

Synthesis, Characterization and Antibacterial Activity of New Complexes of Some Lanthanide Ions with Benzo 18-Crown-6 and 221-Cryptand

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Abstract: Complexes of some lanthanide picrates ($\text{Ln}^{3+} = \text{Pr}^{3+}, \text{Nd}^{3+}$ and Dy^{3+}) with benzo-18-crown-6 and 221-cryptand were synthesized and characterized by elemental analysis, FTIR, and UV-Visible. Spectrophotometric methods, thermal analysis (TGA & DTG), melting point, magnetic susceptibility and molar conductance. Also an *in-vitro* study on gram positive (*Staphylococcus aureus*) and gram negative bacteria (*Escherichia coli*, *Salmonella* and *pseudomonas aeruginosa*) was performed and the results were compared to those of the broad spectrum antibiotic Chloramphenicol. The benzo-18-crown-6 complexes have the general formula of $[\text{Ln.L}(\text{Pic})_2]\text{Pic}.n\text{H}_2\text{O}$, where; ($\text{Ln}^{3+} = \text{Pr}^{3+}, \text{Nd}^{3+}$, and Dy^{3+}), ($\text{L} = \text{Benzo-18-crown-6}$), ($\text{Pic} = \text{Picrate anion}$), ($n = 1-2$). In these complexes two picrate anions are coordinated to the metal ion through the phenolic oxygen and oxygen of the ortho nitro group, thus, the metal ions in these complexes have a coordination number of (10). The complexes of 221-cryptand have the general formula of $[\text{Ln.L}(\text{Pic})]\text{Pic}.n\text{H}_2\text{O}$ where; ($\text{Ln}^{3+} = \text{Pr}^{3+}, \text{Nd}^{3+}$, and Dy^{3+}), ($\text{L} = 221\text{-cryptand}$), ($\text{Pic} = \text{Picrate anion}$), ($n = 1, 2$ or 7). In these complexes one picrate anion is coordinated to the metal ion, also through the phenolic oxygen and the oxygen from the ortho nitro group, thus the metal ions in the cryptand complexes have a coordination number of (9).

Keywords: crown ethers, lanthanides, picrates, cryptand

I. Introduction

The coordination chemistry of lanthanides is important. And during the last decades, an increase in the number of publications devoted to the rare earth coordination compounds has been observed [1-6], due to their biological, biochemical, medical and many other applications such as an excellent diagnostic and prognostic probe in clinical diagnostics [7], an anticancer material [2,8], lanthanide complexes based X-ray contrast imaging and lanthanide chelates based contrast enhancing agents for Magnetic Resonance Imaging (MRI) [9] are being excessively used in radiological analysis in our body systems [8], also as shift reagents for NMR spectrometry [9-11], as well as, their potential applications in fundamental and applied science such as organic synthesis, bioorganic chemistry and homogeneous catalysis [9,12-16]. Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups. The most common crown ethers are oligomers of ethylene oxide, the repeating unit is ethyleneoxy, i.e., $-\text{CH}_2\text{CH}_2\text{O}-$ [17]. Since its discovery by Pedersen [18], many variants of those structures have been reported, such as out-in bicyclic amines and cryptands by Simmons and Park, Lehn and coworkers, lariat ethers, aza-crown ethers, calixarenes and calixcrowns, calixtubes [19]. All these compounds are interesting because of their remarkable selectivity on metal cations, especially from alkali and alkaline earth metals [20-24], which is a topic of fundamental interest in both coordination and biological chemistry [25]. Complexation reactions of crown ethers and cryptands with 4f-element salts under anhydrous conditions promote interaction of the metal ion with the crown ether in solution; however these complexes are often very difficult to crystallize [3,4] but we have successfully prepared, characterized and tested the crystallized complexes against gram positive (*Staphylococcus aureus*) and gram negative bacteria (*Escherichia coli*, *Salmonella* and *pseudomonas aeruginosa*) *in-vitro*. They showed good, promising results when compared to the well-known broad spectrum antibiotic Chloramphenicol, in fact chloramphenicol had no activity at all against the gram negative *pseudomonas aeruginosa* while all the tested complexes showed good inhibitions. However further *in-vivo* study is required. The biological activity of these complexes against these bacteria is believed to arise from the crown ligand (The Chelate) effect on the metal ion. The most important property of the chelating agents, in lanthanide chelate complex, is its ability to alter the behavior of lanthanide ion with which it binds in biological systems, and the chelation markedly modifies the bio distribution and excretion profile of the lanthanide ions. The chelating agents increase the proportion of their complex excreted from complexes lanthanide ion from biological systems [2].

