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Tungsten(V) binuclear thiocomplexes with diethyldithiocarbamate. Synthesis, spectral, thermal and kinetic studies

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Abstract

We report the synthesis, using reactions in different solvents, and the study of di-μ-sulfido-bis(sulfido *N,N*-diethyldithiocarbamate) di-tungsten(V) adducts with pyridine or substituted pyridines, with formula assigned as W_2S_4(diethyldtc)$_2$B$_2$, where dtc = dithiocarbamate; B = pyridine (Py), 3-methylpyridine (3-MP), 4-methylpyridine (4-MP), 3,5-dimethylpyridine (3,4-DMP), 3-aminopyridine (3-AP) and 4-aminopyridine (4-AP). The complexes obtained have been identified by IR and electronic spectra, magnetic susceptibility measurements and analytical data. We have also studied the thermal behaviour and kinetic parameters, by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), of the thermal decomposition of these adducts in the solid state. From the DSC curves, the activation energies and pre-exponential Arrhenius factors for the endothermic process corresponding to the loss of two moles of coordinated base were calculated. We have also deduced the mechanism of the reaction using a new non-isothermal kinetic method. The effects of steric hindrance and the inductive effects exercised by the functional groups, amino and methyl of the pyridine, in the formation of the adducts are discussed. The relationship between the basicity of the pyridines, IR and electronic spectral data and activation energies has also been explored.

Introduction

Papers about Mo– and W–S complexes and clusters have increased during the last few years. There is no other transition metal for which so many pure and discrete heterometal–S species are known. The relevance to the bioinorganic chemistry of molybdenum and tungsten and also to heterogeneous catalysis has been stressed several times in the literature [1–8].

Although the chemistry of Mo(V) is dominated by binuclear complexes with monoxo, dioxo, dithio and oxo-thio bridges, curiously, similar binuclear complexes of tungsten(V) are not in general known. However we have recently reported the study and characterization of W(V) dimeric complexes with dithiocarbamates and oxines as ligands [9–15].

In this paper we describe the synthesis using reactions in different solvents, characterization and thermal decomposition of the di-μ-sulfido-bis-(sulfido *N,N*-diethyldithiocarbamate) di-tungsten(V) adducts with pyridine or substituted pyridines (3-methyl, 4-methyl, 3,5-dimethyl, 3-amino and 4-aminopyridine), by direct reaction between the complex and the pyridines. The study of these complexes by IR and electronic spectroscopy, magnetic susceptibilities and analytical data, shows that stoichiometry of the complex is 1:1 (ligand:metal) and 2:1 (base:complex) for these adducts.

We have determined the kinetic parameters and the reaction mechanism of the process to be:

$$W_2S_4(\text{diethyldtc})_2B_2(\text{solid}) \longrightarrow W_2S_4(\text{diethyldtc})_2(\text{solid}) + 2B(\text{gas})$$

and we have calculated the activation energy and the pre-exponential Arrhenius factor, in all the adducts synthesized, using a new non-isothermal kinetic method reported previously by us.

The determination of kinetic parameters by non-isothermal methods offers interesting advantages over conventional isothermal studies [16–23]. Only a single sample and fewer data are required and the kinetics can be calculated over an entire temperature range in a continuous manner.

A disadvantage of the non-isothermal methods, when compared with the isothermal techniques, is that the reaction mechanism cannot usually be de-

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termined, and hence the meaning of the kinetics parameters is uncertain. However, with the new proposed method, the reaction mechanism can be determined [24–26].

A comparison between activation energies (E_a), steric or inductive factors, IR and electronic spectral data and pK_b values of the coordinated bases has also been explored.

Experimental

Synthesis

W_2S_4(diethyldtc)$_2$

This was prepared as previously reported [12].

W_2S_4(diethyldtc)$_2B_2$

0.01 mol of W_2S_4(diethyldtc)$_2$ was dissolved in 0.02 mol of the organic base (3-methyl, 4-methyl and 3,5-dimethylpyridine) or in an ethanolic solution of 0.02 mol of 3-amino and 4-aminopyridine and heated in a water bath for about 15 min. After cooling for 2 days, the adducts, obtained as a brownish powder, were separated by filtration *in vacuo* and dried over P_4O_{10} in a nitrogen atmosphere.

