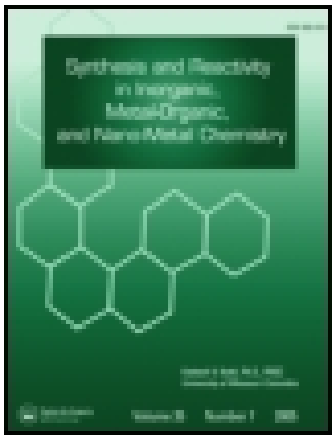

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Synthesis, Characterization, and Kinetic Study of Complexation of Vanadyl Acetylacetone with Some Unsymmetrical N_3O Schiff Bases

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Synthesis, Characterization, and Kinetic Study of Complexation of Vanadyl Acetylacetone with Some Unsymmetrical N_3O Schiff Bases

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This article reports the synthesis and characterization of some new vanadyl Schiff base complexes, ((N-salicylidene-N′-pyrrolidene)-1,2-ethylenediaminato)oxovanadium(IV) [VO (Salpyren)], ((7-methyl-N-salicylidene-N′-pyrrolidene)-1,2-ethylenediaminato) oxovanadium(IV) [VO(Mesalpyren)], ((7-phenyl-N-salicylidene-N′-pyrrolidene)-1,2-ethylenediaminato) oxovanadium(IV) [VO(Phsalpyren)], ((N-salicylidene-N′-pyrrolidene)-1,3-propylenediaminato)oxovanadium(IV) [VO(Salpyrpd)], ((7-methyl-N-salicylidene-N′-pyrrolidene)-1,3-propylenediaminato) oxovanadium(IV) [VO(Mesalpyrpd)], ((7-phenyl-N-salicylidene-N′-pyrrolidene)-1,3-propylenediaminato)oxovanadium(IV) [VO (Phsalpyrpd)]. These complexes were characterized by elemental analyses, IR, UV-Vis, and mass spectra. The kinetics and mechanism of the complex formation in methanol were studied spectrophotometrically. The second order k2 rate constants show the following trend: Mesalpyren > Salpyren > Phsalpyren > Mesalpyrpd > Salpyrpd > Phsalpyrpd The linear plots of kobs vs. the molar concentration of VO(acac)2, the large negative values of $\Delta S\neq$ and the low values of $\Delta H\neq$ suggest an associative (A) mechanism.

Keywords kinetic, mechanism, Schiff base, synthesis, Vanadium complex

INTRODUCTION

In recent years, vanadium chemistry has attracted attention due to its interesting structural features and biological relevance. Oxovanadium complexes have been shown to catalyze a variety of reactions. Vanadium is a bioelement involved in various catalytic (haloproxidasaes, nitrogenases) and inhibitory (e.g., toward phosphatases) processes. There have been great efforts in the past few years to find efficient insulin-mimetic vanadium complexes. There would be highly active, easily absorbable and of low toxicity.[1−7]

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In recent years our group has studied synthesis, thermodynamics and kinetics of adduct formation of many metal Schiff base complexes with donors such as phosphites, amines and Imidazole derivatives. In our previous work, synthesis and characterization of new unsymmetrical Schiff base ligand was reported, and the thermodynamics of incorporation of Ni(II), Cu(II), Zn(II) into Schiff bases in methanol solvent were studied.[8−13]

In the present report, the synthesis and characterization of some new vanadium(IV) Schiff base complexes and the kinetics and mechanism of complexation of vanadyl acetylacetone with new Schiff bases in MeOH were studied spectrophotometrically and explained by an associative (A) mechanism.

EXPERIMENTAL

Materials

All chemicals were used as obtained from Merck, Acros or Fluka. Anal. Grade solvent from Merck was used without further purification.

Instrumental

Light-absorption measurements in the visible region were made with a Jasco-V-530-UV-vis spectrophotometer equipped with a Lauda-ecoline-RE thermostat. FT-IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. Mass spectra (+ion) were obtained with QP 1000 mass spectrophotometer.

