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Thermal studies of Ni(II), Pd(II), Pt(II) and Ru(III) complexes of *N*,*N*-dihexyl-*N*′-benzoylthiourea

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Abstract

Some metal complexes of *N*,*N*-dihexyl-*N*′-benzoylthiourea (DHBT) of the type $M(DHBT)_n$ [M = Ni, Pd, Pt, ($n = 2$), Ru, ($n = 3$)] have been synthesised and studied using DTA and TG. These complexes undergo only the pyrolytic decomposition process. The orders, n, the activation energies, E, the pre-exponential factor, A, and the entropies, ΔS of the thermal decomposition reactions have been derived from thermogravimetric (TG) and differential thermogravimetric (DTG) curves. The characterisation of the end products of the decomposition was achieved by X-ray diffraction. UV–Vis and IR spectra were used for the investigation of characteristic absorption bands and the structural characterisation of ligand and the metals, respectively. Using the Coats and Redfern and Horowitz and Metzger methods performed kinetic analysis of the thermogravimetric data.

Keywords: *N*,*N*-dihexyl-*N*′-benzoylthiourea; Ru(III)-, Ni(II)-, Pd(II)-, and Pt(II)- complexes; Thermal behaviours; Thermal decomposition kinetic; DTA/TG/DTG

1. Introduction

The natural resources of the platinum group metals in the world are very rare. Usage of these metals in industry is increasing and is being used in electricity–electronic industry and as an auto-exhaust catalyst in automobile industry, petroleum–chemical industry, and jewellery industry [1]. One of the most important features of these metals is high-rate hydrogen absorption when they are in metallic form. Therefore, they are used as hydrogenation catalysts [2]. Pt and Pd catalysts are being used for more than ten years. Ruthenium is a good hydrogenation catalyst, the usage of this is not common at present [3]. Some amount of these metals remains in the medium after they are used as catalysts. The regeneration of these metals is achieved by employing a complexing agent. One of such agent is of *N*,*N*-dihexyl-*N*′-benzoylthiourea which can be used successfully for those metals such as Pt, Pd, Ru and Ni [4]. Thermal properties of these metal complexes have not been studied previously. In this study, thermal properties and decomposition kinetics of the metal complexes of Ru(III), Ni(II), Pd(II), and Pt(II) are investigated. In the decomposition kinetic study, the integral method employing the Coats–Redfern equation and the approximation method using the Horowitz–Metzger equation are used for the calculation of kinetic parameters such

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as the reaction order, n, the activation energy, E, entropies, ΔS and the pre-exponential factor, A, from a nonisothermal kinetic study [5,6].

2. Experimental

2.1. Synthesis procedure

The synthesis of ligand and metal complexes is made as given in literature [7]. 0.01 mol Ni(II), Pd(II), Pt(II), Ru(III) solutions are prepared from $NiCl_2$, $PdCl_2$ (60% Merck), K_2PtCl_4 (47% Sigma), $RuCl_3 \cdot H_2O$ (38% Sigma) respectively. Metal complexes are prepared with alcoholic ligand solutions, mixed aqueous metal solutions, and solid complexes are filtered off.

2.2. Instrumentation

X- ray powder diffraction analysis of the solid metal complexes and the final residue were made with a Phillips PW-1010 model X-ray diffractometer using CuKα radiation ($\lambda = 1.5406$ Å) which work in the range of 20–50 kV and 6–50 mA. The characteristic absorption bands of metal complexes are obtained with Hitachi 150-20 model double beam UV–Vis absorption spectrophotometer. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Shimadzu 435 spectrophotometer, using KBr pellets. The DTA and TG curves are obtained with Shimadzu DT-40 model simultaneously with DTA and TG apparatus. The measurements were performed by using a dynamic nitrogen atmosphere at a flow rate of 60 ml min^{-1} up to 1273 K. The heating rate was 10°C min^{-1} and the sample sizes ranged in mass from 5 to 10 mg contained in platinum crucible. α-Al_2O_3 is used as a reference material. Melting points were determined by a digital m.p. instrument from Electrothermal Model 9200.