$W_2S_4(C_5H_{10}NS_2)_2(C_5H_5N)_2$. *Anal.* Calc.: W, 38.72; C, 25.27; N, 5.90; H, 3.16; S, 26.96. Found: W, 37.89; C, 24.45; N, 5.63; H, 3.05; S, 25.45%. Yield: 43%. μ:0.1 BM.

$W_2S_4(C_5H_{10}NS_2)_2(C_5H_4N,3\text{-}CH_3)_2$. *Anal.* Calc.: W, 37.61; C, 27.00; N, 5.73; H, 3.48; S, 26.18. Found: W, 36.67; C, 26.08; N, 4.54; H, 2.80; S, 25.06%. Yield: 49%. μ:0.07 BM.

$W_2S_4(C_5H_{10}NS_2)_2(C_5H_4N,4\text{-}CH_3)_2$. *Anal.* Calc.: W, 37.61; C, 27.00; N, 5.73; H, 3.48; S, 26.18. Found: W, 36.34; C, 26.44; N, 5.06; H, 2.76; S, 25.62%. Yield: 40% μ: 0.03 BM.

$W_2S_4(C_5H_{10}NS_2)_2[C_5H_3N(CH_3)_2]$. *Anal.* Calc.: W, 36.53; C, 28.64; N, 5.57; H, 3.78; S, 25.45. Found: W, 36.43; C, 27.98; N, 5.02; H, 2.98; S, 24.40%. Yield: 48%. μ: 0.00 BM.

$W_2S_4(C_5H_{10}NS_2)_2(C_5H_4N,3\text{-}NH_2)_2$. *Anal.* Calc.: W, 37.53; C, 24.50; N, 8.57; H, 3.27; S, 26.13. Found: W, 37.23; C, 23.32; N, 8.09; H 2.88; S, 25.43%. Yield: 45%. μ: 0.05 BM.

$W_2S_4(C_5H_{10}NS_2)_2(C_5H_4N,4\text{-}NH_2)_2$. *Anal.* Calc.: W, 37.53; C, 24.50; N, 8.57; H, 3.27; S, 26.13. Found: W, 37.12; C, 23.17; N, 7.97; H, 2.02; S, 25.12%. Yield: 52%. μ: 0.02 BM.

Instrumentation

Elemental analyses were performed in a Perkin-Elmer 240 B elemental analyzer. Tungsten was determined by atomic absorption with a Perkin-Elmer 430 atomic absorption spectrophotometer, after decomposing the complexes with a 1:1 mixture of concentrated nitric and sulfuric acid. Magnetic susceptibility determinations were performed at room temperature on a Mettler H-51 AR balance and a type C Newport electromagnet. Reported magnetic moments are corrected for ligand diamagnetism. IR spectra were measured on a Perkin-Elmer 283 spectrophotometer. Vis–near-UV spectra of the compounds were measured on a Beckman DU7 spectrophotometer, using complex solutions in DMSO. Thermogravimetric analysis and differential scanning calorimetry were performed between 25 and 600 °C on a Mettler TA 3000 system fitted with a Mettler TG-50 thermobalance and a Mettler DSC-20 differential scanning calorimeter. The scanning rate used was 2 °C min^{-1} and samples of about 5 mg were used, so as to render insignificant the temperature non-uniformity within the sample. An aluminium pan was used under a dynamic nitrogen atmosphere. The instrument calibration was checked periodically with standard samples of indium (99.99% purity). Several runs were made.

Kinetic studies

The rate of the thermal decomposition reaction of a solid can be expressed by the Arrhenius equation

$$d\alpha/dt = Ae^{E_a/RT}f(\alpha) \qquad (1)$$

In eqn. (1), α is the fraction of material which has reacted at time t, E_a is the activation energy, $f(\alpha)$ is a function which depends on the actual reaction mechanism and A is the pre-exponential Arrhenius factor.

The mathematical expressions of the functions $f(\alpha)$ corresponding to some of the mechanisms of thermal decomposition found in the literature [16] are collected in Table 1.

When the temperature of the sample is increased at a constant rate, we can write eqn. (2), where β is heating rate, dT/dt.

