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The thermal behaviour of nickel, copper and zinc complexes with the Schiff bases *cis*- and *trans*-*N*,*N*′-bis(salicylidene)-1,2-ciclohexadiamine (Salcn)

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Abstract

The Schiff base complexes were prepared and characterised by UV, IR and NMR (^{1}H and ^{13}C) spectroscopy, elemental analysis and X-ray powder diffractometry. Free ligands and some new complexes were submitted to thermal analysis (TG and DSC) under dynamic air atmosphere. The differences in the decomposition profiles were related to the structure of isomers and decomposition intermediates were characterised according to their X-ray diffraction pattern. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Schiff bases are widely used as analytical reactants since they allow simple and inexpensive determination of several organic and inorganic substances [1]. They also form stable complexes with metals that perform important role in biological systems [2].

Due to their importance in analytical and bioinorganic chemistry, complexes of tetra-coordinated Schiff bases and transition metals are extensively studied. Such complexes present many applications in catalysis and oxygen storage devices [3]. Many present antitumoral, antiviral and antibacterial activity [4] and also used as mimetic systems for enzyme models [5].

In this paper, we describe the differences observed in the thermal behaviour of nickel, copper and zinc complexes with *cis*-*N*,*N*′-bis(salicylidene)-1,2-cyclohexadiamine, (*c*-Salcn) and *trans*-*N*,*N*′-bis(salicylidene)-1,2-cyclohexadiamine, (*t*-Salcn) in relation to the structure of the isomers, using thermogravimetry (TG) and differential scanning calorimetry (DSC). Structural representations of the ligands and their abbreviations are given in Fig. 1.

2. Experimental

2.1. Ligand preparation

The ligands were prepared according to Felicio [6]. To a hot ethanol solution of 6.368 g (30 mmol) of *cis*-1,2-diaminocyclohexane sulphate or of 5.613 g

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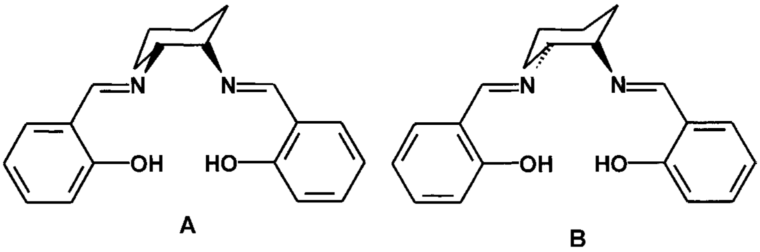

Fig. 1. Structural representations of the ligands: A — (*c*-Salcn) and B — (*t*-Salcn).

(30 mmol) of *trans*-1,2-diaminocyclohexane dihydrochloride and 8.165 g (60 mmol) of sodium acetate trihydrate was added 6.4 cm^3 (60 mmol) of the salicylaldehyde. After stirring and heating at 80°C for 2 h, the resulting solution, a yellow crystalline solid, was obtained. The ligands were used without further purification. (*c*-Salcn): yield, 8.605 g, 89%; m.p., 132–134°C; found: C, 74.7; H, 6.9; N, 8.7. Ca. for $C_{20}H_{22}O_2N_2$: C, 74.5; H, 6.9; N, 8.7. (*t*-Salcn): yield, 8.221 g, 85%; m.p., 115–117°C; found: C, 74.2; H, 6.9; N, 8.8. Ca. for $C_{20}H_{22}O_2N_2$: C, 74.5; H, 6.9; N, 8.7.

2.2. Complex preparation

The complexes were prepared and purified using an adaptation of a method described previously [7]. A solution of the appropriate metal acetate, (5.0 mmol) in 10 cm^3 of distilled water was added to a hot methanol solution, 50 cm^3 containing 5.0 mmol of the Schiff base ligand. Although, a precipitate formed almost immediately, the mixture was refluxed with stirring for 4 h. After cooling slowly to room temperature, the reaction mixture was held at 0°C for 12 h. The resulting precipitate was collected by filtration, washed twice with 20 cm^3 of distilled water and twice with of methanol. The complexes were purified by Soxhlet extraction using the appropriate solvent. The purified complexes were dried in a desiccator over silica gel.

2.3. Characterisation of the complexes

Elemental analyses (C, N, H) were performed in an EA-1108 CHNS-O Fisons apparatus. The infrared spectra were recorded in the range, 4000–200 cm^{-1}, using CsI pellets with a MB-102 Bomem Hart Mann & Braun spectrophotometer, equipped with an Arid Zone detector.

