

Article

New Complexes Of Vanadium And Tungsten With 4-Aminoantipyrine Derivative Synthesis And Spectral Properties

Yahya F. Al-Khafaji¹ and Thamer A.A.M. Alalwani²

¹Department of Chemistry, College of Science, University of Babylon

²Department of Radiological Techniques, Al-Mustaqbal University

E-mail Address: sci.yahya.alkhafaji@uobabylon.edu.iq

Abstract

A new vanadium and tungsten monometallic complexes were prepared, these complexes containing 4-aminoantipyrine derivative namely 1,5-dimethyl-2-phenyl-4-(3-phenylallylidene)amino)-1H-pyrazol-3(2H)-one as ligand. The ultraviolet and infrared were employed to characterize new complex. The optimum pH for complex has been investigated. The V(V) and W(VI) complexes are detected at $\lambda_{\text{max}} = 375 \text{ nm}$ and $\text{pH} = 6$, Beer-Lambert's law is in the range $= (0.3 \times 10^{-5} - 55 \times 10^{-5} \text{ M})$ for V complex, while at $\lambda_{\text{max}} = 385 \text{ nm}$ and $\text{pH} = 7$ and concentration range $= (0.3 \times 10^{-5} - 58 \times 10^{-5} \text{ M})$ for W complex. Different spectrophotometric methods were used to determine the stoichiometry of complexes and the molar conductivity.

Keywords: 4-Aminoantipyrine, Cinnamaldehyde, Vanadium, Tungsten.

Introduction

One of the important class ligands in the coordination chemistry are the Schiff bases due to their vital application in many fields [1, 2], such as catalyst [3], antibacterial [4], industry [5]. A large number of researcher groups have been examined the preparation and characterization of 4-aminoantipyrine and its derivatives due to their use in many

area of applications for example analytical [6], therapeutically [7] and biological [8]. Owing the fact that their various feature[9]. During few decade many article were published by employing of 4-aminoantipyrine derivatives to coordinate with metals[10-12] . 4-aminoantipyrine and their Schiff bases derivative act as multi-dentate ligands[13] can coordinating in neutral formulae, when the metals ion interaction with these ligand can produce complexes with different geometries can fit with many application for example in biologically field[14]. Developing of the complexes of vanadium[15] and tungsten[16] with Schiff base derivative catch more attention due to their ability to application in the biochemical and environmental field. 1,5-dimethyl-2-phenyl-4-(3-phenylallylidene) amino)-1H-pyrazol-3(2H)-one (VAAP) coordinate with vanadium and tungsten by tow bond one of them from Schiff base group and other by oxygen atom in 4-aminoantipyrine to form complex.

Experimental

General

IR and UV-VIS spectra are carried out by FTIR-8400S SHIMADZU spectrometer and UV-1650 Shimadzu spectrophotometer.

Synthesis of the Ligand.

The condensation of (1.32g, 0.01 mol) cinnamaldehyde in ethano with 4-amino-2, 3-dimethyl-1-phenyl-3- pyrozone-5-on (2.03g, 0.01 mol). Follow by refluxing the mixture for 1h, then cool the mixture to form yellow precipitate then the solid was filtered and recrystallized by absolute ethanol[3].

