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STUDIES ON SOME NICKEL(II) AND COBALT(II) MIXED LIGAND COMPLEXES OF ARYLSALICYLALDIMINE AND OTHER LIGANDS

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Abstract

Several new mixed ligand complexes of Ni(II) and Co(II) of *p*-tolylsalicylaldimine (Sal-TH) or *p*-anisylsalicylaldimine (Sal-AH) with 8-hydroxyquinoline (HOx), benzohydroxamic acid (BH_2) or α-picoline (α-*pic*) have been synthesized. The complexes have the general formulae: [M(Sal-T)L], $[M(Sal\text{-}A)L]\cdot H_2O$ or $[Ni(Sal\text{-}T)_2(\alpha\text{-}pic)_2]\cdot H_2O$ where *M*=Ni(II) or Co(II), *Sal-T*=*p*-tolylsalicylaldiminate, *Sal-A*=*p*-anisylsalicylaldiminate, *L*=8-hydroxyquinolinate or benzohydroxamate and α-*pic*=α-picoline. Analytical, conductivity and spectral data support a square planar structure for Co(II) complexes and octahedral structure for Ni(II) complexes. The thermal behaviour of the complexes has been studied by TG and DTG techniques. It was proposed that the decomposition of the complexed Schiff base takes place via a radical mechanism while for 8-hydroxyquinolinate or benzohydroxamate via proton transfer. Kinetic parameters of the thermal decomposition process have been computed by means of Coats–Redfern and Horowitz–Metzger methods.

Keywords: arylsalicylaldimine, 8-hydroxyquinoline, metal benzohydroxamate

Introduction

Several metal complexes of Schiff bases containing N, O donors have been extensively studied [1–5]. This may be due to the reported anticarcinogenic and antiviral activity of these donor ligands and their complexes [6, 7]. The Schiff bases derived from salicylaldehyde and different amines are considered to be suitable models for B_6 vitamins [8], they form stable complexes with metal ions.

Hydroxamic acids have wide use as colorimetric and analytical reagents [9–11]. Furthermore, naturally occurring hydroxamic acids may function variously as antibiotics, antibiotic antagonists and tumour inhibitor [12, 13]. Thermal decomposition of the metal complexes of 8-hydroxyquinoline, hydroxamic acid and Schiff bases has been extensively studied in recent years [14–17]. In this paper we report the synthesis and characterization of some Ni(II) and Co(II) mixed ligand complexes containing

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p-tolylsalicylaldimine or *p*-anisylsalicylaldimine (Fig. 1) with 8-hydroxyquinoline, benzohydroxamic acid or α-picoline. The thermal properties of the solid complexes have been studied as an extension of our work on the thermal decomposition of mixed ligand complexes [18–22].

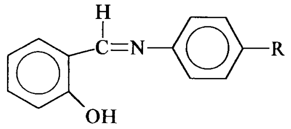


Fig. 1 Structure of the used Schiff bases; *R*=CH_3 (Sal-TH) or *R*=OCH_3 (Sal-AH)

Experimental

All chemicals were of analytical grade. The Schiff base ligands were prepared by the usual condensation method [1]. The IR spectra were recorded on a Shimadzu IR-470 spectrophotometer and electronic spectra were obtained using a Shimadzu UV-2101 PC spectrophotometer. Conductivity were made using a LF Digi 550 conductance bridge. Thermal studies were carried out on 2000 DuPont thermal analyzer, with the heating rate 10°C min^{-1}. The mass spectra were obtained on a $JEOLJMS_{600}$ apparatus.

Preparation of the complexes

The preparation of all mixed ligand complexes containing 8-hydroxyquinolinate or benzohydroxamate followed the same procedure. The preparation of (*p*-anisylsalicylaldiminato)-(benzohydroxamato) cobalt(II) is typical.

To a 20 mL methanolic solution of *p*-anisylsalicylaldimine (0.23 g, 1 mmol), a hot solution of cobalt(II) acetate (0.25 g, 1 mmol) in 15 mL methanol was added dropwise, followed by the addition of 10 mL of a methanolic solution of benzohydroxamic acid (0.14 g, 1 mmol). The reaction mixture was refluxed for 3 h. The product was precipitated by addition of sodium acetate solution (0.2 M). The complex was filtered, washed with methanol (5 mL) and dried over P_4O_{10}.

