

Preparation and Characterization of Biacetyl Monoxime Hydrazone Salicylidene Complexes of Lanthanoid (III) Ions

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CSJI/2021/v30i230216

Editor(s):

(1) Prof. Pradip K. Bhowmik, University of Nevada, USA.

Reviewers:

(1) Juan Ramon Jimenez Gallego, University of Granada, Spain.

(2) Irudaya Antonat Sophia, ST. Mary's College, India.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/66449>

Original Research Article

Received 02 February 2021

Accepted 06 April 2021

Published 23 April 2021

ABSTRACT

The 1:3 complexes of lanthanoid (III) ions as Nd(III), Sm(III), Tb(III) and La(III) with biacetyl monoxime hydrazone salicylidene have been prepared and characterized by elemental analysis, IR, PMR, electronic spectra, molar conductance and magnetic properties. All these complexes of Ln(III) complexes are found to be unique in infrared and solubility to the methanol, chloroform, DMF, DMSO solvents. The results show that the biacetyl monoxime hydrazone salicylidene ligand acts as a bidentate monobasic donor, coordinating through the azomethine nitrogen and deprotonated oximino proton.

Keywords: *Lanthanoid (III); biacetyl monoxime hydrazone salicylidene; Neodymium (III) and Terbium (III).*

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1. INTRODUCTION

Lanthanoids forms a longest series of the periodic table, 4f inner transition series. Lanthanoid (III) ions, forms stable complexes with higher coordination number because their charge and size [1-5]. Coordination number 6-10 of lanthanoid ions of coordination compounds of lanthanoid are reported [6-7].

Metal complexes of Schiff base have played a major role in the development of coordination chemistry [8-11]. Due to their special electronic configuration, lanthanoid complexes have inspired many efforts on the design and synthesis as potential anticancer and antibacterial agents [12-15]. In this work, we wish to reports lanthanoid complexes such as Nd(III), Sm(III), Tb(III) and La(III) complexes with biacetyl monoxime hydrazone salicyalidene [HDMHSA].

2. MATERIALS AND METHODS

Lanthanoid (III) nitrates, such as samarium (III) nitrate, Terbium (III) nitrate, Lanthanum (III) nitrate, Neodymium (III) nitrate, were obtained from Merck and used as such. Solvents were obtained from various sources such as, S.D. Fine Chemicals, Loba Chemie and B.D.H. and were used as such or after distillation if felt necessary. ¹H-NMR spectrum in d₆ DMSO was recorded on Bruker AV300 NMR spectrometer using TMS as internal standard. The FT-IR spectrum was recorded in the range 400–4000 cm⁻¹ by KBr pellet using a 'Perkin- Elmer spectrum 100' model FT-IR spectrophotometer. The UV-Vis spectrum in methanol was recorded with a JASCO V-650 Spectrophotometer.

2.1 Preparation of HDMHSA Ligand

Biacetyl monoxime hydrazone salicyalidene ligand prepared by reported method [16].

2.2 Preparation of Ln(III) Metal Complexes

Complexes were prepared by treating corresponding lanthanoid (III) nitrate (1 mmol) in ethanol with ligand solution (3 mmol) in the same solvent. The resulting solutions were refluxed on the water bath 30 min for about 26 h (50-60°C). The resulting complexes were washed with 50% hot ethanol and separated by filtration.

3. RESULTS AND DISCUSSION

The Schiff base ligand biacetyl monoxime hydrazone salicyalidene (HDMHSA) is yellow crystalline solid, air sensitive in nature and soluble in common organic solvents. The physical and analytical data of ligand and its Ln(III) metal complexes represented in the Table 1. % Element Content, Expected (Observed) is given in Table 2.

Interaction of lanthanoid (III) nitrates with HDMHSA ligand results in the formation of complexes with general composition [LnL₃] (where Ln = Nd (III), Sm (III), Tb (III), La (III) and L = HDMHSA). The general equation for the preparation of the complexes is shown below;

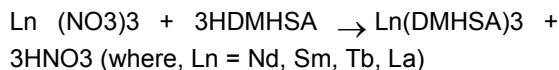


Table 1. Physical and analytical data of HDMHSA ligand and its Ln(III) complexes

Compound	Colour	%Yield	MP/DP in 0c	Molar Conductance
HDMHSA	Yellow	72.68	198	-
[Nd(DMHSA) ₃] ₃ NO ₃	Yellow	72.06	279	20.3
[Tb(DMHSA) ₃] ₃ NO ₃	Yellow	63.98	281	23.6
[La(DMHSA) ₃] ₃ NO ₃	Yellow	69.28	283	19.5
[Sm(DMHSA) ₃] ₃ NO ₃	Green	58.99	297	25.1

Table 2. % Element content, expected (Observed)

