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

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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 CH₂Cl₂ at 400 nm, and 4,5- diphenyl- 3(2- propynyl) 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 CH₂Cl₂ and (CH₃)₂NCHO 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 uλ-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)

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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.

\[
\begin{align*}
[I] & : X = H, \quad R = -CH_2C = CH \\
[II] & : X = H, \quad R = -CH_2C = CH_2 \\
[III] & : X = NH_2, \quad R = H
\end{align*}
\]

Scheme 1

The elemental analysis C, H, N were carried out using Perkin Elmer 240 B Elemental Analyzer. Electronic spectra were measured by Schimadzu 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 λₘₐₓ. A set of solutions was prepared in which the concentration of the metal ion was kept constant (0.001 moldm⁻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 λₘₐₓ = 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 λₘₐₓ = 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 λₘₐₓ = 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.

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” spectroscopic grade. 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).

previously using IR, UV-Vis. Spectra ν₁ = 22973 cm⁻¹ ¹A₁g → ¹B₁g, ν₂ = 24638 cm⁻¹ ¹A₁g ←¹Eg, ν₃ = 34694 cm⁻¹ (CT) with 3.56 μs cm⁻¹. The complex was non conducting (8).
Anal. Caled: 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 [Pd.I.Cl₂(H₂O)₂]. 2H₂O, prepared in CH₂Cl₂, reddish - brown; recrystallized from CH₂Cl₂; % yield 32; decomposed at 212 °C; Anal. Caled: 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 [III]

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 CH₂Cl₂ 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 [Pd.II.(C₆H₅CN).Cl₂] which was characterized previously using different technique IR, uv - vis. Spectra ν₁ = 21656 cm⁻¹ \( ^1A_{1g} \), ν₂ = 28000 cm⁻¹ \( ^1A_{1g} \), ν₃ = 34694 cm⁻¹ (CT). Molar conductance in CH₂Cl₂ 0.4 μscm⁻¹ (9). Anal. Caled: 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 [Pd.II. Cl₂] prepared in CH₂Cl₂, brown in colour; recrystallized from CH₂Cl₂; % yield 30; decomposed at 179 °C; Anal. Caled: 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 CH₂Cl₂ solution and in the solid state (9).

Solutions of [III] in (CH₃)₂NCHO 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 \( \lambda_{max} \) 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; H[Ni.III].4 CH₂Cl₂ which was well characterized previously using (CHN) Anal. Caled. 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 \( \nu₁ = 9800 \text{ cm}^{-1} \), \( \nu₂ = 16600 \text{ cm}^{-1} \), \( \nu₃ = 27500 \text{cm}^{-1} \) \( \beta = 0.79 \). Molar conductance for the ionic complex was (124)μscm⁻¹.

The complex of [III] with Cu (II) ion in (CH₃)₂NCHO 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; [Cu.III.NO₃]. 2(CH₃)₂CO which was well characterized previously using (CHN)
Anal. Caled: C, 48.15; H, 3.96; N, 14.81; Found: C, 48.13; H, 4.61; N, 14.04, IR spectra and uv-vis. spectra.

\[ v_1 = 12500 \text{ cm}^{-1} \quad ^2E_g \rightarrow ^2T_{2g}, \]
\[ v_2 = 23900 \text{ cm}^{-1} \quad \text{CT. L} \rightarrow \text{M}, \]
\[ v_3 = 31501 \text{ cm}^{-1} \quad \text{CT. L} \rightarrow \text{M}, v_4 = 37885 \text{ cm}^{-1} \quad \text{CT & L} \rightarrow \text{M}. \] 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; \([\text{Co} \cdot 4\text{III}.(\text{NO}_3)_2] \cdot 3\text{CH}_2\text{Cl}_2\) which was well characterized previously using (CHN) Anal. Caled: C, 46.24; H, 3.76; N, 16.15; Found: C, 46.82; H, 3.83; N, 16.16., IR spectra, uv-vis. spectra: \( v_1 = 3450 \text{ cm}^{-1} \quad ^4A_{2g} \rightarrow ^4T_{1g} (F) \), \( v_2 = (5747) \text{ cm}^{-1} \) cal.

\[ ^4A_{2g} \rightarrow ^4T_{1g} (F) \quad \beta = 0.62. \] Molar conductance in DMF was (72) \( \mu \text{scm}^{-1} \) (9).

![Figure 1: The Electronic Spectrum of Compound [I] with Pd (II) in CH$_2$Cl$_2$ Solvent.](image1)

![Figure 2: The Molar Ratios vs Optical Densities Plot of the Complex of Compound [I] with Pd (II) in CH$_2$Cl$_2$ Solvent.](image2)

![Figure 3: The Molar Ratios vs Optical Densities Plot of the Complex of Compound [I] with Pd (II) in CH$_2$Cl$_2$ Solvent.](image3)

![Figure 4: The Electronic Spectrum of Compound [I] with Pd (II) in CH$_2$Cl$_2$ Solvent.](image4)

![Figure 5: The Molar Ratios vs Optical Densities Plot of the Complex of Compound [I] with Pd (II) in CH$_2$Cl$_2$ Solvent.](image5)

![Figure 6: The Electronic Spectra of the complexes of Compound [III] with Cu (II), Ni (II) and Co (II) Ions in (CH$_3)_2$NCHO Solvent.](image6)
References


تعيين نسب الكاشف إلى أيون الفنز لبعض معقدات الترايازول

باستخدام الأطياف الإلكترونية بالمذيبات العضوية

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الخلاصة

لقد وجد بأن 4، 5- ثنائي فنيل - 3-(2- بروبينيل) ثابو - 1، 2، 4- ترايازول [I] يكون معقد مع أيون Pd (II) بنسبة 1:1 الذي يمتصل الضوء عند 400 نانومتر بدبي كلوريد المثيلين، وإن 5، 6- ثنائي فنيل - 3-(2- بروبينيل) ثابو - 4- ترايازول [II] يكون معقد مع أيون Pd (II) بنسبة 1:2 الذي يمتصل الضوء عند 430 نانومتر، ومن جهة ثانية، لقد وجد أن المشتق الجديد 4- ثابو - 5-(بارا - أمينو فنيل) - 3-(بريميتو - 1، 2، 4- ترايازول [III] يكون معقد مع أيون Cu (II) بنسبة 1:1 يمتصل الضوء عند 380 نانومتر، ومع أيون Cu (II) بنسبة 1:2 يمتصل الضوء عند 588 نانومتر. لقد تم تعين نسب هذه المعقدات بدبي كلوريد المثيلين وثاني مثيل فوراميد بتركيز مختلفة للكواشف وتركيز ثابتة لأيونات العناصر في كل حالة، ومن ثم تطبيق النتائج وذلك برسما بيانيا، لقد تم التأكد من النتائج بواسطة ترتيب معظم تلك المعقدات وإجراء تحليل العناصر الدقيق لها.