Thermochimica Acta, 82 (1984) 335–343
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS AND CHARACTERIZATION OF MIXED-LIGAND COMPLEXES OF NICKEL(II) WITH 5,5′-THIODISALICYLIC ACID AND AMINES *

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(Received 16 July 1984)

ABSTRACT

The 5,5′-thiodisalicylato complexes of nickel(II) with water, ammonia, methylamine and pyridine were synthesized and their structure established to be $[Ni(TDSA)L_2 \cdot nH_2O]$, where TDSA = 5,5′-thiodisalicylic acid, $[C_6H_3(OH)(COOH)SC_6H_3(OH)(COOH)]$, L = H_2O, NH_3, CH_3NH_2 or pyridine, and $n = 3$ for H_2O, 2 for NH_3 and CH_3NH_2, and 1 for pyridine complexes, from elemental analysis, IR and electronic spectroscopy, and magnetic susceptibility measurement. The thermal behaviour of the complexes has been studied by TG and DTA. TG shows three main steps of decomposition, viz. dehydration, axial base liberation, and decarboxylation leading to the formation of NiO at the final stage.

INTRODUCTION

During the last decade, a number of model coordination compounds containing 5,5′-thiodisalicylic acid (TDSA), $[C_6H_3(OH)(COOH)SC_6H_3(OH)(COOH)]$ have been investigated both spectroscopically and magnetically [1–3]. However, the thermal behaviour on these compounds has not been reported so far. Recently, thermal studies for copper(II)–TDSA complexes with different amines have been reported [4]. It was observed that the decomposition of the above complexes proceeds in nitrogen atmosphere by the loss of axial base and decarboxylation of thiodisalicylato groups. The present study is an extension of earlier work on TDSA complexes. This communication describes the preparation, characterization and thermal behaviour of nickel(II)–TDSA complexes with different amines.

EXPERIMENTAL

Preparation of the complexes

The nickel(II)–TDSA complex, $[Ni(TDSA) \cdot 5H_2O]$ was prepared by mixing a solution of nickel(II) chloride hexahydrate with an ethanolic solution

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* Accepted for presentation in the 29th International Congress of Pure and Applied Chemistry, Cologne, F.R.G., 1983.

0040-6031/84/$03.00

TABLE 1

Analytical data and magnetic moment values of the complexes studied

Complex	Colour	Experimental (%)					Theoretical (%)					Solubility	μ_{eff} (BM)
		Ni	C	H	S	N	Ni	C	H	S	N		
Ni(TDSA)$\cdot$5H_2O	Green	12.86	37.02	3.25	6.84	—	13.02	37.27	3.55	7.10	—	Insol.	3.35
Ni(TDSA)$(NH_3)_2\cdot 2H_2O$	Blue	13.25	38.78	3.50	7.26	6.38	13.62	39.00	3.71	7.40	6.50	Insol.	3.50
Ni(TDSA)$(CH_3NH_2)_2\cdot 2H_2O$	Blue	13.05	41.50	4.50	7.02	5.95	12.79	41.81	4.47	6.97	6.10	Insol.	3.42
Ni(TDSA)$(py)_2\cdot H_2O$	Blue-green	11.20	53.28	3.05	5.95	5.22	10.94	53.66	3.35	5.70	5.22	Insol.	2.58

of TDSA (1 : 1). A green complex formed when this mixture was refluxed in a waterbath. The complex was filtered and washed with water, then ethanol, and dried in vacuum.

The amine complexes of nickel–TDSA were prepared by suspending $[Ni(TDSA) \cdot 5H_2O]$ in ethanol, and then adding slightly more than the calculated quantity of amines. The mixture was shaken for ~5 h. The resulting complex was filtered and washed with ethanol and dried in vacuum.

Detailed elemental analyses are given in Table 1.

Physical measurements

The IR spectra of the complexes have been recorded in the range 4000–250 cm^{-1} with a Beckman IR spectrophotometer (IR-20A), as KBr discs.

The electronic spectra of the complexes were recorded in Nujol mull on a Cary 14 spectrophotometer in the range 250–1200 nm.