Standard Stock solution of V and W ion

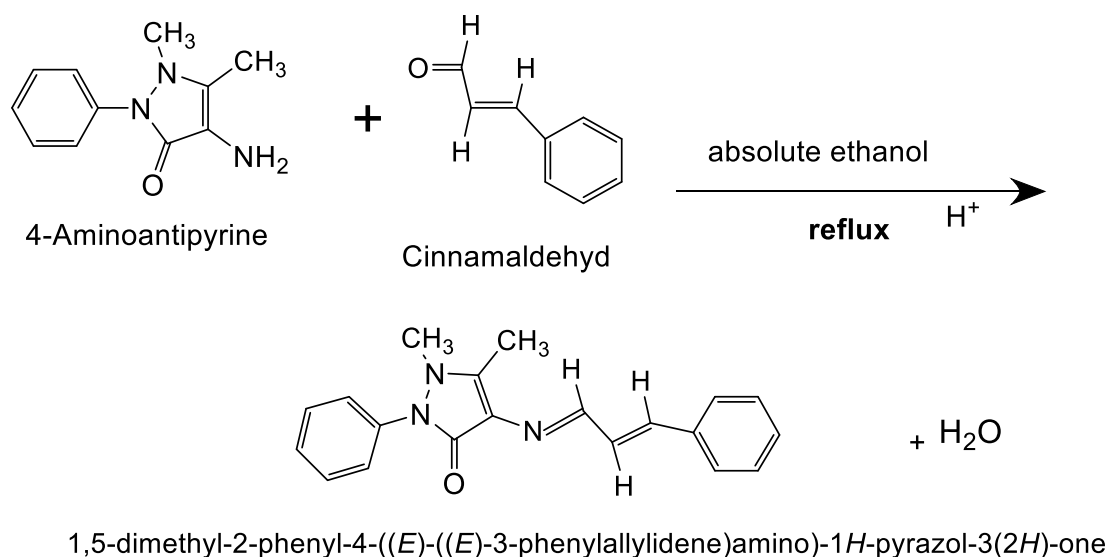
The proper amount of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and NH_4VO_3 were used to prepare required molarity of both starting materials acidic water, and used to prepare dilution solution.

Standard Stock solution of ligand

Dissolve (0.0337 g) of the synthesized ligand in ethanol to prepare(0.001M), this concentration was used to prepare other standard solution.

Results and Discussion

The synthesized Schiff base ligand was prepared according to the scheme below:



Scheme (1) ligand used in this study

Table 1 below represented The physical data of the synthesized compounds

Table 1 Physical data of the prepared compounds

	Color	M.P	Yield %	Molar Conductivity ohm ⁻¹ cm ² mol
Ligand	Yellow	225-227	80.5 %	--
V complex	Yellow- green	200-202	65.1 %	63
W complex	Yellow- green	180-182	55%	70

It is clear from the results (table 1) the electrolyte behavior of these complexes. The metal: ligand ration is 1:1 for both V(V) – L and W(VI) -L complexes according to the table above.

The Electronic Spectra

The ultra-violet of the ligand .

The electronic transitions ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) were appear in Uv-Vis spectrum at 234 nm 337nm respectively, as shown in the Fig.1.

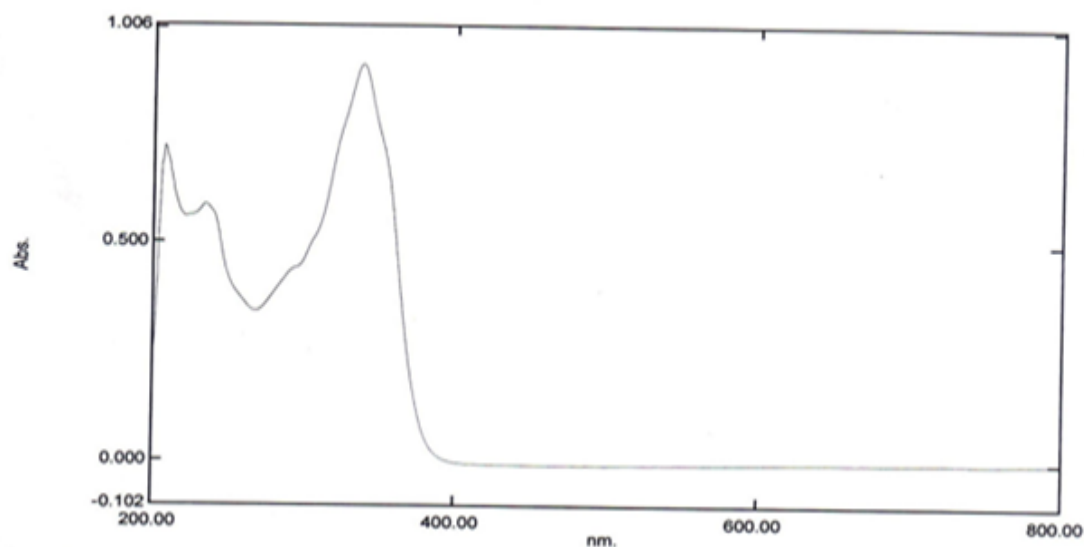


Figure (1) Uv-vis of ligand

Ultra-violet spectra of the complexes:

The Yellow- green complex of V(V) shows peak at 375 nm which belongs to electronic transition, while W (VI) complex shows band peak at 385 nm figure(2).

