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THERMAL STUDIES OF Co(II), Ni(II) AND Cu(II) COMPLEXES WITH SCHIFF BASE DERIVATIVES OF 1H-INDOLE-3-ETHYLENE-SALICYLALDIMINE

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ABSTRACT

Analytical, spectroscopic and magnetic studies of the Co(II), Ni(II) and Cu(II) complexes with Schiff bases containing an indole group have previously been reported. Whereas in the Ni(II) and Cu(II) complexes, the coordination around the metal is *trans*-planar (MO_2N_2 chromophore), the Co(II) complex has an octahedral environment around the metal.

Therefore it is of interest to investigate the thermal stability of these complexes where the ligands have oxygen and nitrogen donor-atoms with different steric requirements. The thermal stability was studied by TG and, in some cases, by DSC. For the same ligand, the stabilities increase in the order: Cu(II) < Co(II) ≈ Ni(II). Finally, the kinetics of the solid-state dehydration of the $Cu(3\text{-MeosalTPA})_2 \cdot H_2O$ complex was studied.

INTRODUCTION

TG and calorimetric techniques have long been applied to inorganic complexes for the determination of kinetic and thermodynamic data for reactions in the solid state. However, until now, few complexes with Schiff bases as ligands with different coordinations of the metallic cation, have been studied with the above techniques [1–3]. Therefore it seemed worthwhile to carry out a comparative study of the thermal stability of this class of complexes, if, as in this case, the ligands contain a large group which may produce some type of distortion.

In the present work, we report on a study of the thermal stability of the complexes of general formula ML_2, where M = Co(II), Ni(II) and Cu(II),

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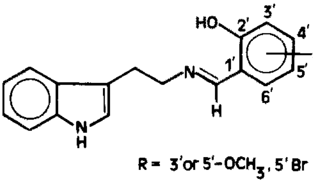

Scheme 1.

and L = 1H-indole-3-ethylenesalicylaldimine (abbreviated: salTPA, Scheme 1) and its derivatives: 1H-indole-3-ethylene-3′-methoxy-salicylaldimine (abbreviated: 3-MeosalTPA); 1H-indole-3-ethylene-5′-methoxysalicylaldimine (5-MeosalTPA); and 1H-indole-3-ethylene-5′-bromosalicylaldimine (5-BromosalTPA).

These compounds have been previously synthesized and the study has been carried out using analytical, spectroscopic, magnetic susceptibility and X-ray diffraction techniques [4–7].

This study of the decomposition in the solid phase of the above complexes allows the degree of thermal stability to be determined for the first time, establishing the relationships between thermal stability, metal coordination and position of the functional groups (3-methoxy, 5-methoxy and 5-bromine).

EXPERIMENTAL

Preparation of the complexes

The Co(salTPA)$_2$, Ni(salTPA)$_2$ and Cu(salTPA)$_2$ complexes were prepared following the method described earlier [4].

Co(5-MeosalTPA)$_2$, Ni(3-MeosalTPA)$_2$, Ni(5-MeosalTPA)$_2$, Cu(3-MeosalTPA)$_2$ · H_2O and Cu(5-MeosalTPA)$_2$ were prepared according to ref. 5. Co(5-BromosalTPA)$_2$ and Ni(5-BromosalTPA)$_2$ were prepared according to ref. 6 and Cu(5-BromosalTPA)$_2$ according to ref. 7. All compounds were recrystallized in the appropriate solvents.

Materials

The starting materials (reagent grade) were obtained commercially and used without further purification.

Analytical methods

Elemental analyses were performed with a Carlo Erba (model 1106) instrument. The averages of the metals were determined by atomic absorp-

