

Versatile Applications of Complexes with Some Lanthanide Elements: A Review

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Abstract

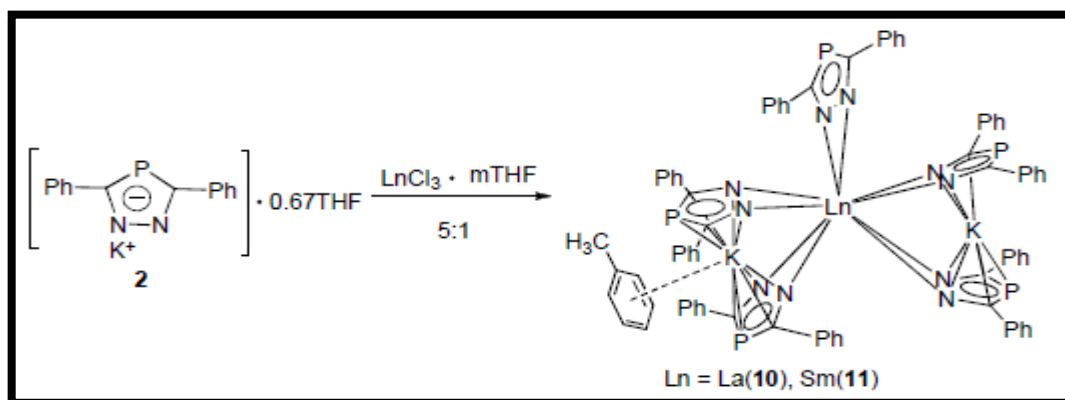
Cerium (III), Neodymium (III) and Samarium (III) Complexes existent a wide range of implementation that stretch from their play in the medicinal and pharmaceutical area because of their major significant pharmacological characteristic such as anti-fungal, anti-cancer, anti-bacterial ,anti-human immunodeficiency virus ,anti-neoplastic, anti-inflammation,inhibition corrosion,in some industrial (polymers, Azo dye).It is likely to open avenuesto research among various disciplines such as physics, electronics, chemistry and materials science by these complexes that contain exquisitely designed organic molecules.This paper reviews the definition, importance and various applications of Cerium (III), Neodymium (III) and Samarium (III) Complexes anddifferent ligands.

Introduction

Lanthanide are the chemical elements in the lanthanide series represented by (15) metal chemical elements with 57–71 (atomic numbers), which start from lanthanum and end with lutetium.The term rare earth elements are used for these elements, in addition to similar chemical elements yttrium and scandium. For the purpose of referring to any lanthanide in the chemistry of the lanthanides, the chemical symbol (Ln) is used. The element lutetium or lanthanum is distinguished by its (d-block), but because of its chemical similarity with (14) elements it was added with them. Depending on the source, all the lanthanides are elements (f-block) agreeing to the electron shell filling (4f) except for the aforementioned element[1-7].Ligands containing harddonor atoms such as oxygen and carboxylates can bond with metal ions such as lanthanide, which are classic hardacids.Because the nature of the ligand-metallic interactions in the lanthanide complexes is linked to the separation of the lanthanide elements and the bonding properties of the ligand, it has been carefully studied[8-14].Lanthanide complexes have been well studied because of their good structure, physical data and different practical uses such as materials chemistry, luminescence, diagnostics and use as catalysts, e.g. in asymmetric peroxidation reactions,in the trans esterification of triglycerides to monoesters, in (P₄)activity by lanthanide naph-thalene complex , in the production of new anti-oxidants with great superoxide scavenging action and important in the making of biodiesel fuel[15-21].

