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Complexation studies of *N*′-[(1*E*)-1-phenylethylidene]isonicotinohydrazide: An aroylhydrazone Schiff base and lanthanides

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ABSTRACT

The interaction of *N*′-[(1*E*)-1-phenylethylidene]isonicotinohydrazide (PHeH) with trivalent Pr, Nd, Gd, Tb, and Ho ions was studied with spectroscopic and potentiometric techniques. Photoluminescence studies of Tb^{3+} and PHeH in ethanol and in solid Tb^{3+}-PHeH complex reveal that PHeH has no sensitizing effect on Tb^{3+} luminescence. The absorption spectral bands of PHeH under different conditions and that of Nd^{3+}- PHeH at different molar ratios were investigated. Potentiometric titrations of 1:4 Ln/PHeH molar ratio carried out at different temperature at a constant ionic strength of $I = 0.1\ \mathrm{mol \cdot dm^{-3}}\ KNO_3$ in aqueous-dioxane medium reveal the moderate thermodynamic stability constants of the complex formation equilibria which follow the order: Pr < Nd < Gd < Tb < Ho. The thermodynamic parameters (ΔG, ΔH, and ΔS) of protonation and complexation reactions are all negative suggesting the spontaneous, exothermic, of unfavorable entropy and enthalpy-driven reactions. Actual synthesis and characterization of Tb^{3+}-PHeH complex, confirmed the veracity of the complex formation equilibria. Finally, the information accrued from the studies is used in the structural elucidation of the complexes.

1. Introduction

Lanthanides and their complexes, due to the arrays of applications and potential uses have not only aroused immense interest in chemistry but on all branches of sciences. Due to their photoluminescence in the visible and near-infrared region under UV excitation, lanthanide organic complexes are of both fundamental and technological interests. A vast treasure of knowledge on their complexes and applications are available in the literature. Among the diverse classes of ligands which constitute the Ln^{3+} complexes, N and O donor molecule like hydrazones and its analogue constitute an important class of ligand [1,2]. Known as privileged ligands [3], the Schiff bases, especially aroylhydrazones have not only simple synthetic process but also interesting spectral and biological activities [4].

In comparison to arrays of literature available with respects to aroylhydrazones transition metal complexes derived from INH or isoniazid, fewer aroylhydrazones lanthanide complexes such as complexes of 2.6-diacetylpyridine-2-thenoyl isonicotinoyl dihydrazone [5], homo binuclear complexes of *N*,*N*′-diisonicotinoyl-2-hydroxy-5-methylisophthalaldehyde dihydrazone [6], nine-coordinate helix like structured complex of 1-phenyl-3-methyl-5-hydroxy-4-pyrazolyl P_H ketone isonicotinoyl hydrazone (H_2O) and its interaction with DNA [7], Ln-complexes of hexadentate 2.6-diacetylpyridine-2-thenoylpicolynoyl dihydrazone [8], complexes of 2-pyridinecarboxaldehyde benzoyl-hydrazone coordinated through the pyridine nitrogen, the azomethine nitrogen and the carbonyl oxygen [9], complexes of N-(2-propionic acid)-salicyloyl hydrazone [10], complexes of 2-carboxybenzaldehyde isonicotinoylhydrazone and it DNA-binding properties [11],complexes of 7-methoxychrom-one-3-carbaldehyde-isonicotinoyl hydrazone and their interactions with calf-thymus DNA [12], tetranuclear Ln^{3+}-complexes in a highly unusual see-saw geometry of 2-methoxy-6-(pyridine-2-ylhydrazonomethyl)phenol [13], a series of 2.6-pyridinedicarboxaldhydebis(p-hydroxyphenylimine) coordinated equatorially with six-coordinate octahedral Ln^{3+} ions orthogonally oriented [14], nine-coordinated La^{3+} complexes of a Schiff-base afforded from 1-phenyl-3-methyl-4-formyl-2-pyrazolin-5-one and isoniazid [15], and a series of Ln_4 clusters with 2.6-(picolinoylhydrazone)pyridine with overall metal core of each cluster comprising of two edge-sharing triangular Ln_3 units linked by μ_3-OH bridges [16] are some of the more notable reported complexes.

