

THERMAL DECOMPOSITION OF COMPLEXES Manganese(II) and vanadyl with *cis*- and iron(II), manga- nese(II) and vanadyl with *trans*-*n,n'*-bis(salicylidene)-1,2- cyclohexanediamine (salcn)

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Abstract

The iron(II) complex of the Schiff bases *trans*-*N,N'*-bis(salicylidene)-1,2-cyclohexanediamine (Salcn), manganese(II) and vanadyl complexes of the Schiff bases *cis*- and *trans*-*N,N'*-bis(salicylidene)-1,2-cyclohexanediamine (Salcn) were prepared and characterized by IR spectroscopy, and elemental analysis. These 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 characterized according to their X-ray diffraction pattern and by their infrared spectrum.

Keywords: differential scanning calorimetry, iron, manganese, Schiff bases, thermogravimetry, vanadyl

Introduction

Metal complexes of Schiff bases and their applications have been widely investigated during the past years [1, 2]. Schiff base complexes have been used as pesticides [3], as antiviral and antibacterial agents [4, 5], and as catalysts [6–8]. The thermal behavior of transition metal complexes of Schiff bases has been widely investigated [9–12].

Recently we presented a report of the thermal behavior of the title ligands and their nickel, copper and zinc complexes [9] relating the thermal properties and the ligand conformation.

The present work describes the differences observed in the thermal behavior of new manganese(II) and vanadyl complexes of *cis*-*N,N'*-bis(salicylidene)-1,2-cyclohexanediamine, (*c*-Salcn) and iron(II), manganese(II) and vanadyl *trans*-*N,N'*-bis(salicylidene)-1,2-cyclohexanediamine, (*t*-Salcn) in relation to the structure of the

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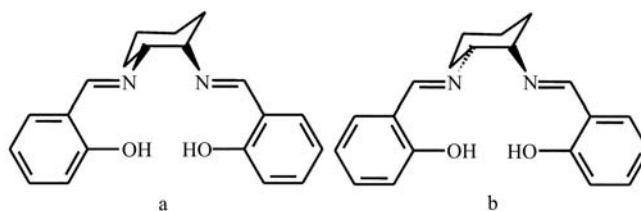


Fig. 1 Structural representations of the ligands: a – *c*-Salcn and b – *t*-Salcn

isomers, using thermogravimetry (TG) and differential scanning calorimetry (DSC). Structural representations of the ligands and their abbreviations are given in Fig. 1.

Experimental

Synthesis

The ligands were prepared as described earlier [9–12]. Salicylaldehyde, 6.4 cm³ (60 mmol) and 8.165 g (60 mmol) of sodium acetate trihydrate were added to either a hot ethanol solution of 6.368 g (30 mmol) of *cis*-1,2-diaminocyclohexane sulfate or a hot ethanol solution of 5.613 g (30 mmol) of *trans*-1,2-diaminocyclohexane dihydrochloride. After stirring and heating at 80°C for 2 h, a yellow crystalline solid was obtained. (*c*-Salcn): Yield 8.605 g, 89%; *m.p.* 132–134°C; Found: C, 74.7; H, 6.9; N, 8.7. Calc. for C₂₀H₂₂O₂N₂: 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. Calc. for C₂₀H₂₂O₂N₂: C, 74.5; H, 6.9; N, 8.7.

The complexes were prepared and purified using adaptations of previously described methods [9–13]. For the iron(II) and manganese(II) complexes a solution of the appropriate metal acetate, (5.0 mmol) in 10 cm³ of distilled water was added to a hot methanol solution, 50 cm³, containing 5.0 mmol of the Schiff base ligand. For the corresponding vanadyl complexes, an aqueous (10 cm³) of oxovanadium(IV) sulfate (5.0 mmol) and sodium acetate trihydrate (11.0 mmol) were added to the hot methanol solution of the 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 cm³ of distilled water and twice with 10 cm³ of methanol. The complexes were purified by Soxhlet extraction using the appropriate solvent. The purified complexes were dried in a desiccator over silica gel.

