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THERMAL STUDIES ON COPPER(II)-5,5'-THIODISALICYLIC ACID COMPLEXES

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Aquo, ammonia and pyridine complexes of copper(II) with 5,5'-thiodisalicylic acid have been investigated by TG and DTG. All these complexes decompose in three distinct steps, viz. dehydration, loss of axial bases and decarboxylation of the aromatic ligand. The thermal curves of the aquo and pyridine complexes show water loss in two distinct steps. The decreasing order of thermal stability of the complexes is py > NH_3 > H_2O.

The structural features of the coordination compounds play an important role in thermal decomposition reactions with linear temperature increase and they can affect their stoichiometry. Recently, systematic studies on the thermal analysis of metal complexes have been reported [1 – 4].

The transition metal complexes of 5,5'-thiodisalicylic acid the

$$[C_6H_3(COOH)(OH)S\ C_6H_3(COOH)(OH)]\ (TDSA)$$

have been the subject of extensive studies due to their interesting stereochemistries [5 – 8]. The preparation and characterization of copper(II) – TDSA complexes by elemental analysis, infrared spectroscopy and magnetic susceptibility studies were reported earlier [9]. No thermal studies, however, have been described. It is therefore of interest to study the thermal properties of the aquo, ammonia and pyridine copper(II) – TDSA complexes.

The object of the present paper is to discuss the possibilities of a correlation between the structure and the stepwise character of the thermal decomposition for aquo, ammonia and pyridine copper(II) – TDSA complexes.

Experimental

The complexes were prepared by the methods already reported [8, 9]. The prepared complexes were analyzed for carbon, hydrogen, nitrogen (micro-analytical method), metal and sulphur to ensure the purity of the complexes. The analytical data are given in Table 1.

The thermogravimetric data were obtained using a Stanton Thermobalance model MF-6. Weighed samples of the dried metal complexes were stored in

Table 1

Analytical data of the complexes

Compounds	Metal, %		Sulfur, %		Carbon, %		Hydrogen, %		Nitrogen, %	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc
$H_2[Cu(TDSA)_2(H_2O)_2 \cdot 7\ H_2O$	7.55	7.60	7.68	7.60	40.17	40.20	3.39	4.30	—	—
$(NH_4)_2[Cu(TDSA)_2(NH_3)_2 \cdot 5\ H_2O$	7.60	7.63	7.80	7.69	40.40	40.41	4.79	4.81	6.64	6.73
$H_2[Cu(TDSA)_2(py)_2 \cdot 4\ H_2O$	7.00	7.02	6.95	7.08	52.00	50.47	3.88	3.98	4.0	3.09

Table 2

Reactions and corresponding temperature ranges observed in thermal decomposition of the complexes

Compounds	DTG Temperature, °C	Observed loss, %	Calculated loss, %	Conclusion
$H_2[Cu(TDSA)_2(H_2O)_2 \cdot 7\ H_2O$	100–180	15	15.08	$-7\ H_2O$ (water of crystalization loss)
	220	19.54	19.62	$-2\ H_2O$, $-H_2$
	300	42.27	40.69	decarboxylation ($-4\ CO_2$)
$(NH_4)_2[Cu(TDSA)_2(NH_3)_2 \cdot 5\ H_2O$	100–180	10.93	10.82	$-5\ H_2O$ (water of crystalization)
	240	19.27	19.24	$-(NH_4)_2$, $-(NH_3)_2$
	300	40.1	40.40	decarboxylation ($-4\ CO_2$)
$H_2[Cu(TDSA)_2(py_2 \cdot 4\ H_2O$	100–200	7.69	7.96	$-4\ H_2O$ (water of crystalization)
	280	25.38	25.67	-2 (py), $-H_2$
	320	46.15	45.15	decarboxylation ($-4\ CO_2$)

freshly tared crucibles placed in a desiccator. For TG studies, the samples were subjected to a heating rate of 5° per min, in an atomsphere of air and data were collected up to 320°. The sensitivity of the balance was 20 mg full scale. The type of volatile products lost during decomposition was computed from the weight losses.

