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A study of synthesis of Schiff bases derivatives: spectral characterization and biological evaluation

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Abstract

In this paper use of metal complexes as diagnostic agents is a relatively new area of medical research and has flourished from last 4-5 decades. Recently Schiff bases have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, anti-proliferative, anti-inflammatory, antiviral, and antipyretic properties.

Keywords: Supramolecular, anti-inflammatory, electrophilic, antipyretic properties

Introduction

Over the past few year a resurgence of interest in coordination chemistry of Lanthanide has been noticed especially in biological application of their element. The nature of the coordination compounds depends on the nature of metal ion, the donor atoms. The structure of the ligand and metal- ligand interaction. The important factor, which contribute to thermodynamic stability of metal complexes, depend considerably on the nature of the ligand and on the metal ion^[1-5].

Schiff bases, named after Hugo Schiff^[5] are formed when any primary amine reacts with an aldehyde or a ketone under specific conditions. The first preparation of imines was reported in the 19th century by Schiff (1864). Since then a variety of methods for the synthesis of imines have been described^[6]. The classical synthesis reported by Schiff involves the condensation of a carbonyl compound with an amine under azeotropic distillation^[7]. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable^[8], while those of aromatic aldehydes having effective conjugation are more stable. In general, aldehydes react faster than ketones in condensation reactions, leading to the formation of Schiff bases as the reaction centre of aldehyde are sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density to the Azomethine carbon and thus makes the ketone less electrophilic compared to aldehyde^[9]. Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, such as biological, inorganic and analytical chemistry^[10, 11]. Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions^[12, 13].

Lanthanides are members of a large family of elements located between barium and hafnium in the 6th row of the periodic table. Lanthanides are no more considered as rare, since industrial processes allow to prepare them in high degree of purity. There is an increasing demand of some lanthanides for modern technology. Rhone Poulenc Company is the world leader for production of purified lanthanides^[14]. The unique spectroscopic and paramagnetic properties of lanthanide ions have made them a fascinating field of research in coordination and supramolecular chemistry^[15]. The design and synthesis of lanthanide (III) complexes with chelating ligands has many potential applications such as light-emitting devices^[16-18], sensors^[19], liquid crystalline materials^[20]. Lanthanide coordination compounds are the subject of intense research efforts due to their applications as contrast agents for NMR imaging, as catalysts in RNA hydrolysis, or as active agents in cancer radiotherapy. It has also been shown that the Eu(III) ion behaves as an extremely sensitive probe responding to faint chemical differences, revealing slightly un-equivalent moieties in molecular solids^[21]. Metal complexes have proven their significance by entering into the field of diagnosis of a wide variety of disease states ranging from heart diseases, brain disorders, cancer and diabetics.

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Metal complexes are also able to determine specific aspects of disease such as tissue hypoxia, as well as to detect molecular phenomena such as multi-drug resistance [22].

The present investigation deals with the preparation of some new dithiocarbazates of 2-Acetylpyridine and their mononuclear La (III), Pr(III), Sm(III) and Nd(III) complexes. The prepared ligands were characterized by elemental analysis, IR, ¹H NMR, and. Elemental analysis, magnetic susceptibility measurements, characterizes the prepared complexes. Prepared complexes were also screened for their antifungal activities against two fungi (*A. niger* and *P. notatum*). The antibacterial activities of the prepared complexes were assessed against gram –positive bacteria *B. subtilis* and *S. aureus* and Gram- negative bacteria *E. coli*

Experimental

Solvents were purified prior to use. All melting points were recorded on KSW (Khera Scientific Work) apparatus. Lanthanum, Praseodymium, Neodymium and Samarium, 2-acetyl pyridine, CDCl₃, DMSO-d₆, TMS, P₄O₁₀, Agar, Peptones, Vacuum desiccator, and Petri-disc were procured from sigma – Aldrich chemical (U.S.A.). Microorganisms were collected from The Indian Agricultural Research Institution (IARI) commonly known as Pusa in New Delhi. Elemental analysis was performed by Regional sophisticated instrumentation centre. Centre drug research institute, Lucknow. India. U.V. visible spectra were run on shimadzu UV 1601 PC UV- Visible spectrophotometer infrared (IR) spectra were recorded on KBr pellets in the 4000-400 cm⁻¹ range on a Perkin Elemer 1620 spectrophotometer. The ¹H NMR spectra were run in CDCl₃ and DMSO-d₆ on Bruker AMX -300 MHz spectro-spin instruments using TMS as internal standard and its values are given in ppm (δ), agar medium for biological studies were used, obtained from Mrunalini's Ayurveda Pvt. Ltd. Nashik Maharashtra India. P₄O₁₀ was used as the drying agent.

