Polynuclear coordination precursor compounds for $\text{M}_3\text{Fe}_5\text{O}_{12}$
garnets (M = Y, Eu, Gd and Er). Part I. Synthesis of the precursors

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Abstract: A new type of complexes compounds $(\text{NH}_4)_6[M_3\text{Fe}_5(\text{C}_4\text{O}_6\text{H}_6)_{6}(\text{C}_4\text{O}_6\text{H}_3)_{6}]$·16$\text{H}_2\text{O}$ (where M(III) = Y, Eu, Gd, Er), $(\text{NH}_4)_6[M_3\text{Fe}_5(\text{C}_4\text{O}_6\text{H}_6)_{6}(\text{C}_4\text{O}_6\text{H}_3)_{6}]$·16$\text{H}_2\text{O}$ (where M(III) = Gd, Er) and $(\text{NH}_4)_6[M_3\text{Fe}_5(\text{C}_6\text{O}_7\text{H}_{10})_{6}(\text{C}_6\text{O}_7\text{H}_9)_{6}]$·x$\text{H}_2\text{O}$
(where M(III) = Y; x = 8; M(III) = Eu, Er; x = 22) [C$_4$O$_5$H$_4^{2-}$ = malate anion; C$_4$O$_6$H$_6^{2-}$ = tartarate anion, C$_6$O$_7$H$_{11}^{2-}$ = gluconate anion] have been synthesized
and characterised by elemental chemical analysis and physico-chemical measurements (IR, UV-Vis spectroscopy and magnetic determinations). The synthetic possibilities offered by the use of these new compounds as potential precursors for garnets have been suggested.

Keywords: garnets precursors, complexation method.

INTRODUCTION

Since their discovery in 1956, important scientific and technological interest have been devoted to ferrimagnetic garnets due to their high resistivity, as well as to their application in microwave and magneto-optical devices.$^1$

Yttrium–iron garnet (Y$_3$Fe$_5$O$_{12}$, YIG) is the most representative and well-known compound among the rare-earth iron garnets. This ferrimagnetic material is used widely in electronic devices for the microwave region, as well as magnetic bubble domain-type digital memories.$^2$ The recent multimedia revolution has increased the need for new, higher density recording media. New blue laser diodes permit the density of recording media to be increased by a factor of four as compared with media which use a conventional red laser. However, the implementation of these improvements requires magneto-optical materials with a high efficiency in the blue region of the visible spectrum. Thin films of rare-earth iron garnets with the general formula M$_3$Fe$_5$O$_{12}$, and, more specifically, their partially substituted (Bi, Dy)$_3$(Fe, Ga)$_5$O$_{12}$ solid state solutions are the most viable candidates for the next generation of efficient magneto-optical media.$^3,4$

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The most common method for ceramic powder synthesis is the grinding of mixed oxide powders followed by solid state reactions. However, this method requires high reaction temperatures and produces particles with large sizes and a limited degree of homogeneity. Also impurities can be introduced during grinding.\textsuperscript{5}

Therefore considerable efforts have been made to develop new synthesis methods for garnets.

Among these methods, the coprecipitation is specially used by Russian researchers,\textsuperscript{6–8} mainly because of its simplicity as compared to the other ones. Inoue \textit{et al.}\textsuperscript{9} investigated the possibility of obtaining rare-earth garnets by the hydrothermal method. They explored the synthesis of garnets in organic media.

In recent years, sol-gel methods have attracted attention due to the lower synthesis temperatures and the finer and more homogeneous particles produced. In sol-gel routes, gelation is frequently attained from solutions of inorganic metal salts and a complexing agent. The concentration of such solutions produces a homogeneous gel if most of the metal ions are in the form of chelate complexes. Therefore, the selection of a suitable chelating agent is important, as are the pH and concentrations in the precursor solution.\textsuperscript{10–14} The most known sol-gel route is the Pechini process.\textsuperscript{15} In this method, the precursor solution contains inorganic metal salts, a chelating agent (citric acid) and a diol (ethylene glycol).

Some research workers admit the existence of citrate precursors\textsuperscript{16,17} or the existence of polynuclear coordination compounds containing urea, hydrazide and hydrazine as ligands (the combustion method),\textsuperscript{18} as garnet precursors. Still, the respective polynuclear coordination compounds are very scantily described and, even more, in some cases they are completely missing.

