SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF SOLID-STATE COMPOUNDS OF BENZOATES WITH SOME BIVALENT TRANSITION METAL IONS

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Solid-state MBz compounds, where M stands for bivalent Mn, Fe, Co, Ni, Cu and Zn and Bz is benzoate, have been synthesized. Simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), infrared spectroscopy and complexometry were used to characterize and to study the thermal behaviour of these compounds. The procedure used in the preparation of the compounds via reaction of basic carbonates with benzoic acid is not efficient in eliminating excess acid. However the TG-DTA curves permitted to verify that the binary compounds can be obtained by thermosynthesis, because the benzoic acid can be eliminated before the thermal decomposition of these compounds. The results led to information about the composition, dehydration, thermal stability, thermal decomposition and structure of the isolated compounds. On heating, these compounds decompose in two (Mn, Co, Ni, Zn) or three (Fe, Cu) steps with formation of the respective oxide (Mn$_3$O$_4$, Fe$_2$O$_3$, CoO, NiO, CuO and ZnO) as final residue. The theoretical and experimental spectroscopic studies suggest a covalent bidentate bond between ligand and metallic center.

Keywords: bivalent transition metals; benzoate; thermal behaviour.

INTRODUCTION

Benzoic acid and some of their derivatives have been used as conservant, catalyst precursors polymers, in pharmaceutical industries, beyond other applications. A survey of literature shows that the complexes of rare earth and d-block elements with benzoic acid and some of its derivatives have been investigated in aqueous solutions and in the solid state.

In aqueous solutions, the publications reported the thermodynamics of complexation of lanthanides by some benzoic acid derivatives\(^1\), the spectroscopic study of trivalent lanthanides with several carboxylic acids including benzoic acid\(^2\), the influence of pH, surfactant and synergic agent on the luminescent properties of terbium chelates with benzoic acid derivatives\(^3\), the thermodynamic of complexation of lanthanides by benzoic and isophthalic acids\(^4\) and the synthesis, crystal structure and photophysical and magnetic properties of dimeric and polymeric lanthanide complexes with benzoic acid and their derivatives\(^5\).

In the solid state the publications reported the vibrational and electronic spectroscopic study of lanthanides and effect of sodium on the aromatic system of benzoic acid\(^6\); the thermal and spectral behaviour on solid compounds of m-methoxybenzoate with rare earth elements\(^2\); the reaction of bivalent copper, cobalt and nickel with 3-hidroxy-4-methoxy and 3-methoxy-4-hidroxybenzoic acids and a structure for these compounds has been proposed on the basis of spectroscopic and thermogravimetric data\(^7\); the thermal decomposition of thorium salts of benzoic and 4-methoxybenzoic acids in air atmosphere\(^8\); the thermal and spectral behaviour on solid compounds of 5-chloro-2-methoxybenzoate with rare earth and d-block elements\(^9\); the synthesis and characterization of 2,3-dimethoxybenzoates of several metal ions\(^10,11\); the spectral and magnetic studies of 2-chloro-5-nitrobenzoates of rare earth elements\(^12\) and thermal behaviour of solid state 4-methoxybenzoates of some bivalent transition metal ions\(^13\).

In an endeavour to extend the literature works, the present publication deals with the synthesis of Mn (II), Fe (II), Co (II), Ni (II), Cu (II) and Zn (II) benzoates, studied by means of infrared spectroscopy, simultaneous thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC) and other methods of analysis. The results permitted to obtain information concerning the structure, thermal stability and thermal decomposition of these compounds.

EXPERIMENTAL

The benzoic acid, C$_6$H$_5$COOH (HBz) 99.9% was obtained from MERCK. Hydrated basic carbonates of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) were prepared by adding slowly with continuous stirring saturated sodium carbonate solution to the corresponding metal chloride or sulphate solution until total precipitation of the metal ions. The precipitates were washed with distilled water until elimination of chloride or sulphate ions (qualitative test with AgNO$_3$/HNO$_3$ solution for chloride ions or BaCl$_2$ solution for sulphate ions) and maintained in aqueous suspension.

Solid state Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) compounds were prepared by mixing the corresponding metal basic carbonates with benzoic acid, in slight excess. The aqueous suspension was heated slowly up to near ebullition, until total neutralization of the respective basic carbonates. The resulting solutions after cooled were filtered through a Whatman nº 40 filter paper. Thus, the aqueous solutions of the respective metal benzoates were evaporated to near dryness in a water bath and kept in a desiccator over phosphorous pentoxide. The same procedure to synthesize the iron (II) compound was unsuccessful, due to oxidation reaction of Fe (II) to Fe (III) during the washing of the precipitate of basic carbonate of Fe (II), even by using solutions and washing water purified with nitrogen gas.

