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SPECTROTHERMAL STUDIES ON Co(II), Ni(II), Cu(II) AND Zn(II) SALICYLATO (1,10-PHENANTHROLINE) COMPLEXES

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Abstract

The cobalt, nickel, copper and zinc atoms in bis(1,10-phenanthroline)bis(salicylato-O)metal(II) monomeric octahedral complexes $[M(Hsal)_2(phen)_2]\cdot nH_2O$, (*M*: Co(II), *n*=1; Cu(II), *n*=1.5 and Ni(II), Zn(II), *n*=2) are coordinated by the salicylato monoanion (*Hsal)* through the carboxyl oxygen in a monodentate fashion and by the 1,10-phenanthroline (*phen*) molecule through the two amine nitrogen atoms in a bidentate chelating manner. On the basis of the DTG_{max}, the thermal stability of the hydrated complexes follows order: Ni(II) (149°C)>Co(II) (134°C)>Zn(II) (132°C)>Cu(II) (68°C) in static air atmosphere. In the second stage, the pyrolysis of the anhydrous complexes takes place. The third stage of decomposition is associated with a strong exothermic oxidation process (DTA curves: 410, 453, 500 and 450°C for the Co(II), Ni(II), Cu(II) and Zn(II) complexes, respectively). The final decomposition products, namely CoO, NiO, CuO and ZnO, were identified by IR spectroscopy.

Keywords: salicylato-phenanthroline complexes, spectrothermal analysis

Introduction

Salicylic acid and metal salicylates have been used for many years as anti-inflammatory, antipyretic and analgesic drugs in medicine [1–4]. Salicylic acid (H_2sal) is a diprotic acid which forms in aqueous solutions hydrogen salicylate ($Hsal^{-}$) and salicylate (sal^{2-}) ions. From a coordination standpoint, salicylate is a versatile ligand, displaying a variety of bonding modes. For example, $Hsal^{-}$ anion is known to bond to metals as a unidentate carboxylate, as a bidentate chelating ligand using one carboxylate oxygen and hydroxyl oxygen and as a bidentate bridging carboxylate ligand. Both the hydroxyl and carboxyl protons can be lost from the parent acid to generate sal^{2-} which seems to be invariably chelating through the hydroxyl and one of the carboxyl oxygens [5].

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Mononuclear metal (II) complexes of salicylate derivatives with basic ligands containing nitrogen donors have been reported and few X-ray structures of them are known [2–6]. It has been found that by increasing the acidity of the alkylcarboxylate ligands or by increasing the basicity of the basic ligands, the tendency towards formation of monomeric complexes increases [2]. The X-ray crystal structure of polymeric $[Mn(Hsal)_2(bipy)]\cdot H_2O$ has also been reported [7].

Experimental

Materials and instrumentation

All chemicals used were analytical reagent products. Elemental analyses for C, H and N were carried out at the TUBITAK Marmara Research Centre in Turkey. The conductivity data were recorded using a Crison conductimeter, model 522. The concentrations of the solutions were approximately 10^{-3} M. Magnetic susceptibility measurements at room temperatures were performed using a Sherwood Scientific MXI model Gouy magnetic balance. UV-VIS spectra were obtained from the ethanol solutions of the complexes with a Unicam UV2 spectrometer in the range of 900–190 nm. IR spectra were recorded in the 4000–200 cm^{-1} region with a Mattson 1000 FT-IR spectrometer using KBr pellets. A Rigaku TG8110 thermal analyzer was used to record simultaneous TG, DTG and DTA curves in a static air atmosphere, at a heating rate of 10 K min^{-1} in the temperature range 20–1000°C using platinum crucibles. Highly sintered α-Al_2O_3 was used as a reference and the DTG sensitivity was 0.05 mg s^{-1}.