Instrumentation

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 characterized by their X-ray diffraction patterns, powder method, using CuK_α radiation between 5 and 75°C with a D5000 Siemens diffractometer and by their infrared spectra.

Thermogravimetric curves of recently dried samples were recorded using a TGA-2050 modulus coupled to a 2000 thermal analyzer, TA Instruments, using ca. 7 mg sample mass in a Pt sample holder, heating rate of 15°C min⁻¹ under dynamic air atmosphere (90 cm³ min⁻¹). Heating rates of 5 and 10°C min⁻¹ did not change the curve shape significantly.

DSC curves were recorded on a DSC 910 modulus coupled to a 2000 thermal analyzer, TA Instruments, in covered aluminum sample holders with a central pin hole and a sample mass of ca. 5 mg under a 15°C min⁻¹ heating rate and 100 cm³ min⁻¹ dynamic air atmosphere. Again, 5 or 10°C heating rates did not change the curve resolution significantly.

Results and discussion

The analytical data for the complexes are resumed in Table 1. The results agree with the general formula $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_2\text{M}\cdot x\text{H}_2\text{O}$ ($M=\text{Fe}^{2+}$, Mn^{2+} , VO^{2+} ; $x=0$ to 1 and H_2O – superficial or hydration).

Table 1 Analytical data for complexes

Compound	Found, (calc.)/%		
	C	N	H
[Fe(<i>t</i> -Salcn)]·H ₂ O	60.0 (60.6)	7.1 (7.1)	5.5 (6.1)
[Mn(<i>c</i> -Salcn)]·H ₂ O	60.0 (60.6)	6.9 (7.1)	5.5 (6.1)
[Mn(<i>t</i> -Salcn)]·H ₂ O	59.0 (60.6)	7.0 (7.1)	5.9 (6.1)
VO(<i>c</i> -Salcn)	61.7 (62.0)	7.7 (7.3)	5.3 (5.2)
VO(<i>t</i> -Salcn)	62.7 (62.0)	7.3 (7.3)	5.2 (5.2)

IR characteristics

The IR spectra of the free ligands and the complexes exhibited several bands in the 4000–200 cm⁻¹ region. The most relevant infrared peaks for ligands and complexes are discussed. 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 [9, 11–13]. The $\nu\text{C}=\text{N}$ band characteristic of Schiff bases [9, 11–13, 15], is observed at 1631 cm⁻¹ for *c*-Salcn and 1634 cm⁻¹ for *t*-Salcn.

The $\nu\text{C}=\text{O}$ is generally observed in the region 1270–1330 cm⁻¹ for free ligands [9, 11–13, 17, 18] and 1305–1330 cm⁻¹ for the complexes [9, 11–13]. 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 [9, 11–13, 17–20]. These IR data are summarized in Table 2.

Table 2 IR data for ligands and complexes

Compound	$\nu\text{OH}\cdots\text{N}=\text{C}/\text{cm}^{-1}$	$\nu\text{C}=\text{N}/\text{cm}^{-1}$	$\nu\text{C}-\text{N}/\text{cm}^{-1}$	$\nu\text{C}-\text{O}/\text{cm}^{-1}$
<i>t</i> -Salcn	2589	1634	1385	1310
<i>c</i> -Salcn	2555	1631	1391	1281
[Fe(<i>t</i> -Salcn)]·H ₂ O	–	1623	1397	1318
[Mn(<i>c</i> -Salcn)]·H ₂ O	–	1627	1398	1310
[Mn(<i>t</i> -Salcn)]·H ₂ O	–	1630	1392	1308
VO(<i>c</i> -Salcn)	–	1614	1392	1308
VO(<i>t</i> -Salcn)	–	1615	1390	1310

Thermal analysis

The TG curves for the ligands and complexes are presented in Fig. 2 while the DSC curves are in Fig. 3. Mass loss (TG and calculated), temperatures ranges and a description of thermal events observed in the studies are summarized in Table 3.

