COMPLEXES OF LANTHANIDE PERCHLORATES WITH THE HYDRAZINE DERIVED LIGANDS—N-ACETYL-N'-BENZOYL HYDRAZINE (ABHyd) AND N-ACETYL-N'-ISOPROPYLIDENE HYDRAZINE (NANIIH)

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Abstract

New complexes of lanthanide perchlorates with the hydrazine derived ligands-N-acetyl-N'-benzoyl hydrazine (ABHyd) and N-acetyl-N'-isopropylidene hydrazine (NANIIH), have been prepared and characterized by chemical analysis, infrared and electronic spectra and electrical conductance data.

From the analytical data the five complexes have the formulae $\text{Ln} (\text{ABHyd})_4 (\text{ClO}_4)_2$ where $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Ho}$ and $\text{Er}$. Complexes of NANIIH are found to have the stoichiometry $\text{Ln} (\text{NANIIH})_3 (\text{ClO}_4)_2$ where $\text{Ln} = \text{La}$ and $\text{Nd}$ and $\text{Ln} (\text{NANIIH})_4 (\text{ClO}_4)_2$ for $\text{Ln} = \text{Sm}$-Er and $\text{Y}$.

Infrared and conductance indicate the noncoordinated nature of all the anions in all the complexes of ABHyd and NANIIH. Infrared data further indicate the bidentate nature of both the ligands, the donor atoms being nitrogen and oxygen in NANIIH and two oxygen atoms in ABHyd.

Introduction

HYDRAZINES, as well as many of their derivatives have been found to yield stable complexes with d-transition metal ions$^{1,2}$. In lanthanide chemistry, however, hydrazine and hydrazine-derived ligands have received little attention$^{2,3}$. In the present work, two new hydrazine derived ligands, namely, N-acetyl-N'-benzoylhydrazine (ABHyd) and the Schiff base N-acetyl-N'-isopropylidene hydrazine (NANIIH) have been used for complexation with lanthanides. The synthesised complexes have been characterised by chemical analysis, electrolytic conductance, infrared and electronic spectral data.

Experimental

Materials

The rare earth oxides were obtained in 99.9% purity from Indian Rare Earths Ltd., Kerala State and their perchlorates were prepared as described in an earlier report$^4$.

Preparation of the ligands

Preparation of N-acetyl-N'-benzoyl hydrazine (ABHyd)

Ethyl benzoate (1 mole) and hydrazine hydrate (1.1 mole) were taken in alcohol (100 ml) and refluxed on a water bath for two hours. Cooling in ice yielded benzoyl hydrazine, m.p. 110° (lit. 111°), which was taken in benzene and acetic anhydride (1:1 mole) was added with cooling. The reaction mixture was heated on a water bath (90° C) under reflux for an hour the precipitate filtered and recrystallise from alcohol, m.p. 169° C lit. 171° C$^*$. Preparation of N-acetyl-N'-isopropylidene hydrazine (NANIIH)

Ethyl acetate (1 mole) and hydrazine hydrate (1 mole) were refluxed on the water bath for an hour. The excess ethyl acetate was evaporated under suction and the residue cooled in ice. The acetyl hydrazine$^5$ has a m.p. 66° C (lit. 65° C). Acetyl hydrazine (1 mole) was then reacted with aceton (1:2 moles) to yield the Schiff base NANIIH, m.p. 137° C, lit. 137° C$^*$. Preparation of the complexes

(a) Complexes of ABHyd: Lanthanide perchlorate (1 mmole) was dissolved in ethyl acetate (10 ml) and added dropwise to the ligand (4.5 mmoles) in chloroform (20 ml) and refluxed on the water bath for two hours when a sticky solid was obtained. The solvent was decanted off, and the residue was washed thrice with hot chloroform. The complex did not crystallise, but the solid was dried at 70° in vacuum when glistening hygroscopic solid was obtained.

(b) Complexes of NANIIH: Lanthanide perchlorate (1 mmole) was taken in triethylorthoformate (15 ml), the ligand (6 mmoles) also was taken in the same solvent. The two were mixed and refluxed for a while on the water bath. The solvent was decanted off from the sticky complex. The complex was then washed well and dried under suction (1 mm) with external heating (~70° C).