The knowledge of Ln^{3+} and Schiff bases interactions, their stability constants and the associated thermodynamics [17–20] would therefore be of paramount importance in pharmaceuticals industry and in understanding the complex biological reactions like transamination, racemization and decarboxylation [2]. The complexation process, in all the Ln^{3+} complexes generally involve displacement of protons (H^+) of the free chelating ligands by metal ions (Ln^{3+}) where Ln^{3+} ions being hard acids inevitably and preferably bind hard bases, like charged ligands or neutral O and N donors generally coordinated with eight to nine donor atoms when available forming complexes that are kinetically and thermodynamically more stable. However, the solution equilibria, the determination of the stability constants [21–23] and the

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associated thermodynamics of the complexation reactions of lanthanides with Schiff bases are limitedly reported.

The coordination behavior of the Schiff bases afforded by condensation of acid hydrazides with hetero aromatic aldehydes or ketones with the transition and lanthanides metals have been studied [24–26] through spectroscopic and pH metric methods in our laboratory. In this work, we have undertaken a series of studies on *N*′-[(1*E*)-1-phenylethylidene]isonicotinohydrazide, PHeH in solution. The spectral properties of the ligand and its interaction with selected lanthanides investigated. The lanthanides were so selected representatively two each from lighter and heavier lanthanides with Gd in the middle so as to arrive at comprehensive generalisation of complexation with the ligands for all the Ln^{3+} series. Nd^{3+} absorption help probe the coordination environment while Tb^{3+} is convenient for photoluminescence studies of the metal complexes. The thermodynamics stability constants of the ligand was evaluated and used for determination of the complex formation equilibria with selected lanthanides and the chemical thermodynamics involved were evaluated. To confirm the veracity of the complex formation equilibria, a terbium complex of PHeH is isolated and characterized and the thermogram investigated. Finally, from the information accrued through the spectral, analytical and formation equilibria studies, the structure of the complexes is proposed.

2. Materials and methods

2.1. Physical measurements

The C, H and N of PHeH and Tb^{3+}-PHeH were micro analyzed using CHNS (O) Analyzer Model: FLASH EA 1112 series made by Thermo finnigan, Italy at IIT Bombay**.** Chlorides ions and Tb^{3+} were estimated as in our earlier work [25]. To estimate hydrazine content, volumetric titrations of PHeH and the complex were done, after subjecting the compounds to acid hydrolysis for 4 h. Shimadzu FTIR-8400 was used for recording the IR spectra in KBr medium. The FAB mass spectrum was obtained on a JEOLSX 102/Da-.6000 mass spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a JEOL AL 300 FT NMR spectrometer in DMSO. A Perkin Elmer LS 55 Fluorescence Spectrophotometer in phosphorescence mode was used for room temperature luminescent studies of Tb^{3+} and PHeH. Conductivity Measurement of the Tb^{3+}-PHeH complex was done with CON 510, Conductivity/TDS/°C/F meter, Eutech Instruments. Magnetic Measurement was carried out with Magnetic Susceptibility Balance, Sherwood Scientific Ltd., UK. The thermal analysis of the complex was done with Perkin Elmer, STA 6000 Simultaneous Thermal Analyzer purged with Nitrogen gas, heated at the rate of 10 °C/min. All the UV–Vis spectra were recorded on a Perkin–Elmer Lambda 25 spectrophotometer keeping the slit width at 2 and scan speed of 120, for all the measurements using glass cell of 1 cm path length, equipped with sample holders, maintained at constant temperatures 303.15 K. Cyberscan pH 1100 model measures the pH of the solutions after calibration using SOP. An Equibath Refrigerated Circulating Bath, from Medica Instrument Mfg.co was used as thermostat during potentiometric titrations

2.2. Materials and solutions

Isonicotinic acid hydrazide, acetophenone, KOH, KNO_3 and 1, 4 Dioxane were obtained from E. Merck, Mumbai, and $LnCl_3.6H_2O$ (Ln = Pr, Nd, Gd, Tb, Ho) from Sigma-Aldrich, USA. All the chemicals used are of A.R. grade. Solutions containing water were prepared with double distilled water. KOH solution standardized with standard oxalic acid solution ($5\cdot10^{-2}$ $mol\cdot dm^{-3}$), was used for standardization of HNO_3. Since the ligand is not soluble in water, stock solution ($5\cdot10^{-3}$ $mol\cdot dm^{-3}$) was prepared in 40% aqueous–dioxane mixture.