II. Materials And Methods

All the Starting materials were commercially available. The ligands (benzo 18-crown-6 and 221-cryptand) were obtained from Sigma Aldrich Company, lanthanide oxides, picric acid and the solvents were obtained from Merck Company and were used without further purification. The lanthanide content was determined by EDTA titration using xylenol orange as an indicator. The carbon, hydrogen and nitrogen content were determined using the Carlo Erba EA 1108 elemental analyzer. The IR spectra were recorded using KBr pellets and an 8400 S – FTIR SHIMADZU spectrometer. The UV – Visible Spectra were recorded using an 1800 – UV SHIMADZU spectrometer. Conductivity measurements were carried out using a HI 9811 – 5 Portable HANNA pH/EC/TDS/°C meters. Thermal analysis of the prepared complexes was performed using SHIMADZU 60-H Thermo Gravimetric Analyzer. The melting points were measured using a GALLENKAMP melting point apparatus. The magnetic properties were measured using a Johnson Matthey MSB MarkI magnetic susceptibility balance.

Preparation of lanthanide picrate:

General procedure: (1 mmole) of lanthanide oxide was placed in a round bottomed flask, followed by the addition of (40 ml) of (0.05 M) picric acid and refluxed at (85 °C) until all the oxide was dissolved, the process took few hours to more than 24 hours. The clear yellow solution was filtered while still hot then the filtrate was concentrated on a heater at (40-50 °C) to half of its volume after that the solution was left over night to be air concentrated (if you want to accelerate the process then evaporate the solution on the heater very slowly and on a low temperature, care must be taken since the metal salts of picric acid are highly explosive more than the acid itself but the slower the rate of the concentration the better yield you get). After the concentration and the evaporation of the solution yellow-dark yellow crystals were formed, all the crystals were collected and stored in a desiccator. The colors of the salts were bright yellow-orange. The general equation for the preparation of lanthanide picrates is shown below:



Where $\text{Ln}^{3+} = \text{Pr}^{3+}, \text{Nd}^{3+}$ and Dy^{3+}

Preparation of B18-crown-6 complexes:

General procedure: a solution of (1 mmole) of B18-crown-6 in (3 ml) of absolute ethanol was added to a solution of (0.5 mmole) of lanthanide picrate in (3 ml) of absolute ethanol and refluxed at (60 °C) for one hour, then the solution was left overnight. The developed precipitate or crystals were collected and stored in a desiccator for 24 hours. In some cases a gummy like precipitate formed. The gummy precipitate was treated with (40-60 °C) petroleum ether for several times till a fine powder precipitate was formed. The obtained crystals were yellow-orange.

Preparation of 221-cryptand complexes:

General procedure: a solution of (2 mmole) of 221-cryptand in (10 ml) of absolute ethanol was added to a solution of (1 mmole) of lanthanide picrate in (10 ml) of absolute ethanol at room temperature. Immediate precipitation occurred along the addition, then the precipitate was filtered and washed with small proportions of ethanol; finally the precipitate was placed in a desiccator and left for 24 hours for complete dryness. The colors of the complexes were yellow-dark orange.

III. Results

Physical and Chemical measurements:

The carbon, hydrogen, nitrogen and metal content data alongside the melting points, colors, conductivity values, and magnetic moments of the prepared complexes are shown in table (1).

