

Thermal behavior of vanadyl complexes with Schiff bases derived from *trans*-*N,N'*-bis(salicylidene)-1,2-cyclohexadiamine (*t*-Salcn)

Pedro E. Aranha^a, João M. Souza^a, Sandra Romera^a, Luiz A. Ramos^b,
Mirian P. dos Santos^a, Edward R. Dockal^{a,*}, Eder T.G. Cavalheiro^b

^a Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905 São Carlos, SP, Brazil

^b Instituto de Química de São Carlos, Universidade de São Paulo, Av. do Trabalhador São-Carlense 400, 13566-590 São Carlos, SP, Brazil

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Abstract

Several Schiff bases coordinated to vanadyl, VO(Schiff base), were synthesized, characterized and studied by thermogravimetry in order to evaluate their thermal stability and thermal decomposition pathways. The number of steps and, in particular, the starting temperature of decomposition of these complexes depend on the equatorial ligand. The intermediates of the thermal decomposition processes were characterized by their IR spectra.

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1. Introduction

In recent years, vanadium chemistry has attracted attention due to its interesting structural features and biological relevance [1–3]. Applications of vanadium compounds in medicine have focused their *in vitro* and *in vivo* activity in the treatment of insulin deficiency, type 1 diabetes, and insulin tolerance, type 2 diabetes. The latter is by far the most common form, frequently found with elderly people and increasingly also as a problem for obese young people. The effects caused by vanadium compounds is usually referred to as insulin-mimetic (or, less correct, insulin enhancing) effect [4]. Several vanadium complexes of the tetradentate Schiff base ligand *N,N'*-bis(salicylidene)ethylenediamine (Salen) have been proposed for potential use as insulin mimetic agents [5].

These ligands are of particular interest because they provide coordination environments which efficiently stabilize different oxidation states of vanadium, while still providing active sites capable of binding other molecules [6]. In addition these complexes exhibit catalytic reactivity towards organic substrates,

oxovanadium complexes have been shown to catalyze a variety of reactions such as the oxidation of alcohols and inorganic compounds like halides and sulfur oxides, the epoxidation of alkenes and allyl alcohols, and the conversion of sulfides to sulfoxides and sulfones [7–14]. These catalytic reactions have been performed chiefly in homogeneous solution system. The homogeneous system has the advantage of the high rate of catalytic reaction, whereas some disadvantages include the difficulty in separation of the reaction product from the catalyst.

As part of our studies [15,16] of complexes of these Schiff bases ligand, this work describes the differences observed in the thermal behavior of vanadyl complexes of *trans*-*N,N'*-bis(salicylidene)-1,2-cyclohexadiamine (*t*-Salcn), *trans*-*N,N'*-bis(4-hydroxysalicylidene)-1,2-cyclohexadiamine (4-OH-*t*-Salcn) and *trans*-*N,N'*-bis(4-diethylaminosalicylidene)-1,2-cyclohexadiamine (4-DEA-*t*-Salcn) derivatives using thermogravimetry (TG) and differential scanning calorimetry (DSC). The free ligands and the corresponding vanadyl complexes with Schiff bases derived from *trans*-*N,N'*-bis(salicylidene)-1,2-cyclohexadiamine (*t*-Salcn) were characterized by elemental analysis (C, H, N), and infrared. Thermal stability is an important feature of the complexes in their potential application as catalysts. Structural representations of the ligands and their complexes with their abbreviations are given in Fig. 1.

* Corresponding author. Tel.: +55 16 3351 8095; fax: +55 16 3351 8350.
E-mail address: dockal@dq.ufscar.br (E.R. Dockal).

