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Study on X-Ray Diffraction and Biological Activity of some Rear Earth Metal Complexes on the Basis of Mixed Ligands

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Abstract

Studies on the Powder x-ray diffraction parameter of metal complexes such as La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) has been synthesized by 4-methoxyplenylmaine and salicylaldehyde, o-vanillin having equiamolar ratio of 1:1:1(metal : ligand : ligand)in the same solvent. The complexes were different physico-chemical properties such as different colour, different melting points and different crystal systems. The x-ray diffraction studies are orthorhombic, monoclinic, tetragonal crystal structure has been proposed for the mixed (L^1 and L^2) ligands and their lanthanide (III) complexes. The x-ray diffraction data suggest that monoclinic crystal system for La(III), Ce(III) complexes and orthorhombic crystal system for Pr(III), Nd(III), Gd(III), Dy(III) and Tb(III) complexes and other were tetrahedral crystal system for Sm(III) complex. The x-ray diffraction data were also being used for the determination of various parameter, unit cell volume and miller indices values (h k l). The screened for their antibacterial activity against bacterium of Staphylococcus aurious, B.subtilis (Gram-positive) and Aspergillus Niger and Fusarium oxysporum (Gram- negative). The result indicated that the complexes exhibited good antibacterial, antifungal active than that of free ligands.

Keywords: Lanthanide (III) complexes, x-ray diffraction studies, antibacterial and antifungal activity.

Introduction

Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields, i.e. biological, inorganic and analytical chemistry¹⁻⁵. Powder x-ray diffraction studies on the lanthanide (III) complexes of an instrumental technique that used to identify crystalline material⁶. X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined⁷.

In this work, we wish to report lanthanide (III) complexes scanned in the range of 5-65° at wavelength 1.540598Å. The diffractogram and associated data depict the 20 value of each peak, relative intensity and inter-planar spacing (d-values), but the systematic study on determination of mixed (L^1 and L^2) ligands and their lanthanide (III) complexes i.e. La (III), Ce (III), Pr (III), Nd (III), Sm (III), Gd (III), Tb (III) and Dy (III). A diffraction pattern plots intensity against the angle of the detector 2θ . In a diffraction pattern, the peak position depends upon the wavelength. X-ray diffractometer with a radiation source of CuK α was used⁸⁻⁹. The objective of x-ray diffraction measurement is to determine the dimensions and shape of unit cell and to identify the detailed structure of the molecule. To achieve this objective, we must be able to express mathematically the nature of the measured interference pattern in terms of the position of the various atoms within the $crystal^{10}$.

Material and Methods

The lanthanide (III) nitrates obtained from Rare Earth Ltd. (India) were used without further purification. Salicylaldehyde, o-vanillin and p-anisidine was obtained from Alfa Acer Chemicals and solvents were obtained from Aldrich Chemical Company. The powders XRD were characterized by recorded on Perkin Elmer TA/SDT-2960 and Philips 3701, respectively.

Synthesis of Schiff base ligands and Metal complexes: The syntheses of Schiff base ligand $(L^1 \text{ and } L^2)$ were prepared by modification of reported method¹¹. In 50 ml solution of ethanol contain 0.001mol (0.122g) of salicylaldehyde, 0.001mol (0.152 g) of o-vanillin and 0.001mol (0.123 g) of 4-methoxyphenylamine were stirred for 4 hours at room temperature at show in scheme-I and scheme-II. The two different color was obtained by gray (L^1) and orange (L^2) . The ligands are collected, filtered by using Buckner funnel, washed with ethanol and dried in the desiccators. Purity of the ligands was checked by TLC plates. The product was purification and recrystallization from a hot ethanol. Yield obtained by 80% L^1 and 78% L^2 .

Synthesis of lanthanide (III) complexes the mixture of hot ethanolic solution (25ml) of ligands L^1 and L^2 in (0.01mol) simultaneously and lanthanide (III) nitrate (0.01mol) was added under constant stirring for 3 hours at room temperature. The precipitated complexes were filtered off washed with ethanol, diethyl ether and dried under vacuum over anhydrous calcium chloride (CaCl₂). Decomposition point of lanthanide (III) complexes was greater than 200 0 C.