The iron (II) benzoate was synthesized by adding solution of sodium benzoate (pH=9.5) to iron (II) sulphate solution, both purified with nitrogen gas. No precipitate was observed during the addition of sodium.

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benzoate; however the precipitation occurred after five day when the solution saturated with N\textsubscript{2} was maintained in a freezer at about 6 °C.

In the solid-state compounds, metal ions, hydration water and benzoate contents were determined from TG curves. The metal ions were also determined by complexometry with standard EDTA solution\textsuperscript{19,20} after igniting the compounds to the respective oxides and their dissolution in hydrochloric acid solution.

Infrared spectra for sodium benzoate as well as for its metal-ion compounds were run on a Nicolet model Impact 400 FT-IR instrument, within the 4000-400 cm\textvision{\textsuperscript{-1}} range. The solid samples were pressed into KBr pellets.

Simultaneous TG-DTA curves were obtained with thermal analysis system model SDT 2960 from TA Instruments. The purge gas was a dry air flow of 100 mL min\textvision{\textsuperscript{-1}}. A heating rate of 20 °C min\textvision{\textsuperscript{-1}} was adopted with samples weighing about 7 mg. Platinum crucibles were used for TG-DTA.

DSC curves were obtained with thermal analysis systems model DSC 25 from Mettler Toledo. The purge gas was a dry air flow of 100 mL min\textvision{\textsuperscript{-1}}. A heating rate of 20 °C min\textvision{\textsuperscript{-1}} was adopted with samples weighing about 5 mg. Aluminium crucibles, with perforated cover, were used for DSC.

Computational strategy

Calculation of theoretical infrared spectrum of nickel benzoate has been necessary to evaluate the structure and wave function computed by the \textit{ab initio} SCF Hartree-Fock-Roothan method\textsuperscript{27} using a split valency (3-21g) basis set\textsuperscript{22,23}. The performed molecular calculations in this work were done by using the Gaussian 98 routine\textsuperscript{21} and the hardware IBM power 3. The geometry optimization was carried out without any constraints. The molecule of benzoate contains rings with conformational flexibility, and all variables optimized. The optimization proceeded more uniformly when all variables were optimized.

RESULTS AND DISCUSSION

Preliminary studies based on TG-DTA curves and infrared spectra, permitted to verify that the synthesized compounds, except iron, were obtained contaminated. The TG-DTA curves also show that the contamination is evolved before the thermal decomposition of the binary compounds. Thus, sample of these compounds were heated in a long test glass tube, and dehydration for manganese and iron compounds, and sublimation for all the compounds were observed. The sublimated material was identified as benzoic acid, m.p. 121 °C (found); 122 °C (literature)\textsuperscript{4}.

The presence of benzoic acid in the compounds must be due to the aggregation phenomenon provoked by the increase of the solubility of benzoic acid in benzoate solution, and it is not recrystallized even an ice bath. Therefore, the procedure used to eliminate the acid in excess is not efficient. This behaviour had already been observed in the 3-methoxybenzoate of the same metal ions, except copper compound\textsuperscript{25}.

Therefore these compounds were heated up to 260 (Mn), 140 (Co), 230 (Ni), 210 (Cu) and 140 °C (Zn), as indicated by the TG-DTA curves and so to obtain binary compounds free from benzoic acid.

Infrared spectroscopic data on benzoate and their compounds with bivalent metal ions. IR spectra /cm\textvision{\textsuperscript{-1}}

\begin{table}
\centering
\begin{tabular}{llll}
\hline
Compound & ν\textsubscript{(\text{OH})} & ν\textsubscript{sym} (COO\textsuperscript{-}) & ν\textsubscript{asym} (COO\textsuperscript{-}) \\
\hline
NaBz & - & 1414 & 1551 \\
Mn(Bz)\textsubscript{2} & - & 1410 & 1533 \\
Fe(Bz)\textsubscript{2} & 3420 & 1410 & 1549 \\
Co(Bz)\textsubscript{2} & - & 1433 & 1541 \\
Ni(Bz)\textsubscript{2} & - & 1435 & 1552 \\
Cu(Bz)\textsubscript{2} & - & 1408 & 1562 \\
Zn(Bz)\textsubscript{2} & - & 1410 & 1549 \\
\hline
\end{tabular}
\caption{Spectroscopic data for sodium benzoate and compounds with some bivalent metal ions. IR spectra /cm\textvision{\textsuperscript{-1}}}
\end{table}

The theoretical infrared spectrum of the Ni(Bz)\textsubscript{2} was calculated by using an harmonic field\textsuperscript{27} and the obtained frequencies were not scaled. The geometry optimization was computed by the optimized algorithm of Bern\textsuperscript{27}. The obtained geometry from calculations is presented in Table 2.