TABLE 1. Kinetic equations

Mechanism (rate-controlling process)	$f(\alpha)$
D1 (one-dimensional diffusion)	$(1/2\alpha)$
D2 (two-dimensional diffusion)	$[-\ln(1-\alpha)]^{-1}$
D3 (three-dimensional diffusion: Jander equation)	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
D4 (three-dimensional diffusion: Ginstling–Brounshtein equation)	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$
F1 (random nucleation)	$(1-\alpha)$
R2 (phase-boundary reaction: cylindrical symmetry)	$2(1-\alpha)^{1/2}$
R3 (phase-boundary reaction: spherical symmetry)	$3(1-\alpha)^{2/3}$

$$\mathrm{d}\alpha/\mathrm{d}T = \alpha' = (A/\beta)\mathrm{e}^{-E_aRT}f(\alpha) \qquad (2)$$

By differentiating the logarithmic form of eqn. (2) with respect to dln(1)α), we obtain eqn. (3).

$$\mathrm{d}\ \ln\ \alpha'/\mathrm{d}\ \ln(1-\alpha) = -(E_a/R)[\mathrm{d}(1/T)/\mathrm{d}\ \ln(1-\alpha)] + [\mathrm{d}\ \ln f(\alpha)/\mathrm{d}\ \ln(1-\alpha)]$$

or

$$\Delta\ \ln\ \alpha'/\Delta\ \ln(1-\alpha) = -(E_a/R)[\Delta(1/T)/\Delta\ \ln\ (1-\alpha)] + [\Delta\ \ln f(\alpha)/\Delta\ \ln(1-\alpha)]$$

and

$$[\Delta\ \ln\ \alpha' - \Delta\ \ln f(\alpha)]/\Delta\ \ln(1-\alpha) = (-E_a/R)[\Delta(1/T)/\Delta\ \ln(1-\alpha)] \qquad (3)$$

Thus, the plots of $[\Delta \ln \alpha') - \Delta \ln f(\alpha)]/\Delta \ln(1-\alpha)$ versus $[\Delta(1T)/\Delta \ln(1-\alpha)]$ should be a straight line with a slope $-E_a/R$, irrespective of the $f(\alpha)$ employed. However, we can select the $f(\alpha)$ that best fits the actual mechanism of the reaction studied by means of the intercept value, which in ideal agreement with eqn. (3) should be zero.

In order to test the validity of the above conclusions we have substituted the seven forms of $f(\alpha)$ into the Arrhenius equation in logarithmic form (2), giving eqn. (4).

$$\ln \alpha' = \ln(A/\beta) - E_a/RT + \ln f(\alpha)$$

or

$$\ln \alpha' - \ln f(\alpha) = \ln(A/\beta) - E_a/RT \qquad (4)$$

The plot of $\ln\alpha' - \ln f(\alpha)$ versus $1/T$ should be a straight line with a slope $-E_aR$ and intercept $\ln(A/\beta)$.

If the proposed mechanism is correct, the activation energy value should be the same as that obtained previously.

Discussion

Magnetic susceptibility

All the complexes studied present very low values for the magnetic moments (0.10–0.00 BM), as occurs in similar W(V) complexes [9–15], which can be attributed to an interaction through the bridge atoms or to the possible formation of a direct metal–metal bond, as has been proved for similar molybdenum(V) oxo complexes [27–29].

IR spectra

The IR spectra show, in all cases, a band in the range 540–504 cm^{-1}, which we attribute to the vibration of the terminal W=S bond. If we compare the complex W_2S_4(diethyldtc)$_2$ with the adducts W_2S_4(diethyldtc)$_2B_2$, one observes that the adducts show the W=S band displaced to lower frequencies (526–504 cm^{-1}) than the complex (540–530 cm^{-1}). This displacement can be attributed to the different basicity of the pyridine or substituted pyridine employed [30, 31]. The pK_b value reflects the basicity of the ligand towards the proton. It may be assumed that the pK_b of the ligand provides a measure of the ability of the ligand to form σ-bonds to metal ions. In general (see Table 2), the greater the basicity the lower the frequency of the W=S vibration.

The IR spectra of the adducts exhibit a band over 349–334 cm^{-1}, which is assigned to the stretching vibration of the W–N(base) bond [32–34]. The frequencies of this band listed in decreasing order are: W_2S_4(diethyldtc)$_2$(4-AP)$_2$ > W_2S_4(diethyldtc)$_2$(3-AP)$_2$ > W_2S_4(diethyldtc)$_2$(3,5-DMP)$_2$ > W_2S_4(diethyldtc)$_2$-(3-MP)$_2$ > W_2S_4(diethyldtc)$_2$(4-MP)$_2$ > W_2S_4(diethyl-dtc)$_2$Py$_2$.