Scheme - II. Synthesis of ligands ligand (L^2)

Results and Discussion

X-ray diffraction study: A good quality x-ray diffractograms of chelate polymers indicates semicrystallinity as well as amorphous nature of complexes. All the reflection has been indexed for h, k, l values using methods reported in the literature¹². On the comparative study on powder x-ray diffraction of lanthanide (III) complexes of La (III), Ce (III), Pr (III), Nd (III), Sm (III), Gd (III), Dy (III) and Tb (III) complexes were mixed (L^1 and L^2) Ligands scanned in the range of 5-65° at wavelength 1.540598Å. The diffractogram and associated data depict the 2θ value each peak, relative intensity and inter-planar spacing (d-values) and lattice constants a, b, and c for each unit cell parameter show in table-1-3, figure-1-2. The x-ray diffraction pattern of these complexes with respect to major peak having relative intensity greater than 10% has been indexed by computer $\operatorname{program}^{13}$. The above indexing method also yields miller indices (h k l), unit cell parameters and unit cell volume; calculate the unit cell volume for each peak in following equation. The diffractogram of La (III) complex of mixed ligands had 14 reflections with maxima at $2\theta = 41.29$ corresponding to d value 2.18Å. The diffractogram of Ce (III) complex of mixed ligands had 12 reflections with maxima at

 2θ =47.28 corresponding to d value 1.92Å. Miller indices (h k l), unit cell parameters and unit cell volume. In x-ray diffractogram figure show percentage of intensity vs. 2 θ values in systematic arrangement of metal complexes. The experimental density values of the complexes were determined by using specific gravity method¹⁴. They'd' values of reflections were obtained using Bragg's equation.

$n \Lambda = 2 dsin \theta$

To calculate the unit cell volume of La (III) and Ce (III) complexes for monoclinic crystal system by the following equation was used.

$V = abcsin \beta$

To calculate the unit cell volume of Pr (III), Nd (III), Gd (III), Tb (III) and Dy (III) complexes for orthorhombic crystal system by the following equation was used. V = abc

To calculate the unit cell volume of Sm (III) complex for tetragonal crystal system by the following equation was used. $V = a^2c=$

| Unit cell of compounds | Lattice Constant a (Å) b (Å) c (Å) | | Unit cell Volume V (Å ³) | Edge length | Inter axial angle | Crystal system | 20 | d- value (Å) | |
|---------------------------|--|-------|---|----------------|-------------------|-----------------------------------|--------------|--------------------|------|
| La (III) | 15.29 | 9.82 | 8.05 | 702.44 | $a \neq b \neq c$ | $\alpha = \beta = 90 \neq \gamma$ | monoclinic | 41.29 | 2.18 |
| Ce (III) | 10.39 | 10.35 | 7.53 | 471.10 | $a \neq b \neq c$ | $\alpha = \beta = 90 \neq \gamma$ | monoclinic | 47.28 | 1.92 |
| Pr (III) | 17.52 | 14.56 | 5.40 | 380.31 | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90$ | orthorhombic | 43.12 | 2.09 |
| Nd (III) | 15.82 | 11.52 | 8.52 | 535.73 | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90$ | orthorhombic | 46.17 | 1.96 |
| Sm(III) | 9.124 | 9.124 | 9.35 | 778.54 | $A = b \neq c$ | $\alpha = \beta = \gamma = 90$ | tetragonal | 44.10 | 2.05 |
| Gd (III) | 17.26 | 14.32 | 10.2 | 533.71 | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90$ | orthorhombic | 34.02 | 2.61 |
| Tb (III) | 8.245 | 9.458 | 7.52 | 586.69 | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90$ | orthorhombic | 49.00 | 1.83 |
| Dy (III) | 9.124 | 9.123 | 7.75 | 645.70 | $a \neq b \neq c$ | $\alpha = \beta = \gamma = 90$ | orthorhombic | 50.89 | 1.79 |