Synthesis of Schiff bases Derivatives

Potassium hydroxide (50 mmol) was dissolved in 90% ethyl alcohol (30ml) and hydrazine hydrate (60mmol) was added into it. Carbon disulphide (60mmol) was added drop wise with constant stirring at 0 °C. During this time two layers had formed, the lower layer (light brown) was separated and dissolved in cold 40% ethyl alcohol (60 ml). The mixture was kept at 0 °C and alkyl halide was added drop wise with stirring. The product formed, was washed with water and dried over anhydrous calcium chloride. Substituted dithio-Carbazates were prepared by mixing S–alkyl dithiocarbazate in hot absolute ethyl alcohol with a solution of 2-acetyl pyridine (15 mmol) in ethyl alcohol (5 ml). The mixture was heated on a steam bath for 40 min. And allowed to stand for one hour where upon the light yellow crystals separated and re-crystallized from benzene [23].

Result and Discussion

Various physicochemical methods have employed to characterize the ligands and their complexes. The spectral data suggests the coordination of the ligand to central Ln atom takes place in tridentate fashion coordination to the metal ions through O N O donor sequence. Melting point determination was carried out to check purity of the compound. Ligands and their Lanthanide complexes percentages of C, H, N, and S were obtained by microanalysis. The analytical data (Table 1) indicates that the complexes have 1:2 (lanthanides: ligand) stoichiometry. The lanthanide complexes are stable and colored. Dithiocarbazates derivatives ligands and their Lanthanide complexes are soluble in benzene, chloroform and slightly soluble in methanol and ethanol. The molar conductance value (Table 1) of the complexes in DMSO and DMF at 10⁻³M are in the range 7.4–7.9 and 10.2–11.1 ohm⁻¹ cm² mol⁻¹ respectively.

Table 1: Analytical data, Magnetic moment, Molar conductance of Lanthanide Complexes

| S. No. | Complexes | Yield% | Colour | Content (Fund/Calcd)% | | | | | DMF | DMSO | μ _{eff} BM |
|--------|--|--------|-------------|-----------------------|-------------|-----------|-------------|-------------|------|------|---------------------|
| | | | | Metal | C | H | N | S | | | |
| 1 | SMDT | 57 | Cream solid | - | 47.65/48.00 | 4.89/4.95 | 18.67/18.44 | - | - | - | - |
| 2 | SBDT | 58 | Brown solid | - | 59.60/59.80 | 4.95/4.98 | 14.32/13.95 | - | - | - | - |
| 3 | [La(SMDT) ₂ (H ₂ O) ₃ Cl ₃] | 87 | Cream solid | 15.17/ 15.25 | 28.76/28.82 | 5.85/5.89 | 11.18/11.22 | 17.04/17.08 | 10.7 | 8.5 | D |
| 4 | [Pr(SMDT) ₂ (H ₂ O) ₃ Cl ₃] | 79 | Cream | 15.62/15.71 | 28.60/28.65 | 5.82/5.85 | 11.12/11.17 | 16.95/17.01 | 11.1 | 8.2 | 3.60 |
| 5 | [Sm(SMDT) ₂ (H ₂ O) ₃ Cl ₃] | 82 | Cream | 16.29/16.35 | 28.38/28.43 | 5.78/5.83 | 11.03/11.07 | 16.81/16.87 | 10.3 | 8.6 | 1.85 |
| 6 | [Nd(SMDT) ₂ (H ₂ O) ₃ Cl ₃] | 80 | Cream | 15.85/15.92 | 28.53/28.61 | 5.81/5.86 | 11.09/11.14 | 16.90/16.95 | 10.4 | 7.9 | 3.55 |
| 7 | [La(SBDT) ₂ (H ₂ O) ₃ Cl ₃] | 75 | Brown | 12.51/12.65 | 39.51/39.56 | 6.58/6.63 | 9.22/9.27 | 14.05/14.11 | 10.5 | 8.8 | D |
| 8. | [Pr(SBDT) ₂ (H ₂ O) ₃ Cl ₃] | 80 | Brown | 12.89/12.95 | 39.34/39.42 | 6.55/6.61 | 9.18/9.24 | 13.98/14.03 | 10.9 | 8.1 | 3.58 |
| 9. | [Sm(SBDT) ₂ (H ₂ O) ₃ Cl ₃] | 85 | Brown | 13.46/13.55 | 39.08/39.14 | 6.51/6.57 | 9.12/9.17 | 13.89/13.94 | 10.2 | 7.4 | 1.92 |
| 10. | [Nd(SBDT) ₂ (H ₂ O) ₃ Cl ₃] | 88 | Brown | 13.08/13.22 | 39.25/39.31 | 6.54/6.59 | 9.16/9.18 | 13.95/13.99 | 10.8 | 8.4 | 3.52 |