TABLE 1

Analytical data

Compound	Calculated (%)				Found (%)			
	C	H	N	Metal	C	H	N	Metal
$Cu(salTPA)_2$	69.20	5.12	9.49	10.77	69.10	5.22	9.60	10.75
$Ni(salTPA)_2$	69.76	5.17	9.57	10.03	69.40	5.15	9.40	10.10
$Co(salTPA)_2$	69.67	5.16	9.57	10.06	69.52	5.20	9.70	9.87
$Cu(3\text{-MeosalTPA})_2 \cdot H_2O$	64.71	5.43	8.38	9.51	64.77	5.41	8.30	9.57
$Ni(3\text{-MeosalTPA})_2$	66.96	5.31	8.68	9.09	66.74	5.35	8.36	9.02
$Cu(5\text{-MeosalTPA})_2$	66.50	5.27	8.62	9.77	66.46	5.20	8.70	9.75
$Ni(5\text{-MeosalTPA})_2$	66.96	5.31	8.68	9.09	66.80	5.38	8.65	9.05
$Co(5\text{-MeosalTPA})_2$	66.97	5.31	8.68	9.13	66.92	5.26	8.73	9.20
$Cu(5\text{-BromosalTPA})_2$	54.59	3.77	7.49	8.49	54.60	3.75	7.37	8.30
$Ni(5\text{-BromosalTPA})_2$	54.97	3.79	7.53	7.89	54.98	3.83	7.41	7.75
$Co(5\text{-BromosalTPA})_2$	54.96	3.79	7.54	7.93	55.08	3.89	7.39	8.09

tion using a Perkin–Elmer (model 3030) spectrophotometer, after decomposing the complexes with a concentrated HNO_3/H_2SO_4 mixture.

The analytical data for the compounds are shown in Table 1.

TG analysis and DSC

The dynamic TG measurements were carried out on a Perkin–Elmer (TGS-2 model) thermobalance with an FDC first-derivative computer. The heating rate was $5\,^{\circ}C\ min^{-1}$ with a sample mass of 4 mg in a nitrogen atmosphere. These conditions were also used for the determination of the kinetic parameters of the dehydration of $Cu(3\text{-MeosalTPA})_2 \cdot H_2O$. Each run was repeated twice, the reproducibility being good.

The instrument was standardized for mass and temperature against standard reference materials. For the thermal stability study the analyses were carried out in a nitrogen atmosphere and in dry air from room temperature to 1073 K.

Calorimetric measurements were made using a Mettler TA 3000 system with a Mettler DSC (DSC 20 model).

Samples of about 5 mg were used, rendering the degree of temperature non-uniformity within the sample insignificant. An aluminium pan was used under a dry nitrogen atmosphere. The scanning rate was $10\,^{\circ}C\ min^{-1}$, and the instrument calibration was checked periodically with a sample of indium.

RESULTS AND DISCUSSION

Thermal stability

The curves of mass loss against temperature and their derivatives indicate two stages in the thermal decompositions of the complexes, except for

TABLE 2

Thermal data for the compounds

Compound	1st step				2nd step				3rd step	
	Temperatures (K) [a]			ΔH (KJ mol^{-1})	Temperatures (K)			ΔH (KJ mol^{-1})	Temperatures (K)	
	T_i	T_p	T_f		T_i	T_p	T_f		T_i	T_f
Cu(salTPA)$_2$	435.1	489,511	610	25.34, −54.11	610	781	831	−9214		
Ni(salTPA)$_2$	533	546	633	70.50	689		931			
Co(salTPA)$_2$	513	540	773	70.06	773		1033			
Cu(3-MeosalTPA)$_2 \cdot H_2O$	303	337	354	21.03	447	470,511	573	64.37, −64.79	573	821
Ni(3-MeosalTPA)$_2$	510	516,569	588	54.64, −111.81	606		783			
Cu(5-MeosalTPA)$_2$	513		703		703		1173			
Ni(5-MeosalTPA)$_2$	522		673		673		1043			
Co(5-MeosalTPA)$_2$	518		648		648		987			
Cu(5-BromosalTPA)$_2$	478	509,751	971	−320.45, −107.94						
Ni(5-BromosalTPA)$_2$	541		570		633		910			
Co(5-BromosalTPA)$_2$	546		569		662					

[a] T_i and T_f refer to temperatures at the beginning and end of each step, respectively. T_p refers to the peak of the DSC curve.