Analysis and physical measurements

Chemical analyses and the physical measurements were performed as described earlier$^6$. 
RESULTS AND DISCUSSION

(a) ABHyd Complexes: Analytical data for the ABHyd complexes conform to the formula Ln(ABHyd₂ClO₄)₃, where Ln = La, Pr, Nd, Ho and Er. All the complexes are extremely hygroscopic and hence handled with usual precautions. All physical measurements were taken using freshly prepared complexes. Complexes are soluble in methanol, acetone and acetonitrile and insoluble in chloroform, ethylacetate, benzene and carbon tetrachloride. Conductivity in acetonitrile started 1:3 electrolytic behaviour.

For the ABHyd molecule, resonance structures (1) and (2) indicate that the electron density is centred on the oxygen atom due to its greater electronegativity compared to nitrogen. This results in a partial negative charge on the oxygen atom and a partial positive charge on the nitrogen atom, thus making oxygen a probable donor towards metal ions.

\[
\begin{align*}
&\text{(1) } & &\text{(2)} \\
\text{R} & \text{C} & & \text{R} & \text{C} \\
\text{N} & \text{H} & & \text{N} & \text{H} \\
& & & & \\
\text{H} & \text{N} & & \text{H} & \text{N} \\
& & & & \\
& & & & \\
& & & & \\
& & & &
\end{align*}
\]

where R = CH₃, R' = COC₆H₅.

In the infrared spectral analysis of ABHyd the NH stretching vibration appears as two bands at 3185 (strong) and 3010 cm⁻¹ (strong) in the free ligand in the solid state, which is found at a higher frequency in the complexes. The spectral region 1500-1800 cm⁻¹ contains absorptions due to amide I, amide II and NH deformation mode of the Hydrazone molecule. The amide I band is found split at 1710 cm⁻¹ and 1650 cm⁻¹ in the solid state and at 1720 cm⁻¹ and 1690 cm⁻¹ in acetonitrile solution. Such observations have been made in many secondary amides and in diacetyl hydrazine.¹⁰⁻¹¹. These bands are shifted to a lower frequency and found as a strong sharp band at 1630 cm⁻¹ in the complexes. The amide II band exhibits shifts to higher frequencies on complexation (from 1545 cm⁻¹ to 1550 cm⁻¹). The amide III band at 1280 cm⁻¹ in the free ligand is shifted by 10 cm⁻¹ to higher frequency in the complex. The above direction of shifts in the ligand bands observed on complexation clearly demonstrates the coordination of the two carbonyl oxygen atoms to the metal ions.

The presence of ionic perchlorate groups is confirmed by the presence of unsplit bands at 1100 cm⁻¹ and 625 cm⁻¹ in the spectra of the complexes.

Further evidence for C = O coordination is obtained from ³¹C NMR data where the C = O resonances are shifted downfield from 169.88 and 171.25 in the ligand to 172.16 and 174.38 respectively in the lanthanum complex.

The electronic spectrum of the Nd³⁺ complex reveals small red shifts of the various bands. The shape of the band both in solid state (null) and in acetonitrile solution representing the hypersensitive transition \( ^3G_{7/2} \rightarrow ^5D_{7/2} \) was the same, indicating similar environment around the metal ion in both the states. It compares reasonably with the shape of the corresponding band in Nd³⁺-β diketone complex reported by Karraker, where a coordination number of eight is proposed. This indicates that the tetraakis ABHyd complexes have a coordination number similar to that in the β-diketones, that is eight. In view of the analysis, conductivity and IR evidence supported by electronic spectra, the present complexes have been assigned a tentative coordination number of eight involving four bidentately bound ABHyd molecules per metal ion.

(b) NANIH Complexes: Analytical data (Table II) indicate a stoichiometry Ln[NANIH]₂(ClO₄)₃, where Ln = La and Nd and Ln[NANIH]₂(ClO₄)₃ for Ln = Sm-Er and Y. The complexes are hygroscopic and soluble in polar solvents like ethanol, methanol, etc. and insoluble in benzene and carbon tetrachloride. Conductivity measurements in acetonitrile show 1:3 electrolytic behaviour suggesting the ionic nature of the perchlorate groups in all the complexes (Table II).