Synthesis

The Schiff base ligands were synthesized according to the literature.[8] The vanadyl complexes were prepared under ambient conditions. To a hot solution of the unsymmetrical ligand (2 mmol) in methanol (20 ml), a hot solution of $VO(acac)_2$ (2 mmol) in methanol (10 ml) was added. The mixture was heated and a few drops of triethylenamine were added. The reaction mixture was refluxed for 30–60 min. The colored solution was concentrated and cooled to yield green powder complexes. The new synthesized complexes (Figure 1) were identified by IR

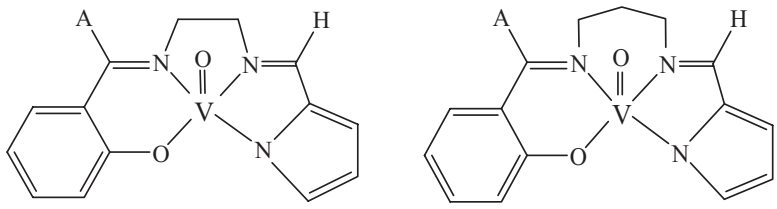

FIG. 1. The structural representation of the oxovanadium(IV) complexes. A=H, CH_3, Ph.

spectra (Figure 2), mass spectra (Figure 3), electronic spectra and elemental analysis.

((N-salicylidene-N'-pyrrolidene)-1,2-ethylenediaminato)oxovanadium(IV) [VO(Salpyren)]. Yield: 54%
IR(KBr, cm^{-1}) : 989($\upsilon_{V=O}$), 1150(υ_{C-O}), 1448, 1537($\upsilon_{C=C}$), 1596, 1620($\upsilon_{C=N}$), 2927(υ_{C-H}).UV.vis : λ_{max}($CHCl_3$, nm) : 362. Mass spectra (m/z) = 306 $(VO\text{-}L)^+$. Anal. Found (Calc.): $C_{14}H_{13}N_3O_2V$ (306.11): C, 55.76(54.93); H, 4.25(4.25); N, 13.84(13.73).

((7-methyl-N-salicylidene-N'-pyrrolidene)-1,2-ethylenediaminato)oxovanadium(IV) [VO(Mesalpyren)]. Yield: 50% IR(KBr, cm^{-1}) : 970($\upsilon_{V=O}$), 1100(υ_{C-O}),1431, 1535($\upsilon_{C=C}$), 1581, 1593($\upsilon_{C=N}$), 3000 (υ_{C-H}).UV.vis: λ_{max}(CHCl3, nm): 364. Mass spectra (m/z) = 320 $(VO\text{-}L)^+$. Anal. Found (Calc.): $C_{15}H_{15}N_3O_2V$ (320.12): C, 56.31(56.28); H, 4.65(4.68); N, 13.21(13.13).

((7-phenyl-N-salicylidene-N'-pyrrolidene)-1,2-ethylenediaminato)oxovanadium(IV) [VO(Phsalpyren)]. Yield: 55% IR(KBr, cm^{-1}): 981($\upsilon_{V=O}$), 1146(υ_{C-O}), 1442, 1535 ($\upsilon_{C=C}$), 1569; 1590($\upsilon_{C=N}$),3062(υ_{C-H}).UV.vis : λ_{max}($CHCl_3$, nm): 362. Mass spectra (m/z) = 382 $(VO\text{-}L)^+$. Anal. Found (Calc.): $C_{20}H_{17}N_3O_2V$ (382.18): C, 63.00(62.86); H, 4.48(4.45); N, 10.84(10.99).

((N-salicylidene-N'-pyrrolidene)-1,3-propylenediaminato) oxovanadium(IV) [VO(Salpyren)]. Yield: 54%

IR (KBr, cm^{-1}): 978 ($\upsilon_{V=O}$), 1068 (υ_{C-O}), 1434, 1541 ($\upsilon_{C=C}$), 1569, 1598 ($\upsilon_{C=N}$), 2923, 3053 (υ_{C-H}). UV.vis: λ_{max}($CHCl_3$, nm): 360. Mass spectra (m/z) = 320 $(VO\text{-}L)^+$. Anal. Found (Calc.): $C_{15}H_{15}N_3O_2V$ (320.24): C, 56.35(56.25); H, 4.72(4.72); N, 13.15(13.12).

