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THERMAL STUDY OF RUTHENIUM(II) COMPLEXES CONTAINING PYRIDINE-2,6-DIIMINES

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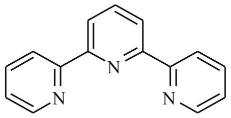
Thermal behaviors of mono- and binuclear Ru(II)-pydim complexes: [PydimCl$_2$RuL] (Pydim: pyridine-2,6-diimine; 2: L=NCMe; 3: L=PPh$_3$) and [PydimCl$_2$Ru(L–L)RuCl$_2$Pydim] (4: L–L=pyrazine; 5: L–L=4,4'-bipyridine) have been studied in nitrogen atmosphere using TG/DTG and DTA techniques. The decompositions of complexes occur in stepwise. The values of activation energy, E_a, and reaction order, n of the thermal decomposition were calculated by means of several methods such as Coats–Redfern (CR), MacCallum–Tanner (MT), Horowitz–Metzger (HM), van Krevelen (vK), Madhusudanan-Krishnan–Ninan (MKN) and Wanjun–Yuwen–Hen–Cunxin (WYHC) based on the single heating rate. Most appropriate method was determined for each decomposition step according to the least-squares linear regression.

Keywords: *activation energy, ruthenium(II) complexes, thermal behaviour*

Introduction

Complexes of transition metals with tridentate triamine ligands are of considerable interest due to their structural and material properties such as terpyridine molecule (I) have been the subject of numerous studies concerning analytical applications [1, 2]. Various pyridine-2,6-diimines (II) (pydim) which are analogs of terpyridine have also been studied as catalyst for many catalytic applications [3–9]. This family of catalysts has attracted great interest, both in academia and in industry [10]. Although a lot of pydim-based transition metal complexes have been reported, examples of the related ruthenium complexes are scarce. While their structural properties have been examined extensively [7, 8, 11, 12], thermal properties of these compounds are rare in the literature. There clearly remains much to investigate in the area of thermal properties of Ru(II)-pydim compounds. In materials science, thermal properties have crucial importance.



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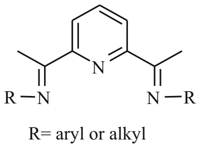

II

The non-isothermal thermogravimetry (TG) with a linear temperature growth is a method frequently used to characterize materials from their thermal behavior standpoint. In addition, it enables to determine apparent kinetic parameters of heterogeneous reactions (the reaction order n, the activation energy E, and the frequency factor A). Considerable attention is paid to the kinetic parameters calculation from TG curves. New calculation methods are still being published [13, 14]. A number of papers are devoted to comparing these methods [15] or to their critical assessment [16]. Strezov [17] was investigated using calorimetric technique the effect of heating rate on the thermal properties of coal. Also, Kök [18, 19] was estimated the thermal analysis and kinetics of several coal and oil shale samples by using the same method based on the single heating rate. Takahashi [20] has investigated the thermal stabilities of the Ni(II)-complexes with 4-iodopyrazole. Kinetic analysis of thermal decomposition of some Co-complexes of unsymmetrical *Vic*-dioximes ligands have been studied by Sahin *et al.* [21] using the various thermoanalytical methods. The thermal stabilities of bis salicylidene adipic dihydrazone derivatives were investigated by Issa *et al.* [22] using thermal and elemental analytical methods. Also, Doğan *et al.* [23] have investigated the thermal behavior, kinetic and thermodynamic parameters of imidazolinium and benzimidazolium bromide salts with pentafluorobenzyl substitutents in a nitrogen atmosphere with TG/DTG and DTA.

On the other hand, a similar study using isothermal function by various methods on rho-

