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A Preparation and Spectroscopic Study for Some Copper and Oxovanadium Complexes of Enaminones

Dhiyaa Kareem Muslem*

Sciences Department, The Open Educational College, Thi-Qar, Iraq

Abstract

Four copper (II) and oxovanadium (IV) complexes of some enaminones derived from acetylacetone or trifluoroacetylacetone with methylamine have been prepared and investigated by physicochemical methods. The results have been proposed that the copper and oxovanadium complexes are in (1:2) (metal:ligand) composition and they have a square planer and square pyramidal structure, respectively. Lewis Acid-Base interaction has been studied for the prepared complexes as acceptors with pyridine as donor, and all the reactions were found as 1:1 interactions. Equilibrium consonants (Keq) for these interactions in chloroform have been measured using visible technique at different temperature. These values are within the range 6.58-16.43 $L.mol^{-1}$. Thermodynamics functions ∆H, ∆G and ∆S for these interactions have also been measured. The ∆H values were within the range (-22.0 to +15.25) $KJ.mol^{-1}$. The ∆G values were within the range of (−5.47 to −6.62) $KJ.mol^{-1}$ while the ∆S within −55.47 to 73.38 $J.mol^{-1}.K^{-1}$.

Keywords: Enaminones; Copper complex; Oxovanadium complex; B-Ketoamine; Schiff bases

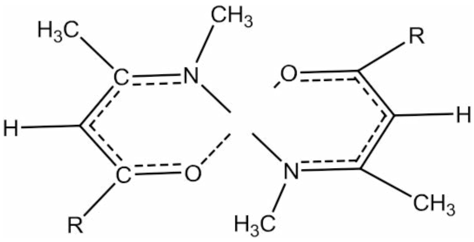
Introduction

There has been an upsurge of interest in the chemistry of chelate compounds owing to their varied application in diverse fields [1-6]. Compounds containing an azomethine group (-CH=N-) are known as Schiff bases. These chemical compounds are distinctive compounds in coordination chemistry and they used in different purposes [7]. They widely used in the development of metal based drugs, analytical, industrial, medicinal, agricultural, biological and clinical areas [8]. For example, Schiff bases are essential materials in the synthesis of number of industrial and biologically active compounds [9]. Also, they are very important ligands from the biological point of view [10] such as they are important intermediates in a number of enzymatic reactions or in the processes of non-enzymatic glycosylations [11]. Also, it has been reported that Schiff bases possessing, antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitumor and anti HIV activities [12-15]. Moreover, these compounds have a great ability to form complexes with amino acids and other materials found in the bodies of living organisms [16-20]. Therefore, the study of the equilibrium constants (Keq) of these complexes is a great importance to understand what is happening in the biological systems.

Although a number of studies have been reported on the metal chelate of tridentate Schiff bases derived by the condensation of amines with β-diketones and related ligands [21,22], the literature reveals little work on physicochemical measurement of these complexes. At the same time, despite there are a number of investigations have been reported on equilibrium constant Keq of the Lewis acid–base interaction in various complexes of ß-diketonats and related ligands as acceptors with amines as donors using different techniques [23-26], but there are a few data have been published about the Keq for adduct formation of enaminoes complexes.

Thus, the present work is an extension for those efforts. In this paper, copper (II) and oxovandium (IV) complexes of some enaminones (structure formula I) have been prepared and characterized using a variety of spectral and analytical methods and also to investigate interaction of the prepared complexes with pyridine and to calculate Keq using visible technique.

R	M	Complex Code
CH3	Cu	Cu-Me
CF3	Cu	Cu-TFA
CH3	VO	VO-Me
CF3	VO	VO-TFA



(I)

Experimental Section

Materials

All chemicals (ethanol, chloroform, pyridine, acetylacetone, trifluoroacetylacetone, methylamine, copper acetate, vandyl sulphate, KBr) were purchased from Aldrich and employed as supplied. All the regents used were Analar or of chemically pure grade. All the solvents were freshly distilled before use.

***Corresponding author:** Dhiyaa Kareem Muslem, Sciences Department, The Open Educational College, Thi-Qar, Iraq, E-mail: dhiyaa99@gmail.com

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Preparation of compounds

The ligands were prepared by the reported method [22], copper (II) and oxovandium (IV) complexes were prepared by adding a calculated amount of the appropriate ligand (0.2 mol) in ethanol to the copper acetate or vandyl sulphate (0.1 mol) in the same solvent. The mixture was refluxed for about 15 min. The solid complexes were filtered, washed with mixture ethanol/water (50:50), dried and re-crystallized with ethanol and dried in vacuum at 80˚C for 24 hr.