Magnetic measurements on solid complexes were made by Gouy's method using mercury tetrathiocyanato cobaltate(II) ($X_g = 16.44 \times 10^{-6}$ CGS units) as calibrating agent.

Thermal studies were carried out as previously described [5].

RESULTS AND DISCUSSION

The analytical data for the prepared complexes $[Ni(TDSA)L_2 \cdot nH_2O]$ ($L = H_2O$, NH_3, CH_3NH_2 or py, and $n = 3$ for water, 2 for amines, and 1 for pyridine complexes) along with their magnetic moment values are given in Table 1. All the complexes decompose without melting at > 200 °C and are insoluble in water and common organic solvents. To determine whether the nH_2O is coordinated or crystalline, information from TG results was taken. The first step in TG, which corresponds to the loss of H_2O from the complex occurs at > 100°C. If the nH_2O is coordinated, the weight loss would take place at a higher temperature and, hence, the nH_2O in the complex must be water of crystallization only.

IR absorption spectra

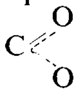
The bonding site of TDSA involved in the complexes has been determined by careful comparison of the IR spectra of the complexes with that of TDSA. The IR absorption bands of diagnostic value and their tentative assignments are given in Table 2. TDSA shows two absorption bands at 1660 and 1600 cm^{-1} due to asymmetric and symmetric  $C\substack{\diagup O\\ \diagdown O}$ stretching vibrations, respectively. The large shift in the asymmetric carboxylate frequency after complexation indicates participation of the carboxylic group in bonding with the metal ion [2]. The νOH band of the complexes is shifted towards the lower wavenumber of about 100 cm^{-1} using the value of 3360 cm^{-1} as reference for νOH for the free ligand TDSA. The broad band of free TDSA arises due to hydrogen bonding between the COOH and OH groups of salicylic acid which disappears after complexation. It suggests a coordination through the oxygen atom of the OH group. The absorption

TABLE 2

IR observed frequencies (cm^{-1}) and assignments for TDSA and its complexes [a]

TDSA	[Ni(TDSA)-(H_2O)$_2$]·3H_2O	[Ni(TDSA)-(CH_3NH_2)$_2$]·2H_2O	[Ni(TDSA)-(NH_3)$_2$]·2H_2O	[Ni(TDSA)-(py)$_2$]·H_2O	Assignment
	3470 (s)	3450 (ms)	3435 (ms)	3450 (m)	νOH for crystalline water
3360 (br)					νOH hydrogen bonded
			3370 (vs)		
		3320 (vs)	3280 (ms)		νNH
	1675 (w)				
1660 (s)		1650 (w)	1640 (w)		νCOO_{asym}
1600 (s)	1605 (s)	1610 (s)	1615 (ms)	1600 (s)	νCOO_{sym}
	1580 (m)	1575 (s)	1570 (m)	1575 (m)	H–O–H bending
				1550 (ms) 1450 (s)	Ring stretching (py)
1470 (s)	1460 (s)	1465 (ms)	1490 (ms)	1480 (s)	νC–C
1440 (s)	1440 (m)	1440 (m)	1435 (s) 1429 (s)	1430 (m)	νC–C + CH scissor
1390 (m)	1370 (s)	1380 (s)	1360 (m)	1390 (s)	νCOO_{sym} + CH bending
1340 (w)	1350 (m)		1340 (s)	1335 (s)	CH bending
1200 (s)	1140 (s)	1150 (ms)	1180 (m)	1170 (s)	νCO
1080 (s)			1080 (s)		
				1045 (s) 1015 (s)	py ring skeleton
960 (w)	975 (w)	965 (w)	969 (w)	985 (w)	C=C deformation
890 (s)	930 (w)			895 (s)	COO scissors
	800 (s)				H_2O coordinated
700 (s)			680 (w)	695 (s)	C–C out of plane deformation
565 (s)	550 (m)	510 (m)	570 (m)	575 (m)	
460 (s)		460 (w) [b]	480 (w) [b]	510 (w) [b]	νNi–N [b]
	445 (w) [c]				νNi–O [c]
395 (s)	410 (vw)	390 (m)	400 (vw)	400 (w)	
370 (w)	380 (m)	350 (w)	385 (w)	370 (w)	

[a] vs, very strong; ms, moderately strong; s, strong; m, moderate; w, weak; vw, very weak; br, broad.

