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Synthesis and characterization of Ln(III) complexes with catechol hydroxamic acid

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Abstract
In this paper, the organic ligand hydroxamic acid derivative *N*-hydroxy-3,4-dimethoxy-*N*-methylnaphthalene-1-carbothioamide was prepared. Thereafter complexation of the newly synthesized ligand with lanthanoids (III) metal has been completed. The complexation of ligand *N*-hydroxy-3,4-dimethoxy-*N*-methylnaphthalene-1-carbothioamide (derivative of hydroxamic acid) with La(III) ion under pH control in (1:3) Molar ratios (M:L) led to the formation of solid complexes which gave analytical data suggested the (1:3) based on elemental analysis, IR and ^{1}HNMR techniques.

Keywords: Hydroxamic acid, catechol, Lanthanoids, IR, NMR

Introduction
Hydroxamic acids are weak organic acids and have a wide range variety of applications. They are used as inhibitors for copper corrosion, antifungal agents, food additives and in nuclear fuel processing. Hydroxamic acids are also important as gravimetric colourimetric reagents and strong chelating [1-5].
In monohydroxamic acid metal complexes, the metal atom is coordinated through the oxygen atoms [2]. Many different types of hydroxamic acids have been synthesized by adopting Blatt's method reported [6] that, in their reaction with transition metal ions, the N-phenylbenzohydroxamic acids may play two different roles depending on the oxidation state of the metal ion. This is well manifested in their reaction with rhodium(I) and rhodium(III). For rhodium(I) the N-phenylbenzohydroxamic acids serve as oxidizing agents, they oxidize rhodium(I) to rhodium(III), and at the same time themselves are reduced to the corresponding amides. With rhodium(III), however, the same hydroxamic acids only undergo complexation in the usual fashion.

Experimental
All materials used for synthesis of N-substituted hydroxamic acids and complexes are of analytical reagent. A digital Philips PW9404 pH meter was calibrated by means of standard buffer solutions (BDH). The IR spectra of the studied complexes were recorded by Perkin-Elmer 580 spectrophotometer using KBr discs. Micro analysis of C, H and N wee recorded by Perkin-Elmer Model 2400 elemental analyzer. ^{1}HNMR spectra were run on Jool JNL-GX-90 FTNMR spectrometer using CDCl3, CD3OD as solvent and TMS as the reference standard.

Preparation of Ligand
The ligand *catechol*-1-carbothioamide (derivative of hydroxamic acid) was prepared by adding catechol (0.1mol) with stirring cooled mixture of KOH (11.2gm, 0.2mol) and *catechol hydroxamic acid* dissolved in methanol (250ml), the resulting mixture was stirred for 5hours. The reaction mixture was extracted with ether and the ethereal layer was evaporated under reduced pressure. The product obtained in the form of shiny white crystals, which recrystallized from chloroform, the melting point is (61-62)C=O.

Preparation of metal complexes
(a) La(L)3.6H2O
Preparation of Lanthanum (III) complexes:
(a (3.18gm, 0.02mol) of octanohydroxamic acid in (50ml) ethanol was added with stirring to (4.33gm, 0.01mol) of $La(NO_3)3.6H_2O$ in (50ml)ethanol, the pH was adjusted between 2.27 to 5.68 using 10% sodium hydroxide solution, white precipitate was allowed to cool then filtered off under nitrogen and dried over calcium chloride.

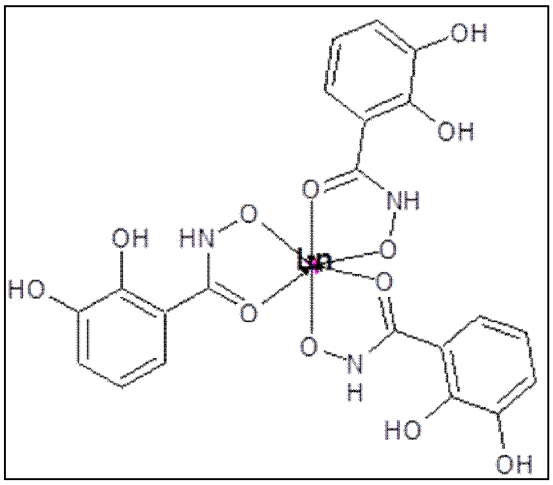
(b) La [(L_3).2OH].3H2O and La [(L_3).2OH].3H2O
The complexes were prepared as discussed before, the pH had adjusted between 3.71 to 6.67 and .48 to 9.38 respectively.

(c) La [(L_3).2OH].6 H2O
0.02mol of catechol hydroxamic acid was (5.39) added to (4.3302 gm, 0.01mol) of La (NO3)3.6H2O in (50ml) ethanol, then the mixture was stirred for one hour. The pH had been adjusted between 1.55 to 9.33, a dark yellow precipitate was obtained.

Results and Discussion
The IR spectra of catechol hydroximic acid ligand show sharp band in the 1645-1615 Cm^{-1} region which attributed[7] to the amide carbonyl frequency, the shift of this band is due to intermolecular hydrogen-bonding on complexation, this band undergoes a shift of about 40-60 wave numbers, which is consistent with chelation by carbonyl oxygen atom. This frequency shift in the carbonyl stretching is due to a reduction of C=O bond order caused by the interaction with metal, abroad band at 3566-2422 Cm^{-1} in the spectra of the free ligands was assigned to free (OH)group, which disappears on complexation in all cases. The free hydroxamic acids are bidentate and the bonding occurs through the two oxygen atom[8]. In the region bellow 950 Cm^{-1} most bands are sensitive to the nature of the metal ion and the substituent.
A strong band at 1430-1455 Cm^{-1} is assigned to C-N

stretching frequency and N-H deformation band [9]. A strong band at 1182-1116 Cm^{-1} is assigned to N-O stretching frequency. The O-H bonded [10] appears at 2957 Cm^{-1} while OH free[11] at 3054 Cm^{-1}. The C-H of N-CH3 stretching appears at 2868-2412 Cm^{-1}.

Lanthanum (III) form 1:3 complexes with ligand octano-N-methyl, N-phenyl and N-(p-chlorophenyl) catechol hydroximic acid. The IR spectra of Lanthanium complexes are listed in Table (2). The IR spectra of the amide carbonyl (C=O) shifted in the solid complexes at lower frequency 1601, 1599, 1560 and 1564 Cm^{-1} in octano, N-methyl, N-phenyl and N-(p-chlorophenyl) catechol hydroximic acids respectively.



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