Preparation of complexes

$[M(Hsal)_2(H_2O)_4]\cdot 4H_2O$, (*M*: Co(II), Ni(II), Cu(II), Zn(II))

A solution of sodium salicylate, $NaC_7H_5O_3$, (1.60 g, 10 mmol) in water (25 mL) was added dropwisely with stirring at 50°C to the solutions of MSO_4 (5 mmol) in water (25 mL). The mixture was stirred for 4 h at 50°C in a temperature-controlled bath and the clear solution was then cooled to room temperature. The crystals formed were filtered and washed with 10 mL of cold water and acetone and dried in vacuo. Yield: 84, 88, 82, 76% respectively.

$[M(Hsal)_2(phen)_2]\cdot nH_2O$, (*M*:Co(II), *n*=1; Cu(II), *n*=1.5 and Ni(II), Zn(II), *n*=2)

A solution of 1,10-phenanthroline (0.748 g, 4 mmol) in ethanol (15 mL) was added dropwisely upon stirring to a solution of $[M(Hsal)_2(H_2O)_4]\cdot 4H_2O$ (2 mmol) in water (15 mL). The solution was heated to 50°C and stirred for 12 h in a temperature-controlled bath. The reaction mixture was then cooled to room temperature. The crystals formed were filtered and washed with a 10 mL of cold water and acetone and dried in vacuo. Yield: 89, 92, 72, 78%; found: C, 63.69, 62.34, 63.14, 62.21; H, 3.99, 4.02, 3.93, 3.91; N, 7.41, 7.48, 7.50, 7.62; calc.: C, 64.14, 62.58, 62.94, 62.01; H, 3.97, 4.15, 4.03, 4.11; N, 7.87, 7.68, 7.73, 7.61 for $C_{38}H_{28}N_4CoO_7$, $C_{38}H_{30}N_4NiO_8$, $C_{38}H_{29}N_4CuO_{7,5}$, $C_{38}H_{30}N_4ZnO_8$, respectively.

Results and discussion

The molar conductivity values of the complexes (Λ=11, 17, 19 and 14 S cm^2 mol^{-1} for the Co(II), Ni(II), Cu(II) and Zn(II) complexes, respectively) indicate that these complexes are non electrolyte in DMF. The Co(II), Ni(II) and Cu(II) complexes exhibit an experimental magnetic moment value of 3.38, 2.32 and 1.36 μ_B, respectively, which are consistent with a weak field octahedral geometry as expected. However, these magnetic moment values are lower than the spin only values for three, two and one unpaired electrons, indicative of some antiferromagnetic behavior [4]. The Zn(II) complex is diamagnetic.

UV-VIS spectra

For the pale-pink complex [Co(Hsal)$_2$(phen)$_2$]·H$_2$O displays the metal-to-ligand charge transfer bands in the 220–273 nm region (ε=4032–3890 dm^3 mol^{-1} cm^{-1}) and a shoulder at 348 nm (ε=1616 dm^3 mol^{-1} cm^{-1}) tailing into the visible region. The occurrence of two *d–d* bands at 482 nm (ε=35 dm^3 mol^{-1} cm^{-1}) as a shoulder and 860 nm (ε=2 dm^3 mol^{-1} cm^{-1}) for the Co(II) complex is consistent with an octahedral structure. The electronic spectrum for the light blue complex [Ni(Hsal)$_2$(phen)$_2$]·2H$_2$O exhibits two weak *d–d* absorption transitions centered at 559 nm (ε=8 dm^3 mol^{-1} cm^{-1}) and 879 nm (ε=6 dm^3 mol^{-1} cm^{-1}) which support octahedral geometry. The spectrum of Ni(II) complex also exhibits a charge transfer band at 317 nm (ε=2850 dm^3 mol^{-1} cm^{-1}) and a shoulder at 345 nm (ε=940 dm^3 mol^{-1} cm^{-1}) tailing into the visible region. The UV spectrum for the turquoise complex [Cu(Hsal)$_2$(phen)$_2$]·1.5H$_2$O exhibits a very broad *d–d* absorption transition centered at 683 nm (ε=98 dm^3 mol^{-1} cm^{-1}). This value was assigned to the $^2E_g \rightarrow ^2T_{2g}$ *d–d* transition, thereby suggesting octahedral geometry around Cu(II). The spectrum also exhibits the bands at ca. 246–309 nm (ε=4523–3560 dm^3 mol^{-1} cm^{-1}) tailing into the visible region and it is assigned to charge transfer. The colorless complex [Zn(Hsal)$_2$(phen)$_2$]·2H$_2$O exhibits no *d–d* absorption band as expected and displays the metal-to-ligand charge transfer bands in the 240–305 nm region (ε=3916–3233 dm^3 mol^{-1} cm^{-1}). A similar band between 400 and 450 nm previously reported for mononuclear copper(II) salicylate compounds was ascribed to a ligand-to-metal charge transfer transition [3, 4, 8].