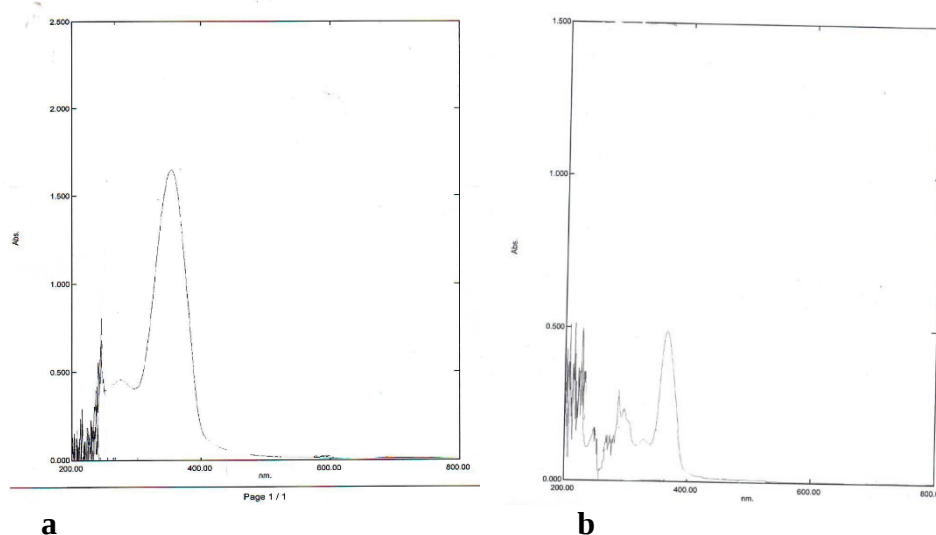


Figure (2): Absorption spectra of V complex(a) and W complex(b)