The application of the method of thermal decomposition of polynuclear coordination compounds (the so-called “complexation method”) requires: (i) a detailed study of their formation in order to establish the parameters influencing the synthesis (the combination ratio of the elements, the nature of the ligand, the pH of reaction medium, the temperature, etc.); (ii) a study regarding the mechanism of their thermal decomposition accompanied by the characterization of the resulting mixed oxide.

The aim of the present work was to study in detail the formation of some polynuclear complex compounds using different ligands selected from the carboxylate acids class as potential precursors of M\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} garnets (M(III) = Y, Eu, Gd and Er). Three ligands were selected: malic, tartaric and gluconic acid.

### EXPERIMENTAL

\textit{Synthesis}

All chemicals: Fe(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O, Y\textsubscript{2}O\textsubscript{3}, Eu\textsubscript{2}O\textsubscript{3}, Gd\textsubscript{2}O\textsubscript{3}, Er\textsubscript{2}O\textsubscript{3}, malic acid, tartaric acid and \(\delta\)-gluconolactone were of reagent quality (Merck). The precursors – polynuclear coordination compounds were prepared as follows.

Lanthanides and iron nitrates were dissolved in the minimum amount of water and mixed with an aqueous solution of carboxylic acid in a 3:5:12 ratio cations/malic (tartaric) acid and 3:5:24 ratio cations/\(\delta\)-gluconolactone, respectively.

Ethanol was added to the final solution until a light brown precipitate was formed. The pH was raised to 5.5–6 by adding NH\textsubscript{4}OH:ethanol (1:1) solution.
The light brown polynuclear compounds were filtered, washed with ethanol and dried over P4O10. Elemental analysis was consistent with the formula:

\[(\text{NH}_4)_6[\text{Er}_3\text{Fe}_5(\text{C}_4\text{O}_5\text{H}_4)_6(\text{C}_4\text{O}_5\text{H}_3)_6]\times16\text{H}_2\text{O} \quad \text{Anal.: Calcd.: Er, 18.19; Fe, 10.16; C, 20.90; N, 3.05. Found: Er, 18.31; Fe, 10.23; C, 20.89; N, 3.03 \%}.

\[(\text{NH}_4)_6[\text{Er}_3\text{Fe}_5(\text{C}_4\text{O}_6\text{H}_4)_6(\text{C}_4\text{O}_6\text{H}_3)_6]\times16\text{H}_2\text{O} \quad \text{Anal.: Calcd.: Er, 17.00; Fe, 9.50; C, 19.54; N, 2.85. Found: Er, 16.88; Fe, 9.44; C, 19.41; N, 2.83 \%}.

\[(\text{NH}_4)_6[\text{Er}_3\text{Fe}_5(\text{C}_6\text{O}_7\text{H}_{10})_6(\text{C}_6\text{O}_7\text{H}_9)_6]\times22\text{H}_2\text{O} \quad \text{Anal.: Er, 13.88; Fe, 7.76; C, 23.95; N, 2.32. Found: Er, 13.75; Fe, 7.69; C, 24.41; N, 2.14 \%}.

The metal content was determined by atomic absorption spectrometry.

Characterization

Diffuse reflectance spectra (200 – 900 nm) were recorded on a UV4 UNICAM spectrophotometer using MgO as the standard.

In order to obtain information about the function of the carboxylate anions, the IR spectra (KBr pellets) of the polynuclear coordination compounds were recorded using a Bio-Rad FTIR 135 type spectrophotometer in the 4000 – 400 cm\(^{-1}\) range.

The room temperature magnetic susceptibility was determined using a Faraday balance with Hg[Co(SCN)]\(_4\) as the calibrant.

RESULTS AND DISCUSSION

In order to establish the optimal conditions for the isolation of some polynuclear coordination compounds the following systems were studied:

\[3\text{M(III)} : 5\text{Fe(III)} : \text{C}_4\text{O}_5\text{H}_4^{2-} ; 3\text{M(III)} : 5\text{Fe(III)} : \text{C}_4\text{O}_6\text{H}_4^{2-} \quad \text{and} \]
\[3\text{M(III)} : 5\text{Fe(III)} : \text{C}_6\text{O}_7\text{H}_{11}^{-} ,\]

where M(III) = Y, Eu, Gd, Er; C\(_4\)O\(_5\)H\(_4\)\(^{2-}\) = malate anion; C\(_4\)O\(_6\)H\(_4\)\(^{2-}\) =tartrate anion; C\(_6\)O\(_7\)H\(_{11}^{-}\) = gluconate anion.

