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Preparation, Characterization and Biological Evaluation of some Lanthanide (III) ions Complexes with 3-(1-methyl-2-benzimidazolylazo)-Tyrosine

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Abstract:

A series of lanthanide metal (III) complexes have been prepared from the new azo ligand, 3-(1-methyl-2-benzimidazolylazo)-Tyrosine (MBT). The structural feature were confirmed on the basis of their elemental analysis, metal content, molar conductance, magnetic measurement, FTIR, ^{1} HNMR and UV-Vis spectra studies. The isolated complexes were found to have a mole ratio (1:2) (metal:ligand) stoichiometry with the general formula $[Ln(MBT)_2]Cl$ (Ln(III) = La, Ce, Pr, Nd, Sm, Eu and Gd). The chelates were found to have octahedral structures. The FTIR spectra shows that the ligand (MBT) is coordinated to lanthanide ions as a N, N, O-tridentate anion via benzimidazole nitrogen, azo nitrogen and oxygen of hydroxyl after deprotonation. Complexes formation in solution were performed after fixing the optimum pH, molar concentration and time. Beer's low was obeyed over a range (7-$9x10^{-5}$) with high molar absorptivity for all the prepared complexes solutions. Stability Constant and Gibbis free energy were also determined. The ligand (MBT) and its prepared complexes were screened invitro against two types of selected bacteria.

Key words: Benzimidazolylazo, lanthanide (III) ions, Structural Studies, Biological Evaluation.

Introduction

The hetrocyclic compounds have a great deals in pharmaceuticals and extensively in organic synthesis [2]. Benzimidazole and its derivatives are potential type of compounds due to their structural similarity to naturally occurring nucleotides which permit them to interact easily with biophores [3]. Diverse biological activities of benzimidazoles derivatives have been described such as; antihypertensive (Candesartan) protonpump inhibitors (Omeprazole), antihistaminics (astemizole), antihelmintics (albendazole) , anticancer and antivirals [4]. Benzimidazole is an important structure in medicinal chemistry and extensive pharmacological and biochemical studies and it's derivatives are efficient against many of micro

organisms [5]. Due to the fact that N-ribosyl-dimethylbenzimidazole is a basic part of the structure of vitamin B12 even though vitamin B12 ability to inducing the growth of bacteria, the benzimidazole derivatives inhibit the bacterial growth [6]. Because of structural similarity to purine, antibacterial ability of these compounds is explained by their contention with purines resulting in repression of the synthesis of bacterial nucleic acids and proteins [7].

2-aminobenzimidazole produces from the guanidine moiety has made it a building block for the preparation of a large number of derivatives of pharmacological compounds [8], and have been found to possess in vitro and in vivo growth inhibition activity against many kinds of yeast, fungi and bacteria [9].

Benzimidazolylazo is a hetrocyclic compounds containing the active azoimine moiety (–N=C–N=N–), this type of organic ligands that contain nitrogen atoms coupled in conjugated system of π-bonds, which have been reacted with metal ions as multidentate ligands [10]. This class of ligands have been used in several applications such as complexion agent, chromogenic reagents, dyes, pharmace and non-linear optics [11-13]. The azo components of 2-aminobenzimidazole derivatives tend to show red shift and high tinctorial strength when compared to analogous dyes derived from other type of aromatic system [14]. The presence of metal ions in biological fluids could have a considerable effect on the therapeutic action for druges [15]. Furtheremore the complexes of many metal ions containing imidazole moiety (benzimidazole) as ligands are commonly found in biological media and play important role in areas like catalysis of drug interaction with bio-molecules [16] and are the principal site responsible for metal binding [17]. Lanthanide complexes of hetrocyclic azo compounds received sporadic intrest [18], and the choice of ligand still acute point because the ligand plays a role of intramolecular sensitizer of lanthanide luminescence [19]. The molecules containing aromatic moieties are very often found to be good sensitizer lanthanide ions. Substance based on lanthanide complexes has been studied with much attention for applications as highly efficient light conversion molecular devices [20]. This work presents synthesis, characterization and biological activity of the ligand (MBT) as a tridentate azo ligand and its prepared Ln-complexes.

Materials and Methods

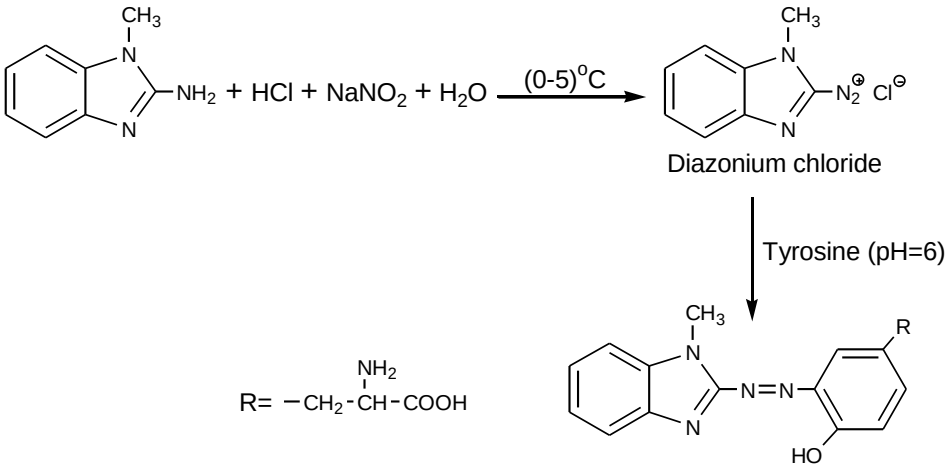
Material and Instrumental analysis

All chmeicals were purchased from BDH, Fluka and Merck. They are chemically pure or analytical grades. Melting points were measured with (Sturat Melting points apparatus). The percentage of chloride ion was determind by Mohr method [13]. The micro elemental analysis (C, H, N) were carried out by using (Eurovector EA 3000A elemental analyzer).The lanthanide content of the complexes was measured using atomic emission spectroscopy measurement by an applied research laboratories model 3410 miniport sequential inductively coupled plasma spectrometer (I.C.P.). The molar conductance measurements were measured by using (10^{-4}M) of Ln-complexes solutions in ethanol and DMF at 25℃ using (HANA instrument/conductivity tester). Magnetic susceptibilities were obtained by using Bruker magnet B.M.G instrument at 25➡C. pH measurements were performed using (HANA instruments pH tester / pocket pH tester). FTIR- spectra were recorded on Shimadzu, FTIR-8400s Fourier form infrared

spectrophotometer (200-4000) cm^{-1} with using CsI discs. UV-Vis spectra for all samples in ethanol (10^{-4}M) were recorded on Shimadzu UV-160A ultraviolet visible spectrophotometer using 1 cm quartz cell in the range (200-1100)nm. The HNMR spectra were recorded on a Jeol using DMSO as a solvent and TMS as a reference.