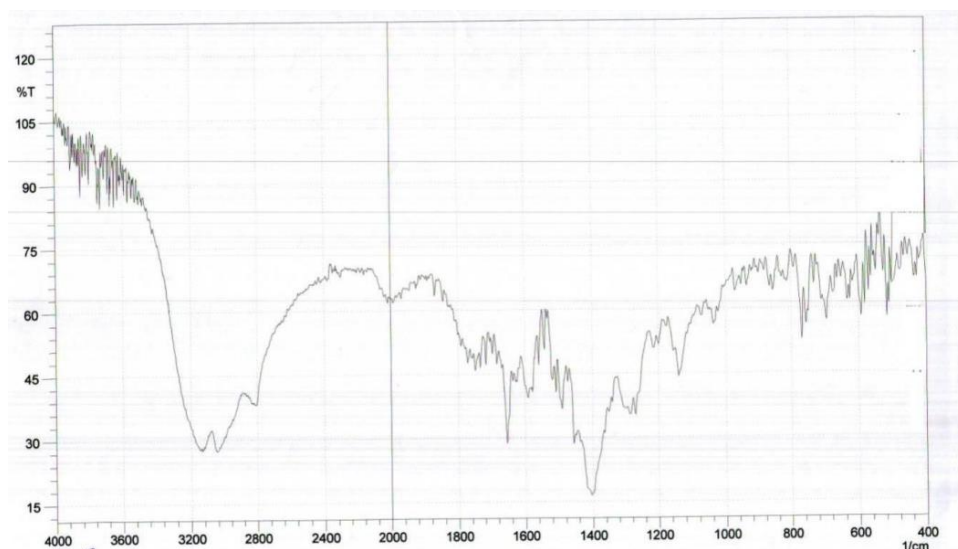
Infrared Spectral Studies

Table(2) are described the important bonds assigned in the infrared spectrum,

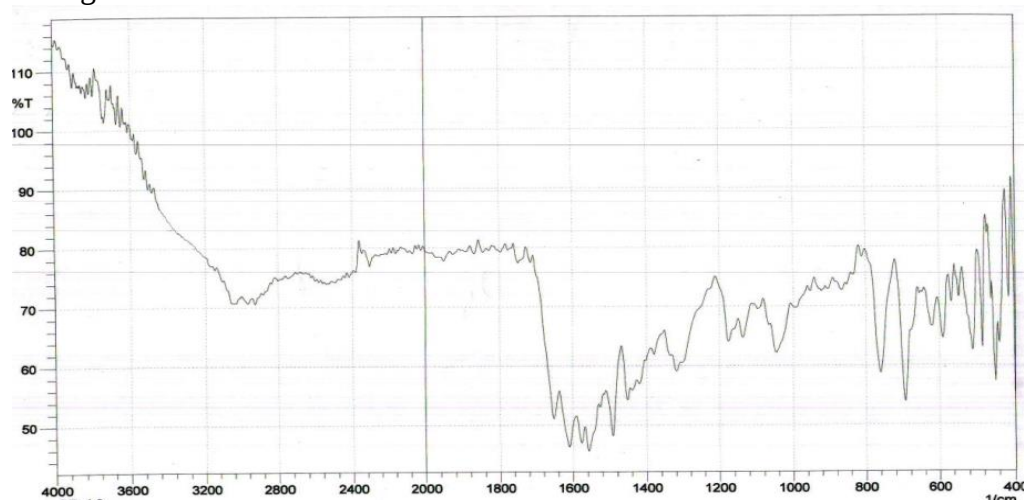
Table 2: IR data

	O-H	C-H	C=N	C=O	C=C	C-O	M-N	M-O
ligand	3114	3029	1579	1624	1499	1274	--	---
V complex	3100	3030	1565	1615	1497	1270	508	480
W complex	3080	3020	1555	1610	1495	1275	510	450

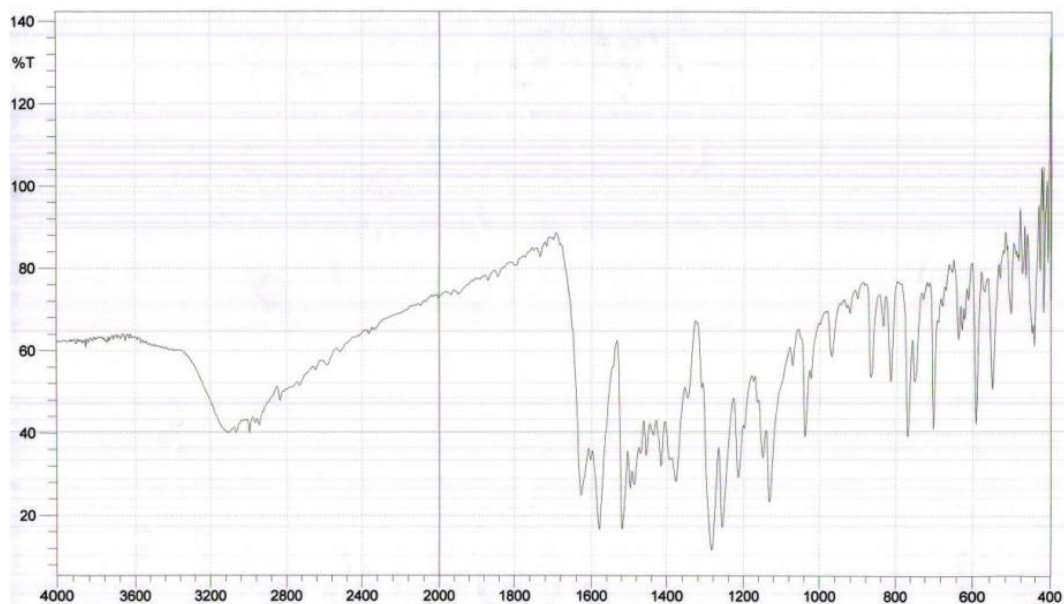
Looking to the spectrum of the ligand (Fig. 3), notice that the weak bands at 3114 cm^{-1} $\nu(\text{O-H})$ and 3029 cm^{-1} $\nu(\text{C-H})$, as compare to the two strong bands at 1627 cm^{-1} and 1627 cm^{-1} attributed to the $\nu(\text{C=O})$ and $\nu(\text{C=N})$ respectively. The bond $\nu(\text{C=C})$ and $\nu(\text{C—O})$ were appear at 1490 cm^{-1} and 1265 cm^{-1} respectively. The characteristic bands for complexes represented in table 2.