These differences can be attributed to the electronic donation of the pyridine or substituted pyridine to the tungsten (N → W) which increases the electron density on the metal d-orbitals and consequently the $p_\pi \rightarrow d_\pi$ donation from the sulfur atom to tungsten is expected to be reduced to an extent which depends upon the donor ability of the base. As a result there

TABLE 2. IR absorption maxima, in cm^{-1}, of tungsten(V) thiocomplexes

Compound	νW=S	ν_aW–S_b	ν_sW–S_b	νC–N	νC–S	νW–N
W_2S_4(diethyldtc)$_2$	540–530	457	365	1517	1080	
W_2S_4(diethyldtc)$_2$(Py)$_2$	526	455	362	1515	1082	334
W_2S_4(diethyldtc)$_2$(3-MP)$_2$	521	459	365	1512	1084	339
W_2S_4(diethyldtc)$_2$(4-MP)$_2$	524	457	367	1516	1075	335
W_2S_4(diethyldtc)$_2$(3,5-DMP)$_2$	515	455	364	1513	1079	342
W_2S_4(diethyldtc)$_2$(3-AP)$_2$	511	460	365	1515	1080	342
W_2S_4(diethyldtc)$_2$(4-AP)$_2$	504	458	367	1511	1078	349

TABLE 3. Electronic absorption spectra of tungsten(V) thiocomplexes

Compound	ν (cm^{-1})	ϵ (M^{-1} cm^{-1})	Transition
W_2S_4(diethyldtc)$_2$	16892	213	$^2B_2 \rightarrow {}^2B_1$
	20202	3640	charge transfer
	22075	3228	charge transfer
	26667	6453	charge transfer
	29940	19548	$n \rightarrow n^*$
	32258	17604	$\pi \rightarrow \pi^*$
	35088	32912	$n \rightarrow \sigma^*$
W_2S_4(diethyldtc)$_2$(Py)$_2$	17422	119	$^2B_2 \rightarrow {}^2B_1$
	20325	2854	charge transfer
	22222	3672	charge transfer
	26316	8043	charge transfer
	30303	21342	$n \rightarrow n^*$
	32051	15322	$\pi \rightarrow \pi^*$
	34843	34307	$n \rightarrow \sigma^*$
W_2S_4(diethyldtc)$_2$(3-MP)$_2$	17606	206	$^2B_2 \rightarrow {}^2B_1$
	20408	3114	charge transfer
	21739	4723	charge transfer
	26525	7529	charge transfer
	30120	14520	$n \rightarrow n^*$
	32362	22719	$\pi \rightarrow \pi^*$
	35714	48065	$n \rightarrow \sigma^*$
W_2S_4(diethyldtc)$_2$(4-MP)$_2$	17422	136	$^2B_2 \rightarrow {}^2B_1$
	20325	2997	charge transfer
	21978	4075	charge transfer
	26316	6428	charge transfer
	30488	17083	$n \rightarrow n^*$
	32154	19768	$\pi \rightarrow \pi^*$
	35971	39640	$n \rightarrow \sigma^*$
W_2S_4(diethyldtc)$_2$(3,5-DMP)$_2$	17699	204	$^2B_2 \rightarrow {}^2B_1$
	20121	2173	charge transfer
	21505	3249	charge transfer
	26667	7983	charge transfer
	30211	16654	$n \rightarrow n^*$
	32258	22473	$\pi \rightarrow \pi^*$
	35211	35245	$n \rightarrow \sigma^*$
W_2S_4(diethyldtc)$_2$(3-AP)$_2$	17857	237	$^2B_2 \rightarrow {}^2B_1$
	20408	2567	charge transfer
	22124	4091	charge transfer
	26596	6971	charge transfer
	30303	14309	$n \rightarrow n^*$
	31746	20017	$\pi \rightarrow \pi^*$
	35587	31376	$n \rightarrow \sigma^*$
W_2S_4(diethyldtc)$_2$(4-AP)$_2$	18349	389	$^2B_2 \rightarrow {}^2B_1$
	20202	2140	charge transfer
	21978	3834	charge transfer
	26455	6213	charge transfer
	29851	13724	$n \rightarrow n^*$
	32573	22054	$\pi \rightarrow \pi^*$
	35461	33515	$n \rightarrow \sigma^*$

will be a lowering of the W=S bond (hence ν(W=S)) and a greater frequency of the W–N bond.