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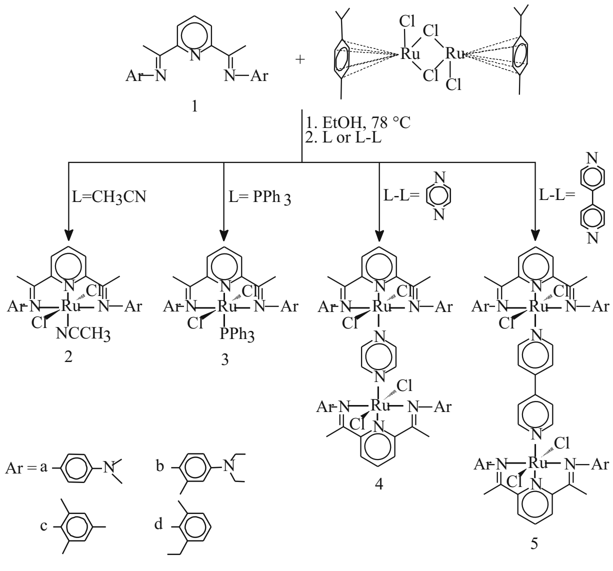
dium(III)-pentamethylcyclopentadienyl and ruthenium(II)-arene derivatives has been reported [24, 25]. In this work, we described the thermal behaviors of mono- and binuclear ruthenium(II)-pydim complexes and determined the kinetic parameters such as the reaction order, *n* and activation energy, E_a of the thermal decomposition by means of CR, MC, HM, vK, MKN and WYHC methods.

Experimental

All compounds have been described elsewhere [26, 27]. Ru(II)-pydim complexes were synthesized by the following general method (Scheme 1): an ethanolic solution (15 mL) of 1.16 Eq. of the respective ligand (1 mmol) was mixed with $[RuCl_2(p\text{-cymene})]_2$ (306 mg; 0.5 mmol). The reaction mixture was refluxed for 10 h. The resulting solution was cooled to room temperature and added L (2: L=NCMe; 3: L=PPh_3) or L–L (4: L–L=pyrazine; 5: L–L=4,4'-bipyridine). The mixture was heated under reflux for further 2 h. The volatiles were removed. The residue was dissolved in CH_2Cl_2 (10 mL) and was precipitated by addition of ether (30 mL).



Scheme 1 Pydims and Ru(II)-pydim complexes studied by thermogravimetric methods

Apparatus

The DTA and TG curves were obtained with TG-DTA Perkin-Elmer Diamond system apparatus. The measurements were performed by using a dynamic nitrogen atmosphere at a flow rate of 200 mL min^{-1} up to 1000°C. The heating rate was 10°C min^{-1} and the sample sizes ranged in mass from 8 to 10 mg contained in platinum crucible. All the experiments were performed twice for repeatability and the results show good reproducibility with the smaller variations in the kinetic parameters. α-Al_2O_3 is used as a reference material.

Results and discussion

Thermal stability

Pydims, the mono- and binuclear Ru(II)-pydim complexes were studied by thermogravimetric analysis from ambient temperature to 1000°C in nitrogen atmosphere. Typical TG/DTG and DTA curves for compounds in the nitrogen atmosphere are present in Figs 1–5. The initial and final temperatures and total mass losses for each decomposition step in the thermal decomposition of complexes are given Table 1, together with temperatures of greatest rate of decomposition (DTG_{max}), evolved moiety and the theoretical percentage mass losses.

Pydim ligands

From TG curves (Fig. 1), 1a–d exhibited one step decomposition process. Also, exothermic thermal effect at 143, 178, 155 and 190°C in DTA profiles correspond to the melting point of 1a, b, c and d ligands, respectively. The reaction orders and activation energies for 1a–d pydim-ligands were found to be 1.90 and 132.96 kJ mol^{-1}, 1.30 and 107.33 kJ mol^{-1}, 0.4 and