Preparation of Ligand 3-(1-methyl-2-benzimidazolylazo)-Tyrosine (MBT)

The ligand (MBT) was prepared as in the literature [21] with some modification (Scheme (1)). 2-amino-1-methylbenzimidazole (0.01 mole, 1.4718) was dissolved in a solution of conc. HCl (4 ml) and distilled water (20 ml). The hydrochloride product was diazotized at (0-5)°C with a solution of $NaNO_2$ (0.2 mole) in distilled water (25 ml) and the resulting diazonium chloride was added to a cooled alkaline ethnolic solution of Tyrosine (0.01 mole, 1.8119 gm) then the mixture was neutralized to pH=6. A brown precipitate was collected by filtration, crystallized by (1:1) (EtOH:H_2O), then washed with acetone.



Scheme (1): Synthesis of the ligand (MBT)

Synthesis of Selcted Lanthanide–MBT Complexes

An ethanolic solution of the ligand (MBT) (2m mole) was added gradually with stirring to (1m mole) of Ln(III) chloride dissolved in buffer solution (ammonium acetate) of the required pH. The reaction mixture was heated under reflux for (30 min). The mixture was cooled until acolored precipitate was formed. The product was filterd and washed several times with (1:1) H_2O:EtOH and followed by acetone and dried in desicator over $CaCl_2$.

Preparation of Buffer Solution

The pH media of the range (4-10) were prepared by dissolving (0.01M, 0.7708 gm) ammonium acetate in (1L) of doubly distilled deionized water. Either acetic acid or ammonium hydroxide solution were added for the adjustment of the pH.

Standard Solutions

An appropriate weight of each of $LnCl_3$ salts (Ln(III)=La, Ce, Pr, Nd, Sm, Eu and Gd) was dissolved in the buffer solution at pH range (4-10) in order to prepare a concentrations range between (10^{-3}-10^{-6}M). A series of ethanolic solutions of ligand (MBT) within the range of concentration (10^{-3}-10^{-6}M) were also prepared.

Determination of the Stiochiometry of Complexes

The mole ratio method [22] was used to determine the stiochiometry (Ln:MBT)

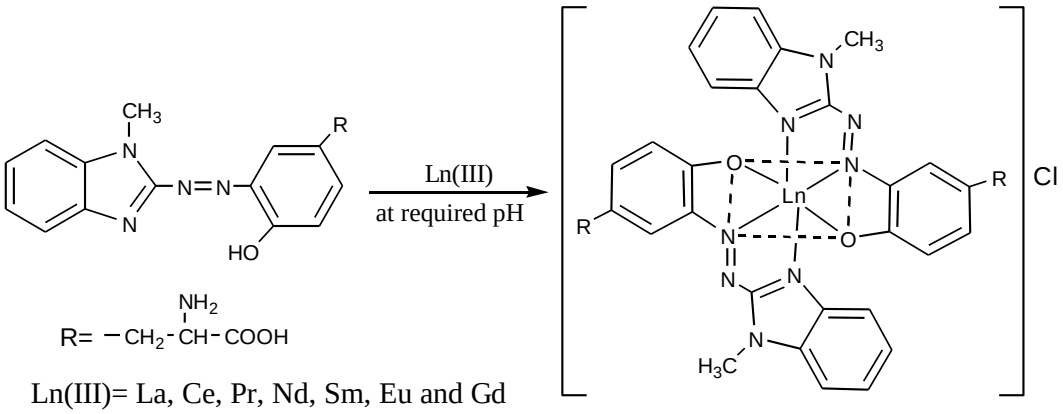
mole ratio. A series of solutions containing constant volume of the Ln(III) solution, prepared at optimum concentration were mixed with different volumes of the ligand (MBT) solution that has been prepared in the same concentration. Then (Ln:MBT) mole ratio was obtained by plotting absorbance of (Ln:MBT) solution against mole ratio.Two straight lines of variable slope are obtained. The intercept of the two straight lines represent the (Ln:MBT) mole ratio .

Biological evaluation:

The in vitro evaluation antibacterial activity was screened using the agar-well diffusion technique [23].Two kinds of bacteria including gram- negative: *Escherichia coli* and gram positive: *Staphylococcus aureus* were grown in nutrient agar .The ligand (MBT) and its Ln-complexes were applied by holes method. In this method the holes were saturated with (20 µL)of tested compound (10 mg/ml) in DMF. The petridishes of each tested compound were incubated at (37°C) for (24hr). Additionally antibiotic discs for Cephalosporin was tested as positive control. The data were recorded by measuring the zones of growth inhibition surrounding the hole of tested compound.

Results and Discussion:

The synthesis of brown crystalline solid of the ligand (MBT) involves coupling of diazonuim salt of 2-amino-1-methyl benzimidazole with Tyrosine as coupling component in an alkaline solution. The coupling mechanism is summarized in the schem(1). The essential intrest of the diazo component for the ligand (MBT) is that the yield is very high, short-time interaction and the method of work involves only one facile step. The presence of azo moiety with lone pair of electrons on the nitrogen atoms provides a binding site for coordination with metal ions. Other coordination site has been also provided by the presence the hetro nitrogen atom in benzimidazole and phenolic oxygen atom on Tyrosin after deprotonation. Therefore the ligand (MBT) was acted as an ionic N,N,O-tridentate ligand when treated with the following lanthanide (III) ions [La, Ce, Pr, Nd, Sm, Eu and Gd] with a (1:2) (Ln:MBT) stiochiometry . The formation of the Ln-complexes can be represented as in the scheme (2):



Scheme (2): The Suggested Octahedral Structure of $[Ln(MBT)_2]Cl$

The ligand (MBT) and it's Ln-complexes were stable solids, non-hygroscopic, possessed good keeping qualities and insoluble in water but shows varying solubility with common organic solvents. Analytical results for

all the prepared compounds are in good agreement with their formulation, and are listed in Table (1). The formulation of all prepared Ln-complexes was made depending on elemental analysis, molar conductance, magnetic susceptibility measurement and various spectral data. Table (1) shows the molar conductance values of Ln-complexes in EtOH and DMF solutions at (10^{-4}M) are in the range(38-43)and(76-86)ohm^{-1}mol^{-2} cm^2 respectively, indicating their electrolytic nature [24]. Therefore the chloride ion was not coordinated with Ln(III), but as a counter ion to neutralize the complex charge.