Elemental chemical analysis and physico-chemical measurements (IR, UV-Vis spectroscopy and magnetic determinations) indicated that the isolated coordination compounds have the following general formula:

\[(\text{NH}_4)_6[\text{M}_3\text{Fe}_5(\text{C}_4\text{O}_5\text{H}_4)_6(\text{C}_4\text{O}_5\text{H}_3)_6]\times16\text{H}_2\text{O}\]

where M(III) = Y, Eu, Gd, Er

\[(\text{NH}_4)_6[\text{M}_3\text{Fe}_5(\text{C}_4\text{O}_6\text{H}_4)_6(\text{C}_4\text{O}_6\text{H}_3)_6]\times16\text{H}_2\text{O}\]

where M(III) = Gd, Er

\[(\text{NH}_4)_6[\text{M}_3\text{Fe}_5(\text{C}_6\text{O}_7\text{H}_{10})_6(\text{C}_6\text{O}_7\text{H}_9)_6]\times x\text{H}_2\text{O}\]

where M(III) = Y, x = 8; M(III) = Eu, Er, x = 22.

IR spectroscopy

\[(\text{NH}_4)_6[\text{Y}_3\text{Fe}_5(\text{C}_4\text{O}_5\text{H}_4)_6(\text{C}_4\text{O}_5\text{H}_3)_6]\times16\text{H}_2\text{O}.\] The most relevant feature in the spectrum of free malic acid is the sharp peak at 1730 cm\(^{-1}\) (\(\nu(\text{CO})\)).
The corresponding IR spectrum of the \((\text{NH}_4)_6[\text{Y}_3\text{Fe}_5(\text{C}_4\text{O}_5\text{H}_4)_6(\text{C}_4\text{O}_5\text{H}_3)_6]\cdot 16\text{H}_2\text{O}\) compound (Fig. 1) suggests that the anion of malic acid is coordinated to the metal ions through both of its two COO– groups and its C–OH group. This statement is supported by the split of the band of free acid carboxylic groups (≈ 1730 cm\(^{-1}\)) into two very strong bands characteristic for coordinated carboxylic groups (\(v_{\text{OCO asym}} ≈ 1610 – 1560\) cm\(^{-1}\) and \(v_{\text{OCO sym}} ≈ 1380\) cm\(^{-1}\)) and by the shift towards lower frequencies (1120 cm\(^{-1}\) → 1040 – 1100 cm\(^{-1}\)) of the band assigned to \(v(\text{C–OH})\).

On the basis of spectroscopic criteria\(^{19}\), the magnitude of the separation \(\Delta \nu = v_{\text{asym}} - v_{\text{sym}}\) may be indicative for establishing the mode of coordination of the carboxylate ions. Thus, \(\Delta \nu\) values in the range 140 – 160 cm\(^{-1}\), i.e., higher than those observed for ionic compounds (\(\Delta \nu_{\text{Na}_2\text{L}} = 120\) cm\(^{-1}\)) suggest a bridging bidentate bonding. On the other hand, values of \(\Delta \nu > 180\) cm\(^{-1}\) are characteristic for unidentate coordination.

For the compound \((\text{NH}_4)_6[\text{Y}_3\text{Fe}_5(\text{C}_4\text{O}_5\text{H}_4)_6(\text{C}_4\text{O}_5\text{H}_3)_6]\cdot 16\text{H}_2\text{O}\), the splitting of the \(v_{\text{OCO asym}}\) and \(v_{\text{OCO sym}}\) vibrations lead to \(\Delta \nu\) values of \(\Delta \nu ≈ 220\) cm\(^{-1}\) and \(\Delta \nu ≈ 170\) cm\(^{-1}\). Such results suggest two different coordination modes of the COO– groups: monodentate bonding (\(\Delta \nu ≈ 220\) cm\(^{-1}\)) and bridging bidentate bonding (\(\Delta \nu ≈ 170\) cm\(^{-1}\)). The \(\text{H}_2\text{O}\) molecules are identified due to the presence of a broad band in the range \(3500 – 3000\) cm\(^{-1}\) (maximum \(≈ 3400\) cm\(^{-1}\)) assigned to the formation of hydrogen bonds.

The IR spectrum also evidenced the presence of \(\text{NH}_4^+\) outer sphere ions (shoulder at 3300 cm\(^{-1}\)). The band appearing at \(≈ 535\) cm\(^{-1}\) is assigned to the M–O stretching vibration.