Preparation of bis(p-tolylsalicylaldiminato)bis(α-picolinato)nickel(II) complex

A methanolic solution (20 mL) of *p*-tolylsalicylaldimine (0.21 g, 1 mmol) was mixed with nickel acetate (0.49 g, 2 mmol), methanolic solution (20 mL). To the above mixture α-picoline (0.18 g, 2 mmol) in 10 mL methanol was added and the reaction mixture was refluxed for 1 h. The complex was precipitated by adding (20 mL, 0.2 M) sodium acetate solution. The product was filtered, washed with (5 mL) methanol and dried over P_4O_{10}.

Results and discussion

The synthesis of the complexes may be represented as follows:

$$\mathrm{M(OAc)_2{\cdot}4H_2O{+}Sal\text{-}TH{+}HL \xrightarrow{\text{sod. acetate}} M(Sal\text{-}T)L{+}2HOAc{+}H_2O}$$

$$\mathrm{M(OAc)_2{\cdot}4H_2O{+}Sal\text{-}AH{+}HL \xrightarrow{\text{sod. acetate}} M(Sal\text{-}A)L{\cdot}H_2O{+}2HOAc{+}H_2O}$$

$$\mathrm{Ni(OAc)_2{\cdot}4H_2O{+}2Sal\text{-}TH{+}2\alpha\text{-}pic \xrightarrow{\text{sod. acetate}} Ni(Sal\text{-}T)_2(\alpha\text{-}pic)_2{\cdot}H_2O{+}2HOAc{+}H_2O}$$

where *M*=Ni(II) or Co(II), *Sal-TH*=*p*-tolylsalicylaldimine, *Sal-AH*=*p*-anisylsalicylaldimine, *HL*=8-hydroxyquinoline or benzohydroxamic acid and α-*pic*=α-picoline.

All of the isolated compounds are air-stable, non-hygroscopic and colored solids; insoluble in water, ethanol and methanol, soluble in DMF and DMSO. The elemental analysis data (Table 1) are consistent with the formation of the complexes in the molar ratio 1:1:1 of the metal salt, the Schiff base and 8-hydroxyquinoline or benzohydroxamic acid while the last complex (Table 1) however, is formed in the molar ratio 1:2:2 between nickel acetate, *p*-tolylsalicylaldimine and α-picoline. The molar conductance of the complexes (2.00–10.00 ohm^{-1} cm^2 mol^{-1}) in DMF (~10^{-3} M) indicates their non-electrolytic nature [23].

Table 1 Color, elemental analyses and melting point of the complexes

Compound	Color	C/	H/	N/	Decomp. *m.p.*/°C
		% found (calc.)			
Ni(Sal-T)(Ox)	light green	66.92 (66.87)	4.35 (4.39)	6.83 (6.78)	290
Co(Sal-T)(Ox)	reddish brown	66.79 (66.83)	4.42 (4.39)	6.75 (6.78)	190
Ni(Sal-T)(BH)	dark green	62.29 (62.26)	4.50 (4.48)	6.95 (6.92)	125
Co(Sal-T)(BH)	reddish brown	62.25 (62.23)	4.46 (4.48)	6.89 (6.91)	185
Ni(Sal-A)(Ox)·H_2O	yellowish green	61.80 (61.78)	4.50 (4.51)	6.24 (6.27)	195
Co(Sal-A)(Ox)·H_2O	reddish brown	61.77 (61.75)	4.48 (4.51)	6.24 (6.26)	192
Ni(Sal-A)(BH)·H_2O	light green	57.41 (57.44)	4.61 (4.59)	6.39 (6.38)	150
Co(Sal-A)(BH)·H_2O	reddish brown	57.38 (57.41)	4.57 (4.59)	6.36 (6.38)	145
Ni(Sal-T)$_2$(α-pic)$_2$·H_2O	yellowish green	70.33 (70.29)	5.91 (5.90)	8.22 (8.20)	191

IR spectra

The infrared spectra of the complexes present the characteristics of both the Schiff base and the other respective ligands. IR spectra (Table 2) show a strong band in the region 1603–1620 cm^{-1} which indicates the coordination of the arylsalicylaldiminate through the azomethine nitrogen [24]. Also a band in the region 1230–1265 cm^{-1} is

Table 2 Main IR bands (cm^{-1}) and electronic spectral data (cm^{-1}) of the complexes

