Thermal and spectral studies of light lanthanide complexes with 2-chloro-5-nitrobenzoic acid

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Complexes of 2-chloro-5-nitrobenzoic acid with light lanthanides of the general formula: Ln(C_7H_5NO_4Cl)_2.2H_2O, where Ln=La, Ce, Pr, Nd, Sm, Eu and Gd have been synthesized and characterized by elemental analysis, IR spectra, thermogravimetric studies and X-ray diffraction measurements. Their solubilities in water at 293K have been also determined.

A survey of literature shows that complexes of 2-chloro-5-nitrobenzoic acid with various metal ions have not been prepared and investigated in solid state. 2-Chloro-5-nitrobenzoates of light lanthanides (La, Ce, Pr, Nd, Sm, Eu and Gd) have not been synthesized in solid state nor have they been studied in solution. Therefore, in this note we present the synthesis of 2-chloro-5-nitrobenzoates of light lanthanide in solid state and their characterization by elemental analysis, IR spectral data, thermogravimetric studies and X-ray diffraction measurements. The solubilities of these complexes were determined in water at 293K. Their determination is valuable because it can give information about the practical use of 2-chloro-5-nitrobenzoic acid for separation of rare earth elements by extraction or ion-exchange chromatographic methods.

Experimental

2-Chloro-5-nitrobenzoates of light lanthanides were prepared by adding the equivalent quantities of ammonium 2-chloro-5-nitrobenzoate 0.1M (pH-5) to a hot solution containing the light lanthanide chlorides. The solid formed was filtered off, washed with hot water to remove ammonium ions and dried at 303K to constant weight. The carbon, hydrogen and nitrogen contents were determined by elemental analysis using Perkin-Elmer CHN 2400 analyser. The chloride content was determined by the Schöniger method. The contents of light lanthanides were analysed by oxalic acid method. The results (Table I) show that the complexes obtained are dihydrates with a metal to ligand ratio of 1:3. The complexes have colours characteristic of Ln^{3+} ions. In order to confirm the chemical composition of the salts, the IR spectra of the hydrated and dehydrated complexes, the spectra of 2-chloro-5-nitrobenzoic acid, its sodium salt and sodium nitrite were run in the range 4000-400cm^{-1} using KBr discs on an M-80 spectrophotometer. In order to estimate the external crystalline form of hydrated 2-chloro-5-nitrobenzoates, X-ray powder patterns were taken on a DRON-2 diffractometer using Ni-filtered CuKα radiation within the range 29 = 5-80° by the Debye-Scherrer-Hull method. The thermal stability of the complexes in air in the range 273-523K was also studied by the use of TG, DTA and DTG techniques. The measurements were made with the use of a Q-1500D derivatograph with Derill converter (MOM-Budapest). The sensitivities of DTG and DTA were regulated by the Derill computer programme worked out by the MOM Budapest Firm (Tables 1, 2).

The solubilities of complexes of light lanthanides with 2-chloro-5-nitrobenzoic acid in water at 293K were determined by measuring the concentration of Ln^{3+} ions in a saturated solution by the oxalic acid method (Table 2).

Results and discussion

2-Chloro-5-nitrobenzoates of light lanthanides were obtained as crystalline substances with a metal to ligand ratio of 1:3 and a general formula: Ln(C_7H_5NO_4Cl)_2.2H_2O for Ln = La - Gd. The colours of the complexes are typical of the appropriate trivalent ions. In the molecules of 2-chloro-5-nitrobenzoates electrons of Cl atom and NO_2 group are conjugated with π electrons of aromatic ring. In these molecules the f→f electronic transitions of the central ions are of the lowest energy and absorption occurs at relatively high wavelengths depending on the nature of the metal ion^{1-7}.

The solid state IR spectra of all complexes are quite similar but they are different from spectrum of the 2-chloro-5-nitrobenzoic acid. In the acid spectrum the
Table 1 Analytical data of 2-chloro-5-nitrobenzoates of lanthanides and the temperature of complex decomposition

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td></td>
<td>H</td>
<td>C</td>
</tr>
<tr>
<td>LaL₃ · 2H₂O</td>
<td>1.53</td>
<td>(1.69)</td>
</tr>
<tr>
<td>CeL₃ · 2H₂O</td>
<td>1.54</td>
<td>(1.68)</td>
</tr>
<tr>
<td>PrL₃ · 2H₂O</td>
<td>1.55</td>
<td>(1.68)</td>
</tr>
<tr>
<td>NdL₃ · 2H₂O</td>
<td>1.51</td>
<td>(1.67)</td>
</tr>
<tr>
<td>SmL₃ · 2H₂O</td>
<td>1.52</td>
<td>(1.66)</td>
</tr>
<tr>
<td>EuL₃ · 2H₂O</td>
<td>1.59</td>
<td>(1.66)</td>
</tr>
<tr>
<td>GdL₃ · 2H₂O</td>
<td>1.60</td>
<td>(1.63)</td>
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</tbody>
</table>