((7-methyl-N-salicylidene-N'-pyrrolidene)-1,3-propylenediaminato)oxovanadium(IV) [VO(Mesalpyren)]. Yield: 54%

IR(KBr, cm^{-1}): 984 ($\upsilon_{V=O}$), 1074 (υ_{C-O}), 1462, 1552 ($\upsilon_{C=C}$), 1625, 1650 ($\upsilon_{C=N}$), 2912, 3030 (υ_{C-H}). UV.vis: λ_{max}($CHCl_3$, nm): 362. Mass spectra (m/z) = 334 $(VO\text{-}L)^+$. Anal. Found (Calc.): $C_{16}H_{17}N_3O_2V$ (334.25): C, 57.42(57.48); H, 5.11(5.12); N, 12.64(12.57).

((7-phenyl-N-salicylidene-N'-pyrrolidene)-1,3-propylenediaminato)oxovanadium(IV) [VO(Phsalpyren)]. Yield: 54%

IR(KBr, cm^{-1}): 980 ($\upsilon_{V=O}$), 1145 (υ_{C-O}), 1462, 1552 ($\upsilon_{C=C}$), 1581, 1593 ($\upsilon_{C=N}$), 2935, 3051 (υ_{C-H}). UV.vis: λ_{max}($CHCl_3$, nm): 364. Mass spectra (m/z) = 396 $(VO\text{-}L)^+$.

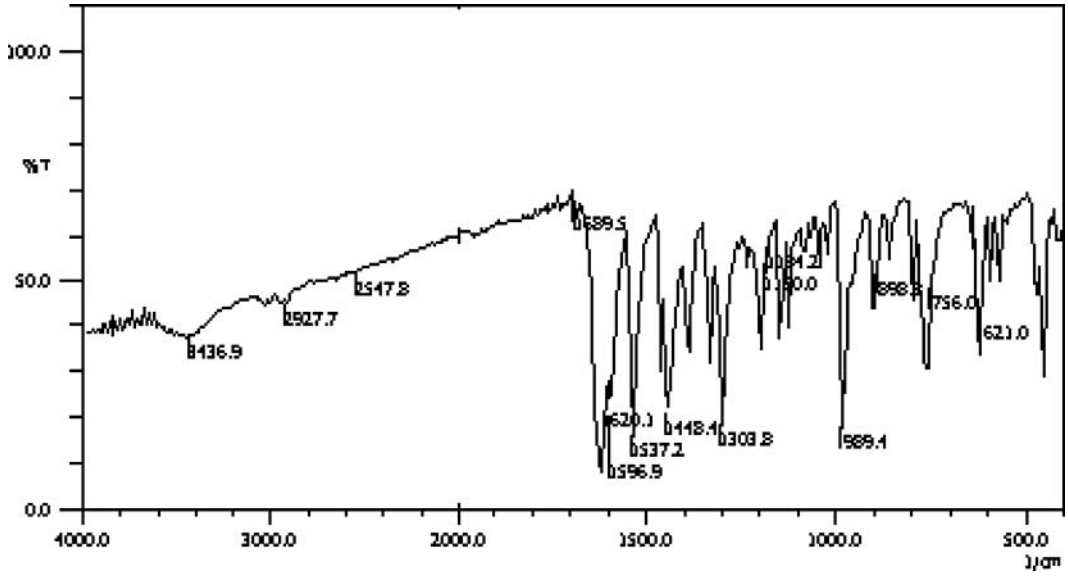

FIG. 2. IR spectra of VO(salpyren).