Physical measurements

The electronic spectra of the complexes were recorded on PHILIPS- PU 8620 UV/VIS/NIR spectrophotometer. Infrared spectra were recorded using KBr disk on a pye unicam SP3-300s-Infrared spectrophotometer. The X-ray diffraction patterns were carried out in the solid state using a PHILIPS X-Ray diffractometer with Cu-K radiation (λ=1.5418). Mass spectra (EI-MS) were recorded by Fiungam Mass spectrometer model M1125. Elemental analyses were determined by the standard combustion method using a Perkin Elmer model 240°C elemental analyzer. Molecular weights were determined by Rast's camphor method [27]. Melting points were recorded on a digital instrument type Gallenkamp and are uncorrected. The molar conductivity was made in DMF solution (1×10^{-3} M) using conductivity meter type JENWAY.

Equilibrium constant

The Keq was determined by visible technique as described already [28]. The measurements were carried out at constant concentration of each complex (0.003 M), while concentration of pyridine were within the range 0.15-0.375 M in chloroform at 15, 25 and 35°C using thermostatic cell holder type MGW LAUDA K4R electronic with thermometer type PHILIP HARRIS precision ± 0.1°C.

Results and Discussion

The resulting complexes were obtained as colored solids and re-crystallized from ethanol. These air-stable complexes are fairly soluble in most organic solvent but very soluble in polar solvent like DMF, DMSO and acetonitrile giving stable solutions. The analytical data given in Table 1 are in good agreement with 2:1 (ligand: metal) composition for these complexes. The molecular weights measurements reveal that the complexes are monomeric in nature. The conductivity measurements in anhydrous DMF (at 296 K) show the complexes are non-conducting, neutral and non-ionic compounds.

Electronic Spectra

The copper and oxovanaduim complexes show a resemblance with two bands in ultraviolet spectra but they differ in visible region (Table 2). The UV spectra of the complexes were characteristic by two bands, band I between (290-320 nm) has been assigned to π-π^* transition, and band II between (235-250 nm) has been assigned to the charge transfer transitions which involve both the metal atom and ligand. Visible spectra of copper complexes were displayed one weak absorption band at (630, 660 nm), while oxovovandium complexes were displayed two weak absorption bands between (623-815 nm) which attributed to d-d transitions. The bathochromatic shift occurs in both the bands in complexes of Cu-TFA and VO-TFA attribute to the substitution of trifluromethyl group [29], which leads to a spread of charge within a larger distance in the molecule and hence to bathochromatic shift [30].

Infrared spectra

Infrared spectra of all complexes showed the absence of the found band in spectra of the ligands near 3360 cm^{-1} account for N-H or O-H vibration [22], which indicates that the metal ion is coordinated through oxygen and nitrogen atoms of the coordinated β-ketoamine. In the IR spectra of Cu-Me and VO-Me complexes (Figure 1) the ν C=O of the coordinated β-ketoamine appeared around 1555 cm^{-1} and 1545 cm^{-1}, respectively. This band shifted to 1580 cm^{-1} and 1576 cm^{-1} in Cu-TFA and VO-TFA complexes, respectively due to the substitution of electron withdrawing CF3 group in these complexes. The characteristic band of the azomethine group C=N observed at 1505 cm^{-1} and 1420 cm^{-1} in the complexes Cu-Me and VO-Me, respectively which shifted to 1510 cm^{-1} and 1430 cm^{-1} in fluorinated complexes on the same order. Further, the appearance of new bands of medium to weak intensity at 450, 482, 425 and 430 cm^{-1} may be attributed to ν (Cu-O), ν (V-O), ν (Cu-N) and ν (V-N) vibrations, respectively in non-fluorinated complexes, while in fluorinated complexes observed at 456, 485, 430 and 436 cm^{-1} on the same order. The spectra of oxovanadium complexes characterized by strong absorption band at 990 cm^{-1} which was assigned to V=O stretching frequency [31].