Table 2 Temperature of decomposition of 2-chloro-5-nitrobenzoates of light lanthanides and their solubility in water at 293K

<table>
<thead>
<tr>
<th>Complex</th>
<th>ΔTᵣ</th>
<th>Tₘᵣ (K)</th>
<th>Time loss (%)</th>
<th>n</th>
<th>Tₑ (K)</th>
<th>Eᵣ (kJ·mol⁻¹)</th>
<th>Solubility (mol·dm⁻³)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaL₃ · 2H₂O</td>
<td>409-439</td>
<td>436.5</td>
<td>4.64</td>
<td>4.29</td>
<td>2</td>
<td>440</td>
<td>85.74</td>
<td>4.0·10⁻³</td>
</tr>
<tr>
<td>CeL₃ · 2H₂O</td>
<td>402-439</td>
<td>431.6</td>
<td>4.63</td>
<td>4.29</td>
<td>2</td>
<td>440</td>
<td>102.20</td>
<td>2.9·10⁻³</td>
</tr>
<tr>
<td>PrL₃ · 2H₂O</td>
<td>404-440</td>
<td>434.0</td>
<td>4.63</td>
<td>4.46</td>
<td>2</td>
<td>442</td>
<td>88.40</td>
<td>2.6·10⁻³</td>
</tr>
<tr>
<td>NdL₃ · 2H₂O</td>
<td>408-443</td>
<td>440.2</td>
<td>4.60</td>
<td>4.55</td>
<td>2</td>
<td>445</td>
<td>94.71</td>
<td>2.2·10⁻³</td>
</tr>
<tr>
<td>SmL₃ · 2H₂O</td>
<td>409-444</td>
<td>434.0</td>
<td>4.57</td>
<td>4.46</td>
<td>2</td>
<td>446</td>
<td>80.81</td>
<td>1.9·10⁻³</td>
</tr>
<tr>
<td>EuL₃ · 2H₂O</td>
<td>399-445</td>
<td>437.8</td>
<td>4.56</td>
<td>4.50</td>
<td>2</td>
<td>447</td>
<td>67.74</td>
<td>1.8·10⁻³</td>
</tr>
<tr>
<td>GdL₃ · 2H₂O</td>
<td>390-442</td>
<td>440.0</td>
<td>4.52</td>
<td>4.48</td>
<td>2</td>
<td>444</td>
<td>66.64</td>
<td>1.7·10⁻³</td>
</tr>
</tbody>
</table>

L = C₅H₅NO₃Cl.

The infrared spectrum of 2-chloro-5-nitrobenzoic acid shows the bands assignable to asymmetric and symmetric vibrations of the NO₂ group at 1540 and 1360 cm⁻¹, respectively, the bands due to ν (C-Cl) vibrations at 750 and 700 cm⁻¹ and the bands due to ν (C-H) vibrations at 3000-3600 cm⁻¹ and 1000-1700 cm⁻¹. The skeleton vibrations occur at 1610, 1480, 1430 and 1265 cm⁻¹. In the IR spectra of 2-chloro-5-nitrobenzoates of light lanthanides the bands due to asymmetric and symmetric vibrations of the NO₂ group are not significantly shifted with respect to those of the parent acid and thus one must conclude that the NO₂ group is not coordinated to the metal ions. The ν (C-Cl) vibrations occur at 750-705 cm⁻¹ and the bands at 540 cm⁻¹ are assigned to the metal-oxygen bond. These bands are not shifted to higher frequencies with increasing atomic number of lanthanide elements. Accordingly, it is possible to suggest that 2-chloro-5-nitrobenzoic acid forms complexes with light lanthanides which have similar stabilities 8, 12, 18. The bands of skel-
etown vibrations in IR spectra of complexes are shifted to lower frequencies compared to those in the acid spectrum. The changes in their positions are caused by the interaction between aromatic ring vibrations and the groups of atoms and ions.

The magnitudes of separation, $\Delta \nu$, between the frequencies $\nu_{\text{sym}}$ OCO and $\nu_{\text{sym}}$ OCO and in the complexes are lower ($\Delta \nu=175-170 \text{ cm}^{-1}$) than those in the sodium salt ($\Delta \nu=185 \text{ cm}^{-1}$) which indicates a smaller degree of ionicity in lanthanide 2-chloro-5-nitrobenzoates. In the spectra of the complexes the bands due to $\nu_{\text{asym}}$ OCO (1570-1565 cm$^{-1}$) and $\nu_{\text{sym}}$ OCO (1395 cm$^{-1}$) occur at lower and the similar positions, respectively, compared to those for sodium 2-chloro-5-nitrobenzoate ($\nu_{\text{asym}}$ OCO =1580 cm$^{-1}$, $\nu_{\text{sym}}$ OCO =1395 cm$^{-1}$). Accordingly, the carboxylate ion appears to be a bidentate chelating ligand.