TABLE 3

Residues of the thermal decomposition

Compound	Atmosphere	Residue	T (K)	Calc. (%)	Found (%)
Cu(salTPA)$_2$	air	CuO	913	10.77	10.79
Ni(salTPA)$_2$	air	NiO	943	10.03	10.15
Ni(salTPA)$_2$	N_2	Ni	913	10.03	10.29
Cu(3-MeosalTPA)$_2$·H_2O	air	CuO	863	9.51	9.57
Cu(3-MeosalTPA)$_2$·H_2O	N_2	CuO	863	9.51	9.38
Ni(3-MeosalTPA)$_2$	air	Ni	833	9.09	9.38
Cu(5-BromosalTPA)$_2$	air	CuO	863	8.49	8.25
Cu(5-BromosalTPA)$_2$	N_2	CuO	933	8.49	8.32
Ni(5-BromosalTPA)$_2$	air	NiO	865	7.89	7.76
Ni(5-BromosalTPA)$_2$	N_2	NiO	1024	7.89	8.08
Co(5-BromosalTPA)$_2$	air	Co_3O_4	845	7.93	8.36
Co(5-BromosalTPA)$_2$	N_2	Co_3O_4	916	7.93	8.17
Co(5-MeosalTPA)$_2$	N_2	CoO	987	9.13	9.11

Cu(3-MeosalTPA)$_2$ · H_2O and Cu(5-BromosalTPA)$_2$, which have three stages and one stage, respectively. The results are shown in Table 2.

In the DSC curves of the complexes Cu(salTPA)$_2$, Ni(salTPA)$_2$, Co(salTPA)$_2$, Cu(3-MeosalTPA)$_2$ · H_2O and Ni(3-MeosalTPA)$_2$, the first endothermic effect is observed between 300 and 900 K (Table 2). This may correspond to a phase change, probably the melting of the solid together with the solid decomposition, except for Cu(3-MeosalTPA)$_2$ · H_2O in which the effect corresponds to loss of the water molecule, as confirmed by the mass loss from the TG curves (theoretical loss: 2.69%; experimental loss: 2.70%). The value of ΔH (21.03 kJ mol^{-1}) together with the low temperature (337 K) for the dehydration reaction indicates that the water molecule is weakly bonded in the complex, probably by means of one hydrogen bond to an electronegative atom of the ligand [5]. The kinetics of dehydration is described below.

For the complexes Cu(salTPA)$_2$, Ni(3-MeosalTPA)$_2$ and Cu(5-BromosalTPA)$_2$ in the temperature range 300–900 K, an exothermic process is observed corresponding to the decomposition. This decomposition is completed at the second step, with the exception of the Cu(MeosalTPA)$_2$ · H_2O which exhibits three steps. The final residue was identified by metal analysis (Table 3).

In accordance with the values of the initial temperatures of decomposition (TG curves) and the peaks of the DSC curves (Table 2), the order of thermal stability of the complexes for the same ligand is: Cu(II) < Co(II) ≈ Ni(II).

The higher thermal stability of Ni(II) and Co(II) is because of the type of ligand, which favours planar coordination around the metal, as occurs with Ni(II) [4,5]. Whereas in Co(II) oligomerization takes place with octahedral coordination around the metal [4,5]. In both metals, the *trans*-planar chromophore MO_2N_2 is less distorted than in the Cu(II) complexes [4,5]. Thus, Ni–O and Ni–N distances for Ni(3-MeosalTPA)$_2$ are 1.84(2) and 1.94(2) Å, respectively [7], whereas the Cu–O and Cu–N distances for Cu(5-MeosalTPA)$_2$ are 1.88(1) and 2.01(1) Å, respectively [5]. Sawodny et al. [3] have found that the order of thermal stability for polymeric metal chelates with Schiff bases is: Co(II) < Cu(II) < Ni(II). In this case, the ligand conformation is different from that of the complexes described here and, moreover, the metal coordination is five.

For the complexes described in this paper, considering the same cation, the order of thermal stability is: 3-MeosalTPA < salTPA < 5-MeosalTPA < 5-BromosalTPA, with the exception of Cu(5-BromosalTPA)$_2$ which is less stable than Cu(5-MeosalTPA)$_2$. The sequence found may be explained by considering that the $-OCH_3$ group in position 3 decreases the thermal stability of the complexes with respect to position 5, because of the larger hindrance by steric repulsion due to the greater proximity of this group to the chelate ring (Scheme 1).