Table (1): Physiochemical properties, conductivity, magnetic moment, and mole ratio for the ligand (MBT) and its Ln-complexes

Compound (M.wt. gm/mole)	Color	M.P. [➡C] (yield%)	Elemental analysis found (cal.)					↶ ohm^{-1}.mol^{-2}. cm^2		↘ B.M	↙$_{max}$ (nm)	M:L
			C	H	N	M	Cl	EtOH	DMF			
$C_{17}H_{17}N_5O_3$ (339.37)	Brown	212 (88)	60.09 (60.11)	4.97 (5.00)	17.66 (17.67)	-	-	-	-	-	430	1:2
[La($C_{17}H_{17}N_5O_3)_2$]Cl (853.14)	Deep red	279 (72)	47.81 (47.82)	3.97 (3.98)	16.38 (16.40)	16.25 (16.28)	4.41 (4.16)	40	77	Dia	510	1:2
[Ce($C_{17}H_{17}N_5O_3)_2$]Cl (854.34)	Redish orange	248 (78)	47.73 (47.75)	3.95 (3.97)	16.36 (16.38)	16.38 (16.39)	4.09 (4.15)	42	79	2.49	489	1:2
[Pr($C_{17}H_{17}N_5O_3)_2$]Cl (855.14)	Purple bluish	280 (81)	47.75 (47.77)	3.96 (3.97)	16.34 (16.37)	16.46 (16.47)	4.11 (4.15)	38	86	3.49	598	1:2
[Nd($C_{17}H_{17}N_5O_3)_2$]Cl (858.48)	Pink	255 (79)	47.74 (47.75)	3.95 (3.96)	16.28 (16.30)	16.78 (16.8)	4.11 (4.13)	38	82	3.48	517	1:2
[Sm($C_{17}H_{17}N_5O_3)_2$]Cl (864.6)	Violet	246 (84)	47.16 (47.18)	3.92 (3.93)	16.16 (16.19)	17.38 (17.39)	3.99 (4.10)	39	76	1.62	535	1:2
[Eu($C_{17}H_{17}N_5O_3)_2$]Cl (866.2)	Redish purple	235 (75)	46.99 (47.10)	3.90 (3.92)	16.15 (16.16)	17.52 (17.54)	4.07 (4.09)	41	80	3.51	562	1:2
[Gd($C_{17}H_{17}N_5O_3)_2$]Cl (871.49)	Purple	290 (80)	46.78 (46.81)	3.89 (3.90)	16.04 (16.06)	18.01 (18.04)	4.05 (4.07)	43	82	7.85	572	1:2

The Effect of pH and concentration on [Ln(MBT)$_2$]Cl solutions

The electronic spectra were measured for a series of mixed solutions containing equal quantities of the same concentration of MBT, dissolved in ethanol, with the studied lanthanide (III) ions dissolved in buffer solutions at pH range (4-10). The electronic spectra of the mixed solutions were studied in a molar concentration range (10^{-6}-10^{-2}M). Only the molar concentrations of (7-9×10^{-5}M) obeyed the Lambert-Beer's law and showed a clear intense color. A calibration curve of absorbance against molar concentration was plotted and a straight line was obtained for each solution mixture Figure (1). The correlation factor R>0.9802 .

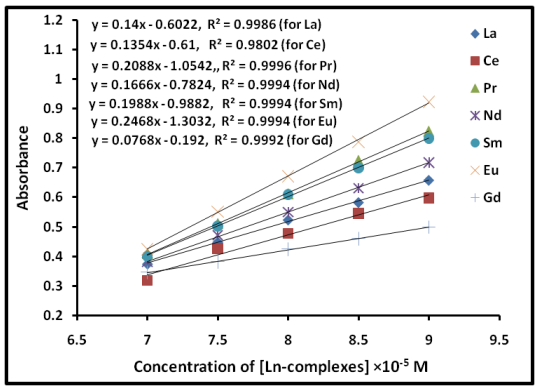


Fig. (1): Calibration graph of the ligand (MBT) and its Ln-complexes

The optimum molar concentration which was chosen when the Ln-complexes solutions giving rise to a constant (λ_{max}) at different pH, was (8×10^{-5}M).

The effect of pH on absorbance for the Ln-complexes formed by the reaction of (MBT) with the studied lanthanide ions was studied at pH range (4-10). It was found that all Ln-complexes were formed at pH (6.5) with higher absorbance, which represented the

optimum pH Figure (2) and was performed at certain (λ_{max}) for optimum molar concentration. At the optimum pH the color of the mixed solutions were changed from brown to red or purple. No such results were observed at pH range lower or higher than pH 6.5 which may be attributed to the dissociation of complexes.

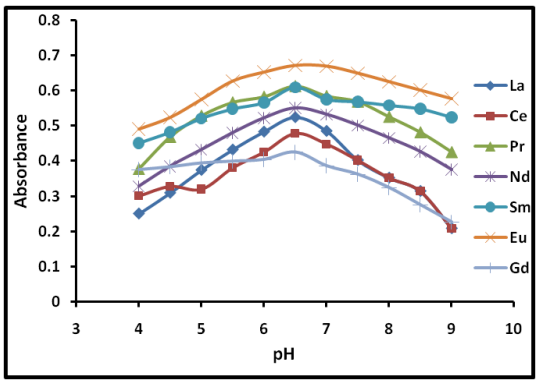


Fig. (2): pH effect at optimum concentration and (λ_{max}) for [Ln-complexes] solutions

Electronic Spectra

Rapid changes in color and a large bathochromic shift in the (λ_{max}) were noticed in the spectra of the prepared Ln-complexes solutions under optimum conditions with respect to that of the free ligand. The shift in (λ_{max}) gave a good indication for the coordination and complex formation, as is shown in Figure (3).