Compound	C	H	N	O	M
HDMHSA	59.84 (59.76)	6.24 (6.09)	17.87 (17.61)	13.27 (12.96)	-
[Nd(DMHSA) ₃] ₃ NO ₃	47.09 (46.54)	4.28 (4.41)	14.98 (14.55)	11.41 (11.00)	17.15 (16.70)
[Tb(DMHSA) ₃] ₃ NO ₃	46.28 (46.11)	4.21 (4.39)	14.72 (14.60)	11.22 (10.63)	18.57 (18.55)
[La(DMHSA) ₃] ₃ NO ₃	47.39 (47.21)	4.31 (4.30)	15.08 (14.61)	11.49 (11.00)	16.62 (16.17)
[Sm(DMHSA) ₃] ₃ NO ₃	46.67 (46.18)	4.25 (4.00)	14.87 (14.63)	11.33 (11.33)	17.75 (17.55)

All synthesized complexes are stable and can be stored for a long time. They are non-hygroscopic in nature and sufficiently soluble in common organic solvents. The molar conductivity values of these complexes were in the range of $19.5\text{-}25.1 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$, indicating the 1:1 electrolyte nature of these complexes [17].

Magnetic moments data shows Lanthanum (III) complex is essentially diamagnetic in nature [18], while all other complexes are paramagnetic due to presence of unpaired electrons $4f$ which are effectively shielded by $5s^2 5p^2$ electrons. This shows that $4f$ electrons do not participate in the bond formation [19].

3.1 Spectroscopic Studies

3.1.1 Electronic absorption spectra

The UV absorption spectra of the free ligand HDMHSA and its Ln(III) metal complexes were measured in DMF and displayed an absorption maxima at 298 and 233 nm with high extinction coefficient for the azomethine and oximino linkages of the free ligand HDMHSA assigned as $\pi^* \leftarrow \pi$ transition (Table 3).

The visible spectral bands of Ln (III) complex were hypersensitive to stereochemistry. This may be probably attributed to the fact that the $f-f$ transitions are very weak. The electronic spectra of the aqueous solutions of the nitrates of Tb (III), Nd (III) and Sm (III) are compared with the corresponding complexes. The data are summarized in Table 3. The data indicate that the energy of $f-f$ transitions in the complexes is slightly reduced compared to the corresponding aqua ions either because of the slight covalent interaction of the $4f$ orbitals with vacant ligand orbitals, leading to some delocalization with consequent reduction in interelectronic repulsion (correlation energy) [20] or by increased nuclear shielding of the orbitals due to a slight covalent ligand-metal electron drift. The bonding parameter ($b_{1/2}$), the covalency parameter (d) and nephelauxetic ratio (b) have been calculated using the literature procedures [21-22]. The value of (b) being less than unity [23] for the complexes, the small and positive values of the bonding parameter $b_{1/2}$ and Sinha's parameter $d\%$ suggest the possibility of a partial covalent nature of the metal-ligand bond [21,24]. Based on electronic spectral studies, a coordination number of six around the metal ion is suggested [25-26].

3.1.2 The PMR spectra of ligand HDMHSA and its La (III) metal complex

PMR spectra were recorded using d_6 DMSO as solvent and TMS was used as an internal standard. Spectral data of HDMHSA reveals two singlet peaks at 11.80 and 11.50 δ . The intensity of the peaks suggests that these are due to single deshielded protons and assigned as oximino and phenolic protons respectively. The peak observed in free ligand HDMHSA at 11.80 δ is absent in all prepared La (III) metal complex, suggested that oximino group deprotonated in complex formation [27-28]. Multiplet observed at in the region 7.10-7.50 δ (4H), 1, 2- disubstituted benzene ring and free methyl protons 2.10 δ (6H). Another singlet peak reveals at 9.08 δ (1H) assigned as methane ($-\text{CH}=\text{}$) group of HDMHSA. All these group unchangeable in La (III) metal complex, indicated that their non-involvement in complex formation and also suggest monobasic character of HDMHSA ligand [29]. The information is tabulated in Table 4.

3.1.3 FT (IR) spectra ligand HDMHSA and its Ln(III) metal complexes

The important IR stretching frequencies are given in Table 5. The spectrum of HDMHSA ligand has broad absorption band at 3500 cm^{-1} which assigned as oximino $-\text{OH}$ is disappeared in metal complexes, indicated successfully complex formation through deprotonation. In case of complexes a notable peak at 1604 cm^{-1} of HDMHSA shows positive shift and appears in the range of $[1644\text{-}1658 \text{ cm}^{-1}]$, this is attributed to azomethine ($>\text{C}=\text{NN}-$) [30-31] stretching and its shift indicates that coordination of ligand in complexes through azomethine nitrogen atom [32-33] Oximino group ($>\text{C}=\text{NO}-$) observed at 1558 cm^{-1} in HDMHSA ligand is shifted to higher frequencies ($1558\text{-}1593 \text{ cm}^{-1}$) indicates that oximino nitrogen involve in complex formation [33]. FT (IR) spectral data of ligand HDMHSA and its Ln(III) metal complexes indicated that ligand HDMHSA coordinated to Ln(III) ions through nitrogen atoms only [LnN_6]. Some new medium to weak bands were also observed in the range ($507\text{-}691 \text{ cm}^{-1}$) in case of complexes of HDMHSA ligand has no absorption. These new medium to weak bands are assigned as; ν (Ln-N) or/and ν (Ln \rightarrow N) modes observed for various Ln(III) complexes. The partial IR data for HDMHSA ligand and their corresponding complexes are given in Table 5.