IR spectra:

IR spectra of the lanthanide picrates: The data of the absorption frequencies of picric acid and lanthanide picrates are listed in table (2). The most important band shift is the one that belongs to the ν (O-H) stretching vibration which is shifted in the spectra of the salts by (367 – 397 cm^{-1}) towards higher wave numbers when compared to the spectra of picric acid, this may be due to the breaking of the intramolecular hydrogen bonding between the phenolic hydrogen and the oxygen from the adjacent nitro group, and the formation of an ion pair between the Ln^{3+} ion and Pic^- [26, 36]. Some noticeable shifts in the bands of the symmetric and asymmetric stretching vibrations of the nitro groups are observed in the spectra of the lanthanide salts when compared to the

spectra of picric acid as it is shown in table (3), this also may indicate the breaking of the intramolecular hydrogen bonding between the oxygen of the nitro group and the phenolic hydrogen [36-39, 41].

IR spectra of the complexes: The data of the absorption frequencies for the free ligands and their complexes are shown in table (3). The most important band in the spectra of the complexes is that of the (C-O-C) stretching vibration. Compared with the free ligand the ν (C-O-C) bands in the complexes of B18-crown-6 are shifted by (99 cm^{-1}) for the first band and by (35 cm^{-1}) for the second band towards lower wave numbers with changes in shape and intensity of the peaks, while the bands in the complexes of 221-cryptand are shifted by ($29 - 35\text{ cm}^{-1}$) also towards lower wave numbers and are also accompanied with changes in shapes and intensities of the peaks. These shifts and spectral changes give an indication of the interaction between the crown compound and the metal ion and the magnitude of the shift defines the strength of the interaction which varies from one ligand to another due to the size matching between the cavity of the ligand and the size of the metal ion alongside other factors [27-31]. Some new bands appear in the spectra of the complexes which are absent in the spectra of the free ligand at around ($1537 - 1560$ and $1325 - 1337\text{ cm}^{-1}$) these bands belong to the asymmetric and symmetric stretching vibrations of the nitro groups of the picrate anion, this confirms the formation of the complexes and means that the picrate anions are incorporated in the skeleton of the complexes whether coordinated to the metal ion or as a counter ion. Any shift in these bands when compared to the bands of their corresponding metal salts indicates their coordination to the metal ion [37-39, 41]. Significant shifts are observed in the complexes when compared to the spectra of the corresponding lanthanide salt as shown in table (3) indicating that some picrate anions are coordinated to the metal ion which is confirmed by their conductance values. Another new band appeared at ($3092 - 3097\text{ cm}^{-1}$) in the spectra of 221-cryptand complexes which is absent in the spectra of the ligand and is assigned to the aromatic ν (C-H) stretching vibration of the aromatic ring of the picrate anion, and another band appeared at ($932 - 943\text{ cm}^{-1}$) which belongs to the aromatic δ (C-H) bending vibration, the appearance of these two bands mean that the picrate anions are somehow incorporated in the complex. The CH_2 bending vibrations (Scissoring, wagging and rocking) experienced shifts in their bands when compared to the free ligand, some shifts are high and obvious, some are simple and all these shifts are accompanied with changes in shapes and intensities of the peaks. These spectral changes are may be due to the decrease in charge density on the adjacent oxygen atom, which gives an indication of their bonding and interaction with the metal ion [30]. Another new band appeared at ($1610 - 1614\text{ cm}^{-1}$) in the spectra of 221-cryptand complexes, this band is assigned to the ν (C=C) stretching vibration of the benzene ring of the picrate anions, this is absent in the spectra of the free ligand [38, 39, 41].

