New lanthanide(III) complexes of biologically active 2,3-disubstituted quinazoline-4-(3H)-one: Synthesis, characterization and biological studies

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A number of lanthanide(III) complexes with 2-pyridine-2-yl-3-[pyridine-2-carboxylideneaminol]-1,2-dihydroquinazolin-4-(3H)-one (PPCADQ) have been synthesized. On the basis of magnetic studies, thermal studies, IR, NMR, UV-vis and EPR spectra, the complexes have been formulated as [Ln(PPCADQ)+H2Ox(NO3)2][NO3] where Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Y(III). The ligand behaves in tridentate fashion. The ligand and complexes have been evaluated for their antibacterial and antifungal activities.

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The chelating behavior of hydrazones obtained by the reaction of o-aminobenzoylhydrazide and aldehydes has been reported by many workers. However, our attempts to synthesize the hydrazone derived by condensing o-aminobenzoylhydrazide (1) with picinaldehyde (2) did not yield the same (3). Instead we obtained a cyclized product, 1,2-dihydroquinazoline (4) (Scheme 1). The reaction was carried out at room temperature in different polar and non-polar solvents like benzene, THF, ethanol and chloroform with 1:1 equivalents of reactants and yielded quinazoline. Varying the stoichiometry of reactants (1:2) still yielded the same product but with higher yield. These type of cyclization reactions have been proposed by Fülöp et al.9

The coordination chemistry of quinazoline ligands has received much attention because of its biological implications. The 4(3H)-one quinazolines have been tested successfully against cancer and HIV virus. Their synthetic analogues possess antimalarial, anti-inflammatory, CNS depressant, anticonvulsant, hypolipidemic and antiproliferative activities. Recently, the metal complexes of pyrimidine derivative, 5-dimethylamino-2-thiourea have been reported wherein the complexes show enhanced antitumour, antifungal and antibacterial activities compared to the free ligand. In view of the above, it makes this class of compounds interesting for the development of further effective compounds having the quinazoline moiety. Further, the chelating behaviour and crystal structure of a few transition metal [(Cu(I), Co(I) and Cd(II)) complexes of 1,2-dihydroquinazoline (4) is reported in a one-pot synthesis. In case of Cu(II) and Co(II), the ligand shows NNN coordination behaviour ligating through both the pyridine and azomethine nitrogens whereas in Cd(II) complex, it behaves as an ONN donor through carbonyl oxygen, azomethine nitrogen and a pyridine nitrogen. But, to our knowledge no reports exist regarding its ligating behaviour towards lanthanide salts.

Keeping in view the different modes of coordinating behaviour of 2-pyridine-2-yl-3-[pyridine-2-carboxylidene amino]-1,2-dihydroquinazolin-4(3H)-one (PPCADQ) and the role of metal ion in enhancement of activity of ligand, we have carried out studies on the synthesis, characterization and biological evaluation of lanthanide (III) complexes with PPCADQ.

Materials and Methods

All the solvents were of A.R. grade. Hydrazine hydrate and 2-pyridinecarboxaldehyde were procured from Rankem and Merck, respectively. o-Aminobenzoylhydrazide was synthesized as reported already. The lanthanide nitrates were obtained by heating lanthanide oxides (Indian Rare Earths, 99.9%) with dilute nitric acid (50%) and evaporating the excess acid.

For synthesizing the ligand, o-aminobenzoylhydrazide (15.1 g, 100 mmol) and
2-pyridinecarboxaldehyde (9.5 ml, 200 mmol) were refluxed in methanol (150 mL) for 2-3 h. The yellow solid obtained was filtered, washed with alcohol and finally recrystallised from alcohol to get yellow needles of PPCADQ. Yield 88%; m.pt. 203-204°C; m/z (molecular ion peak) 329.