The presence of ionic perchlorate groups in the complexes was found in the form of two bands, a very strong one at 1100 cm⁻¹ (\( ν_{\text{s}} \)) and a strong one at 625 cm⁻¹ (\( ν_{\text{as}} \)) both of which are unsplit. The IR spectra of the complexes do not exhibit any bands indicative of water molecules, lattice held or otherwise, in keeping with the analytical results.

A shift of \( ν_{\text{sh}} \) to higher frequencies in the complexes compared to the ligand has been observed. The shift of the carbonyl frequency (amide I) at 1670 cm⁻¹ in the ligand to ~1630 cm⁻¹ in the complexes proves coordination via the oxygen of the carbonyl group. Further, it is found that the amide III band (\( δ_{\text{sh}} \)) at 1300 cm⁻¹ in the ligand is shifted to ~1315 cm⁻¹ in the complexes and the amide VI at 500 cm⁻¹ in all the complexes. These facts confirm the carbonyl coordination in the ligand. The C = N stretching frequency at 1570 cm⁻¹ in the ligand is shifted to lower frequencies in the complexes. However, the shift is smaller.¹²⁻¹⁴
### Table I

*Analytical and conductivity data for the complexes Ln(ABHyd)₆(ClO₄)₃*

<table>
<thead>
<tr>
<th>Ln</th>
<th>% Metal</th>
<th>% ClO₄⁻</th>
<th>% N</th>
<th>% C</th>
<th>Molar conductance in CH₃CN ohm⁻¹ cm²/mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>11.83</td>
<td>12.09</td>
<td>26.44</td>
<td>25.97</td>
<td>9.58</td>
</tr>
<tr>
<td>Pr</td>
<td>12.04</td>
<td>12.24</td>
<td>25.14</td>
<td>25.92</td>
<td>..</td>
</tr>
<tr>
<td>Nd</td>
<td>12.26</td>
<td>12.47</td>
<td>26.19</td>
<td>25.86</td>
<td>..</td>
</tr>
<tr>
<td>Er</td>
<td>14.41</td>
<td>14.20</td>
<td>24.95</td>
<td>25.34</td>
<td>..</td>
</tr>
</tbody>
</table>

### Table II

*Analytical and conductivity data for the complexes, Ln(NANIH)₆(ClO₄)₃ where Ln = La–Nd and Ln(NANIH)₆(ClO₄)₃ where Ln = Sm–Er and Y.*

<table>
<thead>
<tr>
<th>Ln</th>
<th>% Metal</th>
<th>% ClO₄⁻</th>
<th>% N</th>
<th>% C</th>
<th>Molar conductance ohm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>13.58</td>
<td>13.80</td>
<td>29.31</td>
<td>29.59</td>
<td>13.72</td>
</tr>
<tr>
<td>Nd</td>
<td>14.54</td>
<td>14.23</td>
<td>29.16</td>
<td>29.44</td>
<td>..</td>
</tr>
<tr>
<td>Sm</td>
<td>17.07</td>
<td>16.63</td>
<td>33.18</td>
<td>32.96</td>
<td>..</td>
</tr>
<tr>
<td>Tb</td>
<td>17.21</td>
<td>17.42</td>
<td>32.44</td>
<td>32.63</td>
<td>..</td>
</tr>
<tr>
<td>Ho</td>
<td>17.85</td>
<td>17.96</td>
<td>32.73</td>
<td>32.42</td>
<td>12.01</td>
</tr>
<tr>
<td>Er</td>
<td>18.35</td>
<td>18.13</td>
<td>32.10</td>
<td>32.35</td>
<td>..</td>
</tr>
<tr>
<td>Y</td>
<td>10.28</td>
<td>10.54</td>
<td>35.58</td>
<td>35.35</td>
<td>..</td>
</tr>
</tbody>
</table>

