THERMAL DECOMPOSITION OF COMPLEXES
Manganese(II) and vanadyl with cis- and iron(II), manganese(II) and vanadyl with trans-n,n’-bis(salicylidene)-1,2-cyclohexanedianmine (salcn)

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Abstract

The iron(II) complex of the Schiff bases trans-N,N’-bis(salicylidene)-1,2-cyclohexanedianmine (Salcn), manganese(II) and vanadyl complexes of the Schiff bases cis- and trans-N,N’-bis(salicylidene)-1,2-cyclohexanedianmine (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-cyclohexanedianmine, (c-Salcn) and iron(II), manganese(II) and vanadyl trans-N,N’-bis(salicylidene)-1,2-cyclohexanedianmine, (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.

Experimental

Synthesis

The ligands were prepared as described earlier [9–12]. Salicylaldehyde, 6.4 cm$^3$ (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 C$_{20}$H$_{22}$O$_2$N$_2$: 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. Calc. for C$_{20}$H$_{22}$O$_2$N$_2$: 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 cm$^3$ of distilled water was added to a hot methanol solution, 50 cm$^3$, containing 5.0 mmol of the Schiff base ligand. For the corresponding vanadyl complexes, an aqueous (10 cm$^3$) 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 cm$^3$ of distilled water and twice with 10 cm$^3$ 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.

Fig. 1 Structural representations of the ligands: a – c-Salen and b – t-Salen
The residues and intermediates of thermal decomposition were characterized by their X-ray diffraction patterns, powder method, using CuKα 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 C₂₀H₂₀N₂O₂MₓH₂O (M=Fe²⁺, Mn²⁺, VO²⁺; x=0 to 1 and H₂O – superficial or hydration).

Table 1 Analytical data for complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found, (calc.)/%</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>[Fe(t-Salcn)]H₂O</td>
<td>60.0</td>
<td>7.1</td>
</tr>
<tr>
<td>[Mn(c-Salcn)]H₂O</td>
<td>60.0</td>
<td>6.9</td>
</tr>
<tr>
<td>[Mn(t-Salcn)]H₂O</td>
<td>59.0</td>
<td>7.0</td>
</tr>
<tr>
<td>VO(c-Salcn)</td>
<td>61.7</td>
<td>7.7</td>
</tr>
<tr>
<td>VO(t-Salcn)</td>
<td>62.7</td>
<td>7.3</td>
</tr>
</tbody>
</table>

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 νC=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 νC=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>
<thead>
<tr>
<th>Compound</th>
<th>$\nu_{\text{OH---N=C}}$/cm$^{-1}$</th>
<th>$\nu_{\text{C=N}}$/cm$^{-1}$</th>
<th>$\nu_{\text{C--N}}$/cm$^{-1}$</th>
<th>$\nu_{\text{C--O}}$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Salen</td>
<td>2589</td>
<td>1634</td>
<td>1385</td>
<td>1310</td>
</tr>
<tr>
<td>c-Salen</td>
<td>2555</td>
<td>1631</td>
<td>1391</td>
<td>1281</td>
</tr>
<tr>
<td>[Fe(t-Salen)]$\cdot$H$_2$O</td>
<td>–</td>
<td>1623</td>
<td>1397</td>
<td>1318</td>
</tr>
<tr>
<td>[Mn(c-Salen)]$\cdot$H$_2$O</td>
<td>–</td>
<td>1627</td>
<td>1398</td>
<td>1310</td>
</tr>
<tr>
<td>[Mn(t-Salen)]$\cdot$H$_2$O</td>
<td>–</td>
<td>1630</td>
<td>1392</td>
<td>1308</td>
</tr>
<tr>
<td>VO(c-Salen)</td>
<td>–</td>
<td>1614</td>
<td>1392</td>
<td>1308</td>
</tr>
<tr>
<td>VO(t-Salen)</td>
<td>–</td>
<td>1615</td>
<td>1390</td>
<td>1310</td>
</tr>
</tbody>
</table>

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 residue in the sample holder. Both started decomposing at around 150–160°C, sug-
Table 3 TG mass loss, temperature range, DSC peaks and $\Delta H$ related to the thermal decomposition process of the ligands and metal complexes under air