The residues and intermediates of thermal decomposition were characterised by their X-ray diffraction patterns, powder method, using Cu Kα radiation between 5 and 75° with a D5000 Siemens diffractometer.

2.4. Thermal measurements

Thermogravimetric curves of recently dried samples were recorded using a TGA-2050 modulus coupled to a 2000 thermal analyser, TA Instruments, using ca. 7 mg sample mass and a platinum sample holder. Heating rates of 5, 10 and 15°C min^{-1} under dynamic air atmosphere (90 cm^3 min^{-1}) were investigated. In all experiments a heating rate of 15°C min^{-1} was chosen since it reduces the experiment time without significant change in the curve shape.

DSC curves were recorded on a DSC 910 modulus coupled to a 2000 thermal analyser, TA Instruments, in a covered aluminium sample holder with a central pin hole and a sample mass of ca. 5 mg under a 10°C min^{-1} heating rate and 100 cm^3 min^{-1} dynamic air flow.

3. Results and discussion

3.1. Compound characterisation

The analytical data for ligands and complexes are resumed in Table 1. The results agree with the formula $C_{20}H_{22}N_2O_2$ for the ligands and with a general formula $C_{20}H_{20}N_2O_2M{\cdot}xH_2O$ (where M = Zn, Cu, Ni and $x = 0$ or 2) for the complexes.

The IR spectra of the free ligands and the complexes exhibit various bands in the 200–4000 cm^{-1} region.

Table 1
Analytical data for the complexes

Compound	Found (calculated) (%)		
	C	N	H
[Zn(*c*-Salcn)]·2H_2O	57.0 (56.9)	6.2 (6.1)	5.4 (5.7)
[Zn(*t*-Salcn)]·2H_2O	57.3 (56.9)	6.2 (6.1)	5.6 (5.7)
[Cu(*c*-Salcn)]	61.1 (62.6)	7.3 (7.3)	5.2 (5.3)
[Cu(*t*-Salcn)]	62.4 (62.6)	7.4 (7.3)	5.2 (5.3)
[Ni(*c*-Salcn)]	63.4 (63.4)	7.1 (7.4)	5.3 (5.3)
[Ni(*t*-Salcn)]	63.3 (63.4)	7.3 (7.4)	5.3 (5.3)

The most relevant infrared peaks for ligands and complexes are in Table 2. The O–H stretching frequency of the free ligand is expected in the 3300–3800 cm^{-1} region, however this frequency is generally displaced to the 2555 cm^{-1} *cis*, and 2589 cm^{-1} *trans*, region due to the internal hydrogen bond OH–N=C [6,7]. The νC=N band characteristic for Schiff bases [8–13], is observed at 1631 cm^{-1} for *c*-Salcn and 1637 cm^{-1} for *t*-Salcn.

The νC–O are generally observed in the region 1270–1330 cm^{-1} for free ligands [6–8,12,14] and 1305–1330 cm^{-1} for the complexes [6–8]. The shift of C=N stretching frequencies of the free ligand to lower value as well as of C–O stretching frequencies to higher values in the corresponding complexes was taken as evidence for the coordination of both imino and hydroxyl groups [6,7,12,14–16].

3.2. Results from thermoanalytical techniques

The thermogravimetic (TG/DTG) curves for the ligands and their complexes are presented in Fig. 2 while the differential scanning calorimetric (DSC) curves are in Fig. 3.

Mass loss (TG and calculated), temperatures ranges and a description of thermal events observed in the studies are summarised in Table 3.

From the thermal investigation (TG/DTG) it is possible to observe that the decomposition occurs in different ways for the *cis*- and *trans*-isomers of ligand. The *cis*-isomer decomposed in two steps producing a carbonaceous residue previous to the final burning. The *trans*-isomer decomposed in a single step without residue in the sample holder. However, both start decomposition at around 150–160°C, suggesting similar thermal stability.

The zinc complexes were both hydrated and lost one molecule of water in the first mass loss and afterwards decomposed in two steps. The final decomposition product was ZnO according to the X-ray diffraction pattern. The nickel complexes also decomposed in two steps resulting in NiO and Ni as the final residue. The presence of metallic Ni residue suggests the presence of carbonaceous material as decomposition intermediate.

Copper complexes presented similar TG profiles resulting in CuO as main residue after two decomposition steps.

DSC curves presented a melting process for both ligands, at 121°C for *trans* and 135°C for the *cis*-isomer, followed by decomposition represented by exothermic processes at 350°C. In agreement with TG curves, the *cis*-isomer completed the decomposition above 600°C. The *trans*-isomer presented decomposition peaks at 349 and 568°C in the closed DSC pan while in the open TG crucible it decomposed completely between 147–282°C.