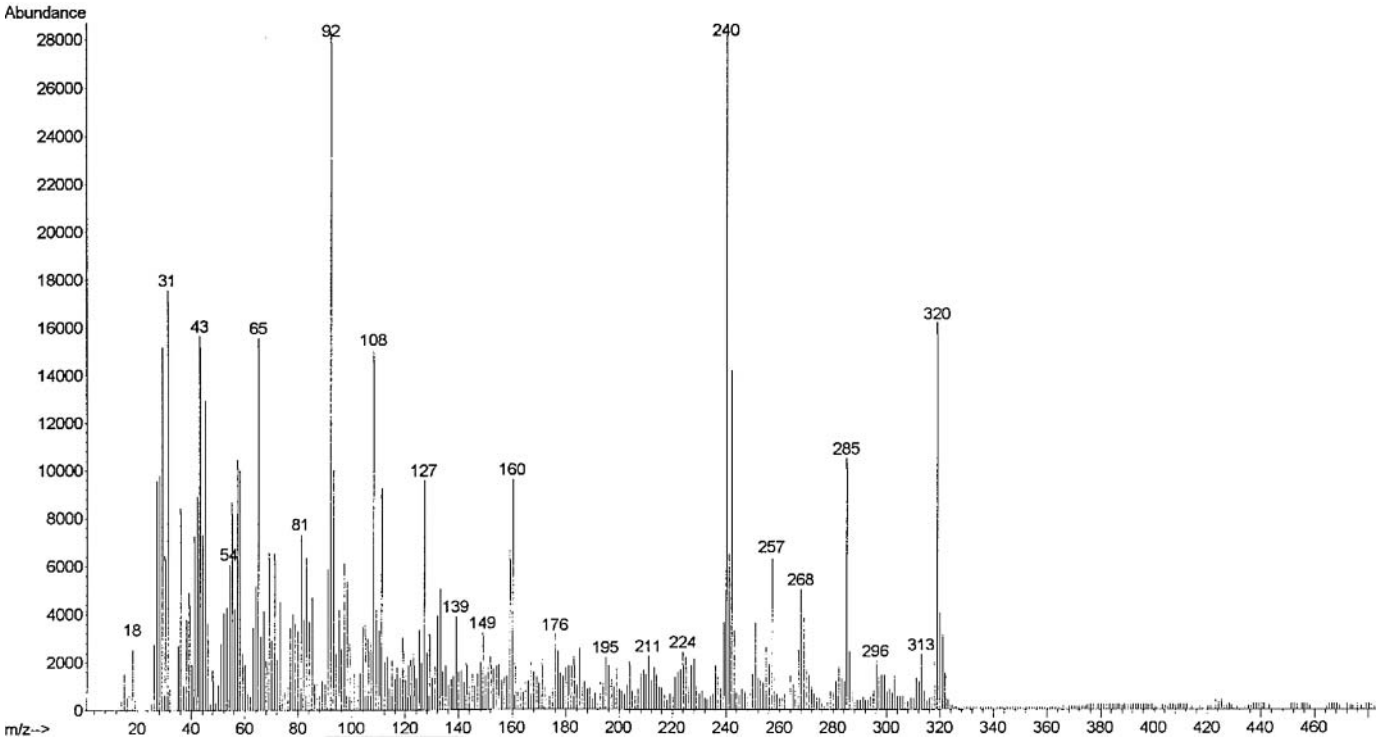

FIG. 3. Mass spectra of VO(mesalpyren).

Anal. Found (Calc.): $C_{21}H_{19}N_3O_2V$ (396.33): C, 63.66(63.64); H, 4.04(4.07); N, 10.62(10.60).

Kinetic Measurements

Kinetic data were determined spectrophotometrically. Pseudo-first-order kinetics for complexation of $VO(acac)_2$ with the ligands were maintained by using much higher $VO(acac)_2$ concentration (∼10–40 times) than that of the ligands. In all cases (runs from 10-40 ± 0.1°C), the procedure involves adding a sample of vanadyl acetylacetone to a solution containing the substrate under N_2 atmosphere. The kinetics were followed at a predetermined wavelength, $\lambda = 362$ nm, where the difference in absorption between the substrate and the product was the largest. The temperature was controlled in a thermostated cell compartment at 10–40 ± 0.1°C, and 10 mm quartz cells were used. The pseudo-first-order rate constants were calculated by fitting the data to $\ln[(A_t\text{-}A_\infty)/(A_0\text{-}A_\infty)]=k_{obs}t$ (where A_t =Absorbance at time t; A_0 =Absorbance at t=0; A_∞ =Absorbance at t= ∞) by means of a linear least-squares computer program. The second order rate constants k_2 were obtained from the slope of the linear plots of k_{obs} *vs*. $[VO(acac)_2]$ (vanadyl conc.). To determine the activation parameters of the kinetics, the absorption measurements were carried out at four different temperatures, i.e., 10, 20, 30 and 40°C, respectively. The activation enthalpy, $\Delta H^{\neq}$ and the activation entropy, $\Delta S^{\neq}$ were obtained from the standard linear Eyring plots of Equation (1):

$$\ln (k_2/T) = -\Delta H^{\#}/RT+\Delta S^{\#} / R + 23.8 \qquad [1]$$

TABLE 1
Pseudo-first-order rate constants 10^3k_{obs} (s^{-1}) for the reaction of mesalpyren with $VO(acac)_2$ in MeOH at different temperatures
[Mesalpyren]= 1.44×10^{-4}M