Compound	Schiff base		Oxinate		Benzohydroxamate			H_2O	Electronic spectral bands
	ν(CO)	ν(CN)	ν(CO)	ν(CN)	ν(CO)	ν(CN)	ν(NO)	ν(OH)	
Ni(Sal-T)(Ox)	1265	1605	1110	1580	–	–	–	–	16129, 24390, 29411, 30769, 34482
Co(Sal-T)(Ox)	1260	1605	1105	1575	–	–	–	–	11764, 18182, 20833, 26666, 29411, 37037
Ni(Sal-T)(BH)	1245	1610	–	–	1565	1465	1145	–	16129, 22222, 28985, 41666
Co(Sal-T)(BH)	1245	1605	–	–	1560	1480	1140	–	12048, 17241, 20408, 31250, 39215
Ni(Sal-A)(Ox)·H_2O	1240	1610	1105	1575	–	–	–	3450	16393, 21739, 29411, 38461
Co(Sal-A)(Ox)·H_2O	1240	1605	1110	1570	–	–	–	3448	11764, 17543, 24390, 29411, 40816
Ni(Sal-A)(BH)·H_2O	1235	1603	–	–	1555	1465	1150	3400	16929, 23255, 28571, 31250, 41666
Co(Sal-A)(BH)·H_2O	1240	1610	–	–	1555	1460	1145	3450	11627, 17543, 24390, 27777, 41666
Ni(Sal-T)$_2$(α-pic)$_2$·H_2O	1230	1620	–	–	–	–	–	3445	16129, 23809, 29411, 35087, 40000

attributable to ν(C–O); this band is shifted to higher frequency in the complexes indicating coordination of the phenolic oxygen to the metal ion [25, 26]. For the oxinate part, ν(C–O) band is found in the range 1105–1110 cm^{-1}, typical of oxinate complexes of metals [27], ν(C=N) occurs in the region 1570–1580 cm^{-1}. Coordination of benzohydroxamate is manifested by the appearance of a 1555–1565 cm^{-1} band due to ν(CO), the shift of which to lower energy indicates coordination of benzohydroxamate through the ketonic oxygen atom [28]. Benzohydroxamate exhibits further two bands in the 1460–1480 and 1140–1150 cm^{-1} regions, apparently associated with ν(CN) and ν(NO), respectively [29]. The presence of secondary coligand (α-picoline) in the complex $Ni(Sal\text{-}T)_2(\alpha\text{-pic})_2\cdot H_2O$ is confirmed from its vibrations as a strong band at 1400 cm^{-1} and a medium band at 530 cm^{-1} which are characteristic for methylpyridine adducts [30, 31]. For *p*-anisylsalicylaldiminate Ni(II) and Co(II) mixed ligand complexes, the absorption at 3400–3450 cm^{-1} is attributed to O–H stretching vibration of lattice water molecules.

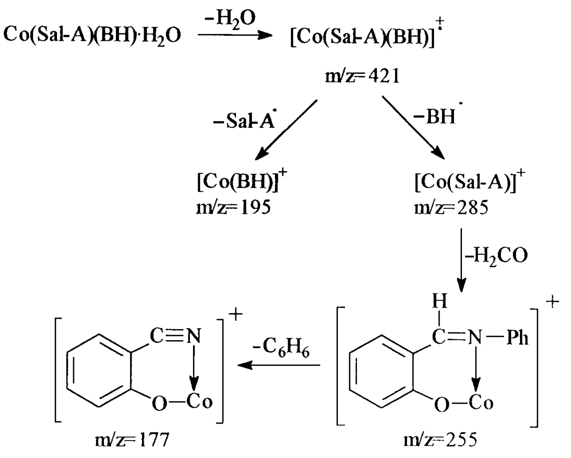
Electronic spectra

The electronic spectra of the complexes were studied in DMF solution and the characteristic bands are summarized in Table 2. Ni(II) complexes show a band in the 16929–16129 cm^{-1} region corresponding to $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) d–d transition. The reddish brown color of the Co(II) complexes and the weak broad band observed at 12048–11627 cm^{-1} region are characteristic of square planar structure [32]. A strong and broad band at 18182–17241 cm^{-1} is also observed in analogy with other square planar Co(II) complexes [33]. Other bands above 11111 cm^{-1} are not observed on our instrument. A band observed in all complexes at 24390–20408 cm^{-1} region is supposed to be charge transfer. Additional bands in the 41666–26666 cm^{-1} region are assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions.