2.3. Potentiometric titration

The Potentiometric titrations of PHeH with the Ln^{3+} ions Pr, Nd, Gd, Tb, and Ho were carried out at a constant ionic strength $I = 0.1$ M KNO_3 solution at three different temperatures 293.15 K, 303.15 K and 313.15 K in 40% aqueous-dioxane medium. The solutions titrated were as follows.

$$\begin{array}{lcl} \text{Solution (a)} & : & 5\text{ mL KNO}_3\left(0.10\ \overset{Ç}{\text{m}}\text{oldm}^{-3}\right) + 2.5\text{ mL HNO}_3\left(\overset{Ç}{1}10^{-3}\ \overset{Ç}{\text{m}}\text{oldm}^{-3}\right) \\ \text{Solution (b)} & : & \text{Solution (a)} + 4.69\text{ mL PHeH}\left(1\cdot\overset{Ç}{2}10^{-4}\ \overset{Ç}{\text{m}}\text{oldm}^{-3}\right) \\ \text{Solution (c)} & : & \text{Solution (b)+x mL Ln}^{+3}\left(\overset{Ç}{3}10\text{--}4\ \overset{Ç}{\text{m}}\text{oldm}^{-3}\right) \end{array}$$

where x mL of Ln^{3+} taken is of the required strength from the stocks solutions. The titrations were done at 1:4 Ln/ PHeH molar ratio to ensure coordinative saturation of the metals during complexation reactions. The titrations were repeated twice for each set.

2.4. UV–Visible absorption studies

For the UV–vis spectra of PHeH as a function of pH, 25 mL PHeH ($8\cdot10^{-5}$ $mol\cdot dm^{-3}$) was titrated with freshly prepared KOH ($5\cdot10^{-2}$ $mol\cdot dm^{-3}$) solution at variable pH in aqueous-dioxane medium. The preparations of solutions follow the same procedures as in potentiometric titrations. After each aliquots addition of KOH, the pH was allowed to stabilize and 4 mL taken in a cuvette to record the spectra. For absorption spectra of PHeH and Nd^{3+} complex, $1\cdot10^{-3}$ $mol\cdot dm^{-3}$ Nd^{3+} (constant) and PHeH (variable) prepared in absolute ethanol were taken for spectral recordings.

2.5. Luminescence studies

The luminescent spectra of $TbCl_3.6H_2O$ and solid Tb^{3+}-PHeH complex were recorded. Solution studies of luminescence were done as outlined earlier [25].

3. Calculations

3.1. Proton ligand and metal ligand formation constants

The protonation constant of PHeH and the formation constants of Ln^{3+}-PHeH complexes (where $Ln^{3+} = Pr^{3+}$, Nd^{3+}, Gd^{3+}, Tb^{3+} and Ho^{3+}) were calculated from the titration curves using Bjerrum's half integral method [27] and as modified by Irving and Rossotti [28,29]. The average number of protons associated with HpEH ($\overline{n_H}$) at various pH meter readings was determined from the acid and ligand titration curves using Eq. (1)

$$\overline{n}_H = Y - \frac{(V_L - V_A)\left(N + E^0\right)}{(V_0 + V_A)T_L^0} \tag{1}$$

where Y is the number of ionisable protons present in PHeH, V_L and V_A are the volumes of KOH ($5\cdot10^{-2}$ $mol\cdot dm^{-3}$) consumed by solutions (a) and (b), respectively, for the same pH reading, and ($V_L - V_A$) measures the difference in position between the ligand curve and the acid curve. V_0 is the initial volume of the reaction mixtures (25 mL), and E^0 and T_L^0 are the concentrations of nitric acid ($1\cdot10^{-3}$ $mol\cdot dm^{-3}$) and PHeH (variables) in the reaction mixtures, respectively.

The average number of PHeH attached per Ln^{3+} ions ($\overline{n}$), and the free ligand exponent, *pL*, were calculated from the experimental titration