In order to verify whether or not the prepared lanthanide 2-chloro-5-nitrobenzoates were converted to the nitrito isomers (during precipitation or on heating to 573K) their IR spectra and IR spectrum of sodium nitrite were recorded. A survey of the literature shows that under the influence of sunlight or with rising temperature the nitro complex may be transformed to the nitrito analogue in an endothermic process. It was found that the isomerization of the nitro group may accompany the dehydration process of the complexes or be connected with the transformation process in its inner sphere. As a monodentate ligand, nitrite ion may be bonded either through a nitrogen atom forming the nitro complex or through one of the oxygen atoms yielding a nitrito compound. The general effect of coordination via nitrogen is an increase in the frequencies of both $\nu_{\text{asym}}$ NO$_2$ and $\nu$ NO$_3$, compared to the values for the free ion ($\approx 1328$ and 1260 cm$^{-1}$, respectively). The IR spectra recorded for all hydrated and dehydrated 2-chloro-5-nitrobenzoates of lanthanides show that the nitro group is not transformed to the nitrito one with increase in temperature. No bands confirming isomerization of the nitro group through the oxygen atom were observed.

In order to estimate the external crystalline forms of the presently studied lanthanide 2-chloro-5-nitrobenzoates, their X-ray powder diffraction measurements were carried out. The diffractogram analysis suggests that they are polycrystalline compounds with low symmetry, large size of the unit cells and different structures. The complexes seem to be isostructural in two groups: La, Ce, Nd and Pr, Sm, Eu. Their structures have not been determined because single crystals of these compounds could not be obtained.

Preliminary studies on the thermal stability of light lanthanide 2-chloro-5-nitrobenzoates have shown that like 2-nitro-, 3-nitro-, 4-nitrobenzoates and 5-chloro-2-nitrobenzoates of those elements these complexes are explosively decomposed when heated in air above 573K. Their great thermal instability during heating above 573K is due to the presence of the NO$_2$ group in benzene ring.

When heated at 273-523K in air, they dehydrate in one-step and form anhydrous salts in the temperature range 390-445K. They start to decompose at 515-523K (Table 1). The dehydration process is connected with endothermic effect as shown by the DTA curves.

The calculated mass loss from TG curves in temperature range 390-445K is about 4.30-4.60% (theoretical values are 4.52-4.64%) corresponding to two molecules of water of crystallization. Thus the TG curves are not horizontal and inflections occur. Above the temperatures 439-445K, the TG curves again attain the constant level which is indicative of the anhydrous complex formation: Ln(C$_7$H$_5$NO$_4$Cl)$_3$2H$_2$O, where Ln(III) = La, Ce, Pr, Nd, Sm, Eu, Gd.

In the case of praseodymium 2-chloro-5-nitrobenzoate decomposition the mass loss starting at 404K corresponds to the beginning of the dehydration process that takes place in the range 404-440K. Accordingly, the TG curve is not horizontal and inflection appears because of the decrease in mass. The loss of mass is about 4.46% (the theoretical value is 4.63%). The DTG peak connected with mass loss is observed and endothermic effect occurs in DTA curve. Next, above 440K the TG curve attains a constant level which is indicative of the anhydrous complex formation that start to decompose at 523K (Table 1).

Considering the temperatures at which the dehydration takes place and the way by which it proceeds it is possible to assume that the molecules of water are in the outer-sphere. According to Nikolaev et al. and Singh et al., water being eliminated below 413-423K can be considered as water of crystallization and water eliminated above 423K may be the one coordinated to the central ion. In the present investigations water is eliminated below 413K and IR studies revealed to be water of crystallization.
From TG and DTA, curves the activation energies of dehydration were calculated with Fatieev and Pletniev method\textsuperscript{13} using the equation:

\[ E = \frac{RT_{\text{max}}^2}{m_o} \ln \left( \frac{m}{m_o} \right) \]

where: \( R \) - gas constant; \( T_{\text{max}} \) - temperature of maximum of the mass loss; \( m_o \) - the mass loss at \( T_{\text{max}} \); \( m \) - the mass loss at \( T \).

The activation energy values are connected with the loss of two water molecules. The difference in these values suggests that molecules of water are bonded with different forces depending on their position. The smallest value of activation energy for gadolinium 2-chloro-5-nitrobenzoate indicates that the water molecules are the most weakly bound whereas its highest value for cerium complex shows that they are presumably most strongly bound in outer-sphere of the complex.