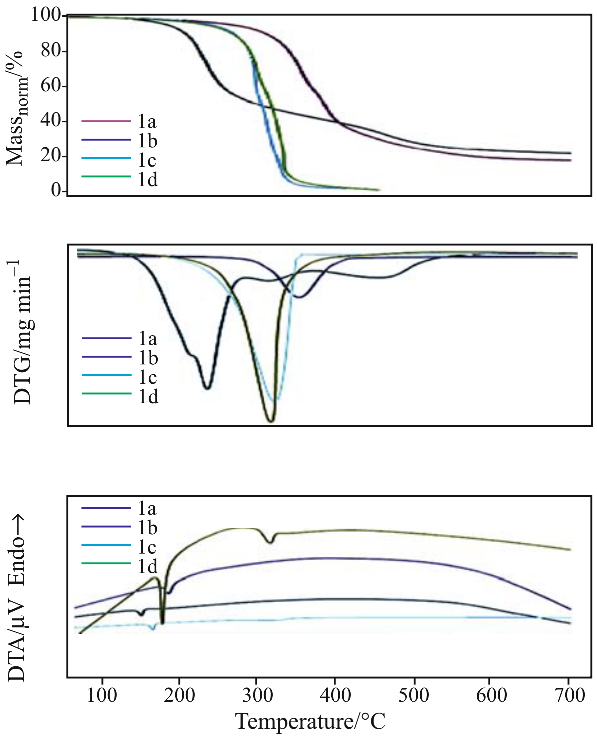


Fig. 1 TG/DTG and DTA curves of pydim ligands

Table 1 TG/DTG and DTA data for the binuclear and mononuclear Ru(II)-pydim complexes

Complexes	Step	DTA$_{max}$/ °C	DTG$_{max}$/ °C	Temperature range/°C	DTA	Mass loss/%, found (calc.)	Assignment
1a	I	178	333	275–362	exo	85.1 (–)	
	residue	>362					
1b	I	143	220	184–261	exo	81.8 (–)	
	residue	>261					
1c	I	155,310	310	227–316	exo, exo	98.2 (–)	
	residue	>316					
1d	I	190,314	301	198–315	endo, endo	99.8 (–)	
	residue	>315					
2a	I		127	53–188		6.6 (6.5)	NCMe
	II	261	272	188–384	exo	14.3 (14.4)	$2NMe_2$
	IIIa	416	427	384–570	exo	13.0 (12.4)	1/2Ph
	IIIb	661	661	592–783	exo	13.3 (12.4)	1/2Ph
	residue	>783				52.8 (54.3)	
2b	I		55	44–140		5.80 (5.1)	NCMe
	II		220	140–340		19.3 (20.6)	$2NEt_2$
	IIIa	400	390	340–520	exo	12.8 (12.5)	$2PhCH_3$
	IIIb		565	546–685		13.4 (12.5)	$2PhCH_3$
	IV		805	715–878		10.2 (11.4)	$1/2Cl_2$
	residue	>878				38.2 (37.9)	
2c	I		32	35–63		4.76 (4.75)	NCMe
	II		169	63–191		6.54 (5.81)	$1/2Cl_2$
	III		277	191–313	exo	6.84 (5.81)	$1/2Cl_2$
	IV	424	424	342–545		19.0 (19.5)	$C_6H_2Me_3$
	residue	>545				62.4 (64.1)	
2d	I		141	55–216		6.60 (6.80)	NCMe
	II		278	216–299		10.2 (11.9)	Cl_2
	III	404	410	299–552	exo	17.2 (19.9)	$4C_6H_3MeEt$
	residue	>552				65.3 (68.4)	
3a	I	343	328	294–377	exo	29.3 (31.4)	PPh_3
	II		416	377–490		11.2 (10.5)	$2NMe_2$
	residue	>490				59.0 (58.1)	
4a	I		406	229–590		36.4 (37.5)	$4PhNMe_2$
	II		609	590–792		12.8 (12.0)	$C_{10}N_2H_8$
	residue	>792				48.7 (50.5)	
4b	I	372	372	302–446	exo	21.5 (20.7)	$4NEt_2$
	residue	>449				78.3 (79.3)	
4c	I		189	97–274	exo	18.5 (19.5)	$1/2C_6H_2Me_3$
	II	364	374	274–441		19.2 (19.5)	$1/2C_6H_2Me_3$
	residue	>441				62.0 (61.0)	
4d	I	402	371	331–440	exo	39.0 (39.1)	$4C_6H_3MeEt$
	residue	>440				59.2 (60.9)	
5b	I	409	423	282–446	exo	44.2 (44.5)	$4PhCH_3NEt_2$
	II		611	497–705		10.7 (10.0)	$C_{10}N_2H_8$
	III		775	719–888		9.36 (9.7)	$2Cl_2$
	residue	>888				37.3 (35.8)	

Table 1 Continues

Complexes	Step	DTA_{max}/ °C	DTG_{max}/ °C	Temperature range/°C	DTA	Mass loss/%, found (calc.)	Assignment
5c	I	253	259	172–296	exo	19.7 (18.0)	$1/2C_6H_2Me_3$
	II	395	384	296–481	exo	18.2 (18.0)	$1/2C_6H_2Me_3$
	residue	>481				63.2 (64.0)	
5d	I	381	366	149–535	exo	34.9 (36.7)	$4C_6H_3MeEt$
	II		603	545–779	exo	11.7 (12.0)	$C_{10}N_2H_8$
	residue	>779				52.7 (51.3)	

105.1 kJ mol^{-1} according to MC method, and 0.3 and 89.10 kJ mol^{-1} according to HM method, respectively.

