CH₂
 [III] ; X = NH₂, R = H

Scheme 1

Experimental

[I] and [II] are known compounds, they were prepared and purified as described elsewhere ⁽⁸⁾, [III] was prepared in our laboratory as described previously ⁽⁹⁾. CH₂Cl₂, (CH₃)₂NCHO, and C₂H₅OH were of "Fluka" spectrosil. Cu (II), Ni (II) and Co (II) were used as nitrates of BDH, Pd (II) as PdCl₂ was of "Fluka", and dichlorodibenzo nitrile palladium PdCl₂ (C₆H₅CN)₂ was prepared and purified as discussed previously ⁽¹⁰⁾.

The elemental analysis C,H,N were carried out using Perkin Elmer 240 B Elemental Analyzer. Electronic spectra were measured by Shimadzu UV-160 A UV-Visible Spectrophotometer using CH₂Cl₂ and (CH₃)₂NCHO as solvents and a quartz cell of 1.0 cm path length. The molar ratio method was followed to determine the ligand to metal ion ratio in each complex at its λ_{max}. A set of solutions was prepared in which the concentration of the metal ion was kept constant (0.001 mol dm⁻³), and the concentration of the ligand was variable (0.00025- 0.004 mol dm⁻³), then the electronic spectrum of each solution in the set was measured.

Results and discussion

Complexes of (I)

Compound (I) forms complexes with Pd (II), a molar ratio of (I) to Pd (II) is 1:1 with 2CH₂Cl₂ in the lattice, i.e [Pd.I.Cl₂].2CH₂Cl₂; and 1:1 with 2H₂O bonded with Pd and 2H₂O in the lattice, i.e [Pd.I.Cl₂(H₂O)₂]. 2H₂O.

These complexes absorb light at λ_{max} = 400 nm. Figures 1 and 2 represent the electronic spectrum of the complex and the variation of the molar ratio of [I]: Pd (II) with the optical density of the complexes at

λ_{max} = 400 nm in CH₂Cl₂ solvent, respectively. Figure 2 shows also that [I] forms another complex in which the molar ratio of I: Pd (II) is 2:1 which also absorbs light at λ_{max} = 400 nm.

In comparison with the solid state, two complexes have been isolated, purified and analyzed elementally. The first was 1:1 which has the structure [Pd.I.Cl₂].2CH₂Cl₂, which was characterized.

previously using IR, UV-Vis. Spectra
 $\nu_1 = 22973 \text{ cm}^{-1} \text{ } ^1A_{1g} \rightarrow \text{ } ^1B_{1g}$,
 $\nu_2 = 24638 \text{ cm}^{-1} \text{ } ^1A_{1g} \leftarrow \text{ } ^1E_g$, $\nu_3 = 34694 \text{ cm}^{-1}$ (CT) with $3.56 \mu\text{s cm}^{-1}$.
 The complex was non conducting ⁽⁹⁾.

Anal. Calcd: C, 35.14; H, 3.04; N, 5.90. Found: C, 35.71; H, 2.66; N, 6.57. The second complex 1:1 which has the structure $[\text{Pd.I.Cl}_2(\text{H}_2\text{O})_2].2\text{H}_2\text{O}$, prepared in CH_2Cl_2 , reddish-brown; recrystallized from CH_2Cl_2 ; % yield 32; decomposed at 212 °C; Anal. Calcd: C, 37.32; H, 3.30; N, 7.92. Found: C, 37.74; H, 3.88; N, 7.77. and which was characterized by appropriate physical method⁽⁹⁾.

We were unable to isolate the complex 2.75:1 in a solid state, this complex is unstable in solution, its colour disappeared after two days, and after nine days it was converted to 1:1 complex which absorbs light at (305) and (360) nm as shown in Figure 3. No attempt has been done to isolate the later 1:1 complex, additional informations are necessary in this respect. Apparently, the investigations of the Pd (II) complexes with [I] in solutions agree very well with that found in the solid state⁽⁹⁾.