[b] Frequencies for the nickel–nitrogen bond.

[c] Frequencies for the nickel–oxygen bond.

band around 3450 cm^{-1} (indicative of the H–O–H stretching frequency) [5] and another around 1575 cm^{-1} (indicative of the bending mode of H–O–H) [6] both confirm the presence of water in the complexes. The very sharp and strong absorption for the complex $[Ni(TDSA) \cdot 2H_2O] \cdot 3H_2O$ at 800 cm^{-1} [7] confirms the presence of coordinated water. For amine complexes, coordination occurs between the nickel and nitrogen atoms of the amine, and the NH_2 vibrations of the amine complex ions are perturbed. The far IR region (500–250 cm^{-1}) of the complexes shows the presence of additional bands due to the Ni–O and Ni–N stretching frequencies [8].

Magnetic moments

The magnetic moments of the complexes are in the range 3.35–3.50 BM, except for the $[Ni(TDSA)(py)_2] \cdot H_2O$ complex, in which the magnetic moment is 2.85 BM. The moments observed in the present complexes are in the range of octahedral complexes [9]. The reduction in the μ_{eff} value of the pyridine complex suggests a distortion due to an exchange interaction.

Electronic spectra

The electronic spectral data of the complexes are summarised in Table 3. The three major absorption bands observed in reflectance spectra are around 26500, 16000 and 10000 cm^{-1}. They are all very weak in intensity. In addition to the above, a band is observed at 21000 cm^{-1} for the $[Ni(TDSA)(py)_2] \cdot H_2O$ complex, due to the splitting of the ν_3 band, arising from the distortion [10]. The above bands in O_h symmetry may be assigned to the transitions $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, ν_3; $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, ν_2; and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ν_1. The ν_2/ν_1 ratios are ~ 1.6 and agree well with reported values for octahedral nickel(II) complexes [11]. The ligand field splitting

TABLE 3

Electronic spectra

Compound	Electronic spectra (cm^{-1})			Dq (cm^{-1})	B' [a] (cm^{-1})	LFSE (kcal mol^{-1})	ν_2/ν_1	β
	ν_1	ν_2	ν_3					
$[Ni(TDSA)2H_2O] \cdot 3H_2O$	9800	16000	26000 (25410) [b]	980	910	33.51	1.63	0.87
$[Ni(TDSA)(NH_3)_2] \cdot 2H_2O$	10100	16200	26700 (26370) [b]	1010	950	34.54	1.60	0.91
$[Ni(TDSA)(CH_3NH_2)_2] \cdot 2H_2O$	10000	16250	26500 (26140) [b]	1000	940	34.32	1.62	0.92
$[Ni(TDSA)(py)_2] \cdot H_2O$	10500	16600 21000	27000 (27300) [b]	1050	980	35.91	1.59	0.94

[a] B' is taken to be 1041 cm^{-1} for nickel(II) ion.

[b] Calculated values.

energy, $10Dq$, is taken to be equal to the energy of the first transition (ν_1) and the Racah parameter, B', was calculated by an empirical method [12]. Table 3 shows the Dq, B', β and ligand field stabilisation energy (LFSE) of the complexes. The ratio (β) of B'/B (0.94–0.87) is comparable to that found for other nickel(II) octahedral complexes.

Thermal studies

The TG, DTG and DTA curves of the $[Ni(TDSA)(H_2O)_2]\cdot 3H_2O$ complex are given in Fig. 1. The TG curve reveals that it is stable up to 80°C after which it starts to decompose without forming any stable isolable intermediate. The weight loss shows the final residue to be NiO (weight loss: exp., 82.90%; theor., 83.43%) at 330°C. The first loss in weight on heating from 80 to 140°C corresponds to dehydration. The intermediate obtained at this temperature $[Ni(TDSA)\cdot 2H_2O]$ could not be isolated since it starts to decompose even before it is completely formed. The DTG curve shows two identifiable dehydration steps at 110 and 140°C, with a mass loss corresponding to H_2O and $2H_2O$, and the stoichiometry of thermal decomposition may be expressed as

$$[Ni(TDSA)(H_2O)_2]\cdot 3H_2O \rightarrow [Ni(TDSA)H_2O]\cdot 2H_2O$$
$$\rightarrow [Ni(TDSA)(H_2O)_2]$$