UV – Visible Spectra:

The electronic spectra of picric acid and lanthanide salts were recorded in ethanol. Picric acid shows two main absorption bands at (λ_{max} 359 and 220 nm). These bands are shifted to lower wave lengths in the corresponding salts. These spectral changes may indicate the formation of ion-pair between Ln^{3+} ion and Pic^- in LnPic_3 which is also confirmed by IR results. The electronic spectra of free ligands and their complexes were recorded in DMSO. Table (4) shows the absorption data of picric acid, Ln salts, ligands and the complexes. All ligands show two typical absorption bands as it is seen in table (4), one of these two bands is shifted to a higher wave length specifically to (380 nm) in all the complexes while the other band is shifted to a lower wavelength table (4). These spectral changes confirms that the complex is formed indicating that there is a change in the environment and leads to the conclusion that Ln^{3+} is maybe incorporated in the ligand causing these spectral changes. The picrate anion also have a pronounced effect on the formation of the complex and the nature of the spectra and since the maximum absorption bands of the lanthanide picrate salts are shifted upon complexation to other wave lengths that means the picrate anions one, or more are coordinated to the metal ions[32,33, 40].

Thermal analysis:

The Pr^{3+} , Nd^{3+} , and Dy^{3+} complexes of B18-crown-6 showed almost similar thermal behavior and results. All the three complexes went through three stages in their thermal decomposition; the first stage was the dehydration step, followed by the second stage which was the decomposition of the anhydrous complex into unidentified intermediates due to the explosive nature of the picrate compounds, and finally the third stage, the formation of Ln oxides [26, 34, 35]. The dehydration process took place at a temperature range of ($66 - 120\text{ }^\circ\text{C}$). The complex $[\text{Pr}(\text{B18-crown-6})(\text{Pic})_2]\text{Pic} \cdot 2\text{H}_2\text{O}$ lost one water molecule when heated to ($73.8\text{ }^\circ\text{C}$) and lost another water molecule when heated to ($120.52\text{ }^\circ\text{C}$), it is really hard to distinguish the coordinated water from the uncoordinated water from the graphical data[30,31], the values of the weight loss found in the process (1.4% and 2.03%) are in good agreement with the calculated values (1.5% and 2.3% respectively). Both Nd^{3+} and Dy^{3+} complexes lost one water molecule when heated to (66.35 and $76.51\text{ }^\circ\text{C}$) respectively, the weight losses found in the process (1.58% and 1.98% respectively) were in good agreement with the calculated values (1.55% and 2.2% respectively). All the three complexes started to decompose at a temperature range of ($260 - 315\text{ }^\circ\text{C}$),

an endothermic peak followed by an adjacent exothermic peak appeared at this range of temperature and multiple explosions took place at the same temperature range due to the explosive nature of picrate compounds forming unidentified intermediates [26]. After this temperature range other weight losses were recorded up to (600 °C), at this temperature Ln oxides were formed [26, 27] which were stable against heating up to more than (800 °C). The complexes of cryptand showed similar behavior, and the data are shown in table (5).

Molar conductance:

The molar conductance values of all the complexes were measured in DMSO at 25 °C. The values obtained lie in the range (50 – 80 Ohm⁻¹.cm².mol⁻¹), this indicates that all the complexes are electrolytes and shows that in benzo-18-crown-6 complexes two picrate anions are coordinated to the metal ion leaving one picrate anion uncoordinated as a counter ion, while in 221-cryptand complexes only one picrate anion is coordinated to the metal ions [42].

Antibacterial assay:

All the prepared complexes were tested *in-vitro* against four types of pathogenic bacteria, one gram positive (Staphylococcus aureus) and three gram negative (Escherichia coli, Salmonella and pseudomonas aeruginosa), and their results were compared to the results of the broad-spectrum antibiotic chloramphenicol. They showed good promising results when compared to the commercial antibiotic, they showed clear inhibition zones some larger than those of the antibiotic, some similar and others smaller. The notice worthy case was that the antibiotic chloramphenicol showed no activity at all against the pathogenic bacteria pseudomonas aeruginosa while all the prepared complexes showed very good results, another case was that the prepared complexes showed greater activity against Staphylococcus aureus than the antibiotic. The inhibition zones measured in millimeters are listed in table (6). Further *in-vivo* studies are required in order to estimate the side effects of these complexes and to study their behavior inside the biological system.

