

Research and Reviews: Journal of Chemistry

The Absorption Spectra of Some Lanthanide (III) Ions

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Short Communication

Received: 18/02/2013

Revised: 13/03/2013

Accepted: 15/04/2013

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Keywords: spectra, lanthanide (III), absorption.

ABSTRACT

Complexes of some lanthanides such as Pr (Praseodymium), Nd (Neodymium), Sm (Samarium) and Tb (Terbium) gives absorption bands in the visible region of the spectrum. The Pr(III), Nd(III), Sm(III) and Tb(III) ions have four, ten, seven and two peaks respectively in their absorption bands. On the other hand Gd (Gadolinium) gives absorption band in UV- region and it has two peaks in its absorption band.

INTRODUCTION

Lanthanide (III) ion is a subject of increasing interest in bioinorganic, biomedical, pharmaceutical and coordination chemistry. The coordination chemistry of lanthanide (III) ions with drugs having amide group, has been widely investigated over last two decades because of their medicinal and biochemical applications. They used as diagnostic tools in biomedical analysis as MRI contrast agents [1, 2]. Lanthanide complexes have been found to exhibit anticancer and fungicidal properties [3].

The 4f-electrons of lanthanides yield two types of transitions such as f-f and f-d transitions. The f-f transitions which give rise to sharp, narrow bands of comparatively weak intensities which are Laporte forbidden, whereas allowed f-d transitions are relatively broad and intense. The observed spectral transitions of the lanthanide ions are f-f transitions. Since the 4f-sub-shell of Ln(III) ions is well shielded by the filled 5s and 5p sub-shells, the energy levels of the 4f-electrons are only little influenced by the environment of Ln(III) ion. The intensity of f-f transition is weak, because these transitions are Laporte forbidden. Relaxation of this selection rule is very less effective than that of d-d transitions. This is because of the weak crystal field interaction.

EXPERIMENTAL

The Ln(III) [Pr(III), Nd(III), Sm(III), Tb(III) and Gd(III)] perchlorate were prepared by heating their oxides with perchloric acid and evaporating off the excess perchloric acid [4]. All glassware's were first washed with chromic acid solution, thoroughly washed with water, rinsed with distilled water, ethanol, acetone, air dried and finally stored in a desiccators. The Ln(III) perchlorates and ligands (Acetaminophen and Indomethacin) were dissolved separately in ethanol and then mixed. The reaction mixture was refluxed with constant stirring for 2h and the solution was concentrated to a viscous mass which was washed many times with distilled water and then ethanol. Finally this viscous mass dried over P₄O₁₀ in desiccator.

RESULT AND DISCUSSION

The absorption bands of Pr(III), Nd(III), Sm(III), Tb(III) and Gd(III) complexes in the UV- visible and near IR region appear due to transitions from the ground levels 3H_4 , $^4I_{9/2}$, $^6H_{5/2}$, 7F_6 and $^8S_{7/2}$ respectively to the excited J-levels of $4f^n$ -configurations. In all these cases nephelauxetic effect or red shift is observed. In all complexes increase in the intensity of the bands have been observed. The small values of bonding parameter ($b^{1/2}$) observed in lanthanide complexes as compared to transition metals, suggest that the very less involvement of $4f$ -orbitals [5]. The ligands which show higher values of $b^{1/2}$ in comparison to other ligands have more covalent than the latter ones and stronger ligands in a nephelauxetic sense [6-17]. Some important data of hypersensitive transitions have been given in tables. For Pr(III), Nd(III), Tb(III) and Gd(III) the hypersensitive transitions are -

For Pr(III)..... $^3H_4 \rightarrow ^3P_2$
 For Nd(III)..... $^4I_{9/2} \rightarrow ^4G_{5/2}$
 For Sm(III)..... $^6H_{5/2} \rightarrow ^6P_{3/2}$
 For Tb(III)..... $^7F_6 \rightarrow ^5D_3$
 For Gd(III)..... $^8S_{7/2} \rightarrow ^6D_{5/2}$