**Preparation of complexes**

A solution of Ln(NO$_3$)$_3$ (1 mmol) and PPCADQ (0.329 g, 1 mmol) was refluxed in methanol (20 mL) for 2 h. The pH of the solution was then raised to 6.5 by addition of alcoholic NH$_3$ (1:1, v/v) and the solution was further refluxed for 3-4 h. The solution was then concentrated to a small volume and the gummy residue obtained macerated with petroleum ether leading to its solidification. The yellow solid obtained was filtered off, washed with water and ether and finally dried in air. Yield 84%; m.pt. >250°C.

**Physical measurements**

Elemental analyses were performed on a Carlo-Erba Strumentazione (Italy) CHN analyzer. IR spectra were obtained on a Nicolet 170 SX FT-IR spectrometer using KBr pellets, in the range 400-4000 cm$^{-1}$. $^1$H NMR spectra were monitored on a JEOL-AMX-400 NMR spectrophotometer using DMSO-$d_6$ as solvent. Mass spectrum of the ligand was recorded on a Thermofinnigan 1020 automated GC MS. Molar conductivities were obtained on an Elico conductivity bridge having platinum electrodes. Room temperature magnetic moments on solid samples were made with a Faraday balance using Hg[Co(NCS)$_3$]$_2$ as calibrant. Diamagnetic corrections were made by using Pascal’s constants$^{19}$. UV-vis spectra were obtained on a Hitachi 2001 spectrometer. EPR spectra of the Gd(III) complex were monitored on a Varian E-4X band spectrometer. TG/DTA thermograms were recorded on a Perkin-Elmer (Pyris Diamond) analyzer in N$_2$ atmosphere at a heating rate of 10°C and a maximum temperature of 1000°C. The metal contents were determined by complexometric titrations with EDTA using xylene orange as the indicator$^{20}$.

Antibacterial and antifungal activities of the ligand and its complexes were carried out against the bacteria *Pseudomonas aeruginosa* (PA, Gram-ve), *Bacillus cereus* (BC, Gram+ve) and *Aspergillus niger* (AN), by the cup-plate method.
Results and Discussion

The analytical data (Table 1) indicate that the complexes have the stoichiometry [Ln(PPCADQ)$_2$ (H$_2$O)$_2$(NO$_3$)$_2$](NO$_3$)$_2$. The lanthanide complexes are stable, non-hygrosopic and orange yellow in color. They are soluble in ethanol, methanol, DMF and DMSO but insoluble in benzene, ether and chloroform. The molar conductance data (Table 1) of the complexes in DMSO at 10$^{-3}$ M is in the range 71.55-80.05 Ohm$^{-1}$ cm$^2$ mol$^{-1}$ indicating that they are 1:2 electrolytes.

All the complexes have been characterized by conductivity measurements, magnetic studies, IR, H and C NMR, UV-vis, EPR and TG/DTA studies. Attempts to grow crystals of the same, however, proved to be unsuccessful.

The ligand PPCADQ acts in tridentate fashion coordinating through carbonyl oxygen, azomethine and pyridine nitrogen. A coordination number of ten is attained on incorporation of two coordinated water and one bidentate nitrate molecule.

Magnetic and EPR spectral studies

The magnetic moments (Table 1) of all the complexes indicate that they are paramagnetic in nature except La(III) and Y(III) which are diamagnetic. The values obtained are similar to the Van Vleck-Frank$^{22}$, and Hund's$^{23}$ values except in case of Sm(III) and Eu(III) where slightly higher values were obtained. This is due to low J-J separation, which leads to thermal population of higher energy levels. The values obtained are similar to those of typical lanthanide ions$^{24}$ and indicate the non-involvement of 4f electrons in bonding due to their very effective shielding by the 5s$^2$5p$^6$ octet.

Gd$^{3+}$ ion has 4f$^7$ electronic configuration with $^8$S$_{7/2}$ single-ion ground state. The energy level of the lowest excited state is very high with no contribution from orbital angular momentum and the anisotropic effect$^{25}$.