Complexes of [II]

Compound [II] form complex with Pd (II) ion after 24 hr from mixing of their solutions, the complex solution is reddish - brown in colour which absorbs light at (390) and (435) nm. Figure (4) represents the electronic spectrum of the complex, whereas Figure (5) shows the variation of the molar ratio of [II]: Pd (II) ion in CH_2Cl_2 solvent at (390) and (435) nm. Figure (5) confirms that there are two types of complexes, one of molar ratio [II]: Pd (II) ion 1:1 which absorbs light at (390) nm, the other of molar ratio 2:1 which absorbs light at (435) nm. Figure (5) clearly illustrates that the two plateau start from molar ratio of 1:1 and 2:1. This observation is in a very good agreement with the experimental findings when we isolate and purify the two complexes in the solid state⁽⁹⁾. The complex of molar ratio 1:1 $[\text{Pd.II.}(\text{C}_6\text{H}_5\text{CN}).\text{Cl}_2]$ which

was characterized previously using different technique IR, uv - vis. Spectra $\nu_1= 21656 \text{ cm}^{-1}$ $^1\text{A}_{1g}$ $^1\text{B}_{1g}$, $\nu_2= 28000 \text{ cm}^{-1}$ $^1\text{A}_{1g}$ $^1\text{E}_{1g}$, $\nu_3= 34694 \text{ cm}^{-1}$ (CT). Molar conductance in CH_2Cl_2 $0.4 \mu\text{scm}^{-1}$ ⁽⁹⁾. Anal. Calcd: C, 42.38; H, 3.55; N, 9.91. Found: C, 41.85; H, 3.48; N, 9.76. The second complex of molar ratio 2:1 $[\text{Pd.II. Cl}_2]$ prepared in CH_2Cl_2 , brown in colour; recrystallized from CH_2Cl_2 ; % yield 30; decomposed at 179 °C; Anal. Calcd: C, 53.44; H, 4.59; N, 10.91; found: C, 53.38; H, 3.94; N, 11.00. Both complexes are very stable in CH_2Cl_2 solution and in the solid state.⁽⁹⁾

Complexes of [III]

Solutions of [III] in $(\text{CH}_3)_2\text{NCHO}$ formed coloured complexes with Ni (II), Cu (II), and Co (II) ions after 24 h from mixing of their solutions, these complexes absorb light at λ_{max} 358, 380, and 588 nm, respectively. The electronic spectra of these complexes are shown in Figure (6). The complex of [III] with Ni (II) ion, yellowish - green in colour, is of molar ratio 3:1, Figure (7). This ratio agrees very well with the structural formula of the complex found in the solid state; $\text{H}[\text{Ni.3III}].4 \text{CH}_2\text{Cl}_2$ which was well characterized previously using (CHN) Anal. Calcd. C,46.65;H,3.10;N,15.52; Found: C, 45.97; H,3.94; N,15.46. IR spectra and uv-vis spectra $\nu_1= 9800 \text{ cm}^{-1}$ $\nu_2= 16600 \text{ cm}^{-1}$, $\nu_3= 27500 \text{ cm}^{-1}$ $\beta= 0.79$. Molar conductance for the ionic complex was $(124)\mu\text{scm}^{-1}$.

The complex of [III] with Cu (II) ion in $(\text{CH}_3)_2\text{NCHO}$ is greenish - yellow in colour, is of ratio 1:1, Figure (8). This ratio agrees very well with the structural formula of the complex found in the solid state; $[\text{Cu.III.NO}_3].2(\text{CH}_3)_2\text{CO}$ which was well characterized previously using (CHN)

Anal. Calcd: C, 48.35; H, 3.96; N, 14.81; Found: C, 48.13; H, 4.61; N, 14.04., IR spectra and uv - vis. spectra.