Ru(II)-pydim complexes

The decomposition processes of Ru(II)-pydim complexes are similar for same type complexes. However the thermal decomposition pattern of each complex shows a different decomposition pattern due to the different pydim ligand.

Type 2 complexes

From the TG curve for complex 2a (Fig. 2), it appears that the sample decomposes in four stages over the temperature range 53–783°C. The first decomposition occurs between 53 and 188°C with a mass loss 6.6% in mass due to the loss of NCMe ligand. This step required an activation energy of 35.29 kJ mol^{-1} with the order of 1.4 according to WHYC method. In the second decomposition step, a mass loss of 14.3% with the order of 1.30 and 46.26 kJ mol^{-1} activation energy according to MC involved the elimination of $4\text{-}NMe_2C_6H_4$ on the pydim ligand in temperature range 195-384°C. In third decomposition step (390–570°C) and fourth decomposition step (592–783°C) $4\text{-}NMe_2C_6H_4$ on the pydim ligand were evolved with mass losses of 13.0 and 13.3%, respectively. 2b is less stable than 2a and decompose at 44, 167, 350, 546 and 715°C, respectively, to give NCMe, $2\text{-}Me\text{-}4\text{-}NEt_2C_6H_4$, $2\text{-}Me\text{-}4\text{-}NEt_2C_6H_4$ and 2 x Cl from the 2b. The reaction order and activation energies for the first and second decomposition steps of 2b were found to be 2.70 and 99.96 kJ mol^{-1}, and 0.4 and 37.57 kJ mol^{-1}, respectively according to MC method. From the TG curve for 2c (Fig. 2), it appears that the sample decomposes in four stages over the temperature range 35–545°C. The first decomposition occurs between 35 and 63°C with a mass loss 4.76% in mass due to the loss of NCMe ligand. This reaction was order of 1.1 with 54.3 kJ mol^{-1} activation energy according to MC method. In second (111–191°C) and third steps (222–313°C), 2xCl were evolved with mass losses of 6.54 and 6.84%, respectively. The reaction order and activation energies for second and third decomposition steps were 1.30, 69.80 kJ mol^{-1} according to MC method and 1.50, 102.10 kJ mol^{-1} according to vK method, respectively. In the fourth step, a mass loss of 19.00% with the order of 1.60 and 62.70 kJ mol^{-1} activation energy involved the elimination of $2,4,6\text{-}Me_3C_6H_2$ on the pydim ligand in temperature range 342–545°C. The 2d is more stable than 2c and decomposes at 55, 231, 308°C, respectively, to give NCMe, 2xCl and $2\text{-}Me,6\text{-}EtC_6H_3$. The first step was order of 1.0 with 17.30 kJ mol^{-1} activation energy according to WHYC method. The second step was order of 0.6 with 96.70 kJ mol^{-1} activation energy according to HM method and the third step was order of 1.0 with activation energy of 75.50 kJ mol^{-1} according to WHYC method.

From the DTA profile three exothermic peaks for 2a are noted. The maximas of these peaks, which are due to the formation of intermediate, are found to be 261, 416 and 661 K, respectively. One exothermic