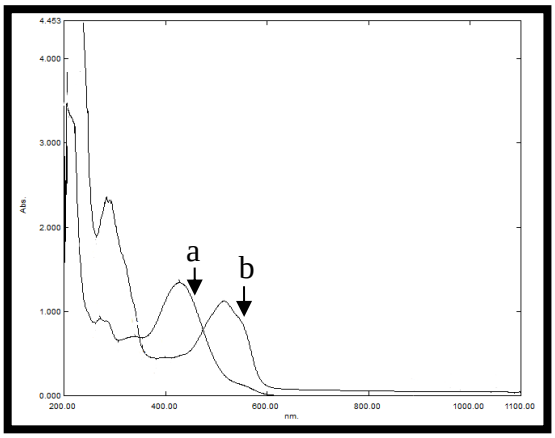


Fig. (3): The electronic spectra of a-MBT; b- [Gd(MBT)$_2$]Cl solutions

Designation of the Nature of the Complex

The stoichiometric reaction of the ligand (MBT) and studied lanthanide ions was investigated applying the mole ratio method [25].The measured absorbance was plotted against molar ratio of the two component when the amount of one component is varied (MBT) while the molar concentration of Ln(III) remained constant. When the complexes formed were stable and there is no retable dissociation, such a plot gives a sharp break. The sharp break indicates the composition of the complex Figure (4). In this work the result revealed (1:2) (Ln:MBT) mole ratio at optimum pH, molar concentration, and λ_{max} as is illustrated in Table (1).

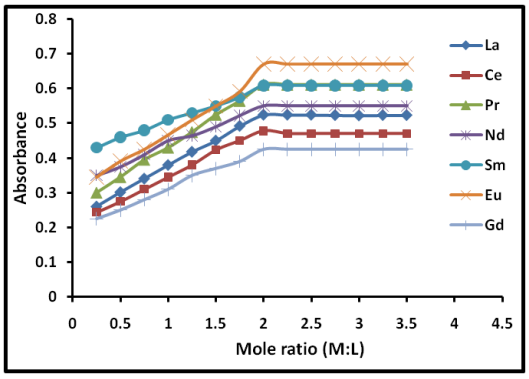


Fig. (4): Mole ratio for [Ln-complexes] solutions at optimum conditions

The Effect of Reaction Temperature and Heating Time

The reaction of MBT with Ln(III) ions of at optimum concentration, pH and λ_{max} was studied at temperature range (25-70℃). The development of color was monitored by UV-Vis spectroscopy. The data were illustrated in Figure (5). The formation of stable colored Ln-complex was achieved at (25℃) after (10 min), which were adopted for further investigated.

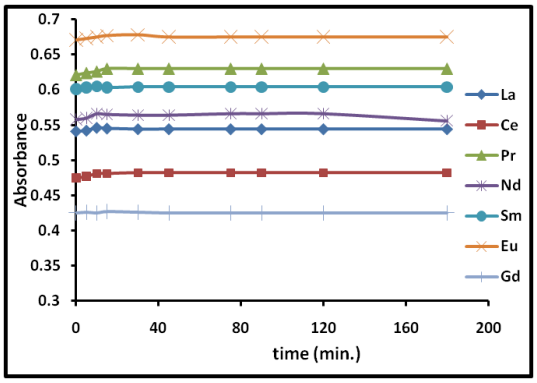


Fig. (5): The relationship between time (min.) and stability of [Ln-complex] solutions

Stability constant and Gibbis Free Energy

Stability constant was calculated spectrophotometrically for (1:2) (Ln:MBT) complexes by using the following equations [26].

$$K = \frac{1-\alpha}{4\alpha^3 C^2} \quad ; \qquad \alpha = \frac{A_m - A_s}{A_m}$$

Where C=molar concentration of the Ln-complexes in molar.

α = degree of dissociation

A_s = the absorption of solution containing a (1:2) stoichiometric (Ln:MBT) at λ_{max}

A_m = the absorption of solution containing (1:1) stoichiometric (Ln:MBT) at $\lambda_{max.}$

All the data were tabulated in Table (2). The high value of K indicate high stability of Ln-complexes.

Gibbis free energy (ΔG) were also investigated, from the equation [27]

$$\Delta G = -RT\ln K$$

where : R=gas constant = 8.3 J.mole^{-1}.K

T= absolute temperature (Kelvin)

The negative value of ΔG Table(2) may reflect that the interaction between the ligand (MBT) and studied lanthanide ions are spontaneous.

Magnetic susceptibility

The magnetic susceptibility of f-block elements are quite difficult to interpret. Their (μ) values are calculated by taking into consideration spin as well as orbital contributions. Due to 4f-electrons are inside the (5s and 5p) electrons and core-like in their behavior. In this report the (μ) values of the complexes showed that lanthanum complex is dia magnetic but the rest are para magnetic, showing close agreement with the calculated values Table (1) [20,28].

The Electronic spectra of isolated solid compounds

The electronic spectra of all the prepared compounds dissolved in ethanol (10^{-4}M) against ethanol as reference within the range (200-1100 nm), have been measured Figure (6 and 7) and the data were included in Table (2). The spectrum of the ligand (MBT) Figure (6) displayed two peaks at (278 nm, 35971.22 cm^{-1}) and (318nm, 31446cm^{-1}) which refered to the moderate ($\pi \longrightarrow \pi^*$) transition of aromatic moiety. A third high intense (λ_{max}) peak was observed at (420 nm, 23809.52 cm^{-1}) which was assigned to the ($\pi \longrightarrow \pi^*$) transition. In the spectra of metal complexes a high intensity bands were observed at wave length in the range (489-572nm) (20489, 1748cm^{-1}) which were assigned to charge transfer (CTML) taken place through the azo moiety (–N=N–) [29], which was suggested to the involvement of the ligand in the complex formation with lanthanide ions Table (2). The sharp bands belong to (f–f) transitions in the partly filled (4f) subshell electrons of the lanthanide ions are only slightly crystal-field affected by direct surroundings of Ln(III). Due to 4f electrons lie deep in the atoms and are inside the (5s and 5p) electrons, and so can't overlap with ligand orbitals and therefore don't participate in bonding. Thus the complexing agents have little effect on the spectral bands [30].