$\nu_1 = 12500 \text{ cm}^{-1} \text{ } ^2\text{Eg} \rightarrow \text{ } ^2\text{T}_{2g}$,
 $\nu_2 = 23900 \text{ cm}^{-1} \text{ CT. L} \rightarrow \text{M}$,
 $\nu_3 = 31501 \text{ cm}^{-1} \text{ CT. L} \rightarrow \text{M}$, $\nu_4 = 37885 \text{ cm}^{-1} \text{ CT \& L} \rightarrow \text{M}$. Molar conductance in DMF was $(38) \mu\text{scm}^{-1}$ (9).

The complex of [III] with Co (II) ion in $(\text{CH}_3)_2\text{NCHO}$ is bluish - pink in colour, of molar ratio above 3.2:1 as illustrated in Figure 9. The ratio obtained in solution is in good agreement with the structural formula of the complex found in the solid state; $[\text{Co}_4\text{III}(\text{NO}_3)_2] \cdot 3\text{CH}_2\text{Cl}_2$ which was well characterized previously using (CHN) Anal. Caid: C, 46.24; H, 3.76; N, 16.15; Found: C, 46.82; H, 3.83; N, 16.16., IR spectra, uv- vis. spectra: $\nu_1 = 3450 \text{ cm}^{-1} \text{ } ^4\text{A}_{2g} \text{ } ^4\text{T}_{2g}(\text{F})$ $\nu_2 = (5747) \text{ cm}^{-1}$ cal.

$^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{F})$ $\nu_3 = 15750, 15525 \text{ cal. Cm}^{-1}$ $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{P})$
 $\beta = 0.62$. Molar conductance in DMF was $(72) \mu\text{scm}^{-1}$ (9)

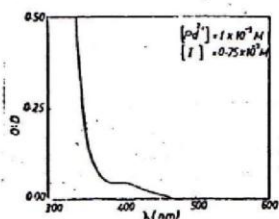


Figure 1: The Electronic Spectrum of Compound [I] with Pd (II) in CH_2Cl_2 Solvent.

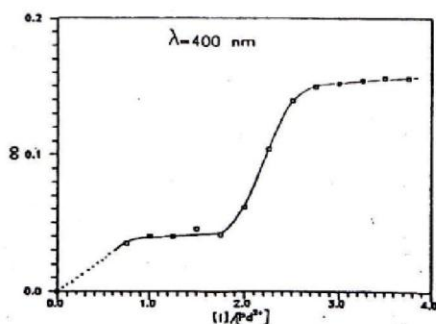


Figure 2: The Molar Ratios vs Optical Densities Plot of the Complex of Compound [I] with Pd (II) in CH_2Cl_2 Solvent.

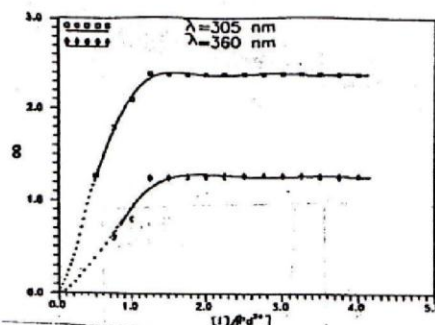


Figure 3: The Molar Ratios vs Optical Densities Plot of the Complex of Compound [I] with Pd (II) in CH_2Cl_2 Solvent.

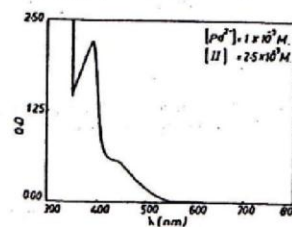


Figure 4: The Electronic Spectrum of Compound [II] with Pd (II) in CH_2Cl_2 Solvent.