IV. Discussion

All benzo-18-crown-6 complexes have the suggested formula [Ln.L.(Pic)₂]Pic.nH₂O, while all 221-cryptand complexes have the general suggested formula [Ln.L.(Pic)]Pic₂.nH₂O where; (Ln³⁺ = Pr³⁺, Nd³⁺, Dy³⁺), (L = B18-crown-6 or 221-cryptand), (Pic = picrate anion), (n = 1, 2 or 7), which is confirmed by their elemental and thermal analysis. The molar conductance values of the complexes lie in a range which confirms that there are two picrate anions coordinated to the Ln³⁺ ion in benzo-18-crown-6 complexes, and one picrate anion coordinated to the metal ions in 221-cryptand complexes which is also confirmed by their IR spectra through the shift in both symmetric and asymmetric (NO₂) stretching vibrations, and also confirmed by their UV – Visible Spectra. The spectral changes and the shifts in the (C-O-C) stretching vibration indicates that the Ln³⁺ ion lies inside the cavity of B18-crown-6 and is encapsulated by 221-cryptand, these shifts also indicate the strong interaction between the Ln³⁺ ions and the ligands, this is due to the size matching between the radius of the ion and the size of the cavity of the ligand, (1.34 – 1.43 Å) for B18-crown-6 and (1.013, 0.995, 0.912 Å) for Pr³⁺, Nd³⁺ and Dy³⁺ respectively. Two picrate anions are coordinated to the metal ion through their phenolic oxygen and the oxygen of the nitro group, to give rise to the coordination number of (10) in B18-crown-6 complexes, and one picrate anion is coordinated to the metal ions in 221-cryptand to give rise to the coordination number (9). These coordination numbers are not uncommon since lanthanides offer the possibility of a wide range of coordination numbers (up to 12), although coordination numbers (8) and (9) are the favorable but other coordination numbers exist too. The UV – Visible Spectra of the prepared complexes confirmed their formation through the simple shifts and changes of intensities of their peaks since it is known that the *f* orbitals are deeply buried inside the atom and are well shielded from the environment so upon complexation with ligands, only minimal changes are observed in the electronic absorption and emission spectra, such as small displacements in the peak positions, and changes in the relative intensities of some of the emission peaks. All the prepared complexes are of explosive nature at a temperature higher than (260 °C) as it is indicated by their thermal analysis which is the nature of all picrate compounds and a common behavior in most nitro compounds. All the prepared complexes were tested *in-vitro* against four types of pathogenic bacteria, one gram positive (Staphylococcus aureus) and three gram negative (E. Coli, Salmonella, and Pseudomonas aeruginosa), and the results were compared to that of the broad spectrum antibiotic Chloramphenicol. The results were very good in comparison to the antibiotic and they were the best against pseudomonas aeruginosa. Pseudomonas aeruginosa is resistant to most of the well-known antibiotics, and chloramphenicol showed no activity at all against Pseudomonas aeruginosa while all the prepared complexes showed very good results, their inhibition zones measured in millimeters are listed in table (6). One of the expected mechanisms for the action of these complexes on the tested bacteria is believed to be related to the metal-chelation or the effect of the chelate (the ligand) on the metal ion. The most important property of the chelating agents (ligands), in lanthanide chelate

complex, is its ability to alter the behavior of lanthanide ion with which it binds in biological systems, and the chelation markedly modifies the bio distribution and excretion profile of the lanthanide ions.

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Table (1): Elemental analysis, colors, melting points, magnetic moments and the conductivity values of the Metal salts and their corresponding complexes