3. Results and discussions

3.1. Thermal analysis

All complexes were studied by thermogravimetric analysis from ambient temperature to 1273 K in nitrogen atmosphere. The temperature ranges and percentage mass losses are given in Table 1, together with the temperatures of greatest rate of decomposition (DTG_{max}) and the theoretical percentage mass losses. Thermal curves obtained for most of the compounds were very similar in character. All complexes show two-stage mass loss. The first mass loss corresponds to the formation of $M(SCN)_2$ and the second mass loss is due to the decomposition of SCN and CN radicals. The beginning and the end products were confirmed

Table 1
Thermoanalytical results on metal complexes of *N,N*-dihexyl-*N′*-benzoylthiourea

Complexes	Stage	Temperature range (K)	DTG_{max} (K)	Mass loss (%)		Evolved moiety
				TG	Theoretical	
$Ni(DHBT)_2$	I	438–651	548	75.9	76.1	2DHB
	II	651–855	793	11.7	11.5	SCN + CN
	Residue	>855	–	12.6	12.5	NiS
$Pd(DHBT)_2$	I	507–682	538	71.8	71.1	2DHB
	II	682–807	738	10.2	10.9	SCN + CN
	Residue	>807	–	18.0	17.9	PdS
$Pt(DHBT)_2$	I	475–691	537	62.1	63.7	2DHB
	II	691–814	723	11.3	9.8	SCN + CN
	Residue	>814	–	26.5	26.6	PtS
$Ru(DHBT)_3$	Ia	421–538	519	49.4	49.9	2DHB
	Ib	538–780	738	25.0	24.9	DHB
	II	780–1113	1025	15.9	15.2	3SCN
	Residue	>1113	–	9.2	9.8	Ru

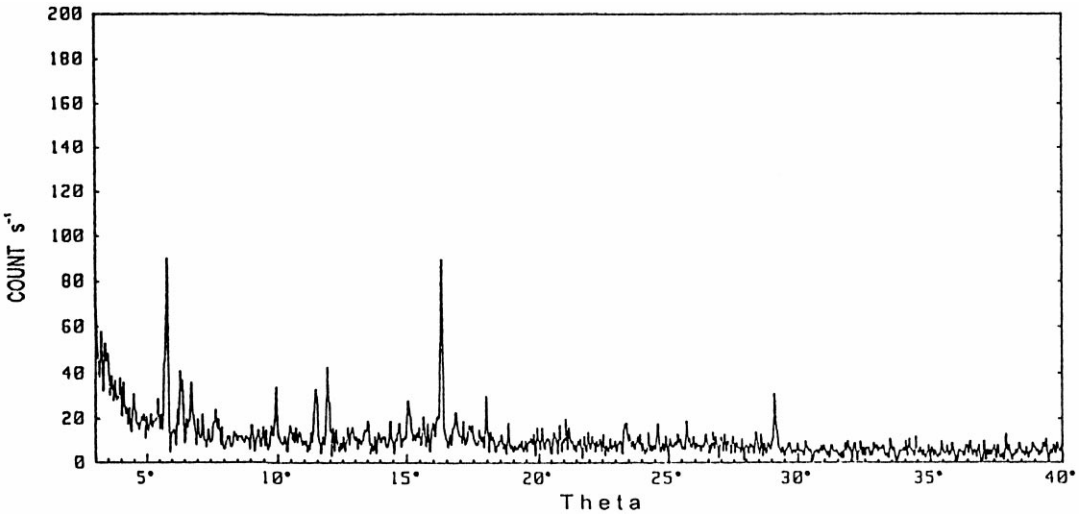

Fig. 1. X-ray powder diffraction pattern of PdS.

via the IR spectrometric and X-ray diffraction data. As an example, X-ray pattern of end product of Pd(II) complex is shown in Fig. 1. It may also be noted here that the absence of dehydration peaks in the DTG curves and the absence of hydroxyl band in the IR spectra indicate that all the compounds under investigation are anhydrous. The IR spectrum of $Pd(DHBT)_2$ is presented in Fig. 2 and the TG and DTG curves of $Ni(DHBT)_2$, $Pd(DHBT)_2$, $Pt(DHBT)_2$ and $Ru(DHBT)_3$ are presented in Fig. 3. The DTA