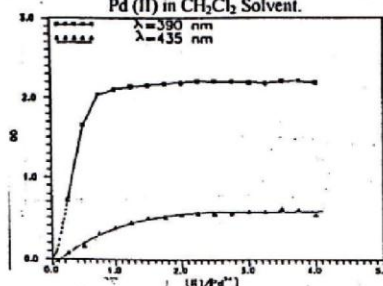


Figure 5: The Molar Ratios vs Optical Densities Plot of the Complex of Compound [I] with Pd (II) in CH_2Cl_2 Solvent.

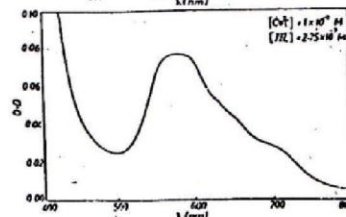
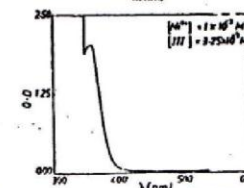
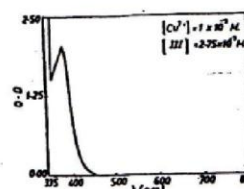


Figure 6: The Electronic Spectra of the complexes of Compound [III] with Cu (II), Ni (II) and Co (II) ions in $(\text{CH}_3)_2\text{NCHO}$ Solvent.

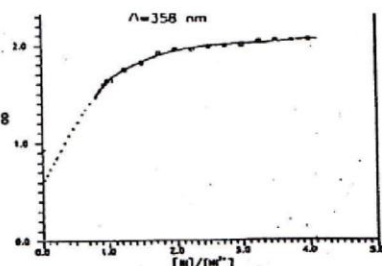


Figure 7: The Molar Ratios vs Optical Densities Plot of the Complex of compound [III] with Ni (II), in $(\text{CH}_3)_2\text{NCHO}$ solvent.

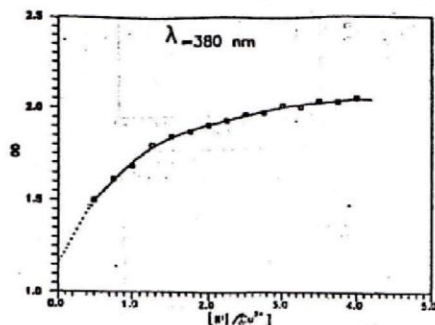


Figure 8: The Molar Ratios vs Optical Densities Plot of the Complex of Compound [III] with Cu (II), in $(\text{CH}_3)_2\text{NCHO}$ Solvent.

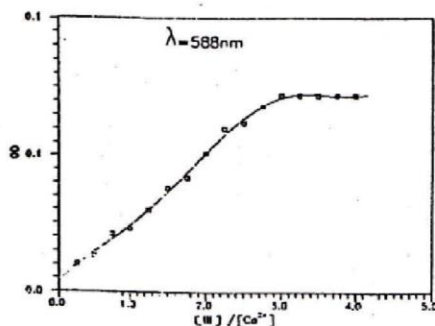


Figure 9: The Molar Ratios vs Optical Densities Plot of the Complex of Compound [III] with Co (II), in $(\text{CH}_3)_2\text{NCHO}$ Solvent.