10^3[VO]/M	0.72	1.44	2.16	2.88	3.60	4.32	5.04	5.76	$k_2/M^{-1}s^{-1}$
10°C	1.3(0.1)	3.2(0.3)	4.7(0.1)	6.7(0.1)	7.0(0.2)	9.11(0.1)	11.3(0.1)	11.9(0.5)	2.1(0.1)
20°C	2.0(0.1)	5.0(0.2)	6.2(0.1)	8.1(0.2)	9.9(0.4)	13.2(0.2)	15.1(0.4)	17.0(0.5)	2.9(0.1)
30°C	3.5(0.1)	5.2(0.1)	7.7(0.2)	10.4(0.2)	12.6(0.3)	16.6(0.1)	18.8(0.5)	21.6(0.6)	3.7(0.1)
40°C	4.7(0.1)	5.8(0.2)	8.3(0.3)	11.6(0.3)	15.5(0.4)	18.6(0.2)	22.8(0.5)	25.2(0.7)	4.4(0.2)

The numbers in parentheses are the standard deviations of k_{obs}.

TABLE 2
Pseudo-first-order rate constants $10^3 k_{obs}$ (s^{-1}) for the reaction of salpyren with $VO(acac)_2$ in MeOH at different temperatures
[Salpyren]= 1.44×10^{-4}M

10^3[VO]/M	0.72	1.44	2.16	2.88	3.60	4.32	5.04	5.76	$k_2/M^{-1}s^{-1}$
10°C	1.2(0.1)	1.9(0.1)	2.8(0.1)	3.1(0.1)	4.3(0.3)	5.2(0.2)	6.2(0.3)	6.9(0.4)	1.1(0.0)
20°C	1.5(0.1)	2.1(0.1)	3.2(0.2)	4.6(0.3)	6.3(0.3)	8.0(0.2)	9.9(0.2)	11.2(0.5)	2.0(0.1)
30°C	2.0(0.1)	3.6(0.2)	5.3(0.3)	7.0(0.2)	9.9(0.6)	12.5(0.3)	13.9(0.2)	15.4(0.6)	2.8(0.1)
40°C	3.5(0.2)	4.1(0.2)	6.8(0.3)	10.2(0.4)	12.7(0.7)	14.7(0.4)	16.7(0.5)	18.8(0.6)	3.2(0.1)

The numbers in parentheses are the standard deviations of k_{obs}.

RESULTS AND DISCUSSION

The observed kinetic data are summarized as a function of [$VO(acac)_2$] and temperature in Tables 1–6.

Under pseudo-first-order conditions, the plots of k_{obs} versus [$VO(acac)_2$] clearly exhibits a zero intercept within the experimental error (Figure 4); confirming firstly the formation of only 1:1 complex and secondly the complex is essentially stable and the reverse reaction is negligible.

The rate law of Equation (2) is compatible with the complex formation according to Equation (3):

$$k_{obs} = k_2[VO(acac)_2] \quad [2]$$

$$VO(acac)_2 + H_2L \rightarrow VO(L) + 2Hacac \quad [3]$$

L = salpyren, mesalpyren, phsalpyren, salpyrpd, mesalpyrpd, phsalpyrpd

The k_2 values in Equation (2) are obtained from the slope of the linear plots of k_{obs} *vs*. the vanadyl concentration [$VO(acac)_2$] (Figure 4).

The spectra in general show clean isosbestic points (Figure 5). For example the isosbestic points observed at 10°C for the reaction of $VO(acac)_2$ with Phsalpyren was at 400 and 341 nm. The deviation in isosbestic points were not observed; these isosbestic points suggest that only one reaction is in progress, (Equation (3)) which indicates that different products have not been produced. Also, the interaction of MeOH solvent with these ligands was tested and it was shown that the interaction was very slow and did not interfere with the direct reaction in Equation (3). The activation parameters $\Delta H^{\#}$, $\Delta S^{\#}$were obtained from the standard linear Eyring plots of $\ln(k_2/T)$ *vs*.1/T (Figure 6).

The results in Tables 1–6 show that there is a linear rate dependence on the concentration of the vanadyl acetylacetone. A typical plot of k_{obs} vs. vanadyl molar concentrations for Mesalpyrpd at different temperature is shown in Figure 4. The linear plots of k_{obs} *vs*. [$VO(acac)_2$] , the large negative values of $\Delta S^{\#}$and the low $\Delta H^{\#}$values(Table 7) suggest an associative (A) mechanism for Equation (3).