<table>
<thead>
<tr>
<th>Process</th>
<th>TG data</th>
<th>Mass loss* or residue**/%</th>
<th>DSC peaks$^\circ$C$^a$</th>
<th>$\Delta H$/g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{range}}$/°C</td>
<td>TG</td>
<td>calc.</td>
<td></td>
</tr>
<tr>
<td>cis-isomers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c-Salen ($s$)→c-Salcn ($l$)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>135 (endo)</td>
</tr>
<tr>
<td>c-Salcn ($l$)→CR$^b$</td>
<td>156–330</td>
<td>90.8*</td>
<td>–</td>
<td>350, &gt;600 (exo)</td>
</tr>
<tr>
<td>CR burning</td>
<td>330–560</td>
<td>9.1*</td>
<td>–</td>
<td>568 (exo)</td>
</tr>
<tr>
<td>[Mn(c-Salcn)]:H$_2$O→[Mn(c-Salcn)]:H$_2$O</td>
<td>25–131</td>
<td>9.8*</td>
<td>10.0</td>
<td>–</td>
</tr>
<tr>
<td>[Mn(c-Salcn)→MnO$_2$</td>
<td>131–714</td>
<td>25.0**</td>
<td>23.2</td>
<td>339, 521 (exo)</td>
</tr>
<tr>
<td>[VO(c-Salcn)→VO$_2$</td>
<td>238–562</td>
<td>21.6**</td>
<td>22.3</td>
<td>294, 350, 478 (exo)</td>
</tr>
<tr>
<td>trans-isomers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-Salen ($s$)→t-Salcn ($l$)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>121 (endo)</td>
</tr>
<tr>
<td>t-Salcn ($l$)→decomposition</td>
<td>147–282</td>
<td>1.10**</td>
<td>0</td>
<td>350, 568 (exo)</td>
</tr>
<tr>
<td>[Fe(t-Salcn)]:H$_2$O→[Fe(t-Salcn)]:H$_2$O</td>
<td>29.9–271</td>
<td>3.4*</td>
<td>3.5</td>
<td>85.7 (endo)</td>
</tr>
<tr>
<td>[Fe(t-Salcn)→Fe$_2$O$_3$</td>
<td>271–473</td>
<td>19.4*</td>
<td>19.7</td>
<td>228, 342, 346, 368, 408, 538 (exo)</td>
</tr>
<tr>
<td>[Mn(t-Salcn)]:H$_2$O→[Mn(t-Salcn)]:H$_2$O</td>
<td>30–149</td>
<td>9.5*</td>
<td>10.0</td>
<td>166 (endo)</td>
</tr>
<tr>
<td>[Mn(t-Salcn)→MnO</td>
<td>149–620</td>
<td>17.4**</td>
<td>17.9</td>
<td>307, 313 (exo)</td>
</tr>
<tr>
<td>[VO(t-Salcn)→VO$_2$</td>
<td>248–580</td>
<td>22.1**</td>
<td>22.3</td>
<td>355, 374, 491 (exo)</td>
</tr>
</tbody>
</table>

$^a$exo – exothermic process; endo – endothermic process
$^b$CR – carbonaceous residue
gesting similar thermal stability. DSC curves revealed a melting process for both iso-
mers around 120–130°C.

Only the iron(II) \( \text{t-Salen} \) complex was synthesized. The TG curves presented de-
hydration 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 sud-
denly \( \text{Fe}_2\text{O}_3 \), confirmed by its infrared spectrum and X-ray diffraction pattern, as fi-
nal 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 300–400°C, followed by burning of the organic mat-
ter, represented by the exothermic peak above 450°C, similar the observed for the
ligand in Fig. 3a.

The Mn \( \text{t-Salen} \) 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 \( \text{cis} \) 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 com-
plexes. The presence of MnO\(_2\) as the decomposition residue for the \( \text{cis} \) isomer should
be related with such a peak and the oxidation occurs just before the decomposition of

\[ \text{MnO} \rightarrow \text{MnO}_2 \]

\[ \text{MnO}_2 \rightarrow \text{MnO} \]

Fig. 3 DSC curves for the complexes: a – \( \text{trans} \)- and b – \( \text{cis} \)-isomers.

Heating rate 15°C min\(^{-1}\), Al-sample holder, air flow 90 cm\(^3\) min\(^{-1}\)
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:

Fe t-Salcn > VO t-Salcn > VO c-Salcn > Mn t-Salcn > Mn c-Salcn

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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References