Formula M.wt.(gm/mole)	C% Cal. (found)	H% Cal. (found)	N% Cal. (found)	M% Cal. (found)	Color	M.P. °C	Magnetic moment BM	$\Omega^1\text{cm}^2.\text{mol}^{-1}$
Pr(Pic) ₃ .6H ₂ O 933.2866	23.165 (23.055)	1.944 (1.823)	13.507 (13.452)	15.098 (14.897)	yellow	98 – 100	4.4
Nd(Pic) ₃ .6H ₂ O 936.6189	23.082 (22.938)	1.937 (1.902)	13.459 (13.323)	15.400 (15.304)	Deep yellow	59 – 62	5.9
Dy(Pic) ₃ .3H ₂ O 900.8333	23.999 (23.713)	1.343 (1.137)	13.994 (13.802)	18.039 (17.754)	Bright yellow	65 – 68	11.1
[Pr(B18C6)(Pic) ₂] ₂ Pic.2H ₂ O 1173.583	34.796 (34.250)	2.920 (2.830)	10.741 (10.410)	12.007 (11.850)	yellow	60 – 62	5.4	50
[Nd(B18C6)(Pic) ₂] ₂ Pic.H ₂ O 1158.9001	35.237 (35.052)	2.783 (2.620)	10.878 (10.680)	12.446 (12.146)	orange	75 – 80	8.9	50
[Dy(B18C6)(Pic) ₂] ₂ Pic.H ₂ O 1177.1601	34.650 (34.450)	2.740 (2.630)	10.709 (10.520)	13.804 (13.680)	Dark yellow	80 – 84	11.2	50
[Pr(221)(Pic)] ₂ Pic ₂ .H ₂ O 1175.645	34.735 (34.087)	3.429 (3.850)	13.105 (12.614)	11.986 (11.542)	Dark orange	110 – 112	5.8	80
[Nd(221)(Pic)] ₂ Pic ₂ .7H ₂ O 1287.0685	31.728 (31.541)	4.072 (3.821)	11.971 (11.432)	11.207 (11.013)	orange	110 – 114	7.1	60
[Dy(221)(Pic)] ₂ Pic ₂ .2H ₂ O 1215.2525	33.603 (33.090)	3.483 (3.247)	12.678 (12.349)	13.372 (13.127)	orange	104 – 108	11.6	70

Table (2): The absorption frequencies of picric acid and lanthanide picrates

Compound	ν (O-H) cm^{-1}	ν (N-O) cm^{-1}	δ (C-H) cm^{-1}	ν (C-O) cm^{-1}
Picric acid	3105	1527 1342	941 919	1088
Pr(Pic) ₃ .6H ₂ O	3502	1541 1360	921 908	1085
Nd(Pic) ₃ .6H ₂ O	3472	1541 1362	943 926	1083
Dy(Pic) ₃ .3H ₂ O	3495	1525 1340	919	1087

Table (3): The absorption frequencies of ligands and complexes

Compound	ν (C-H) aromatic cm^{-1}	ν (C-H) CH ₂ group cm^{-1}	ν (N-O) cm^{-1}	δ Sci. CH ₂ group cm^{-1}	δ wag. CH ₂ group cm^{-1}	δ roc CH ₂ group cm^{-1}	ν (C-O- C) cm^{-1}	δ (C-H) aromatic cm^{-1}	ν (C=C) Stretch cm^{-1}
B18-crown-6	3053	2929	1454	1355 1255	850	1221 1117	1627
[PrB18C6 (Pic) ₂] ₂ Pic.2H ₂ O	3098	2877	1543 1327	1495	1362 1273	847	1122 1082	922 953	1634
[NdB18C6 (Pic) ₂] ₂ Pic.H ₂ O	3102	2874	1539 1327	1425	1364 1273	847	1122 1082	926	1612
[DyB18C6 (Pic) ₂] ₂ Pic.H ₂ O	3110	2872	1537 1325	1425	1364 1277	849	1124 1082	926 947	1630
221-cryptand	2873	1471 1446	1355 1292	829	1099 1029

[Pr (221) (Pic)]Pic ₂ .H ₂ O	3097	2916	1551 1333	1491 1435	1364 1265	845	1070 1038	943	1612 1637
[Nd (221) (Pic)]Pic ₂ .7H ₂ O	3094	2901	1560 1335	1489 1441	1364 1267	849	1064 1036	932	1610 1637
[Dy.(221).(Pic)]Pic ₂ .2H ₂ O	3092	2878	1556 1337	1491 1433	1366 1269	845	1078	943	1636