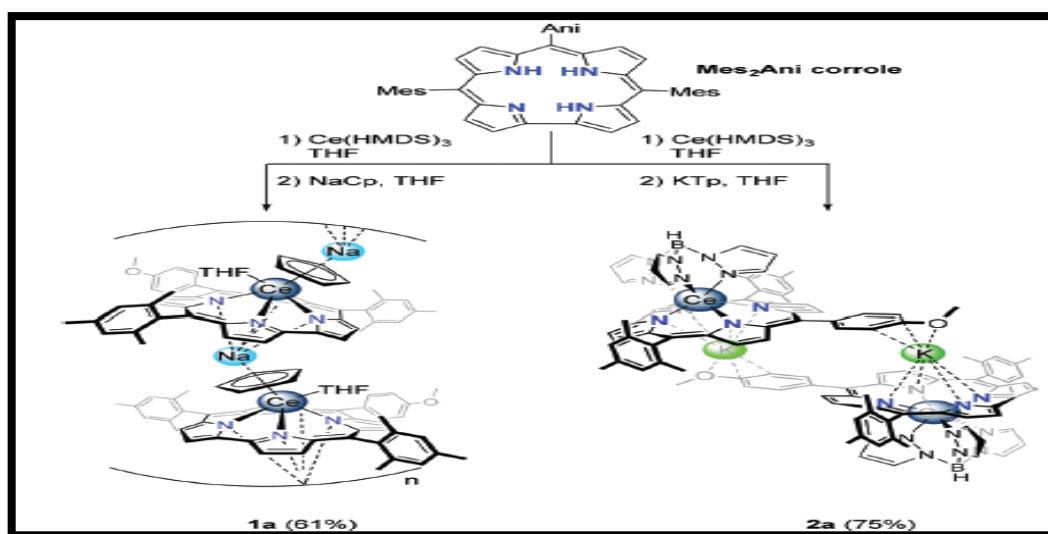
Due to their single optical, organizational, magnetic measurement, used in magnetic resonance image, single molecule magnets, sensing and activity of anti-cancer towards human prostate carcinoma cells, human galactophore carcinoma cells, liver carcinoma cells, Hela cervix carcinoma cells and human stomach carcinoma cells[22-27].

In 2016, Minggang et al. [28] were synthesized of some new complexes of metal ions Ce(III), Nd(III) and Sm(III) with 1,2,4- diazaphospholide derivative in different mole ratio (1:3, 1:4, and 1:5) at lab temperature. All of compounds diagnosis by FT-IR and ^1H , ^{13}C NMR. I found different coordination positions for the prepared complexes. Through magnetic susceptibility, the magnetic properties of many complexes have been studied and a great convergence was found between theoretical and practical measurements of trivalent ions, Scheme (1)



Scheme(1): Preparation of compounds

In 2016, Keith et al. [29] were formed a structure of polymer/1a, and the overall shape $[\text{Cor}-\text{Ce}(\text{T.H.F})-\text{Cp}-\text{Na}]_n$, where Cor = 5,15 - bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl)-corrole, T.H.F= tetrahydrofuran), by sodium cyclopentadienide (NaCp) and a structure of dimer/2a, with the overall shape $[\text{Cor}-\text{Ce}-\text{Tp}]_2$, when (KTp) is employed. The spectroscopic properties and structural of the compounds have been characterized, Scheme(2).



Scheme(2): Production of compounds(1a , 2a).

In 2016, [30] By X-ray diffraction, FT-IR and UV-Vis spectroscopy, new complexes were identified by the extraction of Nd (III) in hydrophobic solvents having acid organophosphorous extracts. In the structure of $[\text{Nd}(\text{D.M.P})_3]$, where D.M.P=dimethyl phosphate where each neodymium atom is bounded by 6O atoms of a compound D.M.P in the octahedral figure. The octahedral co-ordination was conservation from (dilute - saturated) settings and this by persistence of spectral properties crossways a varied range of neodymium applications, Fig.(1).