IR spectra

The bands due to the asymmetric and symmetric stretching ν(COO) of the solid salicylic acid are positioned at 1657 and 1393 cm^{-1}, respectively. The ν(C=O) band at 1657 cm^{-1} is shifted to a lower frequency in the all complexes [e.g. 1595 cm^{-1} for Co(II); 1585 cm^{-1} for Ni(II); 1588 cm^{-1} for Cu(II); 1596 cm^{-1} for Zn(II)] showing that the coordination takes place through the carboxyl group [9, 10]. The difference between the wavenumbers of ν_{asym} and ν_{sym} bands (Δ) is the identifying parameter of the structure of metal-carboxylate anion bond. The observed Δ values for the ligand (H$_2$sal) and its Co(II), Ni(II), Cu(II) and Zn(II) complexes were 264, 205, 196, 185 and 207 cm^{-1}, respectively. The observed Δ values indicate that the coordination is monodentate [3, 11]. The phenolic δ(OH) bending peak for the salicylic acid remained almost in the same position at 1250 cm^{-1} in all complexes suggesting that the phenol group retains the proton. All the complexes show a broad band of strong intensity in the range of 3403–3434 cm^{-1} responsible from the ν(OH) of crystallization water. The sharp absorption bands in the range of 1434–1427 and 858–848 cm^{-1} in complexes are due to the ν(C–N) and δ(C–H) vibrations, respectively. The stretching band for the ν(C=N) of the solid phenanthroline observed at 1643 cm^{-1} [12] was shifted to lower frequencies in the spectrum of the complexes [e.g. 1634 cm^{-1} for Co(II); 1634 cm^{-1} for Ni(II); 1629 cm^{-1} for Cu(II); 1634 cm^{-1} for Zn(II)]. The low intensity bands in the region of 424–391 cm^{-1} are attributed to M–N and M–O vibrations [13]. On the basis of IR spectra, it may be said that the structures of the studied metal complexes are somewhat resemblant.

Thermal analysis

The thermal analysis curves (TG, DTA and DTG) of the studied complexes are shown in Figs 1–4. The thermoanalytical results are summarized in Table 1. The experimental results of TG, DTG, DTA and IR spectra show that the first stages in the decomposition process of all the complexes is related to dehydration. According to the DTG and DTA curves, the dehydration process takes place in a single step which corresponds exactly to the loss of the crystal waters. The dehydration temperature of the complexes lies in the range of 54–189°C. On the basis of the DTG_{max}, the thermal stability of the hydrated complexes follows order: Ni(II) (149°C)>Co(II) (134°C)>Zn(II) (132°C)>Cu(II) (68°C). These hydrated complexes show similar sequence in the nicotinamide-acetylsalicylato mixed-ligand complexes with the identical metal ions [14].

In the second stage, the pyrolysis of the anhydrous complexes takes place. The Co(II) and Ni(II) complexes decompose in a similar manner. The second mass loss stages of these complexes were observed in the range of 196–309°C for the Co(II) complex and 193–286°C for the Ni(II) complex. However, the decomposition process