Table (2): UV-Vis spectra, stability constant and Gibbis free energy

Compound	↙max (nm)	Absorption band (cm^{-1})	⇨×10^4 $L.mol.^{-1}.cm^{-1}$	Transition	log K	⇆G $J.mol^{-1}$
Ligand (MBT)	278 218 420	35971 31446 23809	0.812 0.242 0.406	π•π^*	-	-
$[La(MBT)_2]Cl$	510	19607	0.524	MLCT	9.03	-47683
$[Ce(MBT)_2]Cl$	489	20449	0.478	MLCT	9.11	-47567
$[Pr(MBT)_2]Cl$	598	16722	0.612	MLCT	9.01	-47054
$[Nd(MBT)_2]Cl$	517	19342	0.551	MLCT	8.24	-43030
$[Sm(MBT)_2]Cl$	535	18691	0.609	MLCT	8.3	-43333
$[Eu(MBT)_2]Cl$	562	1779	0.671	MLCT	8.89	-46882.49
$[Gd(MBT)_2]Cl$	572	1748	0.321	MLCT	9.15	-47782.01

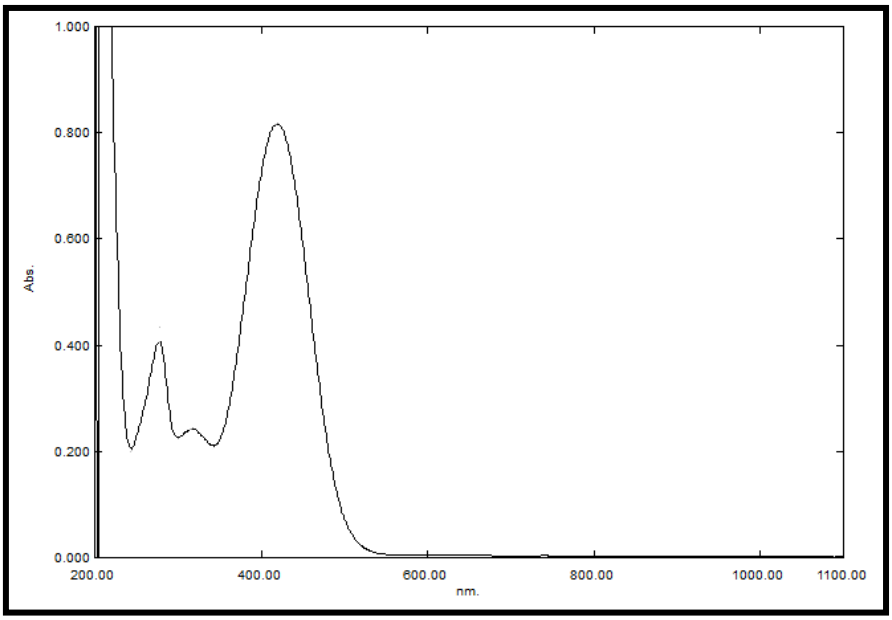


Fig. (6): The electronic spectrum of the ligand (MBT)

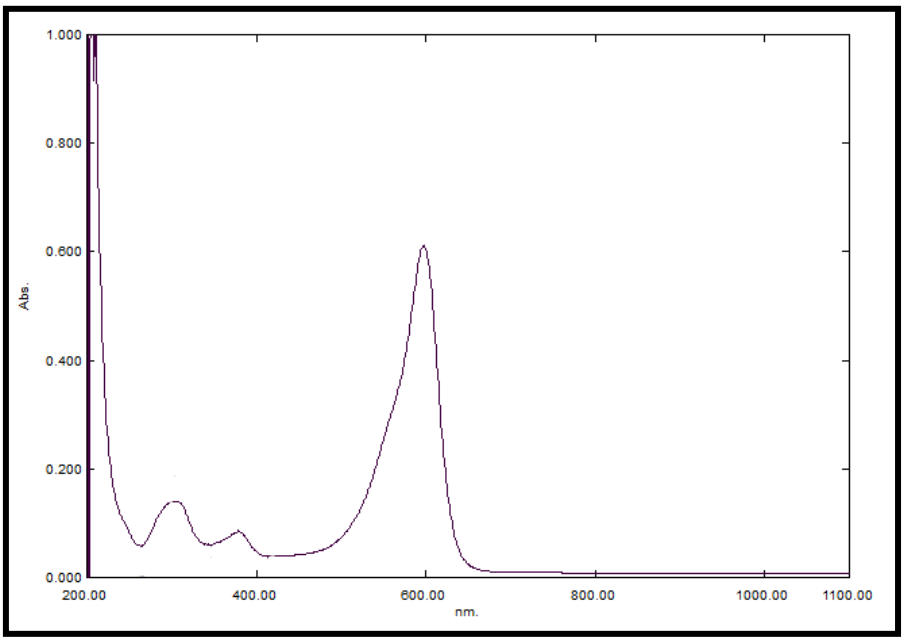
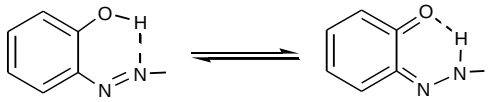


Fig. (7): The electronic spectrum of the $[Pr(MBT)_2]Cl$

FTIR Spectra

The FTIR spectrum of the ligand (MBT) Figure (8) was compared with those of the prepared Ln-complexes Figure (9) in order to detect the coordination sites that may be involved in the chelation. The significant absorption bands are illustrated in Table (3), and explained as follows:

1. It is striking that no other well-defined bands can be found in the spectrum of the free ligand (MBT) at the regions (3570) cm^{-1} and (3460) cm^{-1} related to the stretching vibrations of υ(OH) and υ(NH) respectively [31]. These stretching vibrations bands are known to shift to the lower frequency region with decrease in intensity, but it looks as medium and broad bands Table (3). This may be attributed to the presence of the intra molecular hydrogen bond have been between the hydroxyl proton of the phenol (Tyrosine) moiety and the nitrogen of azo moiety near the benzimidazole moiety, which may lead to have the tautomeric azo-hydrazone.