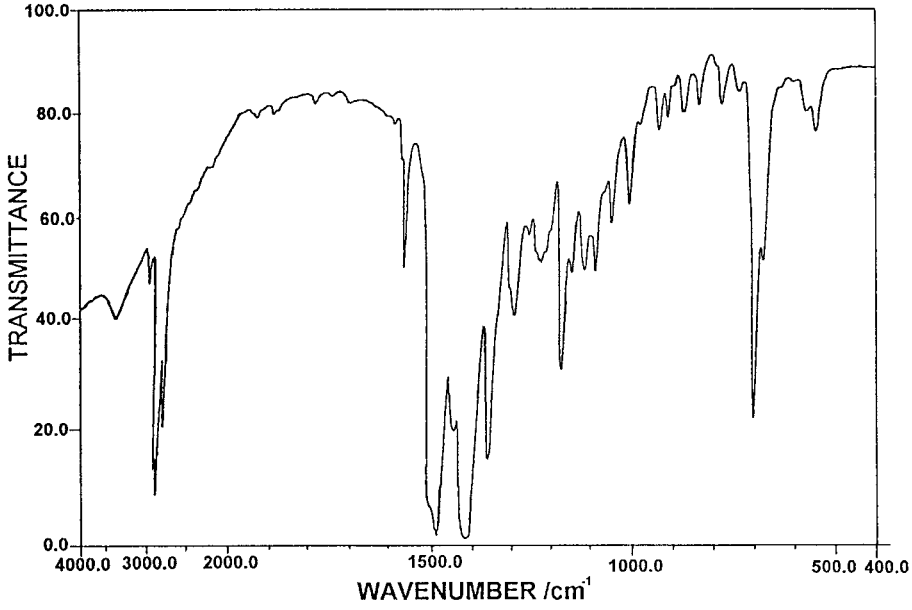

Fig. 2. IR spectra of Pd(II)-*N*,*N*-dihexyl-*N*′-benzoylthiourea complex.

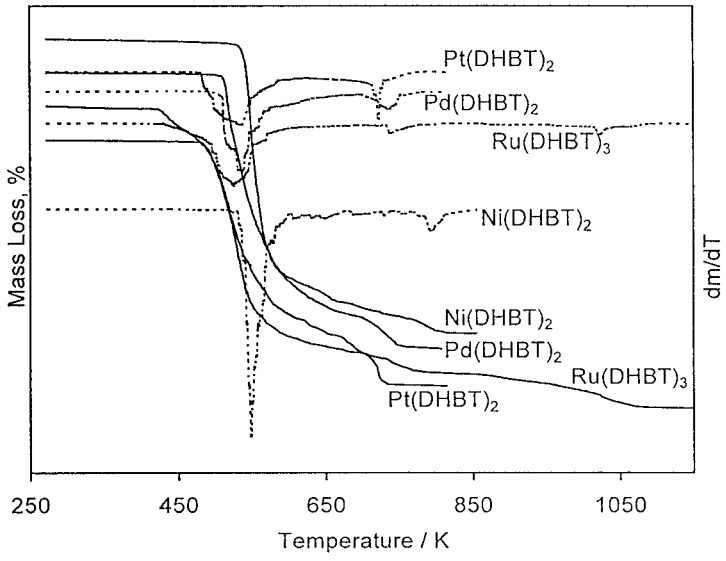

Fig. 3. TG–DTG curves for Ru(III)-, Ni(II)-, Pd(II)-, and Pt(II)-*N*,*N*-dihexyl-*N*′-benzoylthiourea complexes.