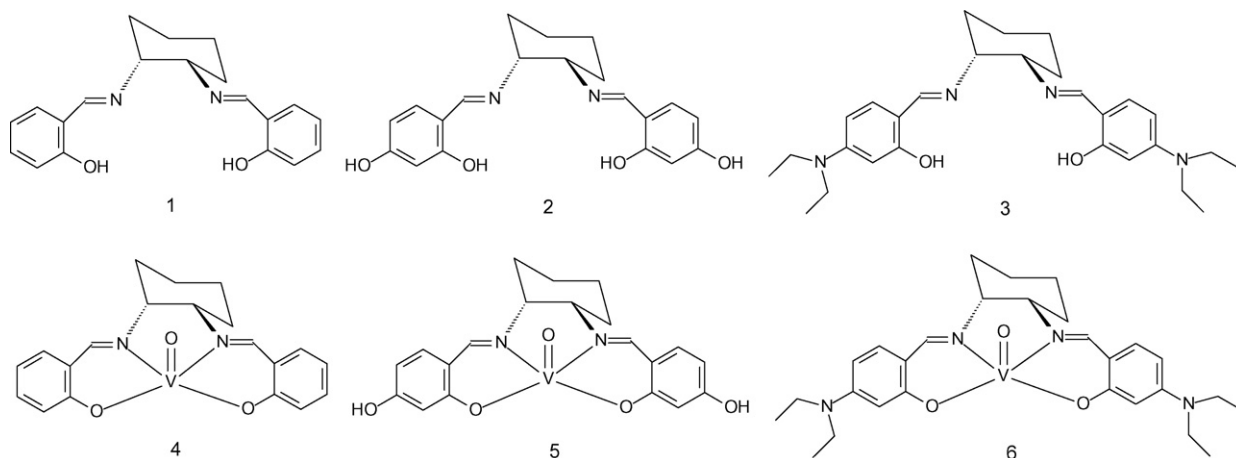


Fig. 1. Structural representations of the ligands and complexes: (1) *t*-Salcn; (2) 4-OH-*t*-Salcn; (3) 4-DEA-*t*-Salcn; (4) [VO(*t*-Salcn)]; (5) [VO(4-OH-*t*-Salcn)]·H₂O; (6) [VO(4-DEA-*t*-Salcn)].

2. Experimental

2.1. Reagents

O-Vanillin, salicylaldehyde 98%, 2,4-dihydroxybenzaldehyde 98%, 4-(diethylamino)salicylaldehyde 98% and (±)-*trans*-1,2-diaminocyclohexane 99%, were purchased from Aldrich and were used as received. All other solvents and reagents with analytical grade (PA) were obtained commercially and used without further purification.

2.2. Physical measurements

Elemental microanalyses (C, H, N) were performed with a Fison EA-1108-CHNS-O instrument. IR spectra were recorded in KBr pressed discs (1 wt.%) with a Bomem Michelson 102 FT-IR instrument.

Thermogravimetric (TG) curves were obtained using a TGA-951 thermogravimetric unit coupled to a TGA-2100 thermal analyzer, both from TA Instruments, using sample mass of ca. 7 mg and a platinum sample holder under a dynamic air flow of 90 mL min⁻¹. In all experiments, a 15 °C min⁻¹ heating rate was used. The TGA-951 was calibrated by using calcium oxalate. Differential scanning calorimetry (DSC) measurements were performed in a DSC-910 unit coupled to a TGA-2100 thermal analyzer, both from TA Instruments, using sample mass of 3.0 mg in a covered aluminum sample holder with a central pin hole under dynamic air flow of 90 mL min⁻¹ and heating rate = 15 °C min⁻¹. The DSC cell was previously calibrated for temperature and energy using indium metal (99.9%) as standard and the peak temperature is reported.

2.3. Preparation of the Schiff bases

The Schiff bases were prepared in a similar manner [17,18] by the following procedure. An aqueous solution (10 mL) of 2 mmol (±)-*trans*-1,2-diaminocyclohexane was added dropwise to a stirred solution of 4 mmol of the appropriate substituted salicylaldehyde in methanol and heated at 80 °C for 2 h. Afterwards the mixture was cooled to room temperature, then held at 5 °C

for 24 h. The solid was filtered and washed with cold ethanol (5 mL at 5 °C) and dried over silica gel in a desiccator. The ligands were used without further purification.

2.4. Preparation of the vanadyl complexes

The vanadyl complexes of the Schiff bases were all synthesized by the same general procedure [19], an aqueous solution of vanadyl sulfate (1 mmol) was added to a stirred methanol solution of the Schiff base (1 mmol) and sodium acetate (2 mmol). The resulting mixture was refluxed during 4 h. After slowly cooling to room temperature, the reaction mixture was held at 0 °C for 12 h. The precipitate was filtered, washed with 20 mL of distilled water and with 10 mL of methanol and dried in a desiccator over silica for 72 h. The compounds were recrystallized from methanol.

3. Results and discussion

The analytical data for the ligands and complexes are summarized in Table 1.