The k_2 values trend in $\mathbf{M^{-1}s^{-1}}$for different ligands with $VO(acac)_2$ at 30°C is as follows:

	mesalpyren	salpyren	phsalpyren	mesalpyrpd	salpyrpd	phsalpyrpd
k_2 ($M^{-1}s^{-1}$)	3.7 ± 0.1	2.8 ± 0.1	2.5 ± 0.1	0.3 ± 0.0	0.2 ± 0.0	0.1 ± 0.0

This trend shows that, the k_2 values for Schiff bases with electron releasing methyl group were more than those with electron withdrawing phenyl group. On the other hand, k_2

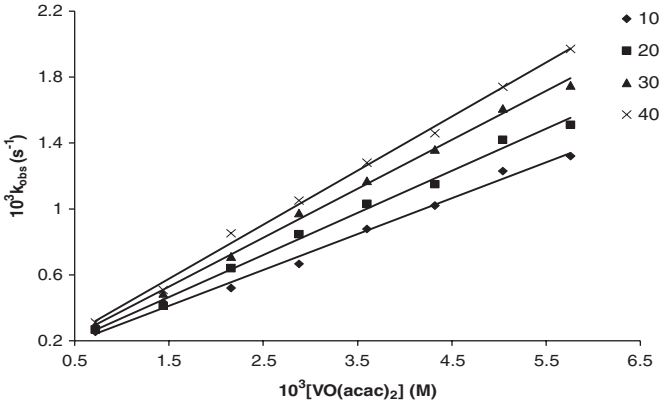

FIG. 4. The plots of k_{obs} *vs*. $VO(acac)_2$ molar concentrations [VO] for mesalpyrpd at different temperatures.

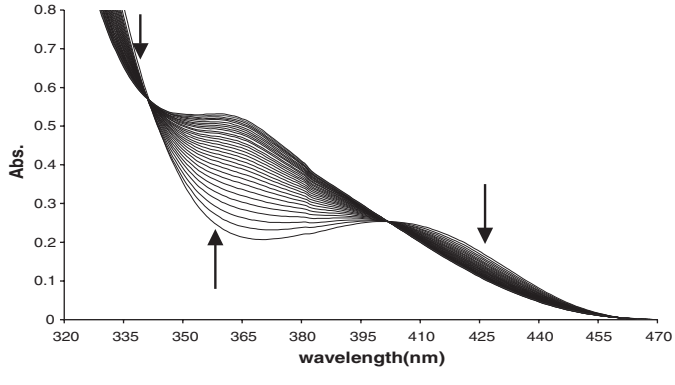

FIG. 5. The absorption spectra of phsalpyren with $VO(acac)_2$ at 10°C in MeOH with the isosbestic points.

TABLE 3
Pseudo-first-order rate constants $10^3 k_{obs}$ (s^{-1}) for the reaction of phsalpyren with $VO(acac)_2$ in MeOH at different temperatures
[Phsalpyren]= 1.44×10^{-4}M

10^3[VO]/M	0.72	1.44	2.16	2.88	3.60	4.32	5.04	5.76	$k_2/M^{-1}s^{-1}$
10°C	0.9(0.0)	1.1(0.0)	1.2(0.0)	2.0(0.1)	2.7(0.1)	3.0(0.2)	3.6(0.2)	4.3(0.3)	0.7(0.0)
20°C	1.0(0.0)	2.2(0.0)	3.9(0.1)	4.8(0.2)	6.0(0.3)	6.8(0.4)	8.1(0.4)	9.1(0.4)	1.6(0.0)
30°C	2.2(0.0)	4.3(0.0)	4.6(0.1)	6.8(0.2)	8.4(0.2)	11.0(0.5)	12.5(0.6)	14.6(0.5)	2.5(0.1)
40°C	2.3(0.0)	4.5(0.1)	6.7(0.2)	8.0(0.4)	11.0(0.6)	13.2(0.6)	15.0(0.7)	17.4(0.7)	3.0(0.1)

The numbers in parentheses are the standard deviations of k_{obs}.