Dehydration kinetics

A study was made of the kinetic process

$$\mathrm{Cu(3\text{-}MeosalTPA)_2 \cdot H_2O(s) \rightarrow Cu(3\text{-}MeosalTPA)_2(s) + H_2O(g)}$$

To obtain the kinetic parameters, four non-mechanism-invoking equations were used.

(1) The Abou-Shaaban–Simonelli equation [8]:

$$\log_{10}\left[\frac{-\mathrm{d}(W^{\mathrm{t}}_{\mathrm{obs}})/\mathrm{d}T}{(W^{\mathrm{t}}_{\mathrm{obs}}) - (W^{\theta}_{\mathrm{obs}})/\gamma}\right] = \log_{10}\frac{Z}{\Phi} - \frac{E_{\mathrm{a}}}{2.303RT}$$

(2) The Horowitz–Metzger equation [9]:

$$\ln\left[\frac{1-X^{1-n}}{1-n}\right] = \frac{E_{\mathrm{a}}\theta}{RT_{\mathrm{s}}^2} - \frac{E_{\mathrm{a}}}{RT_{\mathrm{s}}} + \ln\frac{ZRT_{\mathrm{s}}^2}{\Phi E_{\mathrm{a}}}$$

(3) The Coats–Redfern equation [10]:

$$\ln\frac{1-X^{1-n}}{(1-n)T^2} = \ln\left[\frac{ZR}{\Phi E_{\mathrm{a}}}\left(1-\frac{2RT}{E_{\mathrm{a}}}\right)\right] - \frac{E_{\mathrm{a}}}{RT}$$

(4) The MacCallum–Tanner equation [11]:

$$\log\frac{1-X^{1-n}}{1-n} = \log_{10}\frac{ZR}{\Phi E_{\mathrm{a}}} - 0.485\ \mathrm{E}_{\mathrm{a}}^{0.435} - \frac{(0.449+0.217E_{\mathrm{a}})10^3}{T}$$

where Φ is the heating rate, $\theta = T - T_{\mathrm{s}}$, E_{a} is the activation and Z the preexponential factor. The order parameter, $n = 0.21$, was determined by the Gyulai–Greenhow equation [12]

$$X_{\mathrm{M}} = 1.062n^{1/1-n}$$

TABLE 4

Kinetic parameters and correlation coefficients (r) calculated using the Abou-Shaaban–Simonelli (ASS), Horowitz–Metzger (HM), Coats–Redfern (CR) and MacCallum–Tanner (MT) equations for dehydration of the Cu(3-MeosalTPA)$_2 \cdot H_2O$ compound

	E_a (kJ mol^{-1})	Z (sec^{-1})	r
ASS	113.98	4.12 10^{15}	0.9957
HM	136.20	2.33 10^{18}	0.9548
CR	125.05	8.79 10^{16}	0.9508
MT	122.85	–	0.9548

where the subscript M indicates the value corresponding to X in the DTG peak temperature (T_s).

Using each of the above four equations, the energy of activation and the pre-exponential factor were calculated from the TG curves using a computer. The correlation coefficient, r, was also calculated in each case. The values of E_a, Z and r obtained using the four equations are given in Table 4.

To determine the mechanism of the dehydration we used the nine formulae listed by Satava [13] and also the Johnson–Gallagher equation [14]

$$1/(1-\alpha)-1=Kt$$

The logarithms of these functions $g(\alpha)$ were calculated and plotted against $1/T$(K). The best values of the correlation coefficient, r, when fitted to a straight line using the least-squares method of $g(\alpha)$ versus $1/T$(K) correspond to the equations: random nucleation, one nucleus on each particle; the Johnson–Gallagher equation; and random nucleation, the Avrami–Erofeev I law. This last equation gave values for the kinetic parameters nearer to the values of Table 4, and is, therefore, taken as the model mechanism.

In the complex described here, the water molecule is not bonded to the metal, and therefore E_a does not depend on the crystal field activation energy, but on the transition state formed by the complex and the free water. This water molecule may be more or less able to slip into an interstitial position and to subsequently escape from the crystal.

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