(a) The ligand



(b) Vanadium complex

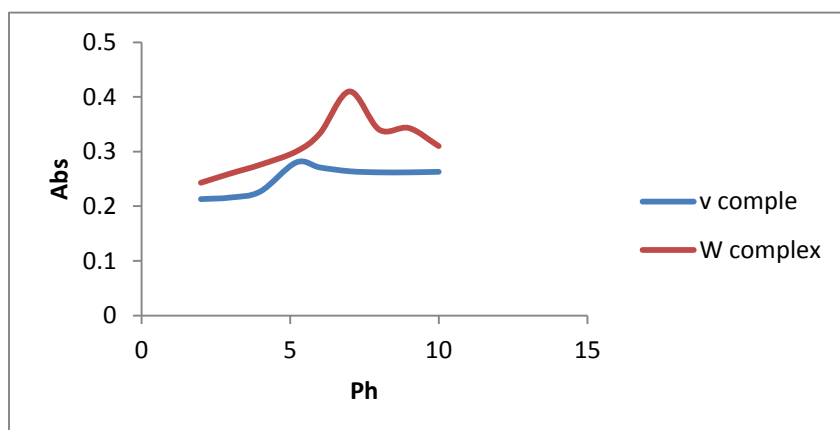


(c) Tungsten complex

Fig. (3) IR for ligand(a) and vanadium complex(b) and tungsten complex (c)**The optimum condition**

The optimum condition of complex was studied

Figure 4 represent the relation between the pH and the absorbance, it is clear from the figure optimum pH for both complexes was in acidic medium, which related with maximum absorbance(Ph(6-7)) for V and W complexes.

**Fig. (4) The PH effect on the absorbance****The effect of temperature**

Refers to the reaction complete at 15 C and the complex stable in the range of 15- 60 C. dissociation of complex absorbed after this temperature. Fig. (5)

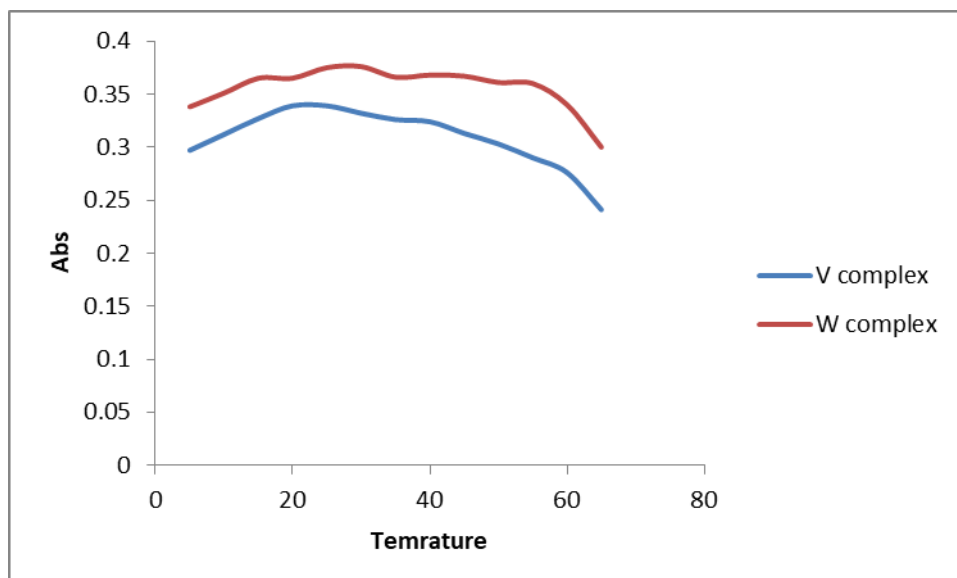


Fig. (5) Temperature effect on the absorbance

The time effect

The absorbance constant for 24 hours refers to the stability of the complex Fig. (6)