Table 2
Infrared data for ligands and complexes (cm^{-1})[a]

Compound	νC=N	νC–N	νC–O	M–N	M–O
c-Salcn	1631 (s)	1391 (m)	1280 (m)	–	–
t-Salcn	1637 (s)	1382 (m)	1283 (m)	–	–
[Zn(*c*-Salcn)]·2H_2O	1634 (s)	1387 (m)	1314 (m)	357 (w)	475 (m)
[Zn(*t*-Salcn)]·2H_2O	1635 (s)	1397 (m)	1305 (m)	357 (m)	472 (m)
[Cu(*c*-Salcn)]	1625 (s)	1393 (m)	1326 (m)	375 (w)	459 (m)
[Cu(*t*-Salcn)]	1632 (s)	1389 (m)	1318 (m)	380 (w)	458 (m)
[Ni(*c*-Salcn)]	1602 (s)	1387 (m)	1330 (m)	384 (s)	471 (m)
[Ni(*t*-Salcn)]	1622 (s)	1388 (m)	1321 (m)	384 (w)	478 (w)

[a] s: strong; m: medium; w: weak.

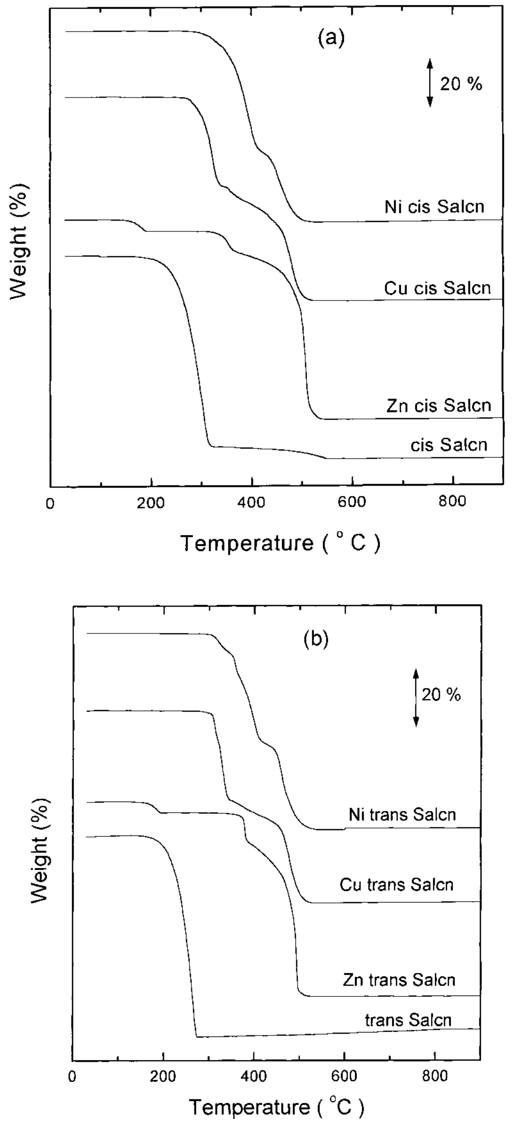

Fig. 2. Thermogravimetric curves for ligands and Ni, Cu and Zn complexes: (a) *cis*-isomers and (b) *trans*-isomers. Heating rate: 15°C min^{-1}; Pt-sample holder; synthetic air: 90 cm^3 min^{-1}.

The zinc complexes presented similar DSC curves, with characteristic endothermic water loss and decomposition in agreement with TG data. An intense exothermic decomposition peak was observed for *trans* copper (315°C) and nickel complexes (356°C). The *cis*-isomers presented a less intense peak at same temperature. The final decomposition is retarded in *cis* copper complex.