Mass spectra

Mass spectra of the complexes Ni(Sal-T)(BH), $Co(Sal\text{-}A)(BH)\cdot H_2O$ and $Ni(Sal\text{-}T)_2(\alpha\text{-pic})_2\cdot H_2O$ have been investigated. The molecular ions for all complexes are not detected probably due to their thermal instability in the ionisation beam. Ni(Sal-T)(BH) and $Co(Sal\text{-}A)(BH)\cdot H_2O$ show similar fragmentation pattern. A representative fragmentation scheme for $Co(Sal\text{-}A)(BH)\cdot H_2O$ is suggested in Scheme I.

For the complex $Ni(Sal\text{-}T)_2(\alpha\text{-pic})_2\cdot H_2O$, the fragment $Ni(Sal\text{-}T)_2^+$ was detected in the mass spectrum, this might be regarded as direct fragments of the molecular ion by the elimination of the water and α-picoline molecules. Evidence for this arises from the existence of the water and the free base as can be deduced from the peaks at $m/z=18$ and $m/z=93$, respectively. This pathway can be simplified as follows in Scheme II.



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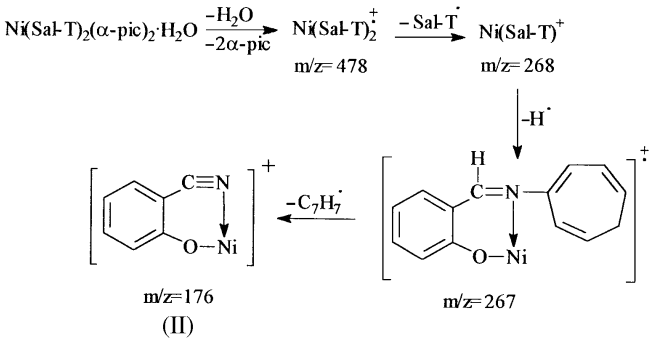


(II)

Existence of the ions $[M(Sal\text{-}A)]^+$ or $[M(Sal\text{-}T)]^+$ and [(2-cyanophenolato)cobalt $(III)^+$] (I) or [(2-cyanophenolato)nickel $(II)^+$] (II) in the mass spectra of all complexes indicates that fragmentation of the complexes proceeds almost with the same mechanism.

In conclusion, a square planar structure is assigned to Co(II) complexes while an octahedral structure is proposed for Ni(II) complexes. The six-coordination geometry may be attained through molecular association. The proposed structures of the complexes are shown in Fig. 2.

Thermal analysis

Thermogravimetric analyses of some of the synthesized complexes were carried out in air with a heating rate of 10°C min^{-1}. The complexes are Co(Sal-T)(Ox), Ni(Sal-T)(BH), Ni(Sal-A)(Ox)·H_2O, Co(Sal-A)(Ox)·H_2O, Ni(Sal-A)(BH)·H_2O and Ni(Sal-T)$_2$(α-pic)$_2$·H_2O. Thermoanalytical data are shown in Table 3. The simultaneous TG-DTG curves of the complexes Ni(Sal-A)(Ox)·H_2O and Co(Sal-A)(Ox)·

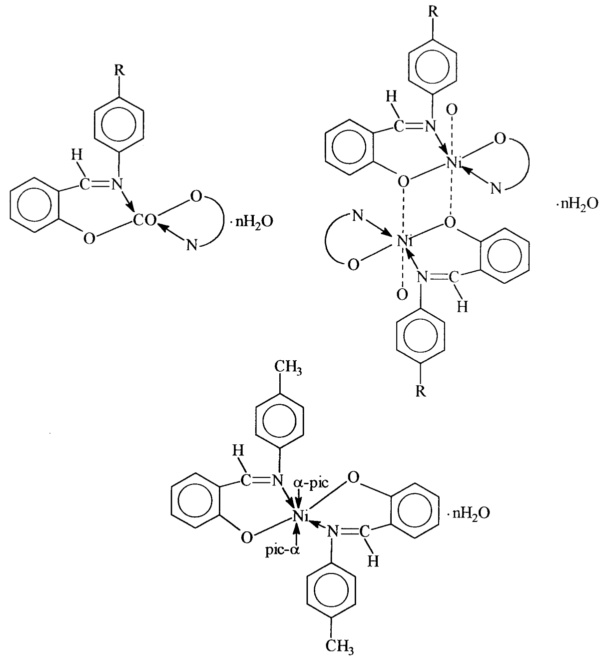


Fig. 2 Suggested molecular structures of the complexes; *R*=CH_3 or OCH_3; *n*=0 for *R*=CH_3 and *n*=1 for *R*=OCH_3; O···N=8-hydroxyquinolinate or benzohydroxamate and α-pic=α-picoline