In the DTA curve the stepwise dehydration of the complex is indicated by the presence of a broad endothermic peak split into two bands at 130 and 140°C. The exothermic peak at 210°C corresponds to the loss of coordinated water molecules, and the other peaks at 240 and 280°C are due to the

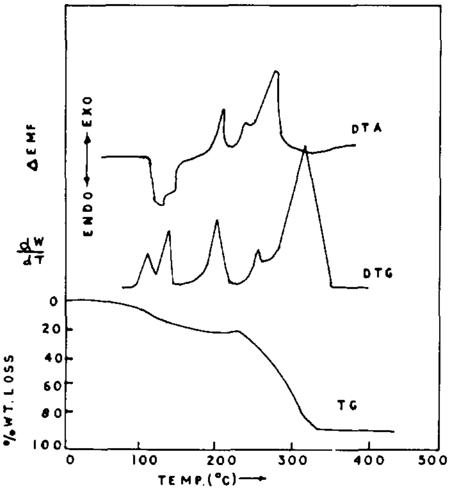


Fig. 1. TG, DTG and DTA curves of the complex $[Ni(TDSA)(H_2O)_2]\cdot 3H_2O$.

decomposition of Ni–TDSA to nickel oxide. The split nature of the strong exothermic peak between 240 and 280°C indicates that the decomposition of Ni–TDSA is a highly complex, multistep process. This is further confirmed by the presence of two peaks at 255 and 320°C in the DTG curve.

The thermal behaviour of ammonia, methylamine and pyridine complexes is comparable to that of $[Ni(TDSA)(H_2O)_2]\cdot 3H_2O$, thereby suggesting that the decomposition of these complexes proceeds in a similar manner. Figures 2 and 3 show the thermal analysis curves of the $[Ni(TDSA)(NH_3)_2]\cdot 2H_2O$ and $[Ni(TDSA)(CH_3NH_2)_2]\cdot 2H_2O$ complexes. The final residue formed after loss of H_2O, amines and TDSA, is NiO (weight loss; exp., 81.78%; theor., 82.66% up to 370°C for NH_3, and exp., 84%; theor., 83.75% up to 340°C for CH_3NH_2 complexes) as confirmed from TG. DTA results show that these complexes undergo an endothermic reaction at about 120°C with the loss of a water molecule, and further exothermic reactions take place with a mass loss corresponding to amines at ~ 200°C and TDSA at ~ 300°C.

The axial base loss of pyridine in the $[Ni(TDSA)(py)_2]\cdot H_2O$ complex occurs between 190 and 250°C. The DTG curve (Fig. 4) shows two peaks at 200 and 235°C, both of a split nature, corresponding to the decomposition of pyridine in two steps

$$Ni(TDSA)py_2 \xrightarrow{I} Ni(TDSA)py \xrightarrow{II} Ni(TDSA) \qquad (2)$$

In the DTA curve the stepwise evolution of pyridine is indicated by a broad exothermic band at 230°C with a shoulder at 200°C. A further exothermic reaction takes place at 330°C with a mass loss corresponding to TDSA and the formation of NiO (weight loss; exp., 85.88%; theor., 86.08%).

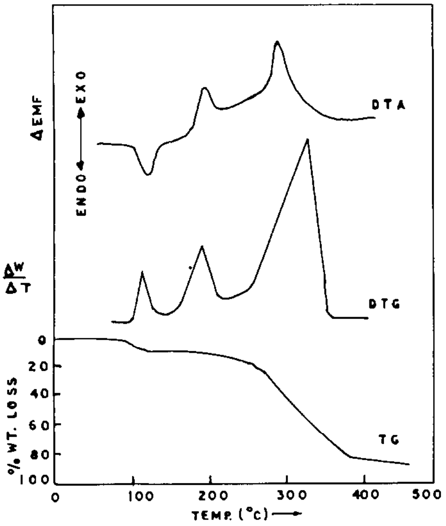


Fig. 2. TG, DTG and DTA curves of the complex $[Ni(TDSA)(NH_3)_2]\cdot 2H_2O$.