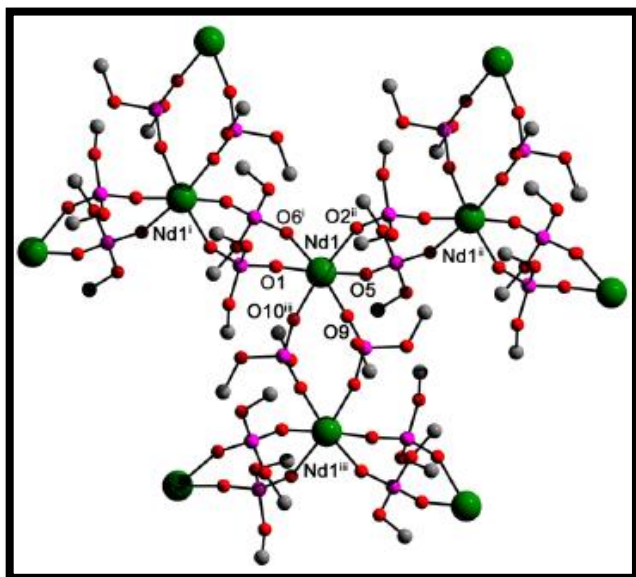


Fig.(1): Structural of complexes

In 2016, Srikanth et al. [31] were synthesized of some new Sr(III) compound, $[\text{Sm}(\text{d.p.q})(\text{D.M.F})_2(\text{H}_2\text{O})\text{Cl}_3]$ (1), $[\text{Sm}(\text{d.p.p.z})(\text{D.M.F})_2(\text{H}_2\text{O})\text{Cl}_3]$ (2) (d.p.q=dipyridoi-3,2-d:2',3'-f]quinoxaline, (d.p.p.z = dipyridoi-3,2- a:2',3'-c]phenazine, (D.M.F = N,N'-dimethylformamide (DMF) and characterized. It was observed that samarium in (1) and (2) takes an eight-coordinated through two donor nitrogen atoms in (dpq/dppz) ligand, three negative chlorine ions, one water molecule and two molecules of DMF. The complexes have been calculated of their reaction with proteins, (DNA) and photosensitive (DNA cleavage) action due to the normalization and photosensitivity capacity of d.p.q and d.p.p.z coordinated bonds ligands, Fig.(2).

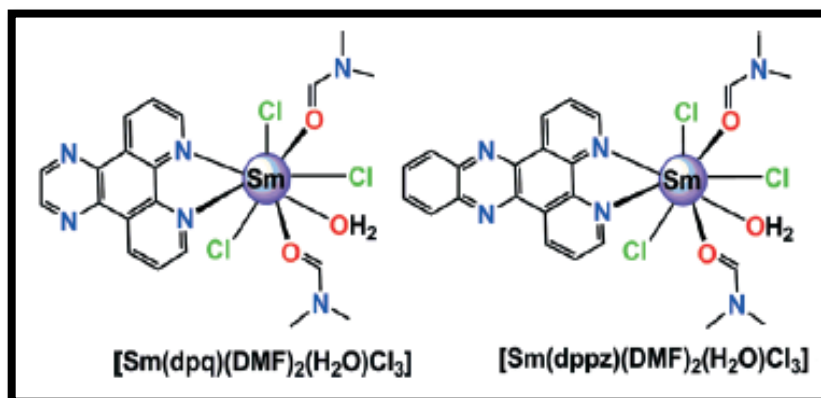


Fig.(2): Synthesis of Samarium(III) complexes

In the same year, Roushan et al. [32] synthesized new in-organic polymers $H_2[\{M(H_2O)_8M(H_2O)_7M(H_2O)_6\}P_2W_{18}Ce_3O_{70}(OH)(H_2O_2)] \cdot x H_2O$; $M = \text{Cerium (iii)}$ (1), Neodymium (iii) (2) and samarium (iii) (3) by synthetic reactions in aqueous solution and diagnosis by C.H.N.S., FT-IR spectra, magnetic measurement, thermal analysis. The 2D form of (1–3) were structure by tri-Cerium (iii) substituted sandwich-form polyoxoanions modified by $6Ln^{+3}$ cations $[M(H_2O)_x]$ ($x = 6-8$) groups. The $[M(H_2O)_x]$ ($x = 6-7$) units acting via bridges to form 2D layer, but the $M(H_2O)_8$ units the 2D layers together by H-bond to form a 3D supramolecular forms, Fig.(3).