\((\text{NH}_4)_6[\text{Er}_3\text{Fe}_5(\text{C}_4\text{O}_6\text{H}_4)_6(\text{C}_4\text{O}_6\text{H}_3)_6]\cdot 16\text{H}_2\text{O}\). The IR spectrum of \((\text{NH}_4)_6[\text{Er}_3\text{Fe}_5(\text{C}_4\text{O}_6\text{H}_4)_6(\text{C}_4\text{O}_6\text{H}_3)_6]\cdot 16\text{H}_2\text{O}\) (Fig. 2) evidenced:

- a broad strong band at 3500 – 3000 cm\(^{-1}\), which is assigned to \(v(\text{H}_2\text{O})\) (with the maximum at \(≈ 3200\) cm\(^{-1}\) assigned to \(v(\text{NH}_4^+)\));
- two strong bands located at \(≈ 1614\) cm\(^{-1}\) (\(v_{\text{OCO asym}}\)) and at \(≈ 1380\) cm\(^{-1}\) (\(v_{\text{OCO sym}}\)) which indicate the coordination of both carboxylic groups of tartaric acid to the metal ions.
In the spectrum of tartaric acid, the peak at 1120 cm\(^{-1}\) is assigned to the C–O stretching vibration of the OH secondary group. In the spectrum of the complex, this band splits and shifts towards lower frequencies (1109 – 1050 cm\(^{-1}\)). The splitting of this band could be the result of different bonding of the two secondary OH groups. The spectrum also exhibited the characteristic band \(\nu(M–O)\) at \(547\) cm\(^{-1}\).

\(\text{(NH}_4\text{)}_6\text{Eu}_3\text{Fe}_5\text{C}_6\text{O}_7\text{H}_{10}\text{C}_6\text{O}_7\text{H}_9\leq 22\text{H}_2\text{O}\). The IR spectrum of \(\text{(NH}_4\text{)}_6\text{Eu}_3\text{Fe}_5\text{C}_6\text{O}_7\text{H}_{10}\text{C}_6\text{O}_7\text{H}_9\leq 22\text{H}_2\text{O}\) (Fig. 3) was recorded and compared to those of single gluconate and glucono-\(\delta\)-lactone.

The IR spectrum of glucono-\(\delta\)-lactone shows a maximum at \(\approx 1720\) cm\(^{-1}\), assigned to the vibration \(\nu(CO)\) of free carbonyl groups. After the formation of the coordination compounds, this band disappears and is replaced by two bands (\(\nu_{\text{OCO}}\text{asym} \approx 1600\) cm\(^{-1}\) and \(\nu_{\text{OCO}}\text{sym} \approx 1380\) cm\(^{-1}\)) assigned to coordinated COO\(^{-}\) groups.

Comparison of the IR spectrum of \(\text{(NH}_4\text{)}_6\text{Eu}_3\text{Fe}_5\text{C}_6\text{O}_7\text{H}_{10}\text{C}_6\text{O}_7\text{H}_9\leq 22\text{H}_2\text{O}\) with that of sodium gluconate indicates a shift of the doublet from 1100 – 1090 cm\(^{-1}\) towards smaller values, according to the literature,\(^{19}\) corresponds to the coordination at one or several OH groups.

**UV-Vis spectroscopy**

The diffusion reflectance spectra recorded in the 200 – 900 nm range for all the studied compounds suggest an octahedral high-spin configuration of the Fe(III) (d\(^5\))
The electronic spectra of (NH₄)₆[Er₃Fe₅(C₆O₇H₁₀)₆(C₆O₇H₉)₆]·22H₂O is given in Fig. 4 as an example. The absorption bands of the Er(III) ion in this compound are due to transitions from $^4I_{15/2}$ (the ground state) to excited states (Table I). The transition $^4I_{15/2} \rightarrow ^2H_{11/2}$ situated at 524 nm suggests a six-coordination geometry of these ions in the complex. This fact is in accordance with literature data.²¹