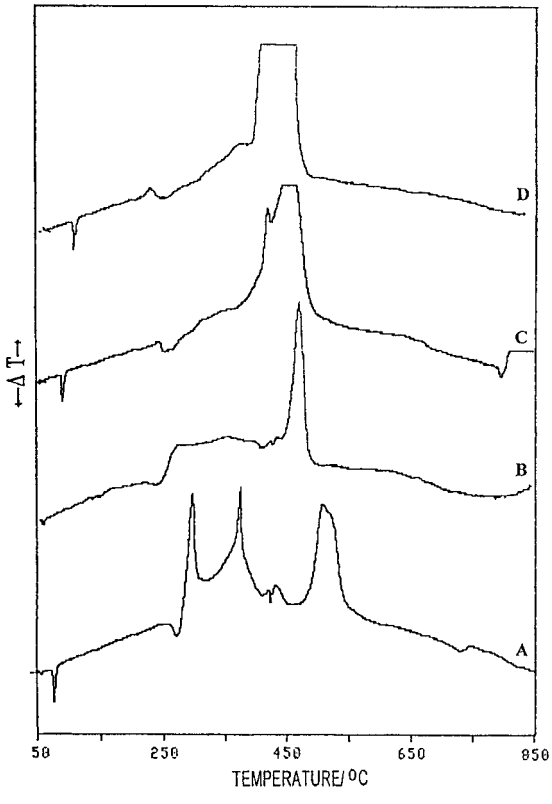

Fig. 4. DTA profiles for (a) Ni(II)-, (b) Ru(III)-, (c) Pd(II)-, and (d) Pt(II)-*N*,*N*-dihexyl-*N*′-benzoylthiourea complexes.

profiles of related complexes are shown in Fig. 4. In the case of $Ru(DHBT)_3$, however, the decomposition of ruthenium complex to metal itself is observed to occur in two. The first mass loss corresponds to the elimination of two dihexylbenzamid (DHB) groups followed by the elimination of other DHB group and the formation of metallic ruthenium after the second mass loss.

3.2. *Ni(DHBT)$_2$*

The complex is thermally stable up to 438 K and decomposition beyond this temperature as indicated by the first loss step in the TG curve. The mass loss at 438 K corresponds to the formation of $Ni(SCN)_2$. Beyond 651 K, continuous mass loss in the TG curve has been observed up to 855 K, which corresponds to the decomposition of $Ni(SCN)_2$ to NiS. The DTA profile shows two endothermic peaks at 351 and 543 K. First peak corresponding to the melting of the complex, second endothermic peak corresponds to the decomposition of the complexes to form $Ni(SCN)_2$. Exothermic thermal effects at 571 and 674 K correspond to the dimerisation of dihexylbenzamid (DHB) which is decomposition product of the complex, and the other exothermic effect corresponds to the decomposition of $Ni(SCN)_2$ to the NiS.

Table 2
Kinetic data on metal complexes of *N*,*N*-dihexyl-*N*′-benzoylthiourea

Complexes	Stage	Reaction order (n)	Parameters	From Coats–Redfern eqn.	From Horowitz–Metzger eqn.
$Ni(DHBT)_2$					
	I	0.959	E^a	158.0	168.1
			A^b	5.7×10^{12}	5.2×10^{13}
			ΔS^c	20.7	12.5
			r^d	0.9996	0.9987
	II	0.514	E^a	55.3	64.0
			A^b	305	215
			ΔS^c	−176.0	−186.6
			r^d	0.9940	0.9957
$Pd(DHBT)_2$					
	I	0.924	E^a	36.4	44.8
			A^b	5.85	43.9
			ΔS^c	−208.9	−218.7
			r^d	0.9987	0.9979
	II	0.556	E^a	52.7	61.5
			A^b	11.3	46.4
			ΔS^c	−203.4	−220.6
			r^d	0.8145	0.8597
$Pt(DHBT)_2$					
	I	0.966	E^a	17.9	21.3
			A^b	0.059	0.141
			ΔS^c	−247.1	−266.3
			r^d	0.9654	0.9837
	II	0.534	E^a	18.7	28.7
			A^b	2.13	0.12
			ΔS^c	−255.6	−269.5
			r^d	0.6065	0.7785
$Ru(DHBT)_3$					
	Ia	0.964	E^a	153.9	153.5
			A^b	2.8×10^{13}	2.7×10^{13}
			ΔS^c	33.8	7.7
			r^d	0.9956	0.9960
	Ib	0.523	E^a	33.9	37.2
			A^b	0.48	1.48
			ΔS^c	−229.7	−248.2
			r^d	0.9333	0.9648
	II	0.710	E^a	107.1	94.9
			A^b	603.4	121.3
			ΔS^c	−170.3	−215.2
			r^d	0.9898	0.9959

[a] Unit of E is in kJ mol^{-1}.
[b] Unit of A is in s^{-1}.
[c] Unit of ΔS is in J mol^{-1} K^{-1}.
[d] r: correlation coefficient of the linear plot.