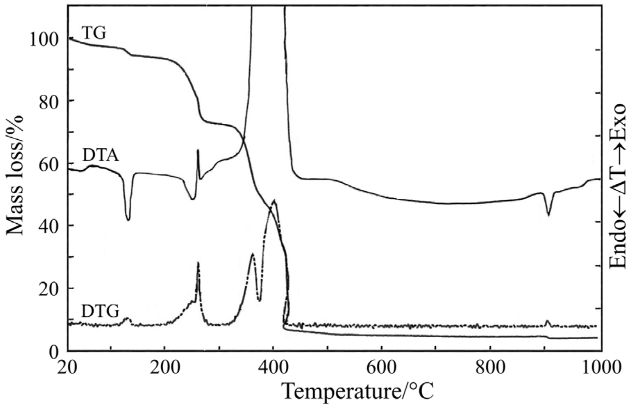

Fig. 1 TG, DTA and DTG curves of $[Co(Hsal)_2(phen)_2]\cdot H_2O$

Table 1 Thermoanalytical results (TG, DTG, DTA) on the Co(II), Ni(II), Cu(II) and Zn(II) salicylato(1,10-phenanthroline) complexes

Complex	Temp. range/°C	DTG$_{max}$[a]/ °C	Rem. group	Mass loss/%		Total mass loss/%		Solid decomp. product	Color
				found	calcd.	found	calcd.		
[Co(Hsal)$_2$(phen)$_2$]·H$_2$O								[Co(Hsal)$_2$(phen)$_2$]	pink
1	98–179	134(+)		2.86	2.53				violet
2	196–309	263(–)	H$_2$O	21.06	–				–
2	309–378	357(–)		28.25	–				–
4	378–443	410(–)		36.50	–	88.67	89.46	CoO	black
[Ni(Hsal)$_2$(phen)$_2$]·2H$_2$O									light-blue
1	104–182	149(+)		4.32	4.93			[Ni(Hsal)$_2$(phen)$_2$]	yellow
2	193–286	253(–)	2H$_2$O	19.15	–				–
3	342–405	376(–)		15.12	–				–
4	405–489	453(–)		52.10	–	90.69	89.79	NiO	green-black
[Cu(Hsal)$_2$(phen)$_2$]·1.5H$_2$O									turquoise
1	54–88	68(+)		3.55	3.72			[Cu(Hsal)$_2$(phen)$_2$]	yellow-green
2	204–253	244(+)	1.5H$_2$O	16.23	–				–
3	253–352	266(–)		27.67	–				–
4	353–562	500(–)		41.33	–	88.78	89.03	CuO	black
[Zn(Hsal)$_2$(phen)$_2$]·2H$_2$O									colorless
1	92–145	132(+)	H$_2$O	2.58	2.44			[Zn(Hsal)$_2$(phen)$_2$]	colorless
2	145–189	161(+)		2.24	2.44				–
3	196–312	266(+)	H$_2$O	37.20	–				–
4	366–426	413(–)		27.91	–				–
5	426–524	450(–)		18.33	–	88.26	88.94	ZnO	colorless

[a] Exothermic and endothermic processes are denoted by (–) and (+), respectively.