H_2O show three-step decomposition process (Fig. 3). For the two complexes, the first step indicates the loss of a water molecule at 100 and 98°C, respectively. Such a dehydration at low-temperature confirms the presence of water of crystallization [34]. The second step involves the loss of 4-methoxyphenyl free radical (III) from the Schiff base moiety at 235 and 231°C, respectively. The loss of a part from arylsalicylaldimine as a free radical is recently reported [18]. The third step is a com-

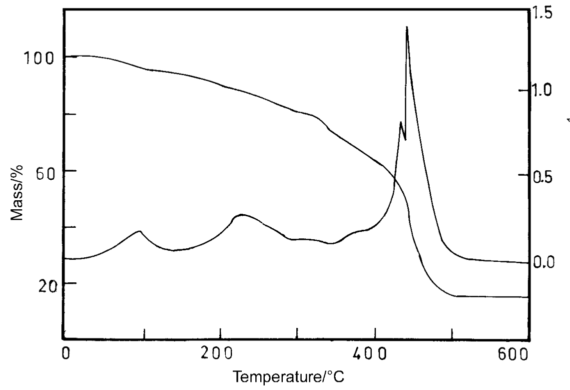


Fig. 3 TG-DTG curves of Co(Sal-A)(Ox)·H_2O

Table 3 Thermoanalytical data of the complexes

Compound	Step	Temperature range/°C	DTG-max/°C	Mass loss/%		Evolved moiety
				found	calculated	
Co(Sal-T)(Ox)	1	200–250	236	22.5	22.3	(IV)[a]
	2	250–398	350	34.6	34.9	HOx
	3	398–460	455	24.6	24.7	rest of complex
	residue	>460		18.3	18.1	CoO
Ni(Sal-T)(Ox)	1	163–230	196	22.3	22.8	(IV)[a]
	2	230–405	337	33.2	33.6	BH_2
	3	405–470	464	26.0	25.2	rest of complex
	residue	>470		18.5	18.4	NiO
Ni(Sal-A)(Ox)·H_2O	1	76–110	100	4.0	4.0	H_2O
	2	110–325	235	24.9	24.2	(III)[a]
	3	325–410	375, 404	54.2	55.1	HOx+rest of complex
	residue	>410		16.9	16.7	NiO
Co(Sal-A)(Ox)·H_2O	1	83–107	98	4.0	4.0	H_2O
	2	107–340	231	24.3	24.2	(III)[a]
	3	340–470	436, 448	54.7	55.0	HOx+rest of complex
	residue	>470		17.0	16.8	CoO
Ni(Sal-A)(BH)·H_2O	1	100–310	257	28.6	28.7	H_2O+(III)[a]
	2	310–382	361	26.6	26.9	BH_2
	3	382–450	442	27.8	27.4	rest of complex
	residue	>450		17.0	17.0	NiO
Ni(Sal-T)$_2$(α-pic)$_2$·H_2O	1	75–195	100	2.5	2.6	H_2O
	2	195–350	325	40.6	40.7	(IV)[a]+2α-pic
	3	350–448	421	45.4	45.5	rest of complex
	residue	>448		11.5	11.2	NiO

[A] Appendix HOx=8-hydroxyquinoline, BH_2=benzohydroxamic acid posite one (Fig. 3), involving the decomposition of the 8-hydroxyquinolinate moiety and the remainder of the complexes at 375 and 404°C for Ni(Sal-A)(Ox)·H_2O and at 436 and 448°C for Co(Sal-A)(Ox)·H_2O with the formation of MO as the end product.