3.3. *Pd(DHBT)$_2$*

The TG curve indicates that the mass change begins at 507 K and continuous up to 682 K. The mass loss corresponds to the formation of $Pd(SCN)_2$. The next decomposition step occurs in the temperature range 682–807 K and corresponds to the formation of PdS. DTA profile shows two endothermic and one exother-

mic peaks. The first, at 357 K corresponds to the melting of the complex, while the second at 521 K corresponds to the decomposition of the complex to $Pd(SCN)_2$. The third broad exothermic peak corresponds to the dimerisation of dihexylbenzamid and also corresponds to the decomposition of $Pd(SCN)_2$ to the PdS.

3.4. $Pt(DHBT)_2$

The TG curve shows an initial mass loss in the temperature range 475–691 K corresponding to the decomposition of the complex to $Pt(SCN)_2$. This is followed by another mass loss in the temperature range 691–814 K due to the thermal decomposition of $Pt(SCN)_2$ to PtS. The DTA curve shows two endothermic, one exothermic effects at 369, 514 and 693 K. The former corresponds to the melting of the complex, the second to its decomposition to $Pt(SCN)_2$, and the third to the dimerisation of dihexylbenzamid which also corresponds to the decomposition of $Pt(SCN)_2$ to the PtS.

3.5. $Ru(DHBT)_3$

The complex is thermally stable up to 421 K and undergoes decomposition beyond this temperature, as indicated by the first mass loss step in the TG curve. The mass loss at 538 K corresponds to the formation of $Ru(DHBT)(SCN)_2$. Beyond 538 K continuous mass loss in the TG curve has been observed up to 780 K which correspond to the decomposition of $Ru(DHBT)(SCN)_2$ to $Ru(SCN)_3$. After this decomposition, the mass loss at 780–1113 K corresponds to the formation of ruthenium metal. The DTA profile shows two endothermic and one broad exothermic peaks at 327, 515 and 693 K. The first appears at 327 K corresponding to the melting of the complex, while the second at 515 K corresponds to the decomposition of the complex to $Ru(DHBT)(SCN)_2$ and the third exothermic peak at 693 K corresponds to the dimerisation of dihexylbenzamid and also corresponds to decomposition of $Ru(SCN)_3$ to Ru.

3.6. Thermal decomposition

The results of TG–DTG studies are presented in Table 2. These results reveal that the first step decomposition of Ni(II), Pd(II) and Pt(II) complexes give corresponding thiocyanates, $Ni(SCN)_2$, $Pd(SCN)_2$ and $Pt(SCN)_2$. The former decomposes to NiS while the second and the third to PdS, and PtS in the final step, respectively. From the TG curves, the order, n, and the activation energy, E, of the thermal decomposition reaction, the pre-exponential factor, A, and the entropies, ΔS, of the decomposition reaction have been elucidated by the methods of Coats–Redfern and Horowitz–Metzger. The linearisation curves are