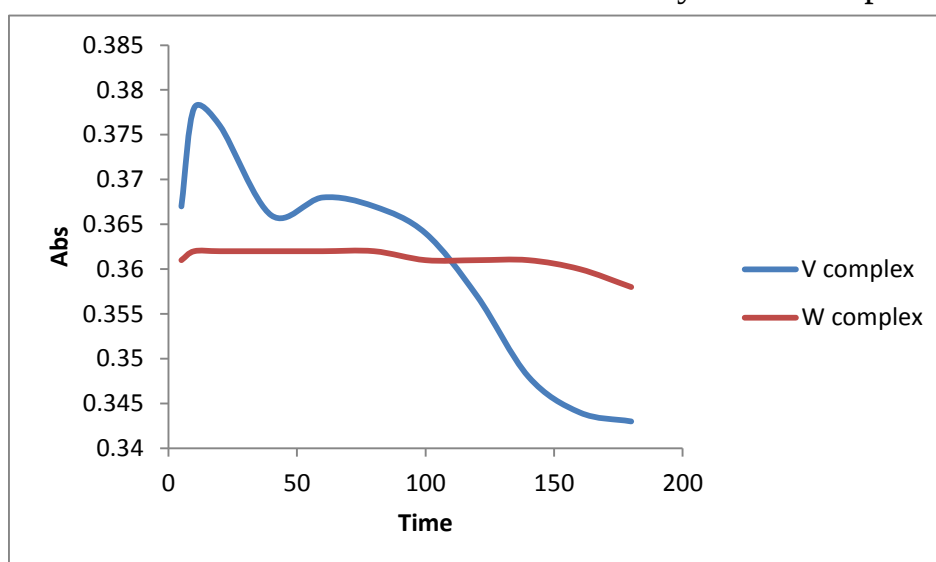


Fig. (6) The time effect on the absorbance

Stoichiometry of complex

Continuous variation and mole ratio methods were employed to determine the stoichiometry of V – VAAP and W-VAAP complexes [17, 18] (Fig. 7) and Fig.(8), the result was (1:1) metal: ligand mole ratio.

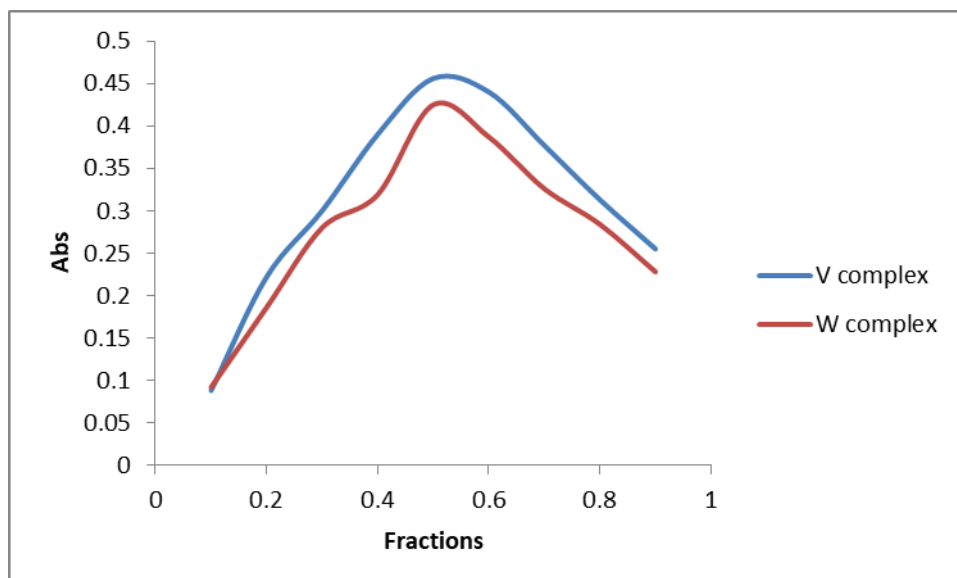


Fig. (7): Job's method.