### Table III

*Electronic and spectral data for Nd(NANIH)₆(ClO₄)₃, Ho(NANIH)₆(ClO₄)₃ and Er(NANIH)₆(ClO₄)₃ in CH₃CN*

<table>
<thead>
<tr>
<th></th>
<th>Nd³⁺</th>
<th>Ho³⁺</th>
<th>Er³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Band energy</td>
<td>J level</td>
<td>Band energy</td>
</tr>
<tr>
<td></td>
<td>KK</td>
<td></td>
<td>KK</td>
</tr>
<tr>
<td>13.47</td>
<td>⁴F₁/₂</td>
<td>15.42</td>
<td>⁴F₆</td>
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<tr>
<td>14.72</td>
<td>⁴F₅/₂</td>
<td>18.50</td>
<td>⁴F₆</td>
</tr>
<tr>
<td>17.01</td>
<td>⁴G₅/₂</td>
<td>20.62</td>
<td>⁴G₅</td>
</tr>
<tr>
<td>18.94</td>
<td>⁴G₇/₂</td>
<td>21.98</td>
<td>³K₆</td>
</tr>
</tbody>
</table>

\[ \beta = 0.9876 \]
\[ \delta = 1.255 \]
\[ \beta = 0.9967 \]
\[ \delta = 0.3311 \]
\[ \beta = 0.9939 \]
\[ \delta = 0.6141 \]
(about 10 cm⁻¹) and suggests the coordination of imine nitrogen to the metal ions.

In ¹³C NMR spectra, the downfield shift of C = O carbon from 173.91 ppm in the ligand to 176.79 ppm in the La⁺⁺ complex confirms coordination of the carbonyl group. The C = N carbon too is shifted downfield from 150.0763 ppm in the ligand to 152.2663 ppm in the La⁺⁺ complex.

The electronic spectra for the Nd⁺⁺, Ho⁺⁺ and Er⁺⁺ complexes reveal the red shift of the f-f bands compared to the aqua ion (Table III). The β and Sinha's δ parameter[15] for the three complexes have been calculated.

The hypersensitive band shapes of Ho⁺⁺ and Er⁺⁺ complexes resemble closely the 8 coordinate shapes reported by Karraker[12]. From analysis, IR, conductance and electronic spectral data, therefore, a probable coordination number of eight can be proposed for all the complexes of NaN₃IH other than La⁺⁺ and Nd⁺⁺ complexes. Although from the consideration of analysis and IR, a coordination number of ten can be assigned to the La⁺⁺ and Nd⁺⁺ complexes, no evidence could be obtained from the electronic spectral shapes, because of lack of suitable model compounds for shape comparison for the Nd⁺⁺ ion.

ACKNOWLEDGEMENT

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8. —, Ibid., 1894, 50, 280.

TASTE RESPONSIVENESS TO PHENYL-THIO-CARBAMIDE AND GLUCOSE DURING MENSTRUAL CYCLE

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ABSTRACT

Taste sensitivity to Phenyl-thio-carbamide (PTC) and gustatory response to glucose have been estimated in different phases of menstrual cycle, in Indian women. The intensity and pleasantness responses to glucose were calculated on the 7-point and 6-point scale respectively. Seven dilutions of the test solution, ranging from 2-0 M with successive half dilution were given to the subjects. The intensity rating increased with an increase in the strength of glucose solution. Maximum pleasantness peak was at 1-0 M solution in all phases of menstrual cycle. During ovulatory phase pleasantness scores were higher. The PTC responses were dynamic and showed a shift from nontasters to tasters during ovulatory phase.

A variety of sensory changes are experienced by women during different phases of menstrual cycle[16]. These changes seem to be linked with the changes in perception[16]. Olfactory sensitivity was found to be most acute in the midcycle period[16]. Several investigators have reported that changes in auditory acuity occurred during menstrual cycle[16]. Changes in detection threshold for light touch and two point discrimination have also been found to vary during follicular and luteal phase[16]. Similarly it has been reported that gonadal hormones influence palatability and spontaneous ingestion of a number of sweet solutions[16], and the difference in ingestion of sweet solution is thought to be caused by the stimulatory