Absorption spectra of the complexes were recorded with a Cary model 14 spectrophotometer, provided with an automatic recording system. The spectra were taken in nujol mull.

Results

The complexes studied here have general formula $M_2[Cu(TDSA)_2L_2]xH_2O$ where M stands for H^+ or NH_4^+, L stands for H_2O, NH_3 or C_5H_5N, and $x = 7.5$ and 4 for aquo, amine and pyridine complexes, respectively. The complexes have octahedral stereochemistry and polymeric structure [9]. The copper is linked to the oxygen of the COO^- groups of the TDSA (bidentate ligand) and to Lewis bases such as H_2O, NH_3 and pyridine in their respective complexes.

Table 2 shows the decomposition behaviour of the complexes.

$$H_2[Cu(TDSA)_2(H_2O)_2] \cdot 7\,H_2O\,. \tag{1}$$

According to the thermal curves of the complex $H_2[Cu(TDSA)_2(H_2O)_2] \cdot 7\,H_2O$ Fig. (1), three step processes occur. The DTG curve shows two identifiable dehydration steps, at 120° and 160°, and its decomposition stoichiometry may be ex-

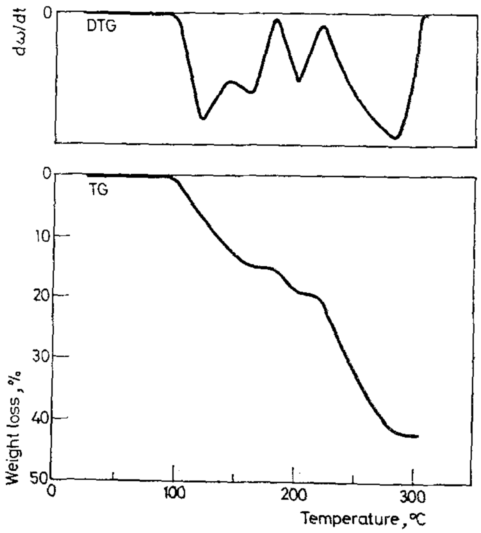

Fig. 1. TG and DTG curves of $H_2[Cu(TDSA)_2(H_2O)_2] \cdot 7\,H_2O$

pressed by the scheme

$$H_2[Cu(TDSA)_2(H_2O)_2] \cdot 7\,H_2O; \quad 7 \rightarrow 2,\ 2 \rightarrow 0\,.$$

This indicates that loosely-bound water molecules are lost first, followed by strongly-held water.

The DTG peak corresponding to the second step indicates a decrease equivalent to two water molecules at 200°. At 260° the breaking of copper-oxygen (COO^- group) bonds takes place due to decarboxylation of the TDSA ligand.

$$(NH_4)_2[Cu(TDSA)_2(NH_3)_2] \cdot 5\,H_2O\,. \tag{2}$$

The thermal curves of the complex $(NH_4)_2[Cu(TDSA)_2(NH_3)_2] \cdot 5\,H_2O$ show three steps of decomposition (Fig. 2). In this case, between the steps I and II, the TG curve of the complex yields horizontal line from 160 to 200°, showing the stability of the dehydrated compounds $(NH_4)_2[Cu(TDSA)_2(NH_3)_2]$ up to 200°. The second step of decompoistion occurs in the temperature range 200–200°. The weight remaining at this stage correspond to $[Cu(TDSA)_2]$. This indicates the lose of NH_3 and NH_4^+ molecules (Table 2). In the third stage of decomposition (240 to 300°) the loss of weight corresponds to the decarboxylation of TDSA.

$$H_2[Cu(TDSA)_2(C_5H_5N)_2] \cdot 4\,H_2O\,. \tag{3}$$

The thermal curves (Fig. 3) of the complex $H_2[Cu(TDSA)_2(C_5H_5N)_2] \cdot 4\,H_2O$ show a similar character of decomposition to that of the aquo and ammonia