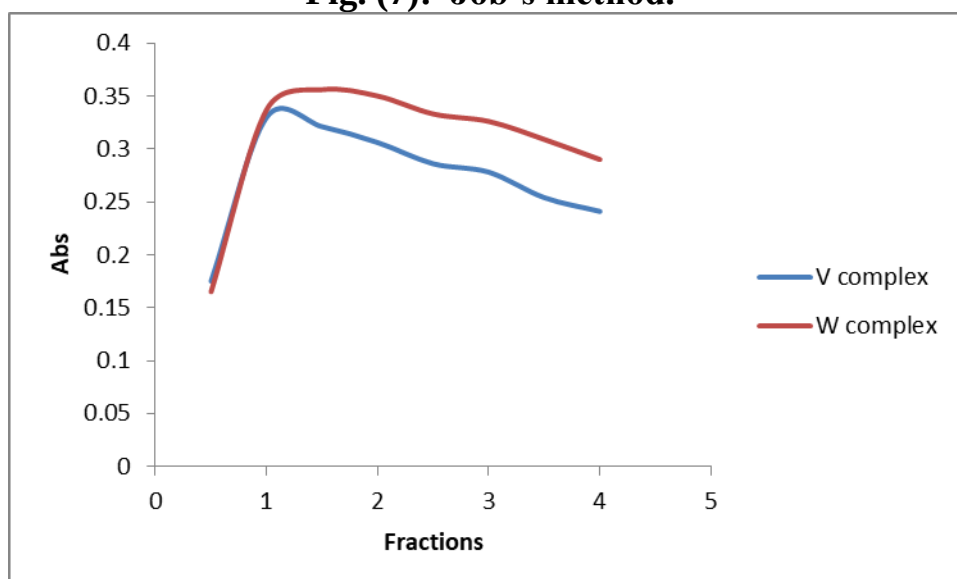


Fig. (8): Mole-Ratio method

The calibration curve

It refers to the complex obey Beer law in the range of $(0.3 \times 10^{-5} - 55 \times 10^{-5} \text{ M})$ for V complex and $(0.3 \times 10^{-5} - 58 \times 10^{-5} \text{ M})$ for W complex Fig.(9)