TABLE 4
Pseudo-first-order rate constants $10^4 k_{obs}$ (s^{-1}) for the reaction of mesalpyrpd with $VO(acac)_2$ in MeOH at different temperatures
[Mesalpyrpd]= 1.44×10^{-4}M

10^3[VO]/M	0.72	1.44	2.16	2.88	3.60	4.32	5.04	5.76	$10^2 k_2/M^{-1}s^{-1}$
10°C	2.5(0.1)	4.3(0.1)	5.2(0.2)	6.7(0.2)	8.8(0.3)	10.2(0.2)	12.3(0.2)	13.2(0.4)	21.7(0.7)
20°C	2.7(0.1)	4.1(0.0)	6.4(0.1)	8.5(0.1)	10.3(0.2)	11.5(0.3)	14.2(0.4)	15.1(0.3)	25.5(0.8)
30°C	2.9(0.1)	4.9(0.1)	7.1(0.2)	9.8(0.2)	11.7(0.3)	13.6(0.3)	16.1(0.4)	17.5(0.5)	29.6(0.6)
40°C	3.1(0.1)	5.1(0.2)	8.5(0.2)	10.5(0.2)	12.8(0.3)	14.6(0.5)	17.4(0.5)	19.7(0.5)	32.7(0.8)

The numbers in parentheses are the standard deviations of k_{obs}.

TABLE 5
Pseudo-first-order rate constants $10^4 k_{obs}$ (s^{-1}) for the reaction of salpyrpd with $VO(acac)_2$ in MeOH at different temperatures
[Salpyrpd]= 1.44×10^{-4}M

10^3[VO]/M	0.72	1.44	2.16	2.88	3.60	4.32	5.04	5.76	$10^2 k_2/M^{-1}s^{-1}$
10°C	2.0(0.1)	3.3(0.2)	4.2(0.4)	5.3(0.2)	5.9(0.0)	6.7(0.1)	9.4(0.1)	9.8(0.4)	15.4(1.4)
20°C	2.1(0.4)	3.6(0.5)	4.0(0.6)	6.4(0.2)	6.9(0.5)	8.0(0.9)	9.6(1.3)	10.8(0.7)	17.0(0.8)
30°C	3.0(0.4)	3.6(0.4)	5.2(0.7)	6.3(0.4)	7.2(0.5)	9.0(0.5)	11.2(0.7)	12.8(0.6)	19.7(1.1)
40°C	3.0(0.4)	4.2(0.3)	5.1(0.4)	7.2(0.3)	9.2(0.4)	10.9(0.5)	11.8(0.5)	13.8(0.6)	21.9(0.8)

The numbers in parentheses are the standard deviations of k_{obs}.

TABLE 6
Pseudo-first-order rate constants $10^4 k_{obs}$ (s^{-1}) for the reaction of phsalpyrpd with $VO(acac)_2$ in MeOH at different temperatures
[Phsalpyrpd]= 1.44×10^{-4}M

10^3[VO]/M	0.72	1.44	2.16	2.88	3.60	4.32	5.04	5.76	$10^2 k_2/M^{-1}s^{-1}$
10°C	1.8(0.1)	2.1(0.2)	2.8(0.3)	3.3(0.2)	4.2(0.0)	6.0(0.1)	6.5(0.1)	7.1(0.4)	11.3(0.9)
20°C	1.9(0.1)	2.0(0.2)	3.3(0.2)	3.7(0.4)	4.4(0.5)	6.1(0.3)	7.5(0.3)	8.1(0.4)	13.2(1.0)
30°C	2.1(0.1)	3.0(0.4)	4.1(0.3)	4.9(0.9)	5.6(0.5)	7.3(0.5)	9.1(0.7)	9.5(0.4)	15.5(0.9)
40°C	2.4(0.2)	3.6(0.3)	4.1(0.4)	5.1(0.6)	7.7(0.4)	8.1(0.5)	9.8(0.9)	11.3(0.6)	17.7(1.0)

The numbers in parentheses are the standard deviations of k_{obs}.