A $\langle g\rangle$ value of 1.99 (at room temperature) and 2.04 (at liquid nitrogen temperature) compared to the free-ion value of tetracyanoethylene (2.00277) with broad resonance lines were obtained. The g values being almost same and similar line widths indicate that the line widths are independent of temperature.$^{26}$

Further, the complete absence of zero-field hyperfine splitting and the presence of broad bands indicate that the Gd$^{3+}$ ion is located in a rather disordered environment caused by strain. These strains (caused by g strain for the g tensor distribution, D-strain for the zero-field splitting distribution) arise due to random hydrogen bonds between water molecules and the complex leading to distortions, which lead to broad resonance EPR lines.$^{27,28}$

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Found (Calcd) (%)</th>
<th>Magnetic moment (B. M.)</th>
<th>Molar conductivity (Ohm$^{-1}$ cm$^2$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) PPCADQ</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) <a href="NO$_3$">La(PPCADQ)$_2$(H$_2$O)$_2$(NO$_3$)$_2$</a>$_2$</td>
<td>13.13</td>
<td>14.42</td>
<td>21.24</td>
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<td>(3) <a href="NO$_3$">Pr(PPCADQ)$_2$(H$_2$O)$_2$(NO$_3$)$_2$</a>$_2$</td>
<td>13.20</td>
<td>14.60</td>
<td>3.29</td>
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<tr>
<td>(4) <a href="NO$_3$">Nd(PPCADQ)$_2$(H$_2$O)$_2$(NO$_3$)$_2$</a>$_2$</td>
<td>13.17</td>
<td>14.40</td>
<td>2.26</td>
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<tr>
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<td>15.51</td>
<td>14.19</td>
<td>3.21</td>
</tr>
<tr>
<td>(6) <a href="NO$_3$">Eu(PPCADQ)$_2$(H$_2$O)$_2$(NO$_3$)$_2$</a>$_2$</td>
<td>14.55</td>
<td>14.21</td>
<td>3.31</td>
</tr>
<tr>
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<td>14.21</td>
<td>14.88</td>
<td>3.33</td>
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<tr>
<td>(8) <a href="NO$_3$">Tb(PPCADQ)$_2$(H$_2$O)$_2$(NO$_3$)$_2$</a>$_2$</td>
<td>16.14</td>
<td>14.82</td>
<td>3.21</td>
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<tr>
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<td>14.51</td>
<td>14.71</td>
<td>3.20</td>
</tr>
<tr>
<td>(10) <a href="NO$_3$">Y(PPCADQ)$_2$(H$_2$O)$_2$(NO$_3$)$_2$</a>$_2$</td>
<td>9.34</td>
<td>47.16</td>
<td>3.49</td>
</tr>
</tbody>
</table>
Infrared spectra

The important IR frequencies of the ligand PPCADaq and its complexes are given in Table 2.

In the free ligand, a strong band observed at 1650 cm\(^{-1}\) is assigned to quinazoline ring >C=O whereas the band at 1613 cm\(^{-1}\) is assigned to the azomethine \(\nu(\text{C} = \text{N})\) group. Due to the presence of intramolecular hydrogen bonding between the oxygen of carbonyl and the hydrogen of N=CH the carbonyl vibration is observed at a lower frequency (1650 cm\(^{-1}\)) compared to the literature report wherein the same was observed at 1700 cm\(^{-1}\) (ref. 29). The \(\nu(\text{C}=\text{N})\) band is observed at 1518 cm\(^{-1}\). The pyridine ring vibrations are doubled due to the presence of two non-equivalent pyridine rings and are observed at 1588, 1566, 1485, 1473, 1449 and 1433 cm\(^{-1}\), the ring breathing mode at 996 and 979 cm\(^{-1}\) and an out-of-plane CH deformation at 749 and 760 cm\(^{-1}\) (ref. 30). The broadness of the 749 cm\(^{-1}\) band is probably due to overlapping with one of the coordinated nitrate bands. A sharp band at 3238 cm\(^{-1}\) is assigned to the \(-\text{NH}\) stretching frequency.