References

1. Saeed A.A.H., Abbo H.S., Haddad H.H, H. and Matti, G.Y., "UV-1985 Visible Spectrophotometric Determination of Microgram Quantities of Iron Using New Schiff Bases Derived From 2,2- Dipyridyl Ketone" *Can. J. Spectro Sc.*, 30, 46.
2. Saeed A.A.H. and Ritha, S.M.A.1991 "Spectrophotometric Investigation of Some Unstable Metal Complexes of Di-2,2-Pyridylglyoxylidene Anilines in Neutral 95% Ethanolic Solutions" (1991) *Iraqi J. Chem.*, 16, 73.
3. Saeed A.A.H. and Ritha, S.M.A. 1993 "Spectrophotometric Investigation of Some Unstable Metal Complexes with the New Schiff Base Di-2,2-Pyridylglyoxylidene -P-N,N-Dimethylaminoaniline and Related Compounds in Neutral Ethanolic Solutions" *Can. J. Appli. Spectro Sc.*, 38, 15.
4. Saeed A.A.H. and Khedar, A.Y. "Synthesis and Spectral Characterization of Metal Complexes of Some New Schiff Bases Derived from 2,2- Dipyridyl Ketone and Diamine" 1994 *Can. J. Appli. Spectro Sc.*, 39, 173.
5. Grases F., Estela J.M., Garcia-Sanchez F., and Valcarcel M., "Determination Espectrofluorimetrica De Trazas De Co (II) Con Las Hidrazanas De La Fenil-2-Piridilcetona Y Dipiridilgloxal. Methodws No-Cinetico Y Cineticos" 1981 *Analisis*, 9, 66.
6. Kate T. and Ikukawa K., Bunseki Kagaku, "Complexes of 2,2- Dipyridyl Ketoxime with Fe (II)" 1981 30, 256.
7. Grases F., Garcia - Sanchez F., and Valcarcel M., 1981 "Complexes of 2,2- Dipyridyl Ketonylidene-Aromatic Amins with Fe (II) and Fe (III) *Anal. Chim. Acta*, 125, 21.
8. Rasol N., "Synthesis of Some acetylenic derivatives of 1,2,4-triazole and their expecion of biological activity M.Sc. Thesis, University of Baghdad, Iraq. 1987 and reference cited therein.
9. Ahmed M. F., "Preparation and Sudies of Some Metal Complexs of Mercapto Triazoles in Solid States and Solutions", M .Sc. Thesis. University of Baghdad. 1996.
10. Rochow E. G., "Inorganic Synthesis", 1960 4, 218.

تعيين نسب الكاشف إلى أيون الفلز لبعض معقدات الترايزول باستخدام الأطياف الإلكترونية بالمذيبات العضوية

علي عبد الحسين سعيد * أيد حمزة جاسم ** محاسن فيصل احمد ***

*قسم الكيمياء-كلية العلوم-جامعة بغداد

**قسم الكيمياء-كلية العلوم-جامعة النهرين

***قسم الكيمياء-كلية العلوم للبنات-جامعة النهرين

الخلاصة

لقد وجد بأن ٤، ٥ - ثنائي فنيل - ٣ (٢- بروبنيل) ثايو - ١، ٢، ١ - ترايزول [I] يكون معقد مع أيون Pd (II) بنسبة ١:١ الذي يمتص الضوء عند ٤٠٠ نانومتر بمذيب كلوريد الميثيلين، وإن ٥، ٤ - ثنائي فنيل - ٣ (٢- بروبنيل) ثايو - ١، ٢، ٤ - ترايزول [II] يكون معقد مع أيون Pd (II) بنسبة ١:١ الذي يمتص الضوء عند ٣٩٠ نانومتر وبنسبة ١:٢ الذي يمتص الضوء عند ٤٣٥ نانومتر، ومن جهة ثانية، لقد وجد أن المشتق الجديد ٤- فنيل - ٥ (بارا - أمينو فنيل) - ٣ - مركبتو - ١، ٢، ٤ - ترايزول [III] يكون معقدات مع أيون Cu (II) بنسبة ١:١ يمتص الضوء عند ٣٨٠ نانومتر، ومع أيون Ni (II) بنسبة ١:٣ يمتص الضوء عند ٣٥٨ نانومتر، ومع أيون Co (II) بنسبة ١:٣، ٢ يمتص الضوء عند ٥٨٨ نانومتر. لقد تم تعيين نسب هذه المعقدات بمذيبي كلوريد الميثيلين وثنائي مثيل فوراميد بتركيز مختلفة للكواشف وتراكيز ثابتة لأيونات العناصر في كل حالة، ومن ثم تطبق النتائج وذلك برسمها بيانياً، لقد تم التأكد من النتائج بواسطة ترسيب معظم تلك المعقدات وإجراء تحليل العناصر الدقيق لها.