We assign the bands corresponding to the W–S–W bridge, which appear at 460 and 365 cm^{-1}, to the antisymmetric and symmetric stretching mode, respectively.

The IR spectra of these complexes show the C–N and C–S vibrations at 1515 and 1080 cm^{-1}. The

TABLE 4. ΔH, α, T and α' obtained from the DSC curve of the complex W_2S_4(diethyldtc)$_2$Py$_2$

ΔH (mJ)	α	T (°C)	α' (K^{-1})
184.51	0.10383	120.0	0.01293
236.37	0.13301	122.0	0.01580
297.60	0.16746	124.0	0.01940
375.82	0.21148	126.0	0.02442
469.57	0.26423	128.0	0.02823
578.19	0.32536	130.0	0.03376
709.13	0.39904	132.0	0.03915
857.08	0.48229	134.0	0.04526
1030.10	0.57965	136.0	0.05100
1217.60	0.68516	138.0	0.05531
1416.20	0.79692	140.0	0.05388
1588.30	0.89376	142.0	0.04238

TABLE 5. Results obtained by using the seven mechanisms for the plot of $\Delta\ln\alpha' - \Delta\ln f(\alpha)/\Delta\ln(1-\alpha)$ vs. $\Delta(1/T)/\Delta\ln(1-\alpha)$ for the complex W_2S_4(diethyldtc)$_2$Py$_2$

Mechanism	r	m	i	E_a (kJ mol^{-1})
D1	−0.99774	−36935.22	0.76519	307 ± 2
D2	−0.99776	−37222.88	0.36008	309 ± 3
D3	−0.99776	−37189.72	−0.15077	309 ± 3
D4	−0.99776	−37189.77	0.18256	309 ± 3
F1	−0.99988	−17519.59	−0.48593	145 ± 1
R2	−0.99999	−17519.59	0.00654	145 ± 1
R3	−0.99989	−17519.59	−0.15259	145 ± 1

displacement to greater frequencies for the C–N band and to lower frequencies for the C–S band, in comparison with the sodium dithiocarbamate, is indicative of bidentate ligands.

Visible and UV spectra

The electronic spectra of the compounds obtained is in accordance with the Ballhausen–Gray and Gray–Hare schemes [35, 36] for a square pyramidal structure for the complex and a distorted octahedral structure for the adducts.

The electronic spectra for all the complexes present a band in the 18 300–16 900 cm^{-1} region, which can be assigned to a $^2B_2 \rightarrow {}^2B_1$ transition. This band shows a greater or lesser bonding force from the tungsten to the ligand. Therefore the band is displaced to higher frequencies in the adducts, because the introduction of the base in the six-coordination position and the '*trans*' effect strengthen the ligand–tungsten σ-bond, as we have observed in the IR spectra (see Table 3).

In the visible zone we can detect three other bands at 20 000, 22 000 and 27 000 cm^{-1} that we attribute to charge transfer transitions. The band which appears at 22 000 cm^{-1} can be attributed to a $S^{2-} \rightarrow W(V)$ charge transfer, as has been observed in other transition metal complexes with sulfur bridge [37, 38].

In the UV zone, three transitions are detected at 30 000, 32 000 and 35 000 cm^{-1} attributable to intraligand transitions like $n \rightarrow n^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$, respectively.

DSC, TGA and kinetic studies

On the DSC curves of all compounds, a first endothermic peak is observed. The mass loss accompanying this transition, corresponds on the TG curves to the loss of two moles of coordinated base to tungsten atoms, the residue being W_2S_4(diethyldtc)$_2$ in all cases.

Table 4 shows the data obtained from the DSC curve of the adduct W_2S_4(diethyldtc)$_2$Py$_2$, α being the reacted fraction at time t and $\alpha' = d\alpha/dt$.

We have plotted $[\Delta\ln\alpha' - \Delta\ln f(\alpha)]/\Delta\ln(1-\alpha)$ versus $\Delta(1/T)/\Delta\ln(1-\alpha)$. From these representations, we can calculate the activation energy of the process. Table 5 shows the results for r (correlation coefficient), m (slope), i (intercept value) and E_a (activation energy) obtained for the seven mechanisms.