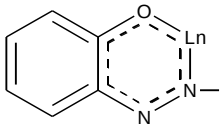
Azo form **Hydrazone form**

Scheme (3): The tautomeric structure

In the spectra of Ln-complexes, the stretching vibrations of hydroxyl group was disappeared due to breaking of hydrogen bond and the coordination of the oxygen atom to the studied lanthanide ions after the deprotination of hydroxyl group [8,21].

2. The weak band located at (3150) cm^{-1} in the spectrum of the free ligand (MBT) which was assigned to the aromatic (C-H) stretching vibrations.

3. A triplet strong bands were observed in the spectrum of the ligand (MBT) at (1685, 1649, 1625) cm^{-1}. These bands were attributed to the combination of the υ(C=O) and υ(C=N) formulated in the hydrazo form [32]. Although the free carbonyl band (C=O) is expected at around (1700-1750) cm^{-1}, such a bathochromic shift is often observed in hydrogen bonded ring systems. In the Ln-complexes, this band is observed at around (1644-1587)cm^{-1}, as the result of involvement of the (C=O...) bond in the lanthanide chelate ring as it is shown below:



The shift of this band from the original position of the ligand probably is attributed to the increased mass of the metal bonded to the oxygen atom relative to that of the proton and addition to the electro negativity of the metal ions [10].

4. The strong characteristic bands in the free ligand (MBT) spectrum at (1413 and 1521) cm^{-1} were due to the azo moiety (–N=N–) stretching and (CNNC) [3]. These band suffered a great change in the intensity and shifts to lower frequencies Table (3) in the spectra of complexes. The obtained results propose that the binding of studied lanthanide ions with the ligand took place through oxygen of hydroxyl group after deprotination, the nitrogen atom of azo moiety of the benzimidazole and nitrogen of benzimidazole (Scheme (2)). Medium and weak bands in the spectra of the prepared Ln-Complexes were obsereved at (547-555)cm^{-1} and (422-430)cm^{-1} which may be attributed to the $\upsilon(M-O)$, $\upsilon(M-N)_{azo}$ and $\upsilon(M-N)_{bnzimidazole}$ [7, 9, 32]. The ionic bond of $\upsilon(M-Cl)$ appeared at (219-235)cm^{-1} [9].

Table (3): Selected FTIR bands (200-4000) $cm^{-1}$for the ligand(MBT) and its Ln–complexe(CsI)

Compound	↔(OH), υ(NH)	↔(C=O) ↔(C=N)	↔(C-N=N-C)	↔(N=N)	↔(M-O)	↔(M-N)	↔(M-Cl)
Ligand (MBT)	3514, 3413 } br, s 3122w	1685, 1649 } t, st 1625	1521 w	1413 w	-	-	-
$[La(MBT)_2]Cl$	- 3121w	1620, 1587 } d, w	1479 m	1409 m	550 m	420 w	235 s
$[Ce(MBT)_2]Cl$	- 3120w	1635, 1590 } d, w	1483 w	1404 m	555 m	427 w	230 s
$[Pr(MBT)_2]Cl$	- 3118w	1626, 1587 } d, m	1475 m	1399 m	548 m	423 w	225 m
$[Nd(MBT)_2]Cl$	- 3120w	1630, 1583 } d, m	1480 w	1400 m	551 m	422 w	219 s
$[Sm(MBT)_2]Cl$	- 3114w	1641, 1592 } d, w	1469 m	1395 w	553 w	430 w	234 m
$[Eu(MBT)_2]Cl$	- 3119w	1644, 1589 } d, m	1467 m	1389 w	551 w	425 w	233 m
$[Gd(MBT)_2]Cl$	- 3120w	1622, 1594 } d, m	1459 w	1402 w	547 m	422 w	227 s

s= strong; sh = sharp; m = medium; w = weak; d = doublet; t = triplet

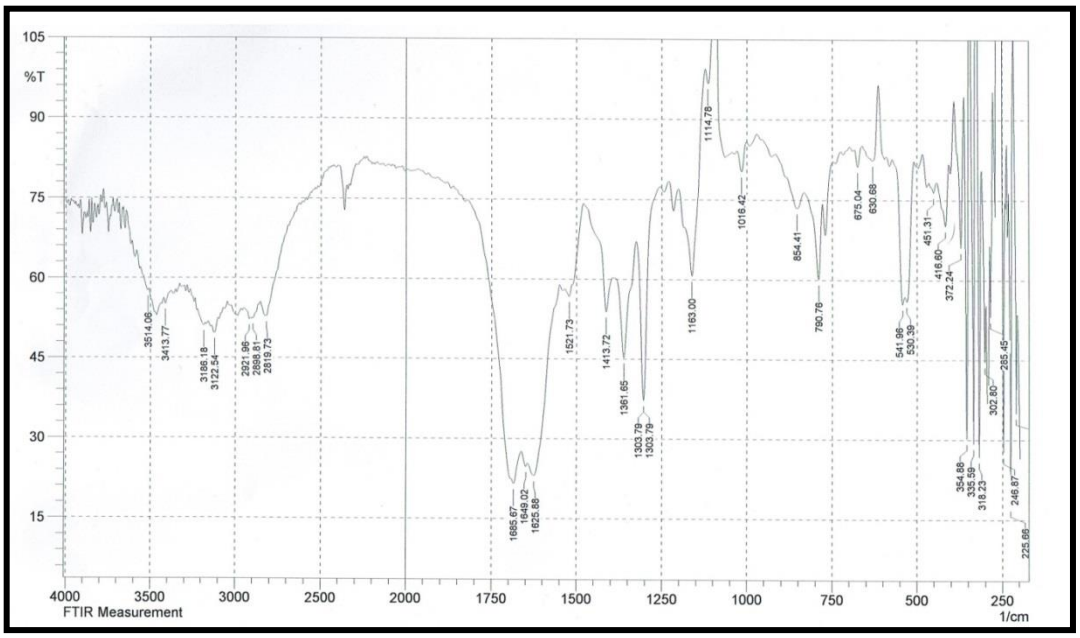


Fig. (8): FTIR spectrum for the ligand (MBT)