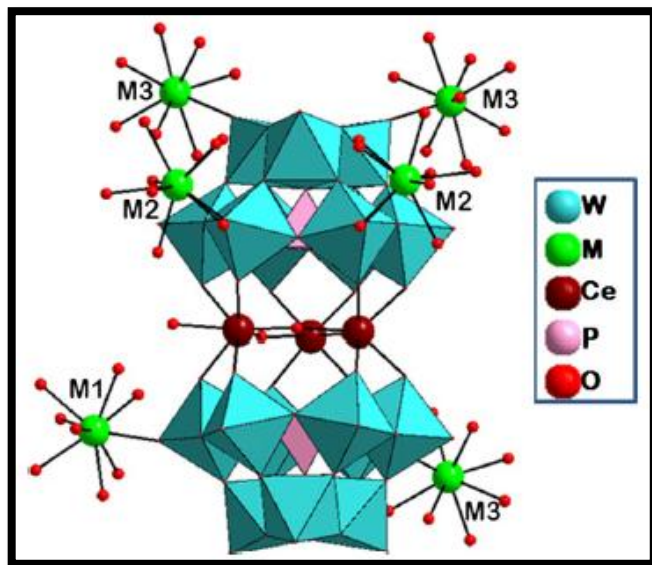
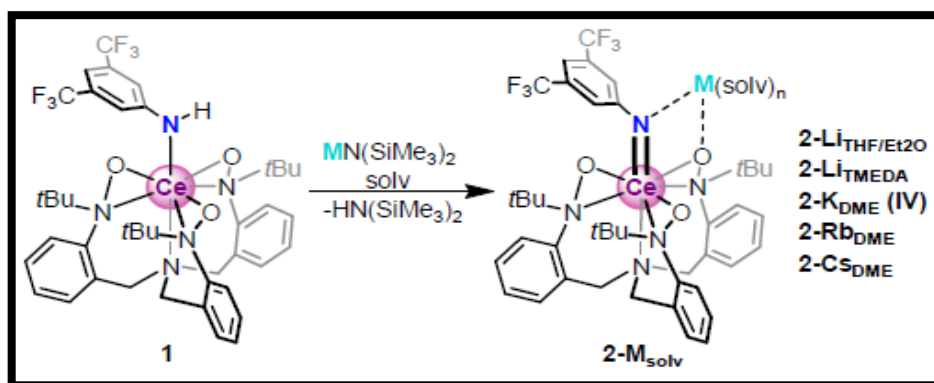


Fig.(3): The structure of compounds (1–3).

In 2017, Lukman et al. were [33] synthesized of some new achain of Ce(IV) imido compound, $[M(SOLV)_x][Ce=N(3,5-(CF_3)_2C_6H_3)(TriNO_x)]$ ($M = \text{Rb, Li, K, Cs}$; $SOLV = Et_2O, D.M.E, T.M.E.D.A \text{ and } T.H.F$) and diagnosis. The complex (first) featuring an un-supported, caudalvarious bind among a Cerium(IV) with a ligand was lonely using en-capsulation of a Cerium⁺ counter ion and 2, 2, 2-cryptand. This compound display the abbreviated detailed (Ce=N) bond length of 2.077(3) Å. computationally data of Ce-imido compounds by D.F.T ways displayed a comparatively greater influence of Ce(5d-orbital) Comparison(4f-orbital) to the (Ce=N) bonds, Scheme (3).



Scheme (3): Preparation of complexes

In 2017, El-Shafiy et al. [34] were synthesized of new series of mono-nuclear VO (IV), Ce(III), Th(IV) and UO₂(VI) compounds of (H₂L), where H₂L= 1-ethyl-4-hydroxy-3- (nitroacetyl)quinolin-2 -(1H)-one . The compounds were diagnosed using various methods via C.H.N.S, TGA, FT-IR, ¹HNMR, mass spectra, UV-Vis and magnetic data, conductance . The ligand acts bi-dentate ligand forming mono-nuclear complexes, general formula [(H₂L)VO(H₂O)₂].0.5H₂O, [(H₂L)M(NO₃)_x(H₂O)_y].nH₂O; M = Th or Ce , x = 2 or 1 , y = 4 or 3 and n = 7 or 2 and [(H₂L)UO₂(H₂O)_x(MeOH)_y].nH₂O; x = 3 or 2, y = 1 or 0 and n = 2.5 or 0.5. The photodata of the syntheses compounds were calculated. Kinetic factors (ΔH, Ea, ΔG, A and ΔS) of the TGA steps have been calculated by (Coats–Redfern) equations. The anti-microbial action of (L) and its complexes was determined towards the micro-organisms *E. coli*, *S. aureus*, *C. albicans*, *K. pneumonia*, and *P. vulgaris* . The antitumor action of (L) and its complexes was examined towards human breast cancer cell lines and human Hepatocellular carcinoma, Fig. (4).