 Table-1

 Lattice constant, Unit cell Volume, Crystal system, Inter-planar spacing of metal

| h | k | | 20 | 20 d | | d | Relative Intensity | |
|---|---|---|----------|------------|----------|------------|--------------------|--|
| | | I | Observed | Calculated | Observed | Calculated | (%) | |
| 1 | 0 | 0 | 9.488 | 9.504 | 9.314 | 9.298 | 100 | |
| 1 | 0 | 0 | 10.137 | 9.504 | 8.719 | 9.298 | 3.38 | |
| 0 | 0 | 1 | 12.491 | 12.541 | 7.080 | 7.052 | 45.72 | |
| 1 | 1 | 0 | 13.530 | 13.101 | 6.539 | 6.752 | 35.39 | |
| 0 | 1 | 1 | 15.210 | 15.456 | 5.820 | 5.728 | 9.15 | |
| 1 | 0 | 1 | 16.272 | 15.759 | 5.443 | 5.618 | 11.45 | |

 Table-2

 Millar indices and interplanar distances of La (III) complex



X-ray diffraction data of $[LaL^1 and L^2(H_2O)_2NO_3]$ complexes

Crystal system: Lattice Type: Monoclinic, Lattice Parameter: a=15.2982, b=9.8211, c=8.0524Å, Volume of unit cell V=702.4431(Å)³.

 Millar indices and interplanar distances of Ce (III) complex

| п | Ŀ | l | 20 | 20 | d | d | Relative | |
|---|---|---|----------|------------|----------|------------|---------------|--|
| п | K | | Observed | Calculated | Observed | Calculated | Intensity (%) | |
| 1 | 1 | 0 | 12.495 | 13.021 | 7.078 | 6.793 | 46.50 | |
| 1 | 1 | 0 | 13.553 | 13.021 | 6.528 | 6.793 | 34.33 | |
| 1 | 0 | 1 | 16.290 | 16.380 | 5.436 | 5.407 | 10.14 | |
| 0 | 2 | 0 | 17.138 | 17.114 | 5.169 | 5.177 | 14.98 | |
| 1 | 1 | 1 | 17.979 | 18.496 | 4.929 | 4.793 | 16.61 | |
| 2 | 0 | 1 | 19.222 | 19.330 | 4.613 | 4.588 | 4.77 | |
| 1 | 2 | 0 | 20.043 | 19.766 | 4.426 | 4.487 | 1.75 | |
| 2 | 1 | 1 | 21.166 | 21.163 | 4.194 | 4.194 | 32.16 | |
| 2 | 1 | 0 | 22.193 | 21.509 | 4.002 | 4.128 | 22.02 | |
| 1 | 2 | 1 | 23.099 | 23.775 | 3.847 | 3.739 | 1.60 | |



Crystal system: Lattice Type: Monoclinic, Lattice Parameter: a=10.3954, b=10.3541, c=7.5384Å Volume of unit cell V=471.1053(Å)³.

Antimicrobial and Antifungal activity: The antibacterial activity of mixed $(L^1 \text{ and } L^2)$ ligand and lanthanide (III) complexes was tested in vitro against bacteria by using paper disc plate method¹⁵. The ligands and Lanthanide (III) complexes have been tested for their antibacterial activity against Staphylococcus aureus and Bacillus substilis and antifungal activity Aspergillus Niger and Fusarium Oxysporum at the same concentration 250 ppm and 500 ppm show in table-4. The antibacterial activity result revealed that the ligands and complexes show good activity. The ligands and metal complexes such as La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) complexes shows highly active as compared to ligands and standard drugs with inhibition zone of 13-17 mm, 13-18 mm, 13-17 mm, 11-15 mm, 12-15 mm, 15-16 mm, 11-17 mm respectively. The Tb (III) complexes have exhibited good activity with the inhibition zone of 14-21mm when compared to the standard drugs ciprofloxacin and ligands. The results show antibacterial activity of Schiff base ligands and its metal complexes of following increasing order Tb(III), > $Gd(III) > L^{1}$ > Ce(III) > La(III) \approx Pr(III) > Sm(III) > Dy (III) > L².