3.1. IR characteristics

The IR spectra of the free ligands and the complexes exhibit several bands in the 250–4000 cm⁻¹ region. The O–H stretching frequency of the ligand is expected in the 3300–3800 cm⁻¹ region, however, this frequency is generally displaced to the

Table 1
Analytical data for ligands and complexes

Compound	Found (calc.) (%)		
	C	N	H
<i>t</i> -Salcn	74.2 (74.5)	8.7 (8.7)	6.9 (6.9)
4-OH- <i>t</i> -Salcn	67.8 (67.8)	8.1 (7.9)	6.5 (6.3)
4-DEA- <i>t</i> -Salcn	72.3 (72.4)	12.3 (12.1)	8.8 (8.7)
[VO(<i>t</i> -Salcn)]	61.7 (62.0)	7.7 (7.3)	5.3 (5.2)
[VO(4-OH- <i>t</i> -Salcn)]·H ₂ O	54.6 (54.9)	6.9 (6.4)	5.1 (5.1)
[VO(4-DEA- <i>t</i> -Salcn)]	63.8 (63.5)	10.3 (10.6)	7.7 (7.2)

Table 2
IR data for ligands and complexes (cm^{-1})

Compound	$\nu\text{OH}-\text{N}=\text{C}$	$\nu\text{C}=\text{N}$	$\nu\text{C}-\text{N}$	$\nu\text{C}-\text{O}$	$\nu\text{V}=\text{O}$
<i>t</i> -Salcn	2591 (w) ^a	1634 (s)	1385 (m)	1310 (w)	–
4-OH- <i>t</i> -Salcn	2532 (w)	1636 (s)	1365 (m)	1294 (w)	–
4-DEA- <i>t</i> -Salcn	2579 (w)	1619 (s)	1388 (m)	1300 (w)	–
[VO(<i>t</i> -Salcn)]	–	1615 (s)	1390 (w)	1310 (m)	978 (s)
[VO(4-OH- <i>t</i> -Salcn)]·H ₂ O	–	1614 (s)	1393 (w)	1306 (w)	985 (s)
[VO(4-DEA- <i>t</i> -Salcn)]	–	1608 (s)	1405 (w)	1312 (w)	979 (s)

^a s: strong; m: medium; w: weak.

2840–2960 cm^{-1} region due to the internal hydrogen bond OH N=C [20,21]. As the hydrogen bond becomes stronger, this band becomes broader and sometimes is not detected. Hydrogen bonds in these Schiff bases are usually very strong. The ligands are relatively planar with an adequate intramolecular distance which favors intramolecular hydrogen bond formation [22]. The C=N stretching frequencies are in the 1592–1640 cm^{-1} region as reported for similar ligands [19,23–25]. The ligands exhibit the characteristic C=N band in 1619–1634 cm^{-1} region. For the complexes the C=N were observed to 1608 and 1615 cm^{-1} region. The C=N stretching frequency in the complexes is generally shifted to a lower frequency, indicating a decrease in the C=N bond order due to the coordinate bond formation between the metal and the imine nitrogen lone pair [26,27].

The C–N stretching frequency has been reported [28–30] in the 1350–1410 cm^{-1} region. For the free ligands the band was assigned as occurring in the 1365–1388 cm^{-1} region and for the complexes in the 1390–1405 cm^{-1} region.

The C–O stretching frequency appears as a weak band within the 1290–1340 cm^{-1} range as reported for similar ligands [20,21,31]. This band occurs in the 1294–1310 cm^{-1} region for the ligands and in the 1306–1312 cm^{-1} region for the complexes. The C–O stretching frequency is generally displaced to a higher frequency, indicating the formation of bond between the oxygen of phenolic group and metal [28,29]. The band at 978–985 cm^{-1} is assigned to $\nu(\text{V}=\text{O})$, this band is observed as a new peak for the complexes and is not present in the spectrum of the free ligand. These IR data are summarized in Table 2.

3.2. Thermal analysis

The thermal decomposition of the ligands and complexes studied in this work presented characteristic pathways, depending on the nature of the ligands, as can be seen from the TG/DTG curves in Fig. 2 and DSC curves presented in Fig. 3.

The *t*-Salcn (**1**) presented an endothermic peak at 123 °C, related to the melting process ($\Delta H_{\text{fus}} = 32.1 \text{ kJ mol}^{-1}$). The compound then decomposed between 150 and 450 °C without residue in the sample holder at 450 °C (Fig. 2, curve a), this decomposition is accompanied by three exothermic peaks at 341, 351 and 414 °C (Fig. 3, curve a).