In the complexes, the quinazoline ring >C=O is shifted to lower wave numbers (20-40 cm\(^{-1}\)) indicating its coordination to the metal ion whereas the azomethine vibration is shifted to lower frequency (1606-608 cm\(^{-1}\)) as a shoulder band on the carbonyl vibration also indicating its involvement in coordination.

In the complexes, the pyridine ring vibrations observed at 1588 cm\(^{-1}\) are shifted to 1585-1591 cm\(^{-1}\) whereas the 1566 cm\(^{-1}\) vibration is also merged in the same region. The 1473 cm\(^{-1}\) band has shifted to 1470 cm\(^{-1}\) whereas the 1433 cm\(^{-1}\) vibrations are now observed between 1413-1416 cm\(^{-1}\). The ring-breathing mode at 996 cm\(^{-1}\) undergoes a shift to higher frequency by 7-16 cm\(^{-1}\). The pyridine out-of-plane vibration undergoes an upward shift of 11-13 cm\(^{-1}\). These changes indicate the coordination of pyridine nitrogen\(^{30}\). The remaining vibrations remain unchanged. However, coordination of one or both pyridine nitrogens was confirmed by \(^1\)H and \(^13\)C NMR spectra. The band due to ionic nitrate could not be assigned due to a strong ligand band which overlaps the ionic nitrate band (1390-1350 cm\(^{-1}\)). The presence of ionic nitrate was however confirmed by conductivity studies.

The coordinated nitrate groups show six absorption bands 1505, 1031, 1307, 816, 750 and 695 cm\(^{-1}\) which are assigned to \(\nu_4, \nu_2, \nu_1, \nu_6, \nu_3\) and \(\nu_5\) vibrations, respectively. The magnitude (\(\Delta\nu\)) between \(\nu_4-\nu_1\) and \(\nu_3-\nu_5\) lies between 198-210 cm\(^{-1}\) and 53-61 cm\(^{-1}\) respectively, indicating the coordination of nitrate group in bidentate fashion\(^{13,2}\). A broad band in the region 3371-3393 cm\(^{-1}\), due to the presence of coordinated water molecules obscures the NH stretching frequency.

\(^1\)H NMR spectra

The \(^1\)H NMR spectra of PPCADaq and its La(III) complex were carried out in DMSO-d\(_6\). The data are summarized in Table 3 and the proton and carbon assignments are given in Scheme 1. The \(-\text{NH}\) signal, which is in close proximity with the -CH=N group of quinazoline ring (6.66 ppm), undergoes a splitting due to the vicinal coupling with the latter (\(J = 4\) Hz) and is observed at 7.97 ppm\(^{31}\). This splitting collapses on D\(_2\)O exchange confirming the coupling of \(-\text{NH}\) proton with the quinazoline ring CH\(^{32}\). The assignment of the \(-\text{NH}\) signal was confirmed by D\(_2\)O exchange. The coupling effect also leads to the

\[
\text{Table 2} - \text{Important IR bands (cm}^{-1}\) of PPCADaq and its La(III) complexes
\]