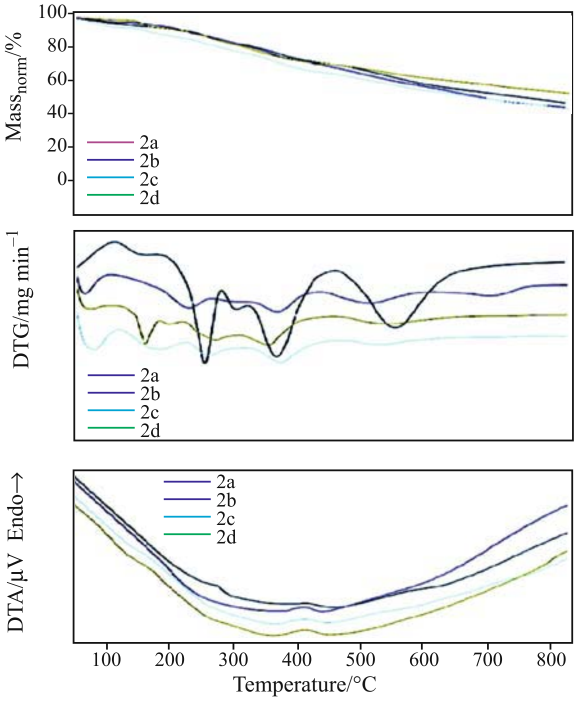


Fig. 2 TG/DTG and DTA curves of type 2 complexes

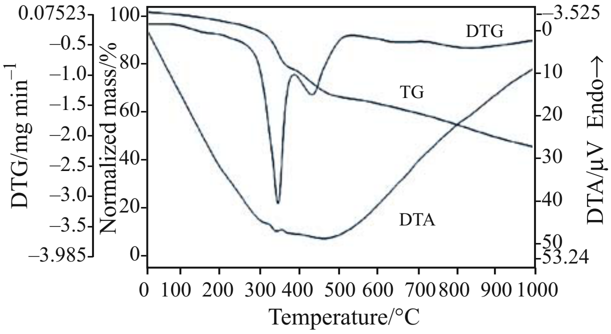


Fig. 3 TG/DTG and DTA curves of type 3 complex

peak for 2b, 2c and 2d are noted. The maximas of these peaks are found to be 400, 424 and 404°C, respectively.

Type 3 complex

3a exhibited two-step decomposition processes. In the first step PPh_3 was eliminated in the temperature range 294–367°C with a 29.30% mass loss. This reaction was in an order of 0.3 with an activation energy of 64.63 kJ mol^{-1} according to HM method. The second decomposition step occurs in the temperature range 396–490°C with 11.20% mass loss and corresponds to the formation of 4-$NMe_2C_6H_4$ on the pydim ligand. Exothermic thermal effect at 343°C corresponds to the formation of PPh_3 which is decomposition product of complex.

Type 4 complexes

As seen in Fig. 4, the complex 4a is thermally stable up to 229°C. The first decomposition step occurs in the temperature range 229–573°C corresponding to the elimination of 4-$NMe_2C_6H_4$. This stage was in order of 1.2 with an activation energy of 40.91 kJ mol^{-1} according to vK method. The next decomposition step occurs in the temperature range 604–792°C and corresponding to the formation of $C_{10}H_8N_2$. Complex 4b shows one decomposition step between 575 and 719 K corresponding to the elimination of 2-Me,4-$NEt_2C_6H_4$ on the pydim ligand with a 21.5% mass loss. The order and activation energy for this decomposition step were 1.0 and 86.85 kJ mol^{-1} according to WHYC method. 4c exhibited two-step decomposition processes. In the first step 1/2 molecule 2,4,6-$Me_3C_6H_2$ was eliminated in the temperature range 97–274°C with 18.5% mass loss. This step required 62.20 kJ mol^{-1} activation energy with the order of 1.0 according to MC method. The second decomposition step occurs in the temperature range 260–441°C with a 19.2% mass loss and corresponds to the formation of 2,4,6-$Me_3C_6H_2$. This step was order of 1.5 with 77.60 kJ mol^{-1} activation energy according to vK method. Exothermic thermal effect at 364°C corresponds to the formation of 2,4,6-$Me_3C_6H_2$ moiety which is decomposition product of complex. 4d shows one decomposition step between 331 and 440°C corresponding to the elimination of 2-Me,6-EtC_6H_3 with a 39.0% mass loss. The order and activation energies for this steps were 1.4, 335.5 kJ mol^{-1} according to vK method. From the DTA profile one exothermic peak for 4b and d are noted. The maximas of these peaks, which is due to the formation of intermediate, are found to be 372 and 371°C, respectively.