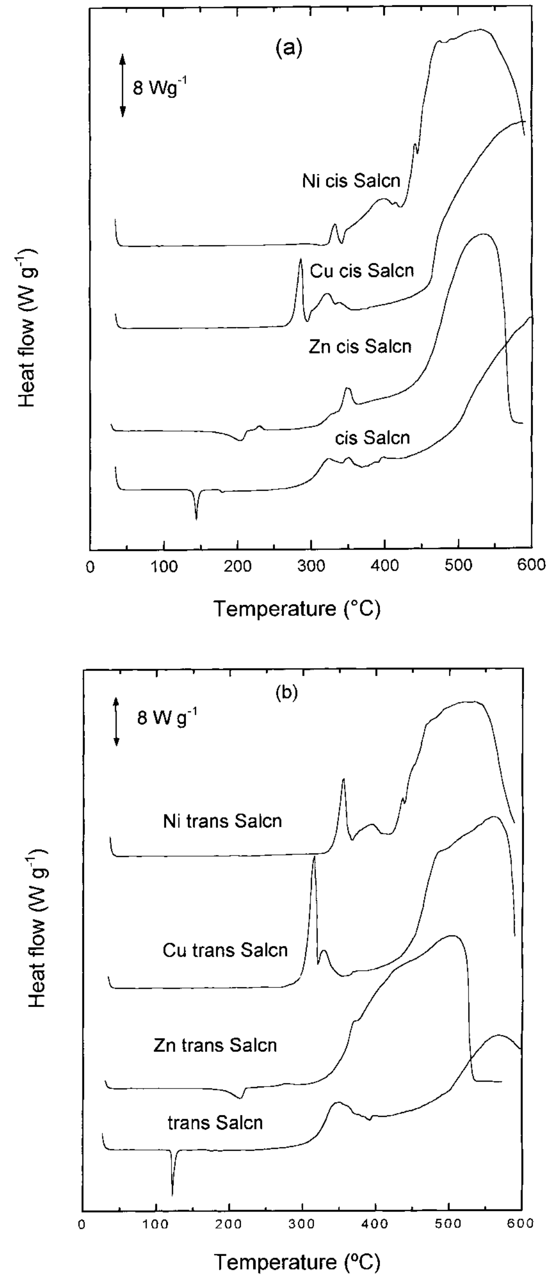

Fig. 3. DSC curves for ligands and Ni, Cu and Zn complexes: (a) *cis*-isomers and (b) *trans*-isomers. Heating rate: 10°C min^{-1}; Al-sample holder; synthetic air: 100 cm^3 min^{-1}.

According to the data in Table 3 after dehydration zinc complexes presented the higher decomposition temperatures for the series of compounds here investigated. The order for thermal stability

Table 3
TG mass losses, temperature range and DSC peaks related to the thermal decomposition processes of the ligands and metal complexes under air

Process	TG data			DSC peaks (°C)[a]
	Temperature range (°C)	Mass loss a or residue b (%)		
		TG	Calculated	
Cis-isomers				
c-Salcn (s) → *c*-Salcn (l)	–	–	–	135 (endo)
c-Salcn (s) → CR[b]	156–330	90.8 a	–	350, >600 (exo)
CR burning	330–607	9.1 a	9.2	568 (exo)
[Ni(*c*-Salcn)] → NiO	274–523	16.3 b	–	332, 339, 533 (exo)
[Cu(*c*-Salcn)] → CuO	248–357	19.0 b	20.7	286, 322, 338, >500 (exo)
[Zn(*c*-Salcn)]·H_2O → [Zn(*c*-Salcn)] + H_2O	121–205	4.55 a	4.46	203 (endo)
[Zn(*c*-Salcn)] → ZnO	292–569	20.3 b	20.1	350, 533 (exo)
Trans-isomers				
t-Salcn (s) → *t*-Salcn (l)	–	–	–	121 (endo)
t-Salcn (l) → decomposition	147–282	1.10 b	0	350, 568 (exo)
[Ni(*t*-Salcn)] → NiO + Ni	295–533	17.43 b	–	
[Cu(*t*-Salcn)] → CuO	247–533	21.3 b	20.7	315, 327, 559 (exo)
[Zn(*t*-Salcn)]·H_2O → [Zn(*t*-Salcn)] + H_2O	147–201	4.24 a	4.46	214 (endo)
[Zn(*t*-Salcn)] → ZnO	327–650	21.6 b	20.5	503 (exo)

[a] Exo: exothermic process; endo: endothermic process.
[b] CR: carbonaceous residue.

found is:

$$\mathrm{Zn}(t\text{-Salcn}) > \mathrm{Zn}(c\text{-Salcn}) > \mathrm{Ni}(t\text{-Salcn}) > \mathrm{Ni}(c\text{-Salcn}) > \mathrm{Cu}(t\text{-Salcn}) \approx \mathrm{Cu}(c\text{-Salcn})$$

This fact should be related with the structure of the ligand and suggests the *cis* as a more unstable isomer. Although, *trans*-isomers started their decomposition process at higher temperatures, the intermediate thermal events associated to these compounds are more intense and occurred at lower temperatures than those observed for *cis*-isomers (see DSC data in Fig. 3).

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