**TABLE I. Absorption bands in the electronic spectrum of (NH₄)₆[Er₃Fe₅(C₆O₇H₁₀)₆(C₆O₇H₉)₆]·22H₂O**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Band position/nm</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₆[Er₃Fe₅(C₆O₇H₁₀)₆(C₆O₇H₉)₆]·22H₂O</td>
<td>338</td>
<td>CT</td>
</tr>
<tr>
<td></td>
<td>366</td>
<td>$^4I_{15/2} \rightarrow ^2G_{5/2}$</td>
</tr>
<tr>
<td></td>
<td>464</td>
<td>$^6A_{1g} \rightarrow ^4A_{1g}, ^4E_g$</td>
</tr>
<tr>
<td></td>
<td>524</td>
<td>$^4I_{15/2} \rightarrow ^2H_{11/2}$</td>
</tr>
<tr>
<td></td>
<td>580</td>
<td>$^6A_{1g} \rightarrow ^4T_{2g}(G)$</td>
</tr>
<tr>
<td></td>
<td>656</td>
<td>$^4I_{15/2} \rightarrow ^4F_{9/2}$</td>
</tr>
<tr>
<td></td>
<td>762</td>
<td>$^6A_{1g} \rightarrow ^4T_{1g}(G)$</td>
</tr>
<tr>
<td></td>
<td>794</td>
<td>$^4I_{15/2} \rightarrow ^4I_{11/2}$</td>
</tr>
</tbody>
</table>

Magnetic measurements

The magnetic properties of the compounds show paramagnetic behavior (Table II). The magnetic moments values are lower than those obtained by summing the individual magnetic moments of the metallic ions and suggest antiferromagnetic interactions.

**TABLE II. Magnetic properties of the compounds (NH₄)₆[Eu₃Fe₅(C₄O₅H₄)₆(C₄O₅H₃)₆]·16H₂O, (NH₄)₆[Gd₃Fe₅(C₄O₅H₄)₆(C₄O₅H₃)₆]·16H₂O, (NH₄)₆[Er₃Fe₅(C₄O₅H₄)₆(C₄O₅H₃)₆]·16H₂O and (NH₄)₆[Er₃Fe₅(C₆O₇H₁₀)₆(C₆O₇H₉)₆]·22H₂O**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\chi$ × 10⁶/cm³/g⁻¹</th>
<th>$\mu$ found/MB</th>
<th>$\mu$ calc/MB</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₆[Eu₃Fe₅(C₄O₅H₄)₆(C₄O₅H₃)₆]·16H₂O</td>
<td>22.6</td>
<td>12.13</td>
<td>13.19</td>
</tr>
<tr>
<td>(NH₄)₆[Gd₃Fe₅(C₄O₅H₄)₆(C₄O₅H₃)₆]·16H₂O</td>
<td>47.8</td>
<td>17.55</td>
<td>19.05</td>
</tr>
<tr>
<td>(NH₄)₆[Er₃Fe₅(C₄O₅H₄)₆(C₄O₅H₃)₆]·16H₂O</td>
<td>52.1</td>
<td>19.08</td>
<td>21.21</td>
</tr>
<tr>
<td>(NH₄)₆[Er₃Fe₅(C₆O₇H₁₀)₆(C₆O₇H₉)₆]·22H₂O</td>
<td>49.1</td>
<td>20.50</td>
<td>21.21</td>
</tr>
</tbody>
</table>
CONCLUSIONS

The complexation method developed in this work were used for the preparation of three different types of compounds:

\[(\text{NH}_4)_6[M_3\text{Fe}_5\text{(C}_4\text{O}_5\text{H}_4)_6\text{(C}_4\text{O}_5\text{H}_3)_6}\] \(16\text{H}_2\text{O}\)
M(III) = Y, Eu, Gd, Er

\[(\text{NH}_4)_6[M_3\text{Fe}_5\text{(C}_4\text{O}_6\text{H}_4)_6\text{(C}_4\text{O}_6\text{H}_3)_6}\] \(16\text{H}_2\text{O}\)
M(III) = Gd, Er

\[(\text{NH}_4)_6[M_3\text{Fe}_5\text{(C}_6\text{O}_7\text{H}_{10})_6\text{(C}_6\text{O}_7\text{H}_9)_6]\cdot x\text{H}_2\text{O}\]
M(III) = Y; \(x = 8\)
M(III) = Eu, Er; \(x = 22\).

The coordination compounds were characterized by elemental chemical analysis and physico-chemical measurements (IR, UV-Vis spectroscopy and magnetic determinations).

The preliminary study on the mixed oxides obtained by the thermal decomposition of these compounds (XRD, IR spectra and magnetic measurements) reveals the possibility of using “the complexation method” as a route to garnets.

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REFERENCES