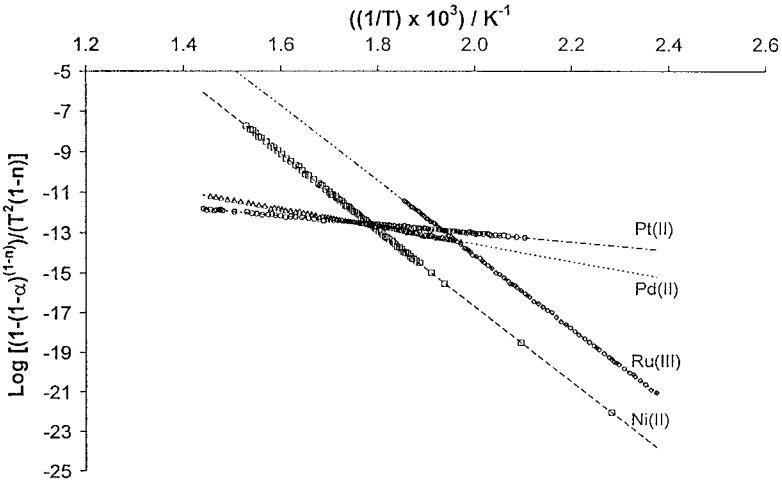

Fig. 5. Linearisation curves of Coats–Redfern method for Ru(III)-, Ni(II)-, Pd(II)-, and Pt(II)-*N*,*N*-dihexyl-*N*′-benzoylthiourea complexes.

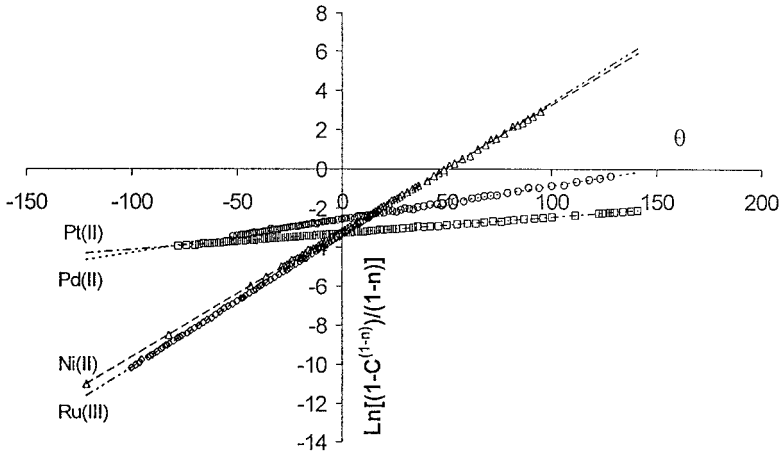

Fig. 6. Linearisation curves of Horowitz–Metzger method for Ru(III)-, Ni(II)-, Pd(II)-, and Pt(II)-*N*,*N*-dihexyl-*N*′-benzoylthiourea complexes.

shown in Figs. 5 and 6, respectively. Among these three complexes having the same square-planar geometry and the same decomposition steps, the smaller size of Ni(II) as compared to Pd(II) and Pt(II) permits a closer approach of the ligand to the Ni(II) ion. Hence the *E* value for the Ni(II) complex is higher than that of Pd(II) and Pt(II). The ionic sizes (*r*) of the metals are shown below [8].

Ions	Ru(III)	Ni(II)	Pd(II)	Pt(II)
r (pm)	69	72	86	96

The *E* values for the first and second thermal decomposition with respect to the method of Coats–Redfern can be put into a descending order as, $E_{Ni} > E_{Pd} > E_{Pt}$.

The *E* value of the first decomposition stage of Ru(III) complex having octahedral geometry and decomposing in two sub-stages is higher than that of all values found for the other complexes. The reaction orders found for the first decomposition stages of all complexes are nearly equal to unity.

References

[1] G.J.K. Ackes, K. Swars, Gmelin Handbook of Inorganic Chemistry, 8th ed., Springer, Berlin, 1985.
[2] Werkgruppe Metalle Precious Metal Catalyst, PCHB 10, Hanau, Hereaus, 1977.
[3] P.N. Rylander, Catalytic Hydrogenation Over Platinum Metals, Academic Press, New York, 1977.
[4] K.H. König, Z. Anal. Chem. 319 (1984) 66.
[5] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[6] H.H. Horowitz, G. Metzger, Anal. Chem. 35 (1963) 1464.
[7] M. Schuster, Ph.D. Thesis, Johann Wolfgang Goethe Universität, Germany, 1986.
[8] N.K. Tunali, S. Özkar, Inorganic Chemistry, Gazi University Publication, Publication No. 185, Ankara, 1993.