Magnetic studies

The magnetic moment of complexes give in (Table 1). The magnetic moment values show that lanthanum (III) complexes are diamagnetic in nature. This observation was actually expected from its closed shell electronic configuration and the absence of unpaired electron. All other tri-positive lanthanide ions are paramagnetic due to presence of unpaired 4f electrons, which are effectively shielded by 5 s² and 5 p⁶ electron. The comparison of these observed magnetic moment values with those observed for 8-hydrated sulphate and those calculated for uncomplexed ions, indicates that the 4f – electrons do not participate in any band formation in these complexes [24]. The values show little deviation from the theoretical values predicted for the

trivalent lanthanide ions. This fact suggests that the 4f electron do not participate in the bond formation of the metal to the ligand [25].

We saw Paramagnetic behavior of the complexes other than that of La (III) is consistent with the presence of unpaired electrons. The observed magnetic moment of the present complexes showed only very little deviation from the calculated values of the corresponding lanthanide ions. This indicates that the 4f electrons are not much disturbed by the ligand filed produced by the Schiff bases. Slightly higher values were obtained in the case of Pr (III) complexes. This could be attributed to law J-J separation, which leads to thermal population of higher every levels.

Electronic spectra

The electronic spectral data of the both compound should a broad at 29860-29782. This broadness of band is probably due to $n-\pi^*$ transition of pyridine as well as azomethine nitrogen of thiocarbazate. Typical spectral data for the solution of some representative lanthanide (III) i.e., 4f metal complexes investigated in lanthanide complexes are recorded (Table 2). All other parameters exhibit positive values suggest some covalent character in metal ligand band, particularly the value of $B \frac{1}{2}$ suggests the comparative

involvement of 4f orbital metal ligand band. The covalence decrease from Pr(III) to Sm (III) complexes which is due to lanthanide contraction ^[26] shift band position towards the lower wave number as compared to those of the metal. Lanthanum (III) has no significant absorption in the visible region. The band observed in the case of Pr (III), Nd (III) and Sm(III) complexes could be assigned to the transition from $3H_4$, $4I_{9/2}$, and $4H_{9/2}$ (ground state) to the excited J-level of the respective 4f configuration ^[27].

Table 2: Typical spectral data for the solution of some representative lanthanide (III) i.e., 4f metal complexes investigated in lanthanide complexes are recorded

| S. No. | Complex | Assignment | λ_{max} of Ln(III) ion CM^{-1} | λ_{max} of Ln(III) complexes CM^{-1} |
|--------|---|-------------------------|--|--|
| 1. | [Pr (SMDT) ₂ (H ₂ O) ₃ Cl ₃] | $n \rightarrow \pi^*$ | 22360, 21385, 20930, 16890 | 22130, 21190, 20800, 16710 |
| 2. | [Sm (SMDT) ₂ (H ₂ O) ₃ Cl ₃] | $\pi \rightarrow \pi^*$ | 27610, 26322, 21470 | 27430, 26140, 21250 |
| 3. | [Nd (SMDT) ₂ (H ₂ O) ₃ Cl ₃] | $n \rightarrow \pi^*$ | 19430, 17310, 16220, 12600 | 19220, 17110, 16020, 12440 |
| 4. | [Pr (SBDT) ₂ (H ₂ O) ₃ Cl ₃] | $\pi \rightarrow \pi^*$ | 22480, 22080, 20590 | 22330, 21980, 20340, 16430 |
| 5. | [Sm (SBDT) ₂ (H ₂ O) ₃ Cl ₃] | $n \rightarrow \pi^*$ | 26930, 25480, 21460 | 26740, 25310, 21251 |
| 6. | [Nd (SBDT) ₂ (H ₂ O) ₃ Cl ₃] | $\pi \rightarrow \pi^*$ | 19280, 17290, 16340, 12580, | 19140, 17120, 16120, 12310 |

Conclusion

We have successfully synthesized the Schiff base Dithiocarbazates derivatives and their lanthanide complexes with La, Nd, Pr, and Sm. All the compounds were characterized by magnetic, electronic, infrared studies and ¹H NMR. The ligand and complexes were analyzed for their antibacterial and antifungal activities. The Schiff base showed considerable activity against all the bacteria while all the complexes showed high antibacterial activity. Comparatively high activity of complexes over the corresponding ligand high inhibition shown by the complexes against the Gram negative bacteria *E. coli* is explained in terms of the effect on LPS found in the cell membrane of such bacteria. The compounds exhibited remarkable antifungal activity against both the species *Penicillium notatum* and *Aspergillus Niger*.

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