<table>
<thead>
<tr>
<th>Comp.</th>
<th>(\nu(\text{OH}))</th>
<th>(\nu(\text{NH}))</th>
<th>(\nu(\text{C}=\text{O}))</th>
<th>(\nu(\text{C}=\text{N}))</th>
<th>Py (\text{N})</th>
<th>Ionic (\text{NO}_3)bands</th>
<th>(-\text{NO}_3)bands</th>
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<tbody>
<tr>
<td>(1)</td>
<td>3462b</td>
<td>3238s</td>
<td>1650s</td>
<td>1615s</td>
<td>1588m</td>
<td>—</td>
<td>1505s 1307m 816w 1031w 750w 695m</td>
</tr>
<tr>
<td>(2)</td>
<td>3393b</td>
<td>—</td>
<td>1621s</td>
<td>1606sh</td>
<td>1588m</td>
<td>1384m</td>
<td>—</td>
</tr>
<tr>
<td>(3)</td>
<td>3371b</td>
<td>—</td>
<td>1620s</td>
<td>1605sh</td>
<td>1588m</td>
<td>1384m</td>
<td>—</td>
</tr>
<tr>
<td>(4)</td>
<td>3382b</td>
<td>—</td>
<td>1620s</td>
<td>1605sh</td>
<td>1588m</td>
<td>1384m</td>
<td>—</td>
</tr>
<tr>
<td>(5)</td>
<td>3382b</td>
<td>—</td>
<td>1621s</td>
<td>1605sh</td>
<td>1590m</td>
<td>1384m</td>
<td>—</td>
</tr>
<tr>
<td>(6)</td>
<td>3387b</td>
<td>—</td>
<td>1626s</td>
<td>1606sh</td>
<td>1591m</td>
<td>1383m</td>
<td>—</td>
</tr>
<tr>
<td>(7)</td>
<td>3387b</td>
<td>—</td>
<td>1622s</td>
<td>1605sh</td>
<td>1587m</td>
<td>1383m</td>
<td>—</td>
</tr>
<tr>
<td>(8)</td>
<td>3393b</td>
<td>—</td>
<td>1622s</td>
<td>1605sh</td>
<td>1595m</td>
<td>1384m</td>
<td>—</td>
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<tr>
<td>(9)</td>
<td>3387b</td>
<td>—</td>
<td>1626s</td>
<td>1605sh</td>
<td>1591m</td>
<td>1383m</td>
<td>—</td>
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<tr>
<td>(10)</td>
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<td>—</td>
<td>1623s</td>
<td>1605sh</td>
<td>1590m</td>
<td>1383m</td>
<td>—</td>
</tr>
</tbody>
</table>

s, strong; b, broad; m, medium; w, weak; sh = shoulder
observation of H_{10} (adjacent to pyridine nitrogen N_3) as a broad singlet at 8.59 ppm whereas the H_3 signal (adjacent to pyridine nitrogen N_1) shows splitting at 8.47 ppm. Presence of hydrogen bonding between carbonyl oxygen and azomethine hydrogen in “free” ligand leads to observation of H_6 of azomethine group at downfield (8.71 ppm). This supports the IR observation. Three triplets at 7.40, 6.80 and 7.80 ppm are ascribed to H_{18}, H_12 and H_3 respectively. A multiplet at 7.28 ppm corresponds to H_2 and H_11. The doublets due to H_{16}, H_9, H_{10} and H_{12} are observed at 7.91, 7.46, 6.73, 7.75 and 7.86 ppm, respectively.

In the \(^1\)H NMR spectrum of La(III) complex, the following changes were observed. The net result of breakdown of hydrogen bonding and complexation to the metal ion through azomethine nitrogen resulted in an upfield shift of H_6 of CH=N. Complexation through azomethine nitrogen is also supported by \(^{13}\)C NMR spectra.

The H_8, H_9, H_{16} and H_12 signals comprising of a triplet and three doublets are now merged to give a multiplet at 7.84 ppm. The H_{10}, H_12 and H_14 signals consisting of a doublet, triplet and a singlet merge to give a multiplet at 6.73 ppm.

The multiplet due to H_2 and H_11 remain unperturbed at 7.28 ppm whereas the doublet and triplet due to H_2 and H_16 are merged to give a multiplet at 7.47 ppm. The H_{10} singlet is now observed as a doublet at 8.58 ppm in the complex.

The signal due to N_4H undergoes a very negligible shift to 7.98 ppm. The H_3 signal is shifted to 8.52 ppm. Further evidence in support of mode of complexation has been obtained from \(^{13}\)C NMR spectral studies.