The values of energies increase in the order: Gd < Eu < Sm < La < Pr < Ce. They do not regularly change with decreasing ionic radii of elements.

From the preliminary investigations on thermal stabilities of the complexes during their heating in air to 1173 K it appears that the hydrates first lose water molecules and then decompose to yield oxides of respective metals through the intermediate LnOCl formation (with the exception of Ce that is directly decomposed to CeO\textsubscript{2}). The oxides of the respective lanthanides are the final products of decomposition. The intermediate products of LnOCl were identified roentgeno-graphically\textsuperscript{32,33}. The roentgenographic measurements revealed them to be Ln\textsubscript{2}O\textsubscript{3} for La, Nd-Gd and Pr\textsubscript{2}O\textsubscript{3}, and CeO\textsubscript{2} for Pr and Ce, respectively.

The solubilities of 2-chloro-5-nitrobenzoates of light lanthanides in water at 293 K were measured and their solubility products determined. They are of the order of \( 10^{-3}\) mol dm\textsuperscript{-3} and \( 10^{-7} - 10^{-10}\) mol dm\textsuperscript{-3}, respectively. The 2-chloro-5-nitrobenzoate of lanthanum is the most soluble salt while that of gadolinium is the least soluble. The solubility decreases from La to Gd (Table 2). Taking into account the presence of nitro- and chloro- substituents in benzene ring of benzoic acid, the solubilities of 2-chloro-5-nitrobenzoates of light lanthanides were compared with those of the corresponding 2-nitro-, 3-chloro- and 5-chloro-2-nitrobenzoates of those elements\textsuperscript{25,26,32,33}. The order of solubilities of 5-chloro-2-nitrobenzoates of these elements is \( 10^{-3}\) mol dm\textsuperscript{-3}. The solubilities of the 2-nitrobenzoates of rare earth elements are in the order of \( 10^{-2}\) mol dm\textsuperscript{-3} and those for 3-chlorobenzoates of the order of \( 10^{-4}\) mol dm\textsuperscript{-3}. The solubilities of the complexes are in the order: 3-chloro- < 5-chloro-2-nitro- = 2-chloro-5-nitro- < 2-nitro-.

The order of magnitude of the solubilities of 2-nitrobenzoates is higher than dissociation constant of the parent acid (6.2 x 10\textsuperscript{-4}). In comparison with the 3-chlorobenzoates, the presence of NO\textsubscript{2} group in benzene ring causes an increase in their solubilities whereas the chloride substituent causes a decrease. The relationship of these values is influenced by inductive and mesomeric effects of substituents on electron density in the molecules. Taking into account the values of complex solubilities it is possible to state that the 2-chloro-5-nitrobenzoic acid cannot be used for separation of rare earth elements by ion-exchange chromatography or extraction methods because complexes formed are not easily soluble. The various positions of substituents in benzene ring do not change the decomposition process\textsuperscript{30}. All hydrated complexes are decomposed in one step. 5-Chloro-2-nitrobenzoates are anhydrous salts (La, Ce, Pr, Nd) or monohydrates (Sm, Eu, Gd), while those of 2-chloro-5-nitrobenzoates form dihydrates.

References
Errata

Paper entitled, "Volumetric and compressibility properties of aqueous solutions of urea and ethylene glycol", *Indian J Chem*, 38A(1999)70-72: On page 71 Figs 1 and 2 have been interchanged inadvertently and these should be exchanged. Within these figures subcaptions a and b should also be interchanged.

Paper entitled, "Solvation of copper(1) perchlorate in benzonitrile + pyridine mixtures investigated by conductometric studies", *Indian J Chem*, 38A(1999)478-481: On page 478 at the end of the right hand side column, Eq.2 has got cut during formatting. It reads as follows:

$$\lambda_0^{\text{Bu,N}} + \lambda_0^{\text{p,N}} = \lambda_0^{(\text{Bu},\text{NBPh}_3)}$$

\[ \text{(2)} \]

Paper entitled, "Sugar vanadates: Synthesis and characterization of a mannopyranoside ester incorporating VO\textsuperscript{3+}", *Indian J Chem*, 38A(1999)405-406: In content page (i) and in page 405, left hand side column, line 9, VO\textsuperscript{2+} should be replaced by VO\textsuperscript{4+}. In the same column in line 2 from bottom, unit of \( \lambda \) is \( \text{A} \) instead of \( \text{A} \) and unit of \( V \) in the first line in the right hand side column is \( \text{A} \).

Paper entitled "Manganese(III) complexes with hexadentate Schiff bases derived from heterocyclic \( \beta \)-diketones and triethylene tetramine", *Indian J Chem*, 38A(1999)427-433: In page 427, at the end of the left hand side column, structure (I) given is incomplete. The complete structure is as follows:

![Manganese(III) complex](image)