

Study of stability constant of lanthanide (iii) metal complexes with some monobasic bidentate ligand

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Abstract

The Bidentate ligand was synthesized from the condensation reaction of 2-hydrazinopyridine and pyridine-2- carbaldehyde, Neodymium and Samarium complexes were isolated when the corresponding nitrate salt was added to the solution of the ligand the isolated compound were characterized by elemental analyses, IR study, room temperature magnetic measurement and single x-ray crystal diffraction of the two crystals. Both complexes crystallize in the monoclinic system with space group P_{21}/c . Both metal centres have distorted tricapped trigonal prism geometry with the schiff base acting as bidentate ligand.

Key words: – Lanthanide complexes hydrazino, antioxidant activity, X-ray structure.

Introduction

In the field of chemistry lanthanide (iii) metal complexes have significance role with monobasic bidentate ligand. In the past decade, the lanthanide coordination chemistry was one of the most focused area of research. The intriguing structure and the potential uses in a wide variety of area as diagnostic tool in biology catalysis, luminescence and magnetism reinforce the interest of chemistry in these area of research. By use of an acyclic schiff's base in presence of acetate groups, it is possible to introduce two identical or different lanthanide ions and to study their physico chemical properties. The flexibility and the multiple coordination site of the acyclic ligand provides several possible structure with lanthanide ions, the carboxylate groups can adopt various coordination mode, which may cause the generation of novel triatomic moiety connection of $-C=N-NH$. They are widely used in the synthesis of complexes to generate original structures, coordination compound from this types of ligand have a variety of application HL is an acyclic hydrazine ligand bearing nitrogen donors containing one coordination cavity which can encapsulate large ions such as lanthanide.

Material and Method

2-Hydrazinopyridine, 2-pyridinecarbaldehyde and the lanthanide nitrate salts were commercial products and were used without further purification. Solvents were of reagents grade and were purified by the usual method. The analyses for carbon, hydrogen and nitrogen were carried out using a LECO CHNS – 932 instrument. ^1H and ^{13}C spectra of the compounds were recorded in DMSO – d_6 with TMS as internal reference on a Bruker Advance operating at 250 MHz. The IR spectra were recorded as KBr discs on a Bruker IFS–66v spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$). The molar conductance of 10^{-3}M solutions of the metal complexes in methanol were measured at 25°C using a WTW LF – 330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance.

Preparation of the Ligand HL

2-Hydrazinopyridine in 20 ml of ethanol was added to a solution of 2-pyridinecarbaldehyde dissolved in 25 ML of ethanol. The resulting mixture was stirred under reflux during 30 min. After cooling, the volume was complete to 100 ML with ethanol and stored in the refrigerator. 10 ml of this solution was evaporated to dryness and the NMR spectrum of the resulting liquid was recorded. δ_{H} (250 MHz, DMSO- d_6)⁺ : 11.185 (1 H, s, H–N–N), 8.542 (1H, d, J 4.75Hz, H–Py); 8.159 (1H, d, J 1.75 Hz, H–Py); 8.144 (1H, s, H–C =N); 7.972 (1H, d, J 7.75 Hz, H–Py); 6.820 (1H, dd, J 4.75 and 7.25 Hz, H–Py). δ_{C} (250 MHz, DMSO – d_6) : 106.500 (C–8), 115.528(C–10), 118–810 (C–4), 122.878 (C–2), 154.257 (C–7), 156.660 (C–5).

Preparation of the complexes

To 10 ML of the solution of the above prepared ligand, a mixture of sodium acetate (3m mol) and $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Ln = Nd or Sm) (1 m mol) in ethanol (10 ML) was added. the mixture was stirred for 30 min and the resulting yellow slightly cloudy solution was filtered – off to discard a small quantity of NaNO_3 and the filtrate was kept at 298 K. yellow powder began to appear after one day and was collected by filtration. Recrystallization by slow evaporation of an ethanol solution gave X–ray quality crystal of two compounds.

The methanol solution of 3.9 ML DPPH (40 mg L^{-1}) was added to test compound (100 ML) at different concentration, the mixture was shaken vigorously and incubated in dark for 30 min at room temperature. After the incubation time, the absorbance of the solution was measured at 517 nm by using UV – vis spectro-photometer mini – 1240 SHIMADZU.

X-ray crystal structure Determinations

Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structure were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Other H atoms (CH and CH_3 groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3. The chain bridging the two pyridine rings was found to be disordered such that the mean bond lengths in the chain are far from the mean values observed. This disorder may be explained by the fact that the sequence of atoms $\text{C(Py)-CH=N-NH-C(Py)}$ overlaps with the sequence $\text{C(Py)-NH-N=CH-C(py)}$, meaning two orientations of the ligand. In such a case for the refinement, one assume that atom C (of CH group) from one chain and atom N (of NH group) from the second chain occupy the same position. The same relates inversely. The instructions EXYZ and EADP of SHELXL were used to have the same atomic coordinates and displacement parameters of the disordered atoms. The occupancy factor refines close to 0.5 in the Nd complex and 60:40% occupancy in the Sm complex.