We can observe that, in all cases the correlation coefficients (r), are very near to unity, consistent with the results of Criado *et al.* [39]. Nevertheless, only when the analysis was performed with the

TABLE 6. Thermal and kinetic parameters for the complexes W_2S_4(diethyldtc)$_2$B$_2$

Compound	Mechanism	ΔH (kJ/mol)	E_a (kJ/mol)	A (s^{-1})	pK_b
W_2S_4(diethyldtc)$_2$(Py)$_2$	R2	22.3 ± 0.6	145 ± 1	$(3.5 \pm 0.3) \cdot 10^{13}$	8.87
W_2S_4(diethyldtc)$_2$(3-MP)$_2$	R2	27.2 ± 0.8	170 ± 1	$(3.6 \pm 0.3) \cdot 10^{20}$	8.32
W_2S_4(diethyldtc)$_2$(4-MP)$_2$	R2	25.6 ± 0.1	163 ± 1	$(7.0 \pm 0.6) \cdot 10^{9}$	7.98
W_2S_4(diethyldtc)$_2$(3,5-DMP)$_2$	R2	35.9 ± 0.8	195 ± 2	$(1.4 \pm 0.2) \cdot 10^{27}$	7.85
W_2S_4(diethyldtc)$_2$(3-AP)$_2$	R2	40.8 ± 0.9	214 ± 2	$(7.8 \pm 0.8) \cdot 10^{32}$	7.49
W_2S_4(diethyldtc)$_2$(4-AP)$_2$	R2	32.5 ± 0.4	270 ± 3	$(2.16 \pm 0.2) \cdot 10^{27}$	4.88

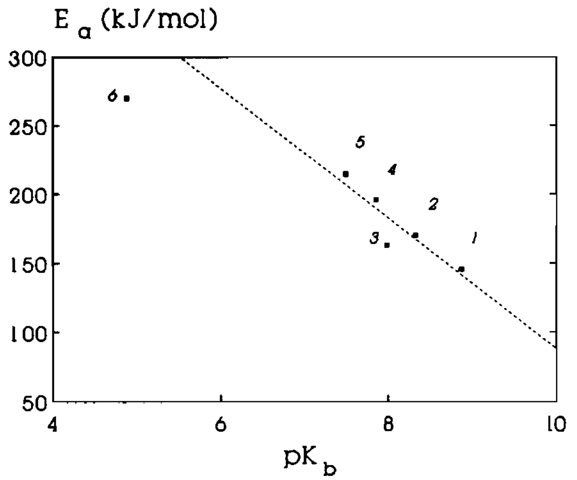

Fig. 1. Activation energy for decomposition of W_2S_4-(diethyldtc)$_2$, B_2, complexes function of pK_b. Points 1–6 correspond to complexes of Py, 3-MP, 4-MP, 3,5-DMP, 3-AP and 4-AP respectively.

mechanism R2 does the straight line present an intercept value close to zero.

Therefore, according with our proposed method, we deduce that the thermal decomposition of the complex [W_2S_4(diethyldtc)$_2$Py$_2$] and the loss of pyridine is carried out by a R2 mechanism (phase boundary reaction: cylindrical symmetry) with a function $f(\alpha) = 2(1-\alpha)^{1/2}$, an activation energy $E_a = 145 \pm 1$ kJ mol^{-1} and a pre-exponential Arrhenius factor $A = 3.5 \pm 0.3) \times 10^{13}$ s^{-1}.

The results obtained for the compounds studied are listed in Table 6.

We can assume that, the thermal decomposition and loss of coordinated base of the adducts with pyridine, 3-methylpyridine, 4-methylpyridine, 3,5-dimethylpyridine, 3-aminopyridine and 4-aminopyridine follows a R2 mechanism.

If we compare the results, in general, as can be seen from the data in Table 6, the greater the basicity of the base employed, the higher the activation energy and the pre-exponential Arrhenius factor for the process of the loss of the base. The outstanding exception is the 4-MP and 4-AP adducts, which can be attributed to the existence of resonance structures and a pronounced effect on the stability of the complex [26, 30, 31]. It can be seen that the steric impediment of the 3,5-DMP does not modify the kinetic parameters.

The plot of pK_b versus activation energy presented in Fig. 1, shows that, except for the 4-MP and 4-AP adducts, a very satisfactory correlation was obtained. It is obvious from this Figure that activation energy is linearly related to the basicity of the ligands.

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