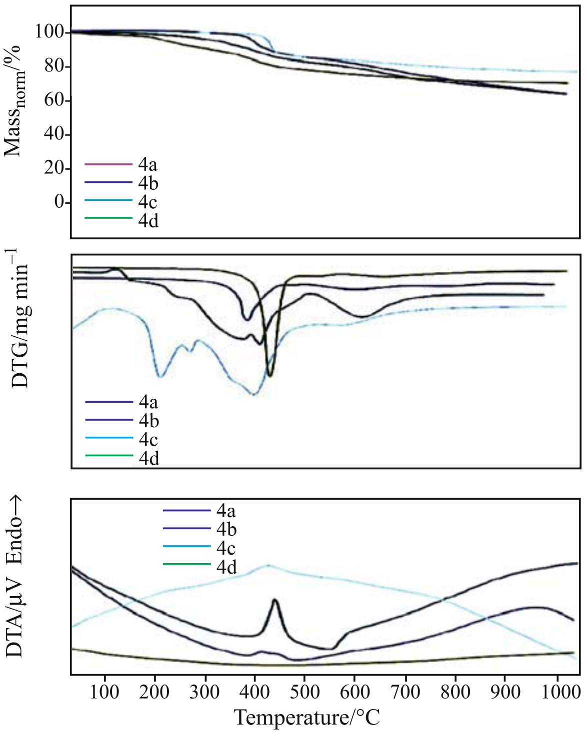


Fig. 4 TG/DTG and DTA curves of type 4 complexes

Type 5 complexes

5c is thermally stable up to 172°C (Fig. 5). The mass loss at the first stage in the temperature range 172-286°C corresponds to the formation of 2,4,6-$Me_3C_6H_2$ with the order of 0.7 and 103.4 kJ mol^{-1} activation energy according to MC method. The next decomposition step occurs in the temperature range 314–481°C and corresponds to the formation of 2,4,6-$Me_3C_6H_2$. 5d again involved two types of decomposition which is similar to 5c.

Kinetic parameters

The six methods investigated in this paper are those by CR, HM, vK, MC, MKN and WHYC.

- The Coats–Redfern method [28]

$$\ln\left[\frac{g(\alpha)}{T^2}\right]=\ln\left[\frac{AR}{\beta E}(1-\frac{2RT}{E})\right]-\left(\frac{E}{RT}\right) \qquad (1)$$

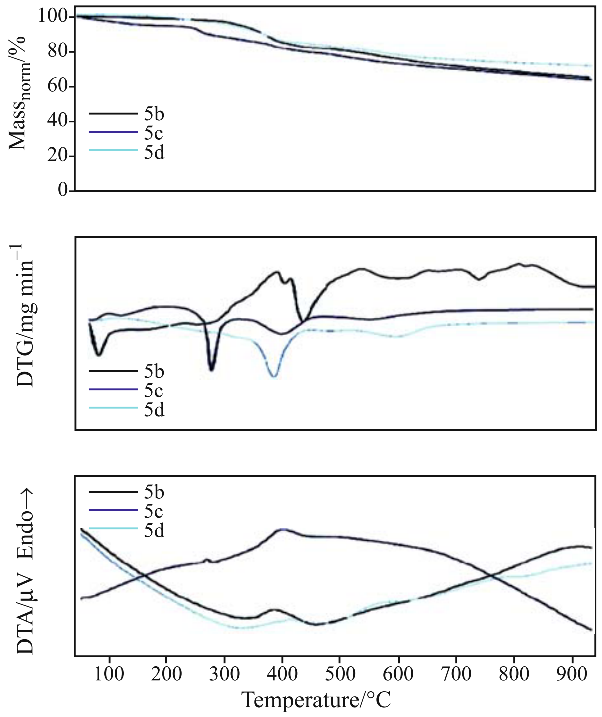


Fig. 5 TG/DTG and DTA curves of type 5 complexes

- The Madhusudanan–Krishnan–Ninan method [29]

$$\ln\left[\frac{g(\alpha)}{T^{1.9206}}\right]=\ln\left(\frac{AE}{\beta R}\right)+3.7678-1.9206\ln E-0.12040\left(\frac{E}{T}\right) \tag{2}$$

- The MacCallum–Tanner method [30]

$$\log g(\alpha)=\log\left(\frac{AE}{\beta R}\right)-0.4828E^{0.4351}-\left(\frac{0.449+0.217E}{10^{-3}T}\right) \tag{3}$$