The TG and DSC curves for the ligands were presented and were discussed earlier [9]. The *cis* isomer decomposed in two steps producing a carbonaceous residue previously to the final burning. The *trans* isomer decomposed in a single step without

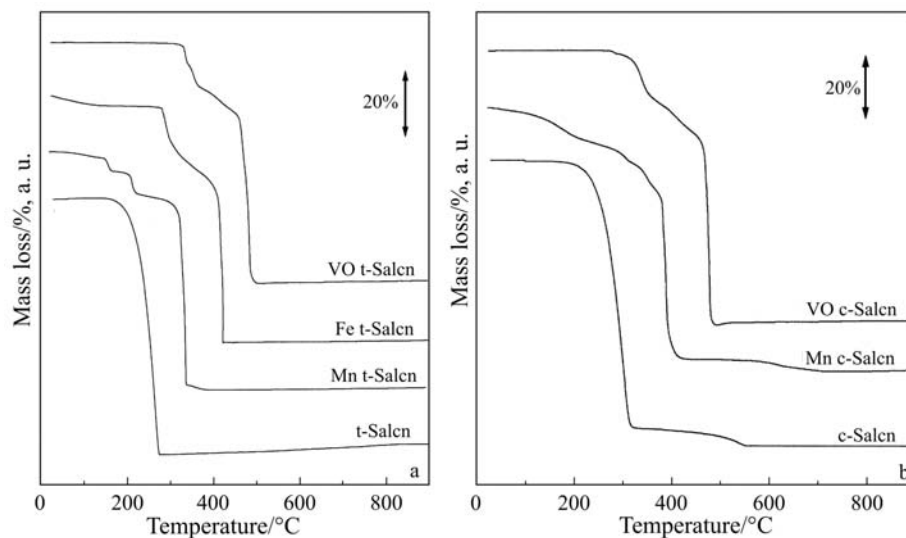


Fig. 2 Thermogravimetric curves for the complexes: a – *trans*- and b – *cis*-isomers. Heating rate 15°C min⁻¹, Pt-sample holder, air flow 90 cm³ min⁻¹

residue in the sample holder. Both started decomposing at around 150–160°C, sug-

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

Process	TG data		Mass loss* or residue**/%		DSC peaks/°C ^a	$\Delta H/J\ g^{-1}$
	$T_{\text{range}}/^{\circ}\text{C}$	TG	calc.	calc.		
<i>c</i> -Salen (<i>s</i>)→ <i>c</i> -Salen (<i>l</i>)	—	—	—	—	135 (endo)	30.11
<i>c</i> -Salen (<i>l</i>)→CR ^b	156–330	90.8*	—	—	350, >600 (exo)	—
CR burning	330–560	9.1*	—	—	568 (exo)	—
[Mn(<i>c</i> -Salen)]·H ₂ O→[Mn(<i>c</i> -Salen)]+H ₂ O	25–131	9.8*	10.0	10.0	—	—
[Mn(<i>c</i> -Salen)]→MnO ₂	131–714	25.0**	23.2	23.2	339, 521 (exo)	488.9
[VO(<i>c</i> -Salen)]→VO ₂	238–562	21.6**	22.3	22.3	294, 350, 478 (exo)	50.93
<i>t</i> -Salen (<i>s</i>)→ <i>t</i> -Salen (<i>l</i>)	—	—	—	—	121 (endo)	37.47
<i>t</i> -Salen (<i>l</i>)→decomposition	147–282	1.10**	0	0	350, 568 (exo)	—
[Fe(<i>t</i> -Salen)]·H ₂ O→[Fe(<i>t</i> -Salen)]+H ₂ O	29.9–271	3.4*	3.5	3.5	85.7 (endo)	—
[Fe(<i>t</i> -Salen)]→Fe ₂ O ₃	271–473	19.4**	19.7	19.7	228, 342, 346, 368, 408, 538 (exo)	—
[Mn(<i>t</i> -Salen)]·H ₂ O→[Mn(<i>t</i> -Salen)]+H ₂ O	30–149	9.5*	10.0	10.0	166 (endo)	247.6
[Mn(<i>t</i> -Salen)]→MnO	149–620	17.4**	17.9	17.9	307, 313 (exo)	—
[VO(<i>t</i> -Salen)]→VO ₂	248–580	22.1**	22.3	22.3	355, 374, 491 (exo)	401.7

^aexo – exothermic process; endo – endothermic process^bCR – carbonaceous residue

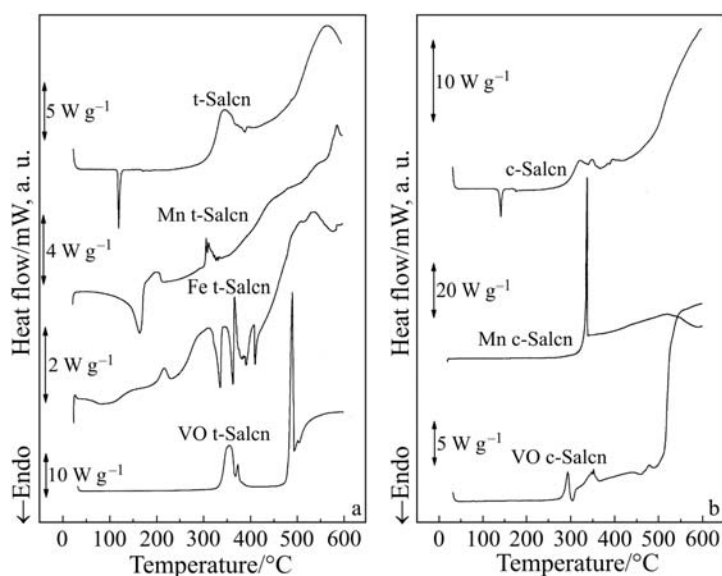


Fig. 3 DSC curves for the complexes: a – *trans*- and b – *cis*-isomers.
Heating rate $15^{\circ}\text{C min}^{-1}$, Al-sample holder, air flow $90\text{ cm}^3\text{ min}^{-1}$

gesting similar thermal stability. DSC curves revealed a melting process for both isomers around $120\text{--}130^{\circ}\text{C}$.

Only the iron(II) *t*-Salcn complex was synthesized. The TG curves presented dehydration from the start of the experiment, referent to the loss of one water molecule. The presence of such water appears also in the IR spectra and in elemental analysis. The anhydrous complex then decomposed in two consecutive steps generating suddenly Fe_2O_3 , confirmed by its infrared spectrum and X-ray diffraction pattern, as final product of thermal decomposition. DSC curves showed that after dehydration, the complex decomposition occurs in a very complicated process via successive endo- and exothermic peaks between $300\text{--}400^{\circ}\text{C}$, followed by burning of the organic matter, represented by the exothermic peak above 450°C , similar the observed for the ligand in Fig. 3a.

The Mn *t*-Salcn complex started decomposition by the loss of one molecule of water followed by two degradation steps and a sudden mass loss that generates MnO at 620°C . The DSC curve shows the dehydration associated to an endothermic event and the rest of decomposition associated with a series of exothermic peaks.

The manganese *cis* isomer presented a TG curve with a slow dehydration step starting in the beginning of the experiment. However, the DSC profile revealed a sharp exothermic peak at 340°C that precedes the decomposition. This intense peak masks the dehydration step, showing a significant difference in the thermal behavior of the isomers, and can be related to the differences in the structures of the Mn complexes. The presence of MnO_2 as the decomposition residue for the *cis* isomer should be related with such a peak and the oxidation occurs just before the decomposition of

the complex, similar results have been observed during the decomposition of dithiocarbamates [21, 22]. The MnO as residue in the *trans* isomer is attributed to the slower decomposition of the organic matter observed in this case.

Vanadium complexes showed similar TG profiles. In the DSC curve for VO *t*-Salcn, a sharp exothermic peak around 500°C, probably related to the decomposition process, is observed. In the *cis* isomer, this process seems to be concomitant with the rest of the decomposition appearing at temperatures higher than 500°C.

Conclusions

Only the iron(II) and manganese(II) complexes presented hydration water molecules. The Fe(II) *c*-Salcn complex could not be obtained under the reaction conditions used. The stability order, after dehydration, is:



In agreement with our previous findings for Ni(II) and Zn(II) *cis* and *trans*-Salcn [9], the *trans* isomers are more stable than the *cis* analogs.

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