Some Spectral Parameters

Ln(III)	Ligand	β	$b^{1/2}$	$\delta\%$	η
Pr(III)	Acetaminophen	0.998969753	0.022696332	0.10313095	0.000515522
	Indomethacin	0.998078173	0.030998605	0.192552753	0.000962301
Nd(III)	Acetaminophen	0.980053	0.099867412	2.035298091	0.01012523
	Indomethacin	0.9790427	0.102365277	2.140591008	0.010646283
Sm(III)	Acetaminophen	0.995186107	0.049060641	0.483717866	0.002415672
	Indomethacin	0.997046662	0.038427451	0.296208604	0.001479948
Tb(III)	Acetaminophen	0.98712	0.080249611	1.3048059	0.006502886
	Indomethacin	0.98812	0.077071395	1.202283124	0.005993455
Gd(III)	Acetaminophen	0.98615	0.083216585	1.404451655	0.006997774
	Indomethacin	0.98426	0.08871302	1.599170951	0.007964141

CONCLUSION

Some complexes of five Ln(III) ions have been prepared with ligands such as Acetaminophen and Indomethacin in ethanolic medium. Solution spectra of each complex have been recorded in UV-Visible and near IR range. By the help of some spectral data, some conclusions have made. The values of various parameters such as nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha's covalency parameter ($\delta\%$) and Covalency angular overlap parameter (η) reveals that the involvement of $4f$ -orbital has negligible for lanthanide complexes as compared to transition metals.

REFERENCES

- Picard C, Geum N and Nasso I. A dual lanthanide probe suitable for optical Tb(III) luminescence and magnetic resonance imaging (Gd^{3+} relaxometry). *Bioorg Med Chem Lett*. 2006;16(20):5309-5312.
- Aime S, Crich SG, Gianolio E, Giovenzana GB, Tei L, Terreno E. High sensitivity lanthanide(III) based probes for MR-medical imaging. *Coord Chem Rev*. 2006;250(11-12):1562-1579.
- Sharma RC, Thripathi SP, Kanna KS, Sharma RS. Biologically active mixed-ligand complexes of rare earths. *Curr Sci*.1981; 50(17):748-750.
- Chakraborty I. Synthesis and Characterization of Some $4f$ -Metal Ion Complexes of 4[N-(3'-Nitrobenzalidene)Amino] Antipyrine Thiosemicarbazone. *Asian J Chem*. 2003;15(2):813-820.
- Solanki AK, Bhandari AM. Indole 3-acetates and indole 3-butyrate of lanthanides. *J Inorg Nucl Chem*. 1979;41:1311-1314.
- Iftikhar K. Hypersensitivity in the $4f$ - $4f$ absorption spectra of lanthanide(III) complexes. *Inorg Chim Acta*. 1987;129:261-264.
- Jorgensen CK. Absorption spectra and chemical bonding in complexes. Pergamon Press, (1962).
- Jorgensen CK. Orbitals in atoms and molecules. Academic press, (1962).
- Singh M, Joshi GK, Vaishnav PP and Misra SN. *Ind J Pure Appl Phys*. 1979;17:554.
- Popli A, Jain R, Bhojak N and Soni K P. SPECTRAL AND Thermodynamical Studies on Doped Pr(III) Ions in Saturated Alcoholic Solutions of Various Semicarbazones Derived from Carbonyl Compounds. *Oriental J Chem*. 2004;20(1):197.

11. Bhojak N, Jain R, Lavi K, Soni K P and Tater PC. Micellar Investigations on Hypersensitive Transitions for Doped Pr(III) Ion in Saturated Alcoholic Solution of Semicarbazones Asian J Chem. 2005;17(4):2765.
12. Bhojak N, Jain R and Soni KP. Characterization of Some PR (III) Complexes of Semicarbazones on the Basis of Electronic Spectral Parameters. Oriental J Chem. 2005;21(2):361.
13. Jain R and Bhojak N. Acta Ciencia Indica. 32(3)(2006)283.
14. Soni K P, Jain R, Popli A, Tater PC, Bhojak N. Electronic Spectral Study and Thermodynamic Characterization of Doped Nd(III) Ions in various Semicarbazones. Asian J Chem. 2005;17:964-968.
15. Popli A, Jain R, Tater P C, Bhojak N, Soni KP. Int J Chem Sci. 2004;2(2):211.
16. Mehta SC, Bhojak N, Jain R. Acta Ciencia Indica. 2006;32C:2.
17. Bhojak N and Singh B. Microwave Assisted Synthesis, Spectral and Antibacterial Investigations on Complexes of Mn (II) with Amide Containing Ligands. Rasayan J Chem. 2008;1(1):105-109.