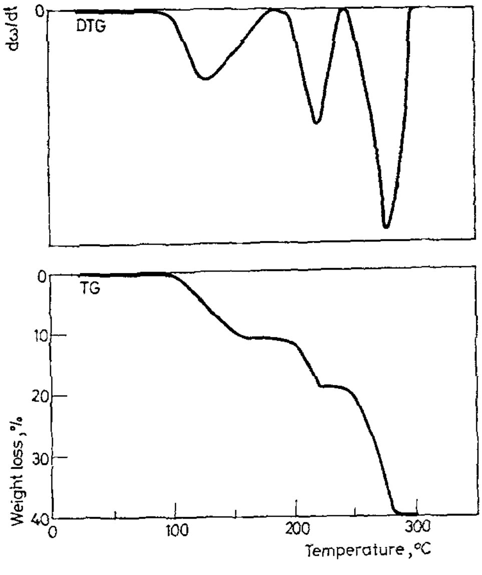

Fig. 2. TG and DTG curves of $(NH_4)_2[Cu(TDSA)_2(NH_3)_2] \cdot 5\,H_2O$

complexes, but at higher temperatures. According to Table 2, the loss of two molecules of pyridine takes place between 220 and 260° i.e. at a temperature higher than those observed in the corresponding complexes with H_2O and NH_3. This elimination leads to the formation of the tetracoordinated complex $[Cu(TDSA)_2]$, found to be stable up to 280° (TG curve, Fig. 3). During the dehydration process (1st step of decomposition) the complex releases the H_2O in two steps in the temperature ranges 100 – 140° and 140 – 200° as is clearly identifiable from the DTG curve (Fig. 3) and its decomposition stoichiometry may be expressed by the scheme

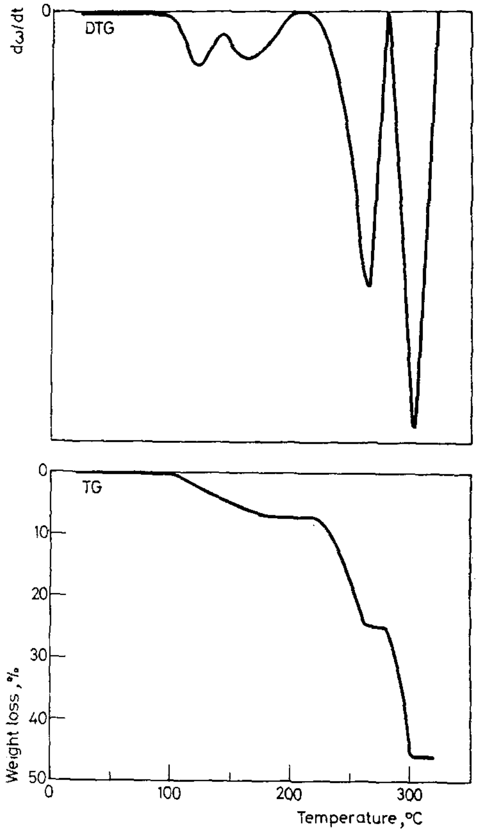

Fig. 3. TG and DTG curves of $H_2[Cu(TDSA)_2(py)_2] \cdot 4\ H_2O$

$$H_2[Cu(TDSA)_2(py)_2] \cdot 4\,H_2O; \quad 4 \rightarrow 2; \quad 2 \rightarrow 0$$

In the third step of decomposition the decarboxylation of TDSA takes place at higher temperature, 300° (DTG curve).

Discussion

The complexes undergo thermal decomposition in the three steps

1	Dehydration
$M_2[Cu(TDSA)_2L_2] \cdot xH_2O$	$M_2[Cu(TDSA)_2L_2] + xH_2O$
2	Decomposition of axial base
$M_2[Cu(TDSA)_2L_2]$	$[Cu(TDSA)_2] + 2M + 2L$
3	
$Cu(TDSA)_2$	Decarboxylation of TDSA.