Table (4): The absorption data of picric acid, lanthanide picrates, ligands and complexes

Compound	λ (nm)	A
Picric acid	359	1.421
	220	1.480
Pr(Pic) ₃	357	1.260
	213	1.385
Nd(Pic) ₃	344	1.127
	203	2.825
Dy(Pic) ₃	357	1.622
	204	3.476
B18-crown-6	337	0.018
	278	2.893
[PrB18C6 (Pic) ₂]Pic.2H ₂ O	380	0.833
	254	1.077
[NdB18C6 (Pic) ₂]Pic.H ₂ O	380	0.785
	255	1.050
[DyB18C6 (Pic) ₂]Pic.H ₂ O	380	0.662
	253	0.820
221-cryptand	340	0.198
	280	1.782
[Pr (221) (Pic)]Pic ₂ .H ₂ O	380	0.956
	267	0.232
[Nd (221) (Pic)]Pic ₂ .7H ₂ O	380	0.976
	259	0.636
[Dy (221) (Pic)]Pic ₂ .2H ₂ O	379	1.069
	258	0.547

Table (5): The data of thermal analysis of the prepared complexes

Compound	Step	Temp. range of the decomposition (°C)	Suggested formula of the resultant compound	$\Delta m(\%)$ mass-loss		Temp. range of thermal stability of the complex (°C)
				Cal.	Obs.	
[PrB18C6 (Pic) ₂]Pic.2H ₂ O	1	73 – 120	[Pr.B18C6(Pic) ₂]Pic	3.10	3.47	120 – 245
	2	245 – 300	*	
[NdB18C6 (Pic) ₂]Pic.H ₂ O	1	49 – 66	[Nd.B18C6.(Pic) ₂]Pic	1.55	1.58	66 – 210
	2	210 – 310	*	
[DyB18C6 (Pic) ₂]Pic.H ₂ O	1	45 – 76	[Dy.B18C6.(Pic) ₂]Pic	2.20	1.98	76 – 223
	2	223 – 317	*	
[Pr (221) (Pic)]Pic ₂ .H ₂ O	1	52 – 120	[Pr.(221).(Pic)]Pic ₂	2.28	2.22	120 – 220
	2	220 – 287	*	
[Nd (221) (Pic)]Pic ₂ .7H ₂ O	1	47 – 205	[Nd.(221).(Pic)]Pic ₂	9.78	10.67	205 – 263
	2	263 – 322	*	
[Dy (221) (Pic)]Pic ₂ .2H ₂ O	1	101 – 175	[Dy.(221).(Pic)]Pic ₂	4.38	4.71	175 – 198
	2	198 – 236	*	...	15.42	
	3	236 – 325	*	

(*): explosive material (unidentified)

Table (6): Inhibition zones of the ligands, prepared complexes and the broad spectrum antibiotic measured in millimeters (concentration of the samples 10 mg/ml=10000 μ g/ml)

Compound	Inhibition zone(mm) Escherichia coli	Inhibition zone(mm) Staphylococcus aureus	Inhibition zone(mm) Salmonella	Inhibition zone(mm) Pseudomonas aeruginosa
DMSO	-	-	-	-
Chloramphenicol	22.5	13.0	25.5	-
B18-crown-6	-	-	-	-
221-cryptand	-	-	-	-
[PrB18C6 (Pic) ₂]Pic.2H ₂ O	19.0	23.0	20.5	20.0

[NdB18C6 (Pic) ₂]Pic ₂ .H ₂ O	16.5	17.5	18.0	20.0
[DyB18C6 (Pic) ₂]Pic ₂ .H ₂ O	12.0	19.0	17.5	18.5
[Pr (221) (Pic)]Pic ₂ .H ₂ O	12.0	18.0	16.0	16.5
[Nd (221) (Pic)]Pic ₂ .7H ₂ O	18.0	20.5	18.5	19.0
[Dy (221) (Pic)]Pic ₂ .2H ₂ O	13.5	17.0	15.5	16.5

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