Mass spectra

Mass spectra of the complexes under study have not been reported before. They are complex and difficult to interpret unequivocally [32]. However, mass spectra of Cu-Me and VO-Me complexes (Figure 2) characterized by the absence of the molecular ion peak. The base peaks of these complexes were displayed at m/e 261 and 265, respectively. It has been concluded probably that the first composition step is the loss of the methyl group on the nitrogen atom. The peaks at m/e 246 and 250 in these complexes may be attributed to loss of CH3 group from one ligand, while the peaks at m/e 162 and 166 may be attributed to loss of one ligand from the complex. The mass spectra of Cu-TFA and VO-TFA were definitely different, these spectra displayed the molecular ion peak at m/e 395 and 399, respectively, while the peak at m/e 229 and 233 may be attributed to loss of one ligand , therefore it is considered this behavior is due to the substation of CF3 group in place of CH3 group.

X-Ray spectra

X-ray spectra of Cu-Me and VO-Me (Figure 3) were showed that the two complexes are in polycrystalline state. The higher reflection in Cu-Me at (2θ=11.5) (d=7.69 A°), which represents appropriate direction of the crystal growing, while higher reflection in VO-Me was at (2θ=13.3) (d=6.75 A°) and (2θ=28) (d=3.18 A°). A comparison of the powder diffraction pattern of the compounds Cu-Me with that of Cu-TFA and Cu-AA (AA=acetylacetone), and also VO-Me with that of VO-TFA and VO-AA show definite similarity, it has been concluded that the crystal structure of unite cell of copper and oxovanaduim complexes are monoclinic and triclinic, respectively [33,34].

Equilibrium constant

Figure 4 shows electronic spectra of free acceptor (complex Cu-Me) (3×10^{-3} M) in chloroform and those obtained by adding increasing concentrations of pyridine (0.15-0.375 M). It can be noted in this figure that there is a isosbestic point which is strong evidence on formation of adduct and it indicates that the reaction of acceptor-donor is from type 1:1 interaction [35], and this also appears in the other reactions. The equilibrium constants Keq for those interactions were determined by visible technique in chloroform at different temperatures using Benesi-Hildebrand (Equation 1) [28].

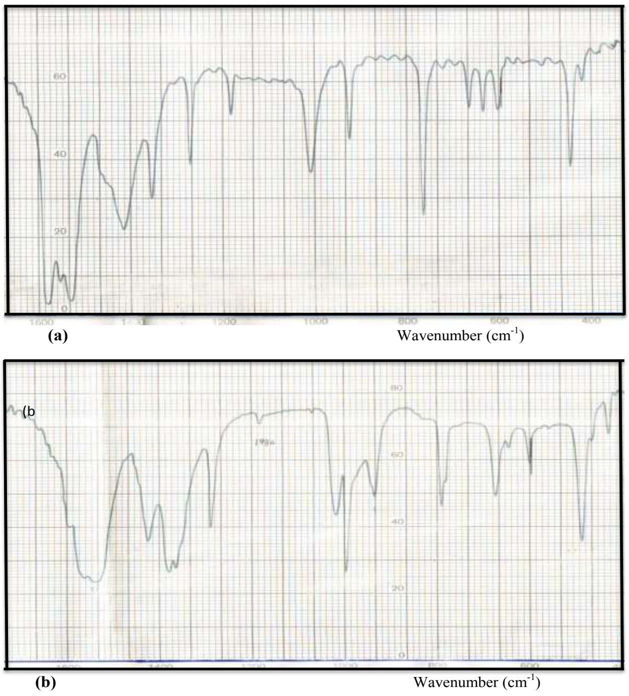

Figure 1: IR spectra of (a) Cu-Me and (b) VO-Me complexes.