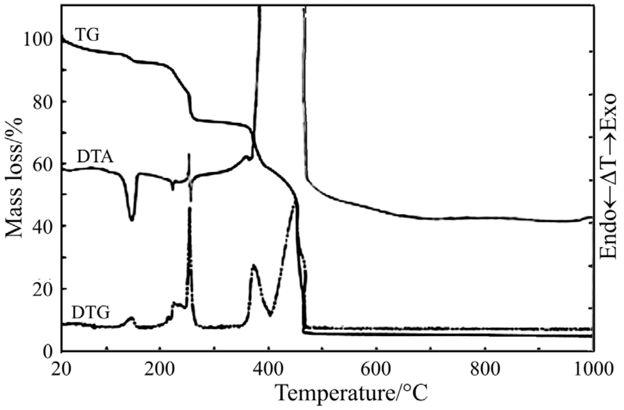

Fig. 2 TG, DTA and DTG curves of $[Ni(Hsal)_2(phen)_2]\cdot 2H_2O$

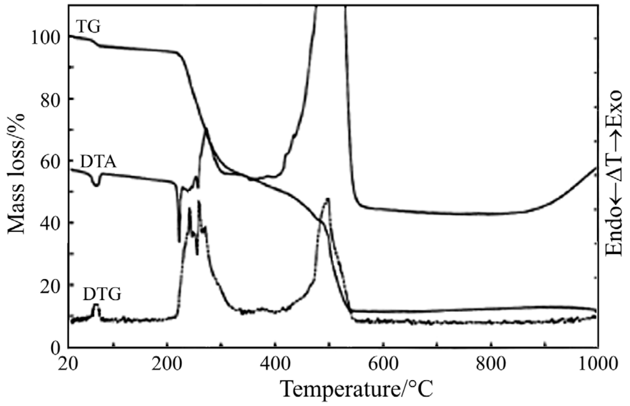

Fig. 3 TG, DTA and DTG curves of $[Cu(Hsal)_2(phen)_2]\cdot 1.5H_2O$

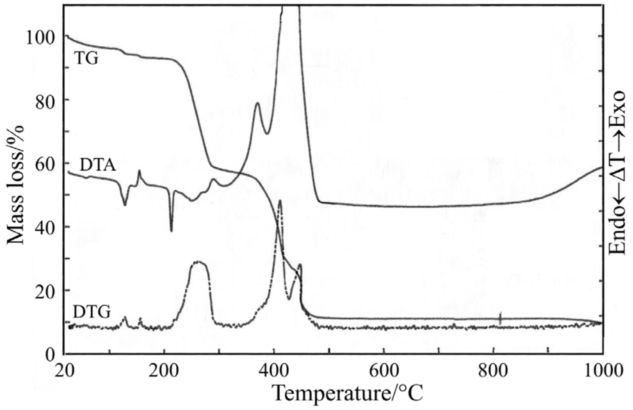

Fig. 4 TG, DTA and DTG curves of $[Zn(Hsal)_2(phen)_2]\cdot 2H_2O$

is initially endothermic, an exothermic contribution is also observed in the DTA curve of the Co(II) complex. The similar but opposite contribution is also observed for the Ni(II) complex. These stages of the complexes are related to the partial decomposition of phenanthroline ligand and the release of CO_2 from the salicylato ligand. The exothermic contribution is likely due to the release of CO_2 [15]. Early reported data on thermal analysis and mass spectrometric studies indicate that the salicylate-metal complexes decompose by releasing of CO_2 [16–18]. A decrease in the CO_2 stretching intensity of the intermediate products was observed in the vibrational spectra of the Co(II) and Ni(II) complexes. In the Co(II) and Ni(II) complexes, the pyrolysis occurred in two successive steps resulting stable intermediate products. Since both ligands decomposed partially in the thermal process, the intermediate products were not identified. The anhydrous Cu(II) and Zn(II) complexes begin to decompose with melting at 222 and 217°C, respectively, according to the DTA curves.

Similar to the other salicylato and benzoate derivative complexes [9, 19–21], the third stage of decomposition is associated with a strong exothermic oxidation process (DTA curves: 410, 453, 500 and 450°C for the Co(II), Ni(II), Cu(II) and Zn(II) complexes, respectively). In the Co(II), Ni(II) and Zn(II) complexes, the strong exothermic mass loss processes occur in two steps, a single DTG peak was observed for the Cu(II) complex. During this stage, the remaining organic part is abruptly burnt in all complexes. In the Co(II) complex, the endothermic peak at 915°C is related to the conversion of Co_3O_4 to CoO. The final decomposition products, namely CoO, NiO, CuO and ZnO, were identified by IR spectroscopy with corresponding spectra obtained under the same conditions as the pure oxides. The values for the final products given in Table 1 show good agreement with the corresponding oxides.

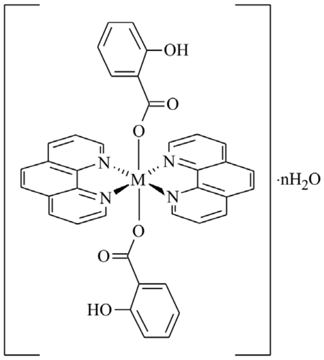

Fig. 5 Suggested structures of the complexes

The structures of the synthesized complexes which are presented in Fig. 5, are consistent with the chemical, thermal and spectroscopic properties which were determined.

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