- Wanjun–Yuwen–Hen–Cunxin method [31]

$$\ln\left[\frac{g(\alpha)}{T^{1.8946}}\right]=\left[\ln\frac{AR}{\beta E}+3.6350-1.8946\ln E\right]-1.0014\left(\frac{E}{RT}\right) \tag{4}$$

- The van Krevelen method [32]

$$\ln g(\alpha)=\ln\left[\frac{A(0.368/T_m)^{\frac{E_a}{RT_m}}}{\beta\left(\frac{E_a}{RT_m}+1\right)}\right]+\left(\frac{E_a}{RT_m}+1\right)\ln T \tag{5}$$

- Horowitz–Metzger method [33]. The Horowitz–Metzger method introduced a characteristic temperature T_m and a parameter Θ such that

$$\Theta=T-T_m$$

If the reaction order is 1, T_m is defined as the temperature at which $(1-\alpha)_m=1/e=0.368$ and the final expression is:

$$\ln\ln g(\alpha)=\frac{E\theta}{RT_m^2}$$

If the reaction order is unknown, T_m is defined for the maximum heating rate.

When $\Theta=0$, $(1-\alpha)=(1-\alpha)_m$ and $(1-\alpha)_m=n^{1/1-n}$ and

$$\ln g(\alpha)=\ln\frac{ART_m^2}{\beta E}-\frac{E}{RT_m}+\frac{E\theta}{RT_m^2} \tag{6}$$

A plot of ln$g(\alpha)$ *vs.* Θ can yield activation energy.

In the equations above, α, $g(\alpha)$, β, T_m, E, A, R are the degree of reaction, integral function of conversion, heating rate, DTG peak temperature, activation energy (kJ mol^{-1}), pre-exponential factor (min^{-1}) and gas constant (8.314 J mol^{-1} K^{-1}), respectively. The kinetic parameters were calculated from the linear plots of the left-hand side of kinetic equations (Eqs (1)–(4) and (6)) *vs.* $1/T$, for van Krevelen equation (Eq. (5)) the left-hand side is plotted *vs.* ln$T$. The values E and A were calculated from the slope and intercept of the straight lines, respectively.

In this study, the several methods based on a single heating rate were used in the thermal analysis. The linearization curves of each decomposition step of the complexes were obtained using the least squares method. From the TG/DTG and DTA curves, the reaction order, n and activation energy, E_a of the decomposition have been elucidated by the first one of the methods mentioned above which has higher linear regression coefficient [34] obtained for Arrhenius plots. The kinetic and thermodynamic parameters related to the ligands and complexes were calculated by the software developed in our laboratory using PHP Web programming language [35].

On the other hand, the value of correlation coefficients of linearization curves of ruthenium complexes are approximately 1.00 and values of reaction orders are around 1.00 for complexes. It is very close to zero for 1c and d ligands. The kinetic data obtained by different methods agree with each other. The thermal stabilities of ligands increase in the following order: 1b<1d<1c<1a. This result shows that 1a are more stable than others. It was found that the thermal stabilities and activation energies of the complexes for the first decomposition stage follow the order 2c<2b<2a<2d<4c<5d<3a<4a<4b<1b<5c<1d<5b<1c<1a<4d and $E_{2d}<E_{2a}<E_{4a}<E_{5d}<E_{2c}<E_{4c}<E_{3a}<E_{5b}<E_{4b}<E_{1d}<E_{2b}<E_{5c}<E_{1c}<E_{1b}<E_{1a}<E_{4d}$, respectively. The highest thermal stability and activation energy for the

first decomposition stage is displayed by the 4d complex. The stabilities of mononuclear complexes with NCMe are very low and consequently, low energy is required for their decomposition. Generally, dinuclear complexes required lower energy than mononuclear complexes to decompose in the first step. 1d ligand increases the stability in mononuclear complexes while it decreases that in binuclear ones. Thermal stability increases from mononuclear complexes to dinuclear ones. Activation energies exhibit a trend of increases for multistep decomposition such as 2a, 2b, 3a, 5b, 4c, 4a, 5d.

Conclusions

In conclusion, *i*) Pydim Ligands are more stable than their corresponding Ru(II) complexes except for 4d and 5b; *ii*) the binuclear complexes appear to be more stable than mononuclear analogs; *iii*) structurally similar complexes have similar thermal decomposition curves; *iv*) the intermediates of different steps are not stable and decompose immediately after their formation.

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