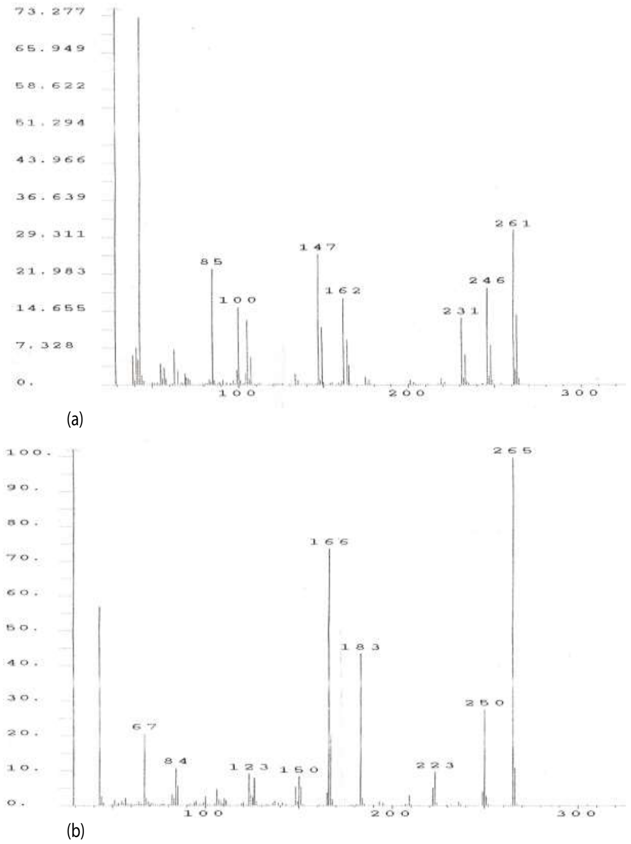

Figure 2: Mass spectra of (a) Cu-Me and (b) VO-Me complexes.

$$\frac{[A]\ell}{A - Ao} = \frac{1}{K(\text{€}c - \text{€}o)} \cdot \frac{1}{[D]} + \frac{1}{\text{€}c - \text{€}o} \quad (1)$$

where [A] is concentration of acceptor, ℓ is cell path length, A0 and A are absorption of acceptor and adduct, respectively, K is equilibrium constant, [D] is concentration of donor, €c and €0 are molar absorptivity of adduct and acceptor, respectively.

Hence a plot of the left- hand side of the Equation 1 Versus 1/[D] should yield a straight line, from the slope and intercept of which Keq can be calculated. Figure 5 shows the plots suggested by Equation 1 for reaction the complexes with pyridine in chloroform as solvent.

The obtained results for Keq given in Table 3 show that the Keq obtained for adduct formation of the Cu-Me complex (9.15 $L.mol^{-1}$) is the smallest compared to the values of Keq for the other complexes, Cu-TFE (10.76 $L.mol^{-1}$), VO-Me (12.01 $L.mol^{-1}$) and VO-TFA (14.4 $L.mol^{-1}$).

The results show that the equilibrium constants for interactions of vanadium complexes with pyridine are bigger than that for analogous complexes of copper, which is concordant with previous studies. For example, Keq for VO-Me is 12.01 $L.mol^{-1}$ while for Cu-Me is 9.15 $L.mol^{-1}$. This is due to the electronic density of copper and vanadium ions. The d orbital in copper ion contains nine electrons while in vanadium ion contains only a single electron [36] and therefore this causes decrease of electronic density on the vanadium ion which becomes a stronger centre than copper ion to accept the electronic pair from the donor and then this leads to increasing of the equilibrium constant. On the other hand, it can be noted that the Keq for fluorinated complexes bigger than that for non- fluorinated complexes, for example Keq for VO-TFA complex is 14.40 $L.mol^{-1}$ while for VO-Me complex is 12.01 $L.mol^{-1}$. This behavior is due to the substitution of CF3 group in place of CH3 group in the ligand and this attributable to the increasing of electronic deficiency on the metal ion and consequently increases value of Keq.

The thermodynamics constants, enthalpies ΔH, Free Energy ΔG and entropies ΔS for the interactions of donor- acceptor in solution have been investigated and obtained by study of the effects of temperature changes on the equilibrium constant. It was found that the interaction of donor- acceptor is accompanied by small changes in enthalpies ΔH and entropies ΔS. Table 4 shows that Keq for the interaction non-fluorinated complexes with pyridine decreases with increasing temperature, for example the Keq for interaction Cu-Me complex with pyridine at 15°C was 12.08 $L.mol^{-1}$ while at 25 and 35°C were 9.15 and 6.58 $L.mol^{-1}$, respectively. This is attributable to the decrease in bonding strength between the acceptor and the donor. At the same time, Table 4 show that Keq for the interaction fluorinated complexes with pyridine increases with increasing temperature, for example the Keq for interaction Cu-TFA complex with pyridine at 15°C was 9.35 $L.mol^{-1}$ while at 25 and 35°C were 10.76 and 12.11 $L.mol^{-1}$, respectively. This may explain that at low temperatures the hydrogen bonding between of hydrogen and fluorine atoms increases and this leads to reduces electronegativity for CF3 group and then increase of electronic density on the matel ion and in other words decrease of the K.