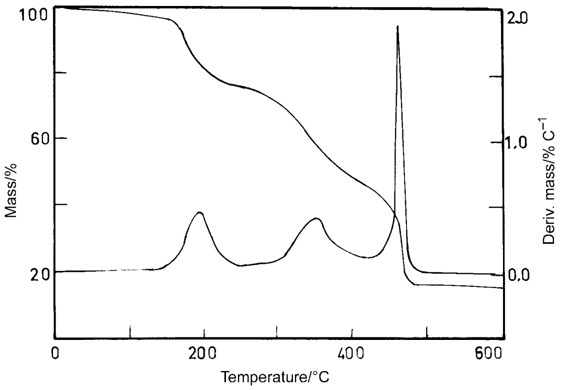


Fig. 4 TG-DTG curves of Ni(Sal-T)(BH)

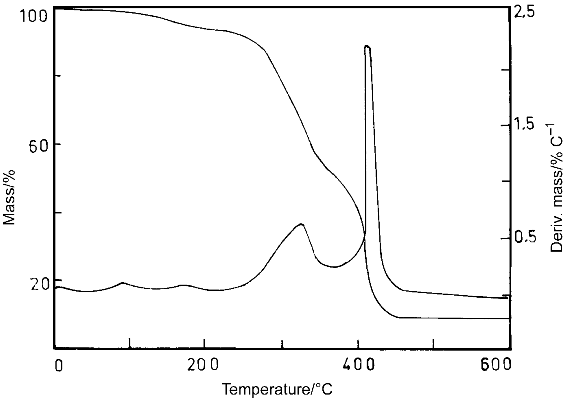


Fig. 5 TG-DTG curves of Ni(Sal-T)$_2$(α-pic)$_2$·H_2O

The complexes Co(Sal-T)(Ox), Ni(Sal-T)(BH) and Ni(Sal-A)(BH)·H_2O decompose in three steps. The first step involves the loss of 4-methylphenyl free radical (IV) or 4-methoxyphenyl free radical (III) for the first two complexes, respectively and with a water molecule for the third complex (Fig. 4). The second step includes the loss of the respective secondary ligand (8-hydroxyquinoline or benzohydroxamic acid) via a proton transfer. This step occurs for the three complexes at 350, 337 and 361°C, respectively. It is proposed that a proton transfers during thermal decomposition from the azomethine group to the other coordinated ligand [35]. The final decomposition occurs at 455, 464 and 442°C, respectively, to produce the corresponding metal oxide. A suggested thermal decomposition mechanism can be explained as follows:

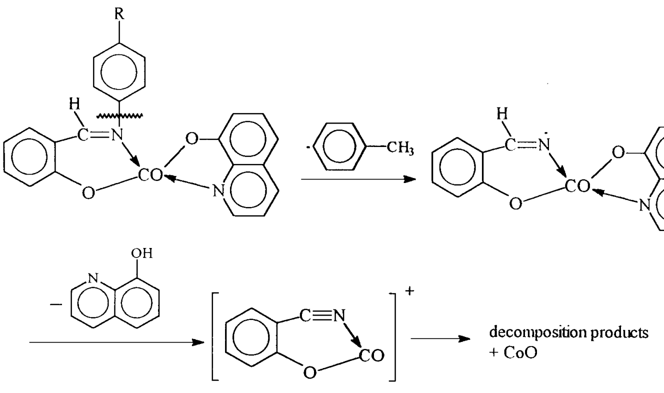


Table 4 Computed kinetic parameters of the complexes

Compound	Step	Method	E^*/	ΔH^*/	ΔS^*/
			kJ mol^{-1}		J mol^{-1} K^{-1}
Co(Sal-T)(Ox)	1	Coats–Redfern	58	68	–65
		Horowitz–Metzger	62	–	–
	2	Coats–Redfern	55	47	–88
		Horowitz–Metzger	56	50	–87
	3	Coats–Redfern	240	134	–69
		Horowitz–Metzger	221	–	–
Ni(Sal-T)(BH)	1	Coats–Redfern	64	41	–87
		Horowitz–Metzger	63	–	–97
	2	Coats–Redfern	148	44	–58
		Horowitz–Metzger	–	–	–
	3	Coats–Redfern	192	135	–39
		Horowitz–Metzger	190	–	–
Ni(Sal-A)(Ox)·H_2O	1	Coats–Redfern	27	88	–44
		Horowitz–Metzger	30	89	–
	2	Coats–Redfern	57	–	–83
		Horowitz–Metzger	55	60	–
Co(Sal-A)(Ox)·H_2O	1	Coats–Redfern	28	89	–67
		Horowitz–Metzger	26	95	–
	2	Coats–Redfern	57	52	–88
		Horowitz–Metzger	55	50	–91
Ni(Sal-A)(BH)·H_2O	1	Coats–Redfern	55	51	–81
		Horowitz–Metzger	56	47	–86
	2	Coats–Redfern	147	171	–50
		Horowitz–Metzger	149	–	–
	3	Coats–Redfern	188	182	–
		Horowitz–Metzger	192	148	–95
Ni(Sal-T)$_2$(α–pic)$_2$·H_2O	1	Coats–Redfern	–	–	–
		Horowitz–Metzger	14	11	–61
	2	Coats–Redfern	62	77	–79
		Horowitz–Metzger	59	–	–88
	3	Coats–Redfern	290	184	–101
		Horowitz–Metzger	289	183	–121