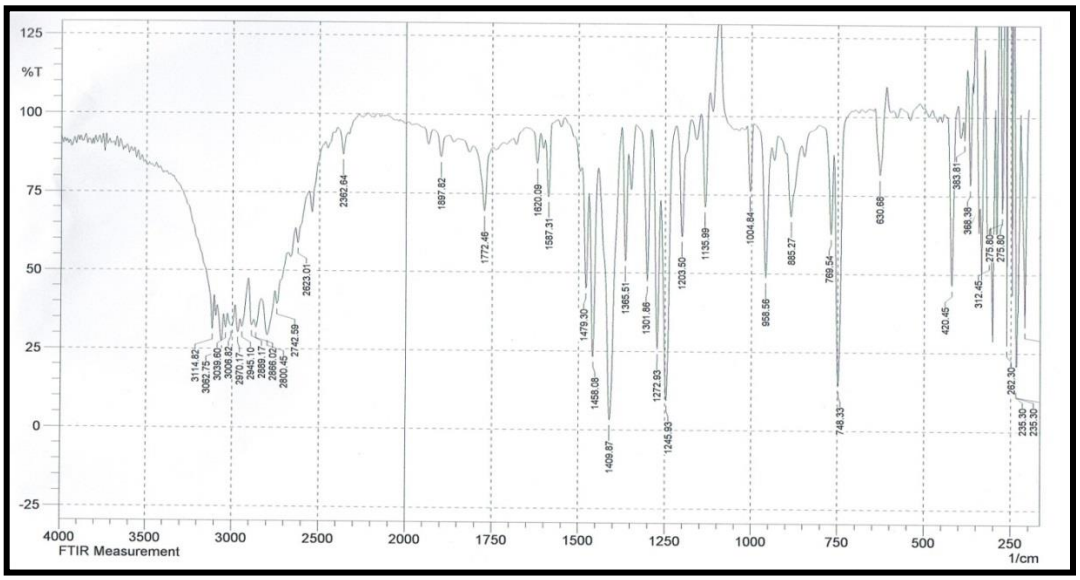


Fig. (9): FTIR spectrum for $[Sm(MBT)_2]Cl$

^{1}HNMR spectra

The ^{1}HNMR spectra are shown in Fig. [10 and 11], for the free ligand (MBT) and for $[Ce(MBT)_2]CL$ complex in DMSO respectively, using (TMS) as an internal Standard. The free (MBT) spectrum shows the main signals at (δ=10.88 ppm, H) and (δ=8.42 ppm, H) which were attributed to (-COOH) and (-OH) group in the Tyrosine moiety[33]. The multiplet signals observed in the region (δ=6.94-7.52 ppm, 7H) were assigned to chemical shifts of aromatic protons for benzimidazole and Tyrosine moieties, while the signal at (δ=3.71 ppm, 3H) belongs to ($N\text{-}CH_3$) of benzimidazole moiety [34]. The spectrum of $[Ce(MBT)_2]Cl$ exhibited no shift in the position of (-COOH) signal (δ=10.81 ppm, H) and ($N\text{-}CH_3$) signal at (δ=3.72 ppm, 3H) which excluded these groups from coordination to Ce(III) ions. But slight shifts in position of the proton signals assigned to aromatic (δ=6.28-7.53 ppm, 7H) protons and disappearance of the signals assigned to (OH) refers to complex formation [22].