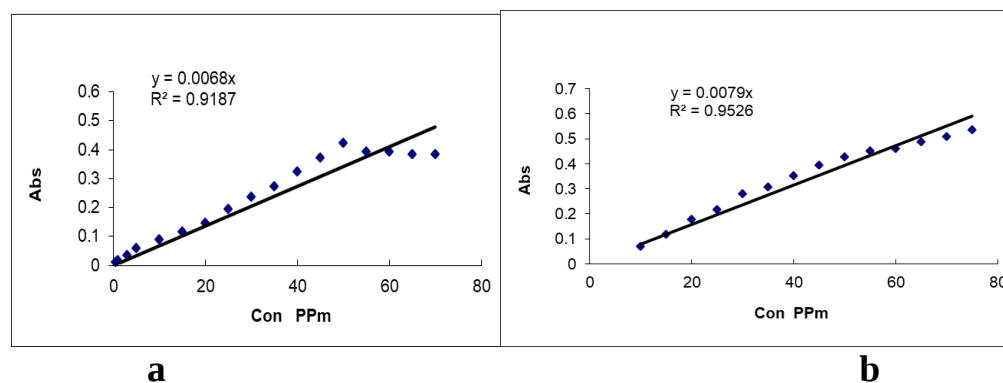


Fig. (9) The calibration curve (a)V complex and(b)W complex

References

- [1] Abu-Dief, A.M. and I.M.A. Mohamed, *A review on versatile applications of transition metal complexes incorporating Schiff bases*. Beni-Suef University Journal of Basic and Applied Sciences, 2015. **4**(2): p. 119-133.
- [2] Wang, X., et al., *Organoaluminium Complexes Derived from Anilines or Schiff Bases for the Ring-Opening Polymerization of ϵ -Caprolactone, δ -Valerolactone and rac-Lactide*. European Journal of Inorganic Chemistry, 2017. **2017**(13): p. 1951-1965.
- [3] Al-Khafaji, Y., et al., *Aluminium complexes as catalysts for ring-opening polymerization of ϵ -caprolactone bearing Schiff base ligands derived from 4,4'-Methylenebis (2,6-diisopropylaniline)*. Journal of Physics: Conference Series, 2019. **1234**: p. 012055.
- [4] da Silva, C.M., et al., *Schiff bases: A short review of their antimicrobial activities*. Journal of Advanced Research, 2011. **2**(1): p. 1-8.
- [5] More, M.S., et al., *Metal complexes driven from Schiff bases and semicarbazones for biomedical and allied applications: a review*. Materials today. Chemistry, 2019. **14**: p. 100195-100195.
- [6] Mohanram, I. and J. Meshram, *Synthesis and Biological Activities of 4-Aminoantipyrine Derivatives Derived from Betti-Type Reaction*. ISRN Organic Chemistry, 2014. **2014**: p. 639392.

- [7] Raman, N., S. Johnson Raja, and A. Sakthivel, *Transition metal complexes with Schiff-base ligands: 4-aminoantipyrine based derivatives—a review*. Journal of Coordination Chemistry, 2009. **62**(5): p. 691-709.
- [8] Tyagi, M., et al., *Synthesis, characterization and anti-fungal evaluation of Ni(II) and Cu(II) complexes with a derivative of 4-aminoantipyrine*. Journal of Taibah University for Science, 2017. **11**(1): p. 110-120.
- [9] Elattar, K.M. and A.A. Fadda, *Chemistry of antipyrine*. Synthetic Communications, 2016. **46**(19): p. 1567-1594.
- [10] Dhanaraj, C.J. and S.S. Salin Raj, *Synthesis, characterization and biological studies of Schiff base metal complexes derived from 4-aminoantipyrine, acetamide and p-phenylenediamine*. Inorganic Chemistry Communications, 2020. **119**: p. 108087.
- [11] Joseph, J., K. Nagashri, and G.A.B. Rani, *Synthesis, characterization and antimicrobial activities of copper complexes derived from 4-aminoantipyrine derivatives*. Journal of Saudi Chemical Society, 2013. **17**(3): p. 285-294.
- [12] Kurdekar, G.S., et al., *4-Aminoantipyrine-based Schiff-base transition metal complexes as potent anticonvulsant agents*. Medicinal Chemistry Research, 2012. **21**(9): p. 2273-2279.
- [13] Mishra, A.P., et al., *Synthesis of New VO(II), Co(II), Ni(II) and Cu(II) Complexes with Isatin-3-Chloro-4-Floroaniline and 2-Pyridinecarboxylidene-4-Aminoantipyrine and their Antimicrobial Studies*. Mycobiology, 2012. **40**(1): p. 20-26.
- [14] El-Megharbel, S.M., A.S. Megahed, and M.S. Refat, *Preparation, physical and chemical studies on metal complexes of Schiff bases as a nucleus key to prepare nanometer oxides have catalytic applications: Nickel (II) complexes derived from 4-aminoantipyrine derivatives*. Journal of Molecular Liquids, 2016. **216**: p. 608-614.

- [15] da Silva, J.A.L., J.J.R. Fraústo da Silva, and A.J.L. Pombeiro, *Amavadin, a vanadium natural complex: Its role and applications*. Coordination Chemistry Reviews, 2013. **257**(15): p. 2388-2400.
- [16] Lunk, H.-J. and H. Hartl, *Discovery, properties and applications of tungsten and its inorganic compounds*. ChemTexts, 2019. **5**(3): p. 15.
- [17] Renny, J.S., et al., *Method of Continuous Variations: Applications of Job Plots to the Study of Molecular Associations in Organometallic Chemistry*. Angewandte Chemie International Edition, 2013. **52**(46): p. 11998-12013.
- [18] Ntoi, L.L. and K.G. von Eschwege, *Spectrophotometry mole ratio and continuous variation experiments with dithizone*. African Journal of Chemical Education, 2017. **7**(2): p. 59-92.