\(^{13}\)C NMR spectra

The \(^{13}\)C NMR spectra of PPCADQ and its La(III) complex were carried out in DMSO-\(d_6\). The data is summarized in Table 3. In the “free” ligand PPCADQ, the peaks at 147.87 ppm is due to C_7, (Scheme 1) of the –CH=N group whereas the C_14 signal of the quinazoline ring –CH was observed at 71.87 ppm as expected for an sp\(^3\) hybridized carbon atom. The C_7 of carbonyl group was observed at 160.7 ppm. The signals observed at 149.43 and 149.16 ppm are ascribed to C_3 and C_10 adjacent to the pyridine nitrogens. The C_8 and C_10 signals are observed as a single line at 117.83 ppm. On complexation, the C_6 of the –CH=N group undergoes a downfield shift to 148.44 ppm indicating the coordination of azomethine group to metal. The C_7 of the carbonyl group also undergoes a significant shift to 161.82 ppm indicating its involvement in coordination. The C_14 signal is shifted by 0.49 ppm towards downfield probably due to the coordination of carbonyl oxygen. The signals of one of the pyridine rings [C_1, C_2, C_3, C_4 and C_5] showed a downfield shift indicating the coordination through N_1 whereas the \(^{13}\)C signals of another pyridine ring showed an upfield shift.
Electronic spectral complexes
Thermal studies

<table>
<thead>
<tr>
<th>Complex</th>
<th>Assignments</th>
<th>$\lambda_{\text{max}}$ of Ln$^{3+}$ ion</th>
<th>$\lambda_{\text{max}}$ of complex</th>
<th>$\beta$</th>
<th>Related parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Nd([PPCDAQ]$_2$NO$_3$)($H_2O$)$_2$]2(NO$_3$)$_2$</td>
<td>2$H_{2O}$ $\rightarrow$ 2$F_{3/2}$</td>
<td>11381</td>
<td>11261</td>
<td>0.98919</td>
<td>$\delta=0.79629$</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$ 2$F_{5/2}$</td>
<td>12475</td>
<td>12444</td>
<td>0.99751</td>
<td>$b^2=0.06284$</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$ 2$F_{7/2}$</td>
<td>13997</td>
<td>13550</td>
<td>0.96806</td>
<td>$\eta=0.08923$</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$ 2$H_{3/2}$</td>
<td>14594</td>
<td>14688</td>
<td>1.06444</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$ 2$G_{9/2}$</td>
<td>17170</td>
<td>17158</td>
<td>0.99930</td>
<td></td>
</tr>
<tr>
<td>[Sm([PPCDAQ]$_2$NO$_3$)($H_2O$)$_2$]2(NO$_3$)$_2$</td>
<td>2$H_{2O}$ $\rightarrow$ 2$H_{5/2}$</td>
<td>21477</td>
<td>21114</td>
<td>0.98390</td>
<td>$\delta=0.79121$</td>
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<tr>
<td></td>
<td>$\rightarrow$ 2$F_{7/2}$</td>
<td>26624</td>
<td>26652</td>
<td>1.00105</td>
<td>$b^2=0.06264$</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$ 2$P_{1/2}$</td>
<td>27264</td>
<td>27412</td>
<td>0.99232</td>
<td>$\eta=0.08985$</td>
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</tbody>
</table>

UV-visible spectra

The electronic spectral data of two representative complexes is given in Table 4. The free ligand shows an intense band at 303 nm and two weaker bands at 365 and 259 nm of which the first two are assigned to the $n-\pi^*$ and the latter to the $\pi-\pi^*$ transitions, respectively. The electronic spectra of the complexes are dominated by ligand bands, with a slight shift to higher or lower energy levels. This slight shift was attributed to the effects of crystal field upon the interelectronic repulsion between the 4f electrons.