The decomposition of $[Ni(TDSA)(H_2O)_2] \cdot 3H_2O$ begins at around 80°C, while the decomposition of $[Ni(TDSA)(CH_3NH_2)_2] \cdot 2H_2O$, $[Ni(TDSA)(NH_3)_2] \cdot 2H_2O$ and $[Ni(TDSA)(py)_2] \cdot H_2O$ starts at 85, 90 and 95°C, respectively. On the basis of their initial decomposition temperatures, their thermal stability follows the order $[Ni(TDSA)(py)] \cdot H_2O > [Ni(TDSA)(NH_3)_2] \cdot 2H_2O > [Ni(TDSA)(CH_3NH_2)_2] \cdot 2H_2O > [Ni(TDSA)(H_2O)_2] \cdot 3H_2O$. From the above studies it can be inferred that the com-

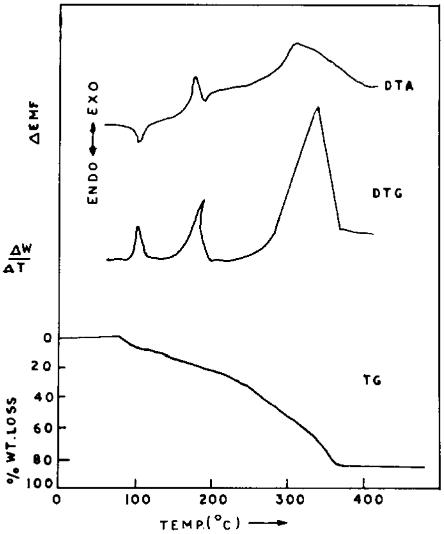


Fig. 3. TG, DTG and DTA curves of the complex $[Ni(TDSA)(CH_3NH_2)_2] \cdot 2H_2O$.

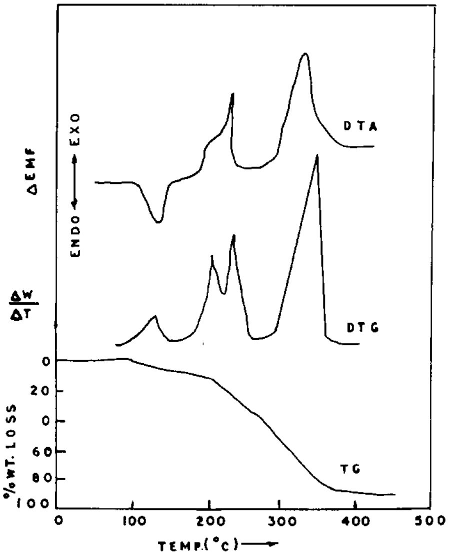


Fig. 4. TG, DTG and DTA curves of the complex $[Ni(TDSA)(py)_2] \cdot H_2O$.

plexes follow three steps in a sequential thermal decomposition process, viz. dehydration, decomposition of axial base, and decarboxylation

$$[\mathrm{Ni(TDSA)L_2}]\cdot n\mathrm{H_2O} \overset{\text{1st}}{\rightarrow} \mathrm{Ni(TDSA)L_2} + n\mathrm{H_2O}$$

$$\mathrm{Ni(TDSA)L_2} \overset{\text{2nd}}{\rightarrow} \mathrm{Ni(TDSA)} + 2\mathrm{L}$$

$$\mathrm{Ni(TDSA)} \overset{\text{3rd}}{\rightarrow} \mathrm{NiO}$$

The order of the thermal stability pyridine > ammonia > methylamine > aquo complexes correlates with the bond strengths of the complexes: Ni–N bonds of pyridine, methylamine and ammonia, and the Ni–O bond of water, as estimated by the vibrational frequencies of the complexes; i.e., νNi–N of pyridine complex (510 $\mathrm{cm^{-1}}$) > νNi–N of ammonia complex (480 $\mathrm{cm^{-1}}$) > νNi–N of methylamine complex (460 $\mathrm{cm^{-1}}$) > νNi–O of aquo complex (445 $\mathrm{cm^{-1}}$).

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