3.2 Structure of Complexes

The preferred coordination number of Ln(III) metal ion is 7. This coordination number depends upon the nature of the ligand. Conductance and molecular weight data show present of nitrate anions inside the coordination sphere in the

complexes. IR spectral data reveal that ligand is coordinated to metal ions nitrogen atoms of oximino and azomethine linkages in all the complexes studied. Hence, coordination number 7 is suggested for metal ion in these lanthanoid complexes [34-37]. The possible structure of the complexes is given Fig. 1.

Table 3. UV-Visible spectral data of HDMHSA ligand and its Ln(III) metal complexes

Compound	λ nm	ϵ (dm ³ /mol/cm)	Transition
HDMHSA	298	7132	$\pi^* \leftarrow \pi$
	233	4595	$\pi^* \leftarrow \pi$
[Nd(DMHSA)3]	816	118	4F9/2 \leftarrow 4H5/2 $\beta_{ave} = 0.9937$
	754	259	4P13/2 \leftarrow 4H5/2 $b_{1/2} = 0.0390$
	587	956	4P9/2 \leftarrow 4H5/2 $\delta\% = 0.6283$
	520	5659	4P7/2 \leftarrow 4H5/2 $\eta = 0.0031$
[Tb(DMHSA)3]	599	1077	7F4 \leftarrow 5D4
	545	2948	7F5 \leftarrow 5D4
	480	7650	7F6 \leftarrow 5D4
[La(DMHSA)3]	392	110	MLCT
	243	13541	MLCT
[Sm(DMHSA)3]	740	89	4F9/2 \leftarrow 4H5/2 $\beta_{ave} = 0.9941$
	466	4952	4P13/2 \leftarrow 4H5/2 $b_{1/2} = 0.03773$
	437	5368	6P7/2 \leftarrow 4H5/2 $\delta\% = 0.5911$
	405	6671	4P9/2 \leftarrow 4H5/2 $\eta = 0.0029$

Table 4. PMR spectrum of HDMHSA and its metal complexes in d6 DMSO

Compound	Oximino - OH	Phenolic - OH	-CH=	Phenyl Ring	-CH3
HDMHSA	11.80	11.50	9.00	7.10-7.50	2.10
[La(DMHSA)3]	-	11.20	9.00	7.20-7.40	2.10

Table 5. IR spectral bands of the ligand (HDMHSA) and its metal complexes (cm⁻¹)

Assignments	HDMHSA	Nd(III)	Tb(III)	La(III)	Sm(III)
vOH Oximino	3500	-	-	-	-
Phenolic -OH	3131	3389	3314	3380	3385
vC=C Ar.	3046	3055	3047	3053	3155
vC=NN	1604	1645	1658	1644	1646
vC=NO	1558	1593	1588	1589	1544
vN-N	974	1008	1064	1008	1014
vN \rightarrow O	---	1212	1229	1210	1228
vM-N	---	547	593	569	606
vM \rightarrow N	---	509	507	541	523

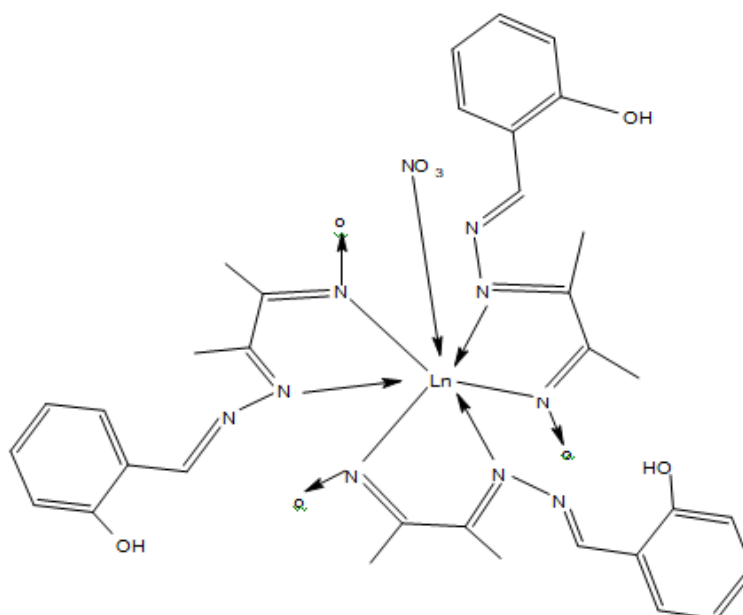


Fig. 1. Structure of metal complexes of HDMHSA ligand

4. CONCLUSION

The results shows that the Biacetyl monoxime hydrazone salicyalidene ligand acts as a bidentate monobasic donor, coordinating through the azomethine nitrogen and deprotonated oximino proton.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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