The various bands in Nd (III) complex at 11261, 12444, 13550, 14688 and 17158 cm$^{-1}$ are due to the transitions from $4H_{5/2}$ to $4F_{5/2}$, $4F_{7/2}$, $4F_{9/2}$ and ($4G_{9/2}$, $4G_{7/2}$). In case of Sm (III) complex, the bands at 21477 cm$^{-1}$, 26624 cm$^{-1}$ and 27264 cm$^{-1}$ correspond to transitions from $4H_{5/2}$ to $4F_{5/2}$, $4F_{7/2}$ and $4F_{9/2}$. The bonding parameter ($\beta$), Sinha's covalency parameter ($\delta$), nephelauxetic parameter ($\beta$) and angular covalency parameter ($\eta$) have been calculated according to literature procedures. $\beta$ values being less than unity and positive values of $\beta$ and $\delta$ indicate metal-ligand covalent bonding. According to Kurraker, the shape of the hypersensitive transition reflects the environment of the metal ion. On comparison of the spectra with that of known compounds, it is concluded that the coordination number of the present complexes is ten.

Thermal studies

The TG/DTA analysis of a few representative complexes was carried out in nitrogen atmosphere at a heating rate of 10°C/min. In the thermogram of [Pr([PPCDAQ]$_2$($H_2O$)$_2$NO$_3$)$_3$][NO$_3$], the initial weight loss of 3.42% (Caled 3.52%) at 250°C corresponds to loss of two coordinated water molecules. The next weight loss in the temperature range 250-350°C is due to loss of two nitrate molecules (Obs. 12.06; Caled 12.14%). A further weight loss in the range 350-600°C corresponds to loss of a coordinated nitrate and two ligand molecules (Obs. 69.89; Caled 70.52%). On continued heating up to 1000°C, the most stable oxide Pr$_5$O$_{12}$ is formed. The percentage of metal obtained is in confirmation with the values obtained by metal determinations.

In case of [Dy ([PPCDAQ]$_2$($H_2O$)$_2$NO$_3$)$_3$][NO$_3$], the TG thermogram exhibits a loss of 3.32% (Caled 3.45%) corresponding to loss of two coordinated water molecules. A loss of 11.72% (Caled 11.89%) between 240-320°C is due to removal of two nitrate molecules. Further weight loss of 69.16%
exhibited enhanced activities, which is due to the synergistic effect that increases the lipophilicity of the complexes. Chelation decreases the polarity of the metal ion, which further leads to enhancement of lipophilicity of the complex. Since the microorganism cell is surrounded by a lipid membrane which favours the passage of lipid soluble materials, increased lipophilicities allows the penetration of complex into, and through the membrane and deactivates the active enzyme sites of the microorganisms.

Based on the above data, structure (I) is proposed for the lanthanide(III) complexes having the formula \([\text{Ln}(\text{PPCADQ})_2(H_2O)_2\text{NO}_3]_2\text{(NO}_3\text)_2\) where \(\text{Ln} = \text{La(II)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Gd(III)}, \text{Tb(III)}, \text{Dy(III)}\) and \(\text{Y(III)}\). In the present complexes, due to rotation about the N-N bond, the ligand changes its conformation to facilitate the coordination in ONN fashion as in case of Cu(II) complex, as reported earlier.

**Acknowledgement**

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**References**


**Biological activity**

The results of the antibacterial and antifungal study are given in Table 5. The concentration of the compound used for testing was 1 mg/ml in DMSO (inactive). Grisofulvin and Norfloxacin were the standards used against fungi and bacteria respectively.

In a typical procedure, a well was made on the agar medium inoculated with microorganisms. The well was filled with the test solution using a micropipette and the plate was incubated at 37°C for 48 h. During this period, the test solution diffused and the growth of microorganisms was affected. The antimicrobial activity was estimated on the basis of size of inhibition zone around the cup.
23 Hund F Z Phys. 33 (1925) 855.