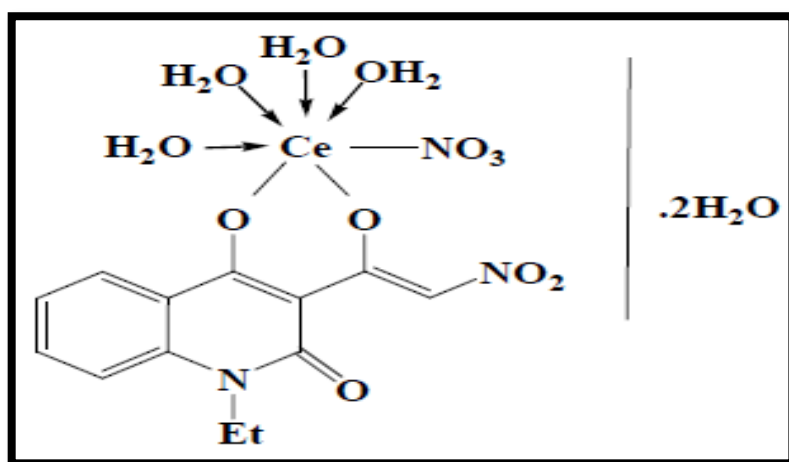


Fig. (4): The structures of complexes cerium ion

In 2017, Mbossé et al. were [35] created of ligand using the reaction for pyridine-2-carbaldehyde with 2- hydrazine pyridine. Nd and Sm complexes were lonely when nitrate salt was in addition to the solution of the ligand. The compounds were characterized by C.H.N.S, FT-IR and magnetic susceptibility of the two crystals. metal centers have distorted tri-capped tri-gonal prism structure, with the Schiff base act tri-dentate ligand. The D.P.P.H (radical scavenging) properties of the Schiff base and their Ln(III) compounds were studied. The Ln(III) compounds were high activity in D.P.P.H compare the ligand (alone), Fig. (5).

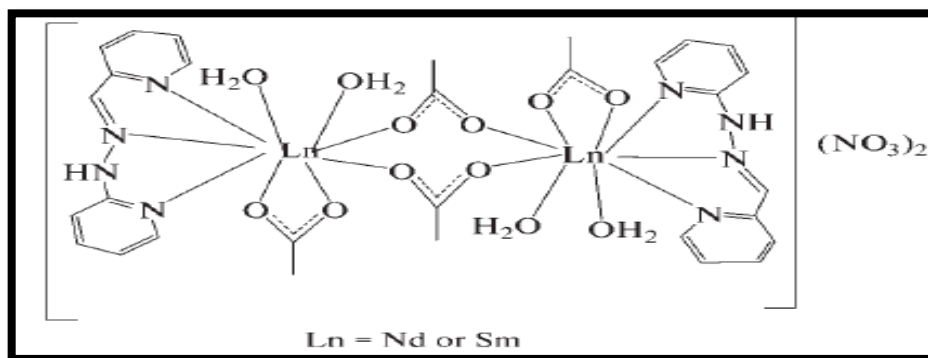


Fig. (5): Synthesis of complexes.

In same year, Oleksandra et al. [36] were synthesized of new Nd(III) complexes of product ligand by reaction(allyl- 3 –oxo –butanoate) and (2-methyl- 5-phenylpenten-1-3,5-dione) .Byfree-radical polymerization, the polycomplexes on their basis and co-polymers with N-vinylcarbazoleand styrene in ratio (5:95) were gotten . The data of measured have displayed that the formation of the coordinatesites isun-changed by the poly-merization. As a product, the kind of co-ordination was studied and the building ofco-ordination polyhedral was supposed.Fluorescence spectra were diagnosed for metallo-complexesand polymers in the solid state and in solutions, Fig. (6).