From the above thermal decomposition studies it can be inferred that the thermal stability of the copper axial base bond in these complexes decreases in the following order:

$$py > NH_3 > H_2O\,.$$

The highest thermal stability is displayed by the complex $H_2[Cu(TDSA)_2(py)_2] \cdot 4\,H_2O$ (280–300°). It is inferred that the thermal stability of the complexes is influenced by the copper-oxial base bond.

Table 3

Thermal decomposition maximum of Lewis bases and absorption maxima of the complexes

Complexes	*Td* (max.), °C	*J* max d–d transition, cm^{-1}
$H_2[Cu(TDSA)_2(H_2O)_2 \cdot 7H_2O$	200	13 890
$(NH_4)_2[Cu(TDSA)_2(NH_3)_2 \cdot 5H_2O$	220	24 100
$H_2[Cu(TDSA)_2(py)_2 \cdot 4H_2O$	260	26 200

Table 3 presents the decomposition temperature maxima (*Td*) of the H_2O, NH_3 and C_5H_5N complexes, obtained from the DTG curves, and the frequencies of the absorption band maxima ν^{max} of the $d-d$ transitions of the electronic spectra of the complexes. A comparison of the *Td* and ν^{max} values shows that with the shift of the $d-d$ transition absorption to higher wavenumber, i.e. $[E_g \rightarrow T_{2g}-]$, in the case of the octahedral copper(II) complexes, the thermal stability of the complexes increases. For the pyridine complex the change in the degree of distortion from the octahedral to the tetracoordinated structure $[Cu(TDSA)_2]$ is higher. The greater distortion in the pyridine complex is due to multiple bond formation between the nitrogen of the pyridine and the copper, and to the increasing metal–metal interaction [10].

References

1. W. W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 245.
2. W. W. Wendlandt and J. P. Smith, J. Inorg. Nucl. Chem., 25 (1963) 843, 985, 1267.
3. S. Sarig, Thermochim. Acta, 7 (1973) 297.
4. R. S. Bottei, H. S. Chang and D. A. Lusardi, J. Thermal Anal., 16 (1979) 389.
5. S. C. Srivastava and M. L. Good, Talanta, 12 (1965) 181.
6. P. C. Srivastava, K. B. Pandeya and H. L. Nigam, J. Inorg. Nucl. Chem., 35 (1973) 3613.
7. P. C. Srivastava, K. B. Pandeya and H. L. Nigam, Technology, 13 (1976) 170.
8. P. C. Srivastava, Technology, 10 (1975) 190.
9. P. C. Srivastava, K. B. Pandeya and H. L. Nigam, Proc. Chem. Symp. DAE, 20 (1972) 103.
10. P. C. Srivastava, S. Banerjee and B. K. Banerjee, Indian J. Chem. (1980) (in press).

Zusammenfassung — Aquo-, Ammoniak- und Pyridinkomplexe von Kupfer(II) mit 5,5'-Thiodisalicylsäure wurden durch TG und DTG untersucht. Diese Komplexe werden in den drei Stufen, Dehydratisierung, Verlust axialer Basen und Decarboxylierung des aromatischen Liganden zersetzt. Die Abbaukurven der Aquo- und Pyridinkomplexe zeigen einen Wasserverlust in zwei Stufen. Die abnehmende Reihenfolge der Thermostabilität der Komplexe ist py $>$ $NH_3 > H_2O$.

Резюме — Методом ТГ и ДТГ были исследованы водные, аммиачные и пиридиновые комплексы меди(II) с 5,5'-тиодисалициловой кислотой. Установлено, что комплексы раз лагаются в три стадии: дегидратация, потеря осевых оснований и декарбоксилирование ароматического лиганда. Термические кривые акво- и пиридиновых комплексов показали, что потеря воды происходит по двум различным путям. Термоустойчивость комплексов уменьшается в следующем порядке: пиридин $> NH_3 > H_2O$.