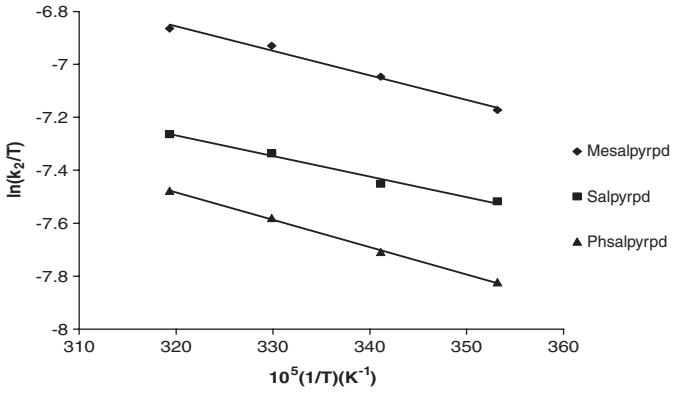

FIG. 6. The Eyring plots for the complexation of $VO(acac)_2$ with different salpyrpd Schiff bases in MeOH.

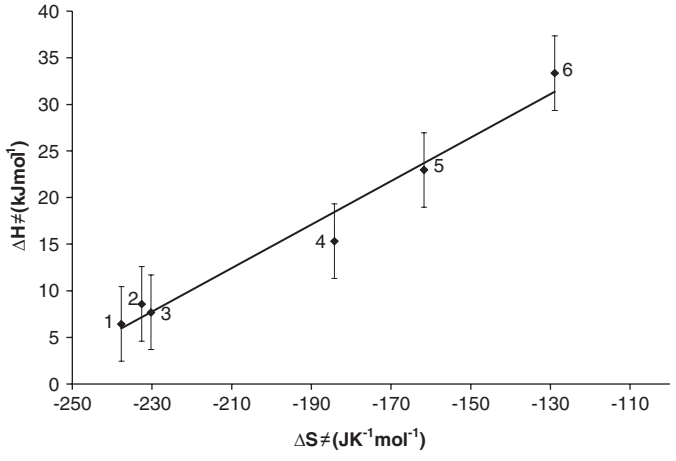

FIG. 7. Correlations between $\Delta H^{\#}$ and $\Delta S^{\#}$ for the complex formation of $VO(acac)_2$ with salpyrpd(1), phsalpyrpd (2), mesalpyrpd (3), mesalpyren (4), salpyren (5), phsalpyren (6).

TABLE 7
Activation parameters $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$ for the reaction of $VO(acac)_2$ with Schiff bases (L) in MeOH

L	$\Delta H^{\#}$/kJmol^{-1}	$\Delta S^{\#}$/JK^{-1}mol^{-1}	[a] $\Delta G^{\#}$/kJmol^{-1}
Mesalpyren	15.3(1.6)	−184.2(5.5)	73.0(2.4)
Salpyren	23.0(4.5)	−161.8(15.1)	73.6(6.5)
Phsalpyren	33.3(6.6)	−128.9(22.1)	73.7(9.5)
Mesalpyrpd	7.7(0.6)	−230.3(1.9)	79.8(0.8)
Salpyrpd	6.4(0.5)	−237.7(1.7)	80.8(0.7)
Phsalpyrpd	8.6(0.2)	−232.6(0.7)	81.4(0.3)

[a]Calculated from $\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$ at T=313 K, the numbers in parentheses are the standard deviations.

values for phsalpyrpd, salpyrpd, mesalpyrpd were lower than phsalpyren, salpyren, mesalpyren, which shows that the trimethylene derivatives are considered to produce a weaker ligand field than the dimethylene derivatives. This is may be due to higher flexibility caused by the trimethylene chain on complex formation.

The plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$gives a good linear relationship for the reaction of $VO(acac)_2$ with salpyren, mesalpyren, phsalpyren, salpyrpd, mesalpyrpd, phsalpyrpd, as shown in Figure 8. The good compensation correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$suggests that an isokinetic relationship exists, which supports the claim that the same mechanism operates for the complex formation.

CONCLUSION

By considering k_2, $\Delta S^{\#}$and $\Delta H^{\#}$values for complexation of six new Schiff base ligands with $VO(acac)_2$the following conclusions have been drawn:

1. The k_2 values for dimethylene derivatives change according to the following trend due to electronic properties: mesalpyren > salpyren > phsalpyren. Also, this trend is observed for trimethylene derivatives.
2. The k_2 values for the trimethylene derivatives are lower than the dimethylene derivatives due to their higher flexibility.
3. The linear plots of k_{obs} *vs*. $[VO(acac)_2]$, the large negative values of $\Delta S^{\#}$and the low values of $\Delta H^{\neq}$ suggest an associative (A) mechanism.

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