The values of ΔH have been calculated using Equation 2 from the slopes of liner plots of the type depicted in Figure 6, while Free Energy ΔG and ΔS were calculated at 25°C using Equations 3 and 4

$$\ln k = \frac{\Delta S}{R} - \frac{\Delta H}{R} - \frac{1}{T} \quad (2)$$

$$\Delta G = -RT \ln Keq \quad (3)$$

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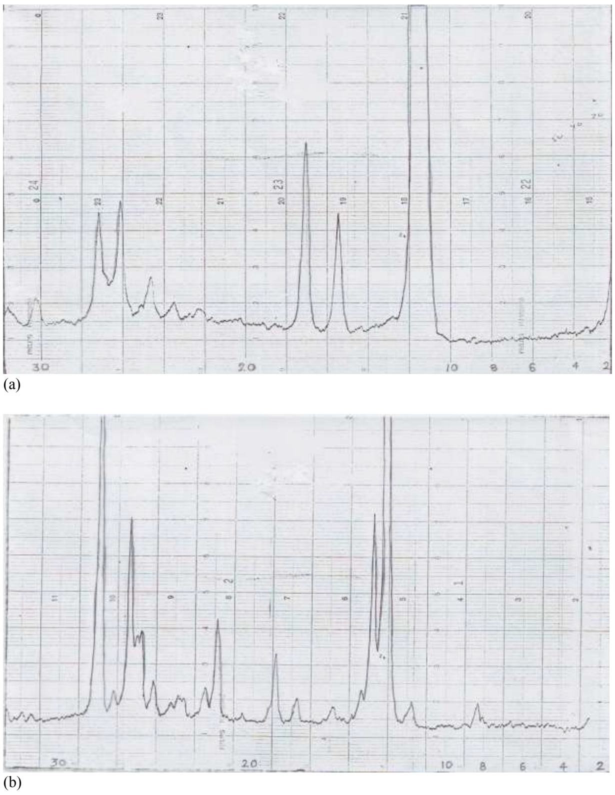

Figure 3: X-ray diffraction patterns of (a) Cu-Me and (b) VO-Me complexes.

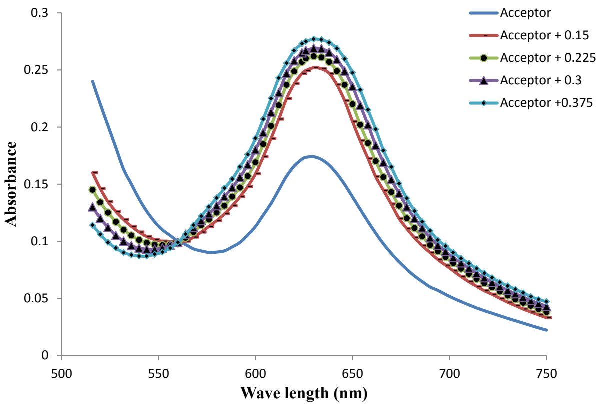

Figure 4: Electronic spectra of acceptor (Cu-Me complex) with increasingly concentrations of pyridine (015-0.0375) M in chloroform at 25°C.

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

The calculated thermodynamics constants were listed in Table 5, the ΔH are negative for interactions the non-fluorinated complexes with pyridine and within (−14.40)-(−22.0) KJ.mol^{-1}, while for fluorinated complexes are positive within the range (+9.04)-(+15.25) KJ.mol^{-1}. The ΔG values are negative for all the interactions, which indicate that the occurrence of interactions was spontaneously. On the other hand, the ΔG were small within (-5.47)-(-6.62) KJ.mol^{-1} relate low values of the equilibrium constants. Table 5 also show that ΔS are negative for non-fluorinated complexes within (−27.61)-(55.47) J.mol^{-1}.K, while are

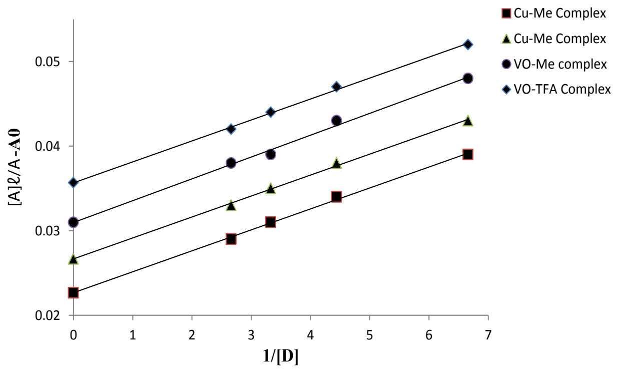

Figure 5: Plot of Equation 1 for the interaction prepared complexes with pyridine in chloroform at 25°C.