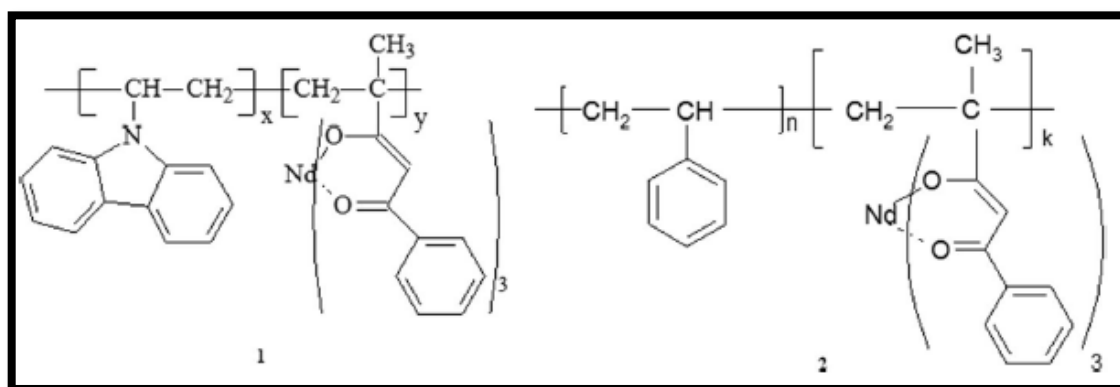


Fig. (6): The structure of (1) and (2)

In 2018, Sajjad et al. [37]were synthesized of new aCe(iii) compound, $[\text{Ce}_2(\text{NA})_6(\text{H}_2\text{O})_4]$ (1) , where (NA = nicotinic acid) and diagnosed by X-ray diffraction, FT-IR and thermo-gravimetric analysis. In compound (1), the Ce(iii) ions are linked by (COOH)sets of ligands. Every oneCe(atom) in compound (1) is 9 – co-ordinate and shown a (mono – capped - square) anti-prism structure. The Cerium (iii) ions are co-ordinated through7(O) atoms of (COOH) groups and 2(O) atoms of H_2O molecules,Fig. (7).

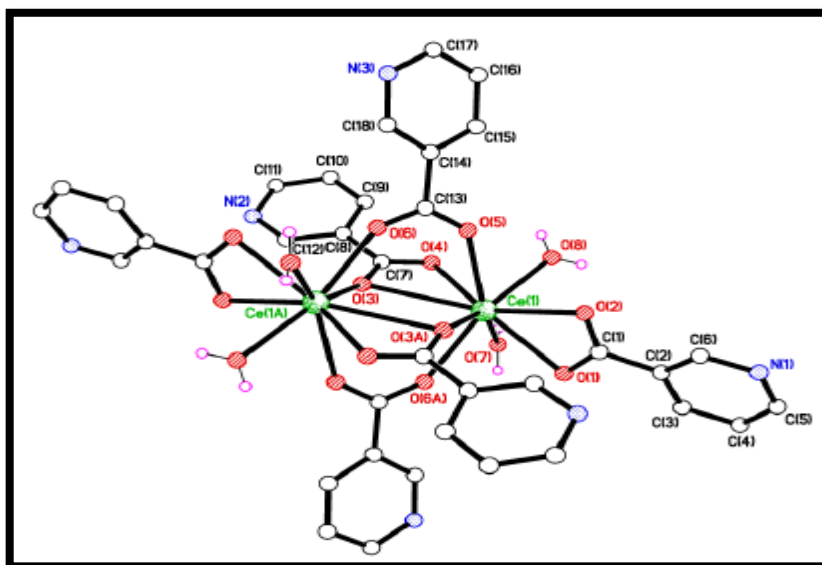


Fig.(7): Molecular structure diagram of complex.

In 2018, Zhichun et al. [38] were synthesized of anewsamarium (iii) compound $[\text{Sm}(\text{L.