Results and Discussion

The acyclic Bidentate ligand, 1-(pyridin-2-yl)-2-(pyridine-2-ylmethylene) hydrazine, abbreviated as HL, was prepared by the 1:1 condensation reaction of 2-hydrazinopyridine and 2-pyridine carbaldehyde in ethanol. The reaction of $\text{Ln}(\text{NO}_3)_3 \times \text{H}_2\text{O}$ and NaOOCCH_3 , with the prepared ligand solution, with a 1:3:1 molar ratio in ethanol gave yellow powder. The formulae of these powders are further confirmed as $\{[\text{Ln}(\text{HL})(\text{n}^2\text{-CH}_3\text{COO})(\text{H}_2\text{O})_2](\mu\text{-CH}_3\text{COO})_2[\text{Ln}(\text{HL})(\text{n}^2\text{-CH}_3\text{COO})(\text{H}_2\text{O})_2]\}(\text{NO}_3)_2$, with $\text{Ln} = \text{Nd}$ and Sm (Scheme 1) by spectroscopic and X-ray analysis.

The ^1H and ^{13}C NMR spectra of the hydrazinopyridine derivative ligand and its diamagnetic Nd (III) and Sm(III) complexes are recorded in DMSO-d_6 . In the spectrum of the ligand a singlet appearing at 11.185 ppm is attributed to the H-N proton. No shift of this signal was observed in the spectrum of both complexes indicating no deprotonation of the ligand and the nitrogen atom supporting this proton is not involved in the coordination. The

signal attributed to the H-C = N proton is slightly shifted to higher field from 8.144 ppm in the free ligand to 8.096 and 8.135 ppm respectively in the spectra of the Nd and Sm complexes. This fact is indicative of an involvement of the azomethine in the complexation. The pyridine ring protons show also little difference shifts in the spectra of the complexes. Upon complexation the signals of the ^{13}C NMR spectra of the complexes show little difference with those of the spectrum of the free ligand. The signal of C = N carbon atom appearing at 139.164 ppm for the free ligand is slightly shifted to 139.171 ppm for Nd(III) complex and 139.153 ppm for Sm(III) complex. The spectrum of Nd(III) complex shows new broad signal at 4.722 ppm due to the protons of the water molecules. The signals of the methyl groups of the acetate moieties are not observed in the NMR spectra of the complexes. They are probably obscured by the intense signal of the DMSO solvent.

Both IR spectra of the two complexes reveal bands which are assigned respectively to asymmetric V_{as} (COO) and symmetric V_{s} (COO) stretching vibrations of the acetate group in the ranges 1565–1550 and 1450–1440 cm^{-1} . The positions of these asymmetric and symmetric bands are very close proximity in the two spectra of the complexes indicating that the coordination modes of the different acetate groups are similar in all these compounds. The values of $\Delta = V_{\text{as}} - V_{\text{s}}$ are in the range admitted for multiple coordination modes of acetate groups. This coordination behaviours of the acetate groups were further confirmed by X-ray studies of the complexes. In the X-ray structure of these binuclear complexes, each Ln(III) (Ln=Nd, Sm) ions have one acetate behaving as bidentate chelating and two others acting as bridges between the two lanthanide (III) ions. In both spectra medium bands in the range [1583–1590 cm^{-1}] are observed and assigned to the $V(\text{C}=\text{N})$ stretching vibration which was expected for the free ligand at $\sim 1630 \text{ cm}^{-1}$ as observed in the literature. This observation is a consequence of the decrease of the stretching force constant of the C=N bond, indicating the involvement of the imino nitrogen in the lanthanide ion coordination sphere. The presence of band of medium intensity at ca. 3220 and 820 cm^{-1} are due to the coordinated water molecules.

The absorption bands at $\sim 1580 \text{ cm}^{-1}$ are attributed to stretching vibration of the pyridine rings. The strong and sharp band observed in all the spectra at around 1370 cm^{-1} is characteristic of uncoordinated nitrate ion. Molar conductivities were measured for freshly prepared solutions in DMF and after standing for two weeks. The conductivities increased very slightly with time in DMF for all the complexes. The conductance values lie in the

range observed for 1:1 electrolytes ($70\text{--}90\text{ cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$) in DMF. The u_{eff} values of the lanthanide complexes show that they are paramagnetic. This paramagnetic behaviour is consistent with the presence of unpaired 4f electrons. The observed u_{eff} values are in close proximity to the values for the free metal ions reported by Van Vleck and Frank. This shows that the magnetic moments of the Ln^{3+} ions are not affected by the ligand field. The 4f-electrons are not involved in the coordination. These facts observed from the spectroscopy study are in accordance with the measured molar conductivities.

Conclusion

A Bidentate ligand (N_4) was synthesized and reacted with lanthanide nitrate and sodium acetate to yield binuclear lanthanide compounds of Nd and Sm. These complexes were characterized by spectroscopic studies, elemental analyses, molar conductivity and room temperature magnetic moment measurements. Suitable X-ray crystals diffraction were obtained for the Nd and Sm complexes. The X-ray structure determination reveal that the Ln^{3+} ion is nine-coordinated with two pyridine nitrogen atoms, one imine nitrogen atom, four oxygen atoms from acetate groups and two water oxygen atoms resulting in a distorted tricapped trigonal prism geometry, these lanthanide complexes show activity concentration dependence.

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