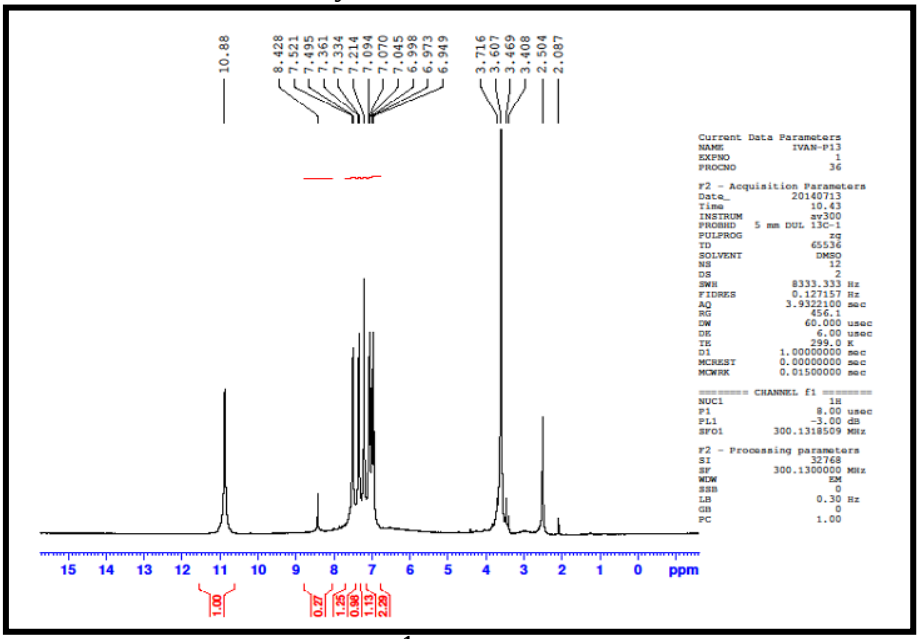


Fig. (10):The^{1}HMNR of the ligand

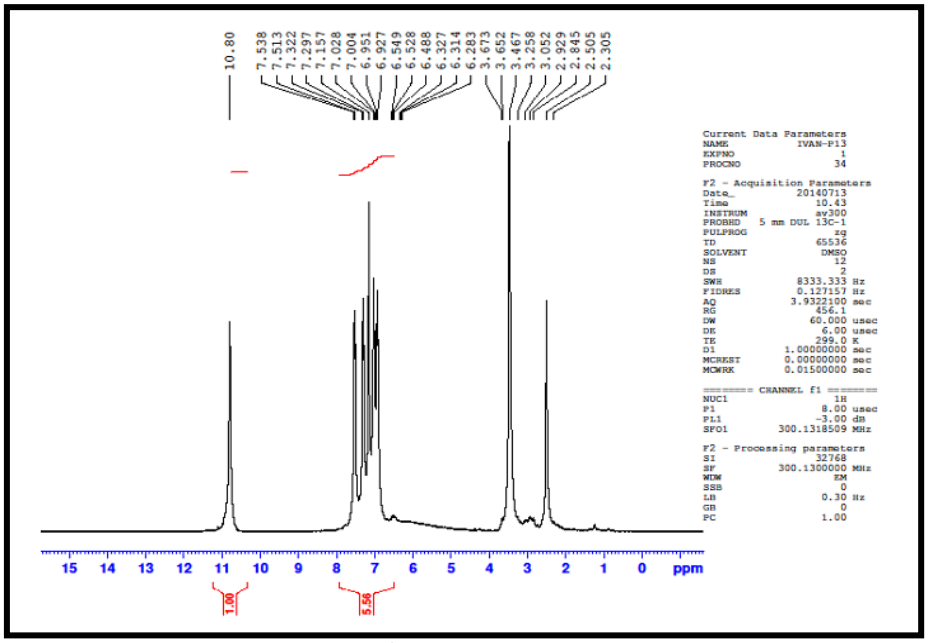


Fig. (11): The ^{1}HMNR of [Ce(MBT)$_2$]Cl

The in Vitro Biological Evalution

Two types of bacteria were selected to study the bacteriological activity of the ligand (MBT) and it's Ln-complexes dissolved in DMF (10 mg/ml). One type of bacteria was gram negative, which is *Escherichia coli* and the second one was gram positive, which is *Staphylococcus areus* using Cephalosporin as refrences all the results are summarized in Table (4). The ligand (MBT) and it's Ln-complexes enhanced antimicrobial activity against the tested bacteria. With the expception of Eu(III) complex, the Ln-complexes showed moderate to higher activity especially the La(III) and Sm(III) which were comparable Cephalosporin (Cephalexin) showed appreciable inhibition against the tested bacteria. A reasonable exposition for the observed increased activity upon chelation is that the positive charge of Ln-complex in coordinated complex is partially shared with the ligand's donor atoms, thus there is an electron delocalization over the whole chelate ring, which leads to increase of lipophilic character of the lanthanide chelate and favorous its penetration through the biolipid layers of the cell membranes of bacteria. It's supported that some complexes deactivate different cellular enzymes, which play a vital roles in different metabolic pathways of these micro organisms. Moreover, there are other factors that affect the biological activity of the complexes as compared to the corresponding ligand, such as solubility, conductivity and dipole moment [7,11,35].

Table (4): Influence of the ligand (MBT) and it's Ln-complexes on the growth of tested bacteria (mg/ml) with Cephalosporine as reference

Compound	Bacteria	
	E. coli **gram (-)**	***Staphylococcus aureus*** **gram (+)**
Cephalexin	+++	+++
Ligand (MBT)	++	++
[La(MBT)$_2$]Cl	+++	+++
[Ce(MBT)$_2$]Cl	+++	++
[Pr(MBT)$_2$]Cl	++	++
[Nd(MBT)$_2$]Cl	+++	++
[Sm(MBT)$_2$]Cl	+++	+++
[Eu(MBT)$_2$]Cl	+	+
[Gd(MBT)$_2$]Cl	++	+++

(+++) = Highly inhibition zone >12 mm
(++) = Moderately inhibition zone 6-9 mm
(+) = Slightly inhibition zone 6-8 mm

Conclusion:

Coupling reaction of 2-amino-1-methylbenzimidazole with Tyrosine in alkaline medium gave an ionic N, N, O-tridentate azo ligand (MBT). The reaction of this ligand with lanthanide(III) ions (La, Ce, Pr, Nd, Sm, Eu and Gd) was gave complexes with a (1:2) (Ln:MBT) mole ratio at optimum pH, Concentration and λ_{max}, with the general formula $[Ln(MBT)_2]Cl$. Beers law was obeyed over concentration range ($7\text{-}9x10^{-5}$ M). All the prepared compounds were identified by analytical and spectroscopic methods as well as magnetic susceptibility and conductivity measurements. All the prepared compounds except the Eu(III) exhibited good antibacterial activity, against two selected bacteria.

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تحضير، تشخيص ، ودراسة الفعالية البايولوجية لبعض معقدات ايونات اللانثانات (III) مع 3- (1- مثيل – 2- بنزايميدازوليل آزو) تايروسين

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الخلاصة:

حُضرت متسلسلة من معقدات ايونات اللانثانات (III) مع ليكاند جديد 3- (1- مثيل بنز ايميداوليل آزو) تايروسين (MBT) . وشخصت جميع المركبات المحضرة استنادا الى تحاليل العناصر ، ونسبة الفلز ،قياسات التوصلية المولارية ، قياسات الحساسية المغناطيسية ،و دراسة اطياف الاشعة تحت الحمراء و الاشعة فوق البنفسجية- المرئية وطيف الرنين النووي المغناطيسي اظهرت بان جميع المعقدات لها النسبة المولية (2:1) (فلز : ليكاند) وذات الصيغة العامة$[Ln(MBT)_2]Cl$حيث ان (Ln(III) = La, Ce, Pr, Nd, Sm, Eu and Gd).وذات شكل هندسي ثماني السطوح .ولقد وجد ان الليكاند ايوني ويتناسق من خلال O,N,N - ثلاثي السن عن طريق نيتروجين مجموعة البنزايميدازول ونيتروجين مجموعة الآزو واوكسجين مجموعة الهيدروكسيل بعد فقدانها البروتون .جميع المعقدات حُضرت بعد تثبيت الظروف المثلى من pH و تركيز مولاري عند الطول الموجي الاعظم وكان التركيز الذي يطيع قانون لامبرت - بير ضمن المدى ($7-9\times10^{-5}$ مولاري) ولها امتصاصية مولارية عالية. اضافة لذلك فقد دُرست مدى استقرارية المعقدات المحضرة من خلال دراسة ثابت الاستقرارية والطاقة الحرة لكبس وكذلك دراسة تأثير درجة الحرارة والوقت عليها . وفي ذات الوقت تم تقييم الفعالية البايولوجية لليكاند ومعقداته ضد صنفين من البكتيريا.

الكلمات المفتاحية : بنز ايميداوليل آزو، ايونات اللانثانات (III)، دراسة طيفية ،فعالية بايولوجية.