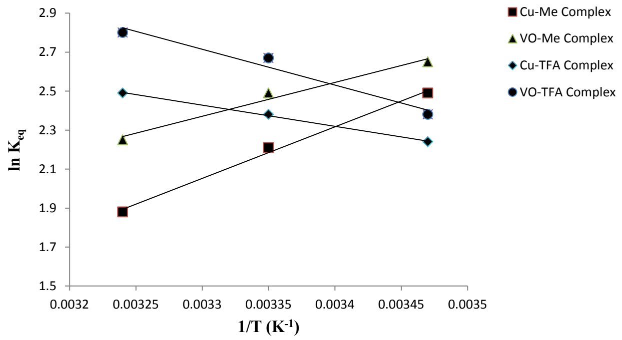

Figure 6: Plot of Equation 2 for the interaction prepared complexes with pyridine in chloroform at 25°C.

Complex	Colour and state	Mp (°C)	Analysis (%)			M.Wt.
			C/ Found (calcd.)	H/ Found (calcd.)	N/ Found (calcd.)	Found (calcd.)
Cu-Me	Light blue Solid	246 (dec.)	49.82 (50.08)	6.41 (6.95)	9.18 (9.73)	271.0 (287.5)
VO-Me	Blue Solid	248	50.11 (49.48)	6.06 (6.87)	9.43 (9.62)	308.0 (291.0)
Cu-TFA	Light blue Solid	198	36.26 (36.40)	3.91 (3.53)	6.84 (7.07)	388.0 (395.5)
VO-TFA	Blue Solid	204	35.06 (36.09)	3.69 (3.50)	7.67 (7.01)	383.0 (399.0)

Table 1: Properties and analyses data of the complexes.

Complex	λ max (Ɛ l mol^{-1} cm^{-1})
Cu-Me	250 (24400), 290 (21020), 630 (58)
VO-Me	246 (1980), 311 (16450), 623 (52), 805 (91)
Cu-TFA	241 (1041), 295 (1045), 660 (54)
VO-TFA	235 (105), 320 (120), 645 (48), 815 (95)

Table 2: Spectrophotometric data of the prepared complexes in methanol.

Complex	Cu-Me	Cu-TFA	VO-Me	VO-TFA
Keq (L.mol-1)	9.15	10.76	12.01	14.40

Table 3: Data of Keq for the interaction the prepared complexes with pyridine at 25°C.

Complex	Keq (L.mol-1) At 15°C	Keq (L.mol-1) At 25°C	Keq (L.mol-1) At 35°C
Cu-Me	12.08	9.15	6.58
Cu-TFA	9.35	10.76	12.11
VO-Me	14.21	12.01	9.45
VO-TFA	10.81	14.40	16.43

Table 4: Data of Keq for the interaction the prepared complexes with pyridine at 15, 25 and 35°C.

Complex	∆H (KJ.mol-1)	∆G (KJ.mol-1)	∆S (J.mol-1.K-1)
Cu-Me	-22.0	-5.47	-55.47
Cu-TFA	9.04	-5.89	50.10
VO-Me	-14.40	-6.17	-27.61
VO-TFA	15.25	-6.62	73.38

Table 5: Values of ∆H (from the slope-Figure 4), ∆G and ∆S (at 25°C) for the interaction the prepared complexes with pyridine.

positive for fluorinated complexes within (+50.10)-(+73.38) J.mol^{-1}.K.

Conclusion

Based on these results, it is concluded that the copper and oxovanaduim complexes are mononuclear complexes having square planer and square pyramidal, respectively geometry around metal center with 2:1 (ligand; metal) composition. The results also indicate that the reaction of acceptor-donor is from type 1:1 interaction.

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