The antifungal activity result revealed that the mixed ligands and its La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) complexes have exhibition shows highly active with the inhibition zone of 16-19 mm, 22-24 mm, 20-24 mm, 14-20 mm, 16-26 mm, 22-24 mm, 14-24 mm, 15-23 mm as compared to the standard drug ciprofloxacin. The antifungal activity of Schiff base ligand and the mixed (L¹ and L²) ligand complexes is following order Ce (III) \approx Gd (III) >Pr (III) > Sm (III) > La (III) >Dy (III) > Tb (III) > Nd (III) > L² > L¹. From the result obtained it clearly indicates that the antibacterial activity of metal salts is high. From table-4 it is found that the inhibition by metal complexes is higher than that of a free ligand and results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes¹⁶. The corresponding metal salts against the same organism under experimental conditions. The metals salt used for the synthesis of complexes exhibit negligibly high antimicrobial activity¹⁷⁻¹⁸. The comparative study of all compounds both ligands and its all metal complexes shows higher antifungal activity against *Aspergillus Niger* at 500 ppm and at 250 ppm against *Fusarium Oxysporum*.

Conclusion

The synthesis of mixed ligand metal complexes like La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Tb(III) complexes with N and O donor Schiff base ligand derived from 4-methoxyphenylanaline,salicylaldehyde and o-vanilline were synthesized. A comparative study of crystal system, unit cell volume, edge length and Miller indices of powder XRD. The powder XRD study suggested that orthorhombic crystal system for Pr(III), Nd(III), Gd(III), Dy(III), Tb(III) complexes and monoclinic crystal system for La(III), Ce(III) complexes and tetragonal crystal system for Sm(III) complex. The mixed ligands and their metal complexes of antibacterial and antifungal activity are highly active compared to free ligand.

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| Table-4 | |
|---------|--|
|---------|--|

| | Tuble 4 | | |
|-----------------------------|---------------------------------------|-----------------|---|
| Antibacterial and Antifunga | al activity of ligands and Lanthanide | e (III) complex | xes [Diameter of inhibition Zone in (mm)] |

| | Antibacterial activity | | | | Antifungal activity | | | |
|--------------------------------------|------------------------|---------|--------------------|---------|---------------------|---------|--------------------|---------|
| Compounds | Staphylococcusaureus | | Bacillus Substilis | | Aspergillus Niger | | Fusarium Oxysporum | |
| | 250 ppm | 500 ppm | 250 ppm | 500 ppm | 250 ppm | 500 ppm | 250 ppm | 500 ppm |
| $C_{14}H_{13}NO_2(L^1)$ | nil | 14 | nil | 16 | nil | 11 | 16 | 19 |
| $C_{15}H_{15}NO_3(L^2)$ | nil | 16 | nil | 17 | 16 | 16 | 15 | 18 |
| $[La(L^1 L^2)(H_2 O)_2 NO_3]$ | 17 | 16 | 17 | 13 | 16 | 19 | 19 | nil |
| $[Ce(L^{1}L^{2})(H_{2}O)_{2}NO_{3}]$ | 13 | 18 | 14 | 15 | 24 | 22 | 22 | nil |
| $[\Pr(L^1 L^2)(H_2 O)_2 NO_3]$ | 15 | 17 | nil | 13 | 20 | 24 | 24 | nil |
| $[Nd(L^1L^2)(H_2O)_2NO_3]$ | 14 | 14 | 11 | 15 | 18 | 20 | 19 | 14 |
| $[Sm(L^1L^2)(H_2O)_2NO_3]$ | 12 | 16 | 14 | 15 | 21 | 16 | 26 | 19 |
| $[Gd(L^1L^2)(H_2O)_2NO_3]$ | 16 | 15 | nil | 16 | 22 | 22 | 24 | 22 |
| $[Tb(L^{1}L^{2})(H_{2}O)2NO_{3}]$ | 11 | 16 | 17 | 15 | 24 | 14 | 17 | nil |
| $[Dy(L^1L^2)(H_2O)_2NO_3]$ | 14 | 14 | 21 | 15 | 23 | 18 | 15 | Nil |
| Ciprofloxin | 29 | nil | 27 | nil | 30 | 21 | 32 | nil |