For the complex Ni(Sal-T)$_2$(α-pic)$_2$ the decomposition proceeds in three steps (Fig. 5). In the first step one molecule of water is lost at 100°C. The second step includes the loss of 4-methylphenyl free radical accompanied by two α-picoline molecules at 325°C. The remainder of the complex is decomposed in the third step at 421°C to produce NiO as the end product (Table 3).

A computer program [36] which enables the determination of kinetic and thermodynamic parameters from experimental TG/DTG data has been used. This program allows the Coats–Redfern and Horowitz–Metzger methods [37, 38] to be performed, the results are summarized in Table 4. From the results obtained we can conclude the following:

1. From the observation that the obtained activation energy values for the loss of 4-methylphenyl free radical and 4-methoxyphenyl free radical are slightly different (Table 4), it is assumed that the attack in these compounds is not directly at the metal-ligand bonds but frequently at a point in the Schiff base moiety and indicates that the decomposition takes place through the same mechanism [39].
2. The loss of 8-hydroxyquinoline is much easier than the loss of benzohydroxamic acid which confirms the high thermal stability of benzohydroxamato complexes.

Microbiological activities

The biological activities of some of the prepared complexes were tested against a number of fungi and bacteria. The used fungi were *A. niger* and *Penicillum* while the tested bacteria were *P. aeruginosa* and *E. coli*. The culture media were nutrient agar (N.A.) supplemented with one gm yeast/liter. The antifungal and antibacterial activity of each compound were evaluated by the classical filter paper technique. For each complex, a mass of 0.01 g was dissolved in 5 mL DMF. The complexes show variable antibacterial and antifungal activities against the used bacteria and fungi (Table 5).

Table 5 Microbiological activities of the complexes

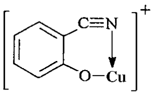
Complex	Fungi		Bacteria	
	A. niger	*Penicillum*	*P. aeruginosa*	*E. coli*
Ni(Sal-T)(BH)	+	++	++	++
Co(Sal-T)(Ox)	+	+	++	++
Co(Sal-A)(Ox)·H_2O	+	–	+	+
Ni(Sal-T)$_2$(α-pic)$_2$·H_2O	+	–	+	++

The diameter (*D*) of inhibition zone (in nm) is expressed as '+' and '–'; '++': *D*=15–20; '+': *D*=1–15; '–': *D*=0

Conclusions

All the studied complexes undergo thermal decomposition firstly via the loss of 4-methylphenyl free radical or 4 methoxyphenyl free radical from the Schiff base moiety, this is accompanied by the release of H_2O molecule or two α-pic molecules in the complexes Ni(Sal-A)(BH)·H_2O and Ni(Sal-T)$_2$(α-pic)$_2$· H_2O, respectively. TG curves show evolution of the secondary ligand (HOx or BH_2) in a separate stage for the complexes Co(Sal-T)(Ox), Ni(Sal-T)(BH) and Ni(Sal-A)(BH)·H_2O or with the remainder of the complex for Ni(Sal-A)(Ox)·H_2O and Co(Sal-A)(Ox)·H_2O. This can be occurred via proton transfers from the azomethine group to the other coordinated ligand. All the complexes form the corresponding metal oxide as the end product.

Appendix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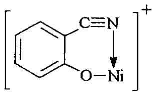
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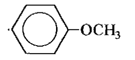
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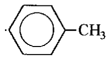
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