\begin{table}
\centering
\begin{tabular}{llllllll}
\hline
Compound & ν\textsubscript{sym} (COO\textsuperscript{-}) & ν\textsubscript{asym} (COO\textsuperscript{-}) & ν\textsubscript{(\text{OH})} \\
\hline
NaBz & - & 1414 & 1551 \\
Mn(Bz)\textsubscript{2} & - & 1410 & 1533 \\
Fe(Bz)\textsubscript{2} & 3420 & 1410 & 1549 \\
Co(Bz)\textsubscript{2} & - & 1433 & 1541 \\
Ni(Bz)\textsubscript{2} & - & 1435 & 1552 \\
Cu(Bz)\textsubscript{2} & - & 1408 & 1562 \\
Zn(Bz)\textsubscript{2} & - & 1410 & 1549 \\
\hline
\end{tabular}
\caption{Theoretical geometries parameters of Ni(Bz)\textsubscript{2} compound}
\end{table}

Theoretical infrared spectrum of the Ni(Bz)\textsubscript{2} (electronic state \textit{A}) was obtained with frequency values (cm\textvision{\textsuperscript{-1}}), relative intensities, assignments and description of vibrational modes. The theoretical frequency, assignments and description was visualized by using graphic software Molden 4.2 for Linux\textsuperscript{28}. It was compared with the experimental infrared spectrum of the NiBz\textsubscript{2}.

A comparative analysis between the experimental and theoretical spectrum permitted to verify that: (a) the first assignment shows a strong contribution at 1552 cm\textvision{\textsuperscript{-1}} suggesting a \textit{ν}\textsubscript{sym} (COO\textsuperscript{-}) assignment, while the theoretical results show the corresponding peak at 1562 cm\textvision{\textsuperscript{-1}} with discrepancies of 0.64%; (b) the second assignment shows a strong contribution at 1435 cm\textvision{\textsuperscript{-1}} suggesting a \textit{ν}\textsubscript{asym} (COO\textsuperscript{-}) assignment, while the theoretical results show the corresponding peak at 1487 cm\textvision{\textsuperscript{-1}} with discrepancies of 3.6%. The theoretical and experimental data suggesting that compounds considered in this work have a covalent bidentate bond.

The thermal behaviour of the compounds is heavily dependent on the nature of the metal ion and so the features of each of these compounds are discussed individually.
Manganese compound. The TG-DTA and DSC curves are shown in Figure 1(a). The TG curve shows mass losses in two overlapping steps and thermal events corresponding to these losses or physical phenomenon. The small endothermic peak at 260 (DTA) or 265 °C (DSC) is attributed to the fusion. The mass loss, between 260 and 500 ºC, corresponding to the exothermic peak at 470 (DTA) or 440 and > 500 ºC (DSC) is attributed to the oxidation of organic matter. The total mass loss up to 500 ºC is in agreement with the formation of Mn3O4, as final residue (Calcd = 74.34%; TG = 74.31%).

Iron compound. The TG-DTA and DSC curves are shown in Figure 1(b). The TG-DTA and DSC curves are shown in Table 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Metal Oxide (%)</th>
<th>ΔBz (%)</th>
<th>H2O (%)</th>
<th>Final Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(Bz)2</td>
<td>25.66</td>
<td>25.39</td>
<td>25.18</td>
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</tr>
<tr>
<td>Fe(Bz)2.0.5H2O</td>
<td>26.00</td>
<td>26.16</td>
<td>26.19</td>
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</tr>
<tr>
<td>Co(Bz)2</td>
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<td>26.74</td>
<td>26.83</td>
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<tr>
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<td>24.85</td>
<td>24.67</td>
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</tr>
<tr>
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<td>26.01</td>
<td>25.99</td>
<td>26.17</td>
<td>CuO</td>
</tr>
<tr>
<td>Zn(Bz)2</td>
<td>26.45</td>
<td>26.27</td>
<td>26.00</td>
<td>ZnO</td>
</tr>
</tbody>
</table>

*All the residues was confirmed by X-ray powder diffractometry; Key: Bz means benzoate

Figure 1. TG-DTA and DSC curves of the compounds: (a)MnBz2, (b)FeBz2.0.5H2O, (c)CoBz2, (d)NiBz2, (e)CuBz2, (f)ZnBz2. Bz = benzoate
CONCLUSION

The TG-DTA curves, infrared spectra and chemical analysis, permitted to verify the presence of benzoic acid in all the synthesized compounds, showing that the procedure used to eliminate the benzoic acid in excess is not efficient.

The TG-DTA, also permitted to verify that the binary compounds can be obtained by thermosynthesis, because the benzoic acid is eliminated before the thermal decomposition of these compounds.

The theoretical and experimental infrared spectroscopic data suggest that the benzoate acts as a bidentate ligand towards the metal ions considered in this work.

The TG-DTA and DSC provided previously unreported information about the thermal stability and thermal decomposition of these compounds.

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