Reference

- 1. Cimerman Z, Miljanic S and Galic N, Croatica *Chemical* Acta., 73(1), 81-95 (2000)
- Singh P, Goel R.L. and Singh B.P., J Indian Chem. Soc., 52, 958-959 (1975)
- **3.** Perry BF, Geezer AE, Miles RJ, Smith BW, Miller J and Nascimento MG, Microbois., **45**, 181 (**1988**)
- 4. Elmali A, Kabak M and Elerman Y.J., *Mol. Strut*, 477, 151 (1999)
- 5. Patel P.R., Thaker B.T. and Zele S, *Indian J Chem.*, **38**A, 563-566 (**1999**)
- 6. Klop E.A. and Lammers M., *Polymers*, **39**, 5987 (1998)
- 7. Cullity B.P., Elements of X-ray diffraction, Addison: Wesley Inc., (1978)
- 8. Bish DL and Post JE, Editors Modern Powder Diffraction, Reviews in Mineralogy, v. 20. Mineralogical Society of America (1990)
- **9.** Wall B., Driscoll C., Strong J. and Fisher E., The Suitability of Different Preparations of Thermo luminescent Lithium Borate for Medical Dosimetry, *Physical Medical biology*, 1023-1034, (**1982**)
- **10.** Azaroff and Burger, The Powder Method, McGraw Hill London (**1958**)
- Munde A.S, Jagdale A.N, Jadhav S.M. and Chondhekar T.K; *Journal of the Korean Chemical society.*, 53, 407 (2009)
- 12. Saxena N., Juneja H.D. and Munshi K.N., *J. Indian Chem. Soc.*, **70**, 943 (1993)
- **13.** Carvajal J.R., Roisnel T. and Winplotr A, Graphic Tool for Powder Diffraction, Laboratories Leon brillouin (ceal / enrs) 91191 gif suryvette cedex, France, (**2004**)
- 14. Bhattacharya K.C., An Elementary Physics for Indian School, The Indian Press Ltd. Allahabad, 105 (1934)

- **15.** Munde A.S., Jagdale A.N., Jadhav S.M., Chondhekar T.K., *J. Serb. Chem. Soc.*, **75(3)**, 349 (**2010**)
- Madhure A.K. and Aswar A.S., Am. J. Pharm. Tech. Res., 3(6), 462-484 (2013)
- Singh P., Geol R.L. and Singh B.P., *Indian J. Chem.* Soc., 52, 958 (1975)
- Patel P.R., Thaker B.T. and Zele S., *Indian J. Chem.*, 38A, 563, (1999)
- **19.** Prabhumirashi L.S. and Khoje J.K., *Indian J. Chem.*, **43**a, 299 (**2004**)
- 20. Nakamura T., Niwa K., Fujiwara M. and Matsushita T., *Chem. Lett.*, 1067 (1999)
- **21.** Choi Y.K., Kim W.S., Chung K.I., Chung M.W. and Nam H.P., *Microchem. J.*, **65**, 3, (**2000**)
- 22. Yoon H., Wagler T.R., O'Connor K.J. and Burrows C.J., J. Am. Chem. Soc., 122, 4568 (1990)
- 23. Pan N.T.S., Brown D.H., Adams H., Spey S.E. and Styring P., *J. Chem. Soc.*, Dalton Trans., 9, 1348 (2004)
- 24. Hussain R. and Juneja H.D., Int. J. Chem. Sci., 7(2), 632-638 (2009)
- 25. Nagasudha B., Yellasubbaiah N. and Bharathi K., *Int. J. Chem. Sci.*, **13**(2), 837-848 (2015)
- 26. Ubani O.C., Oforka N.C., Ngochindo R.I. and Odokuma L.O., Synthesis, Characterization and Antimicrobial Studies of Cinnamaldehydebenzylamine Schiff base Metal ion Complexes *Res. J. of Chem. Sci.*, Vol. 5(3), 14-22, March (2015)
- Malik GM1, Patel BA1 and Patel NC, Synthesis, Spectroscopic and Physico-chemical Characterization of Cu (II), Ni(II), Co(II) and Mn(II) Coordination compounds with 4-methoxy salycylaldehyde-4-(2'carboxy-5'-sulphophenyl)-3-thiosemi-carbazone (4-MSCST)., *Res. J. of Chem. Sci.*, Vol. 5(3), 49-52 (2015)