The 4-OH-*t*-Salcn (**2**) decomposed between 195 and 305 °C with a residue of 78.2%. According to the DTG curve the decomposition involves more than one step (Fig. 2, curve b). The DSC peaks (Fig. 3, curve b) appeared at 245 (endothermic) and 275 °C (exothermic). Then another decomposition process takes place

from 325 to 650 °C with a residue of 1.6%, associated with a DSC exothermic peak at 330 °C.

The thermal decomposition of 4-DEA-*t*-Salcn (**3**) occurs in three steps (curve c in Fig. 2). The first mass loss (3.1%), can be seen between 100 and 150 °C, and was attributed to the elimination of the surface water since the elemental analysis does not suggested water of hydration. The second mass loss (TG = 38.2%) was observed between 220 and 350 °C. The third step occurred between 350 and 700 °C (TG = 58.8%) without residue in the sample holder. The DSC curve (curve c in Fig. 3) presented an endothermic peak related to the loss of the water, followed by a melting process at 207 °C represented by an endothermic peak ($\Delta H_{\text{fus}} = 52.5 \text{ kJ mol}^{-1}$). The exothermic peaks at 340 and 352 °C are related to the decomposition.

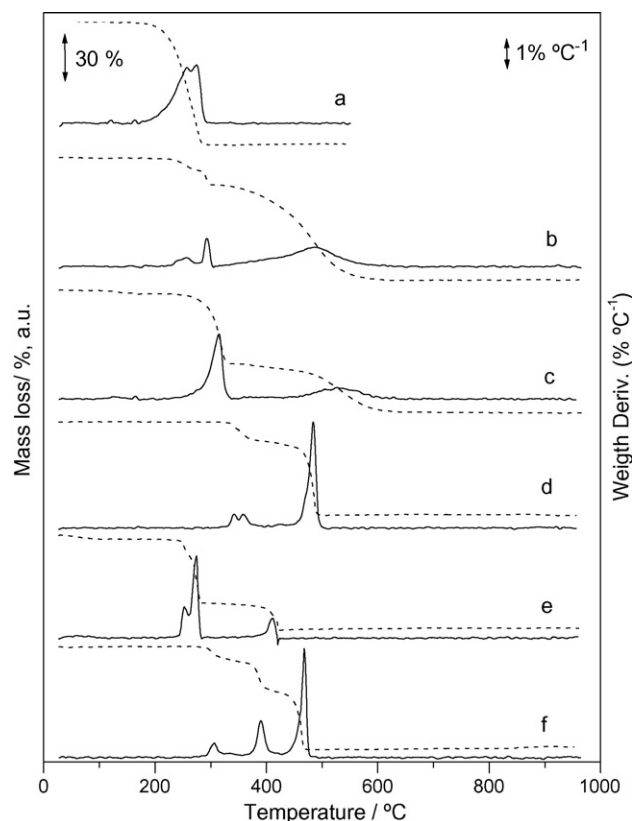


Fig. 2. TG (dash) and DTG (solid) curves: (a) *t*-Salcn; (b) 4-OH-*t*-Salcn; (c) 4-DEA-*t*-Salcn; (d) [VO(*t*-Salcn)]; (e) [VO(4-OH-*t*-Salcn)]·H₂O and (f) [VO(4-DEA-*t*-Salcn)]. Sample mass: ca. 7 mg; heating rate: 15 °C min⁻¹; under air flow of 90 mL min⁻¹; in a Pt sample holder.

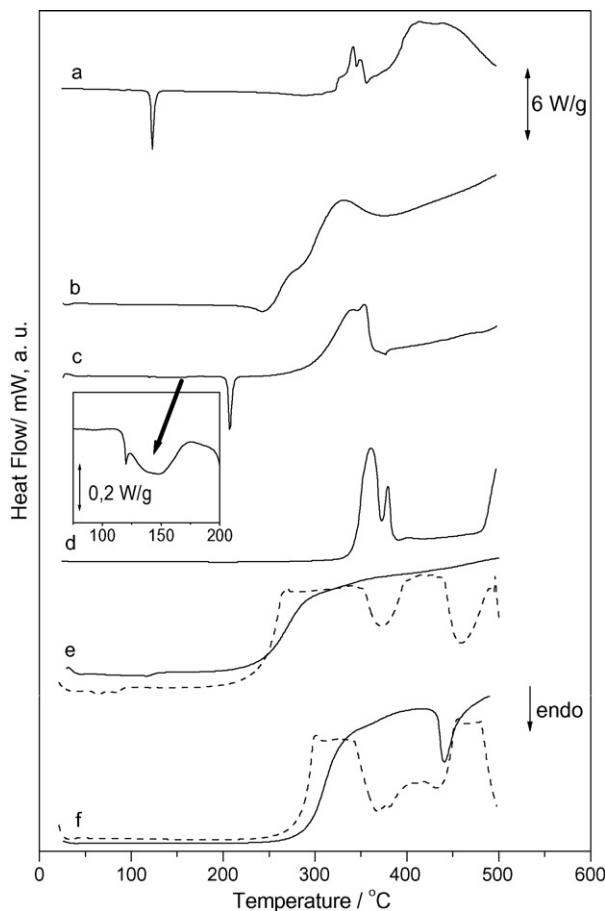


Fig. 3. DSC curves: (a) *t*-Salcn; (b) 4-OH-*t*-Salcn; (c) 4-DEA-*t*-Salcn, insert: enlargement for 75–200 °C; (d) [VO(*t*-Salcn)]; (e) [VO(4-OH-*t*-Salcn)]·H₂O and (f) [VO(4-DEA-*t*-Salcn)]. Sample mass: 3 mg; heating rate: 15 °C min⁻¹; under air flow: 90 mL min⁻¹; in a covered aluminum sample holder with a central pin hole. The dashed curves in (e) and (f) were run using open pans.

The complex, [VO(*t*-Salcn)] (**4**), decomposes in two steps (Fig. 2, curve d). The first step occurs between 310 and 380 °C (TG = 15.1%). The second step of the thermal decomposition, which occurs in the range 420–500 °C, resulted in the formation of the V₂O₅ at 950 °C (TG = 25.9%; calc. = 23.5%). The presence of V₂O₅ is confirmed when the IR spectra of the final residue was compared with the IR spectra of the commercial oxide, however some other vanadium oxides can be present causing the difference between the calculated and experimental values. The DSC curve (Fig. 3, curve d) showed no melting and exothermic decomposition at 360 and 379 °C, followed by the beginning of a new exothermic event not complete at the end of the experiment (500 °C).

The [VO(4-OH-*t*-Salcn)]·H₂O (**5**) presented three steps in the TG curve (Fig. 2, curve e) The first mass loss occurred up to about 150 °C and was attributed to the release of the hydration water (TG = 3.0%; calc. = 4.0%). The second thermal event was observed between 240 and 280 °C is probably a partial decomposition of the ligand (TG = 52.8%). The third mass loss between 385 and 420 was assigned to the loss of the rest of the ligand with the formation of the V₂O₅ (TG = 23.6%; calc. = 20.8%). This is confirmed by IR data as described above. In agreement

with the TG/DTG curves, the DSC data using open sample holders presented the release of water at 64 and 84 °C followed by exothermic decomposition with peak at 269 °C and endothermic events at 371 and 457 °C for the [VO(4-OH-*t*-Salcn)]·H₂O complex.

Three consecutive steps were observed during the thermal decomposition of [VO(4-DEA-*t*-Salcn)] (**6**) (Fig. 2, curve f). The first mass loss (TG = 10.2%) occurs between 280 and 330 °C. A comparison of the IR spectra of the initial complex and of this residue showed the presence of the C=N peak of the original Schiff base. The second step that occurred between 370 and 400 °C suggested the loss of the substituted group based on the absence of the stretching C–H bands of the diethylamine in the IR spectra of the residue (TG = 26.4%). The last mass loss occurred between 440 and 480 °C with formation of V₂O₅ (TG = 17.4%; calc. = 17.2%), confirmed according to the IR data. The DSC curves for the [VO(4-DEA-*t*-Salcn)] using open sample holders presented an exothermic peak at 301 °C related to the decomposition followed by four endothermic events at 369, 380, 415 and 432 °C, all related to mass losses in the TG/DTG curves.

The differences were attributed to the gas release in the open sample holder, which is more difficult in the hermetic ones. The trapping of gases in the closed pans give the non-peak shape in the DSC-curves.

3.3. Conclusions

According to the results discussed above, the order for thermal stability found for the ligands is: *t*-Salcn < 4-OH-*t*-Salcn < 4-DEA-*t*-Salcn and for the complexes is: [VO(4-OH-*t*-Salcn)]·H₂O < [VO(4-DEA-*t*-Salcn)] < [VO(*t*-Salcn)].

The number of decomposition steps of the ligand depends on the substituent group leading to differences in thermal process for the complexes, the number of steps and, in particular, the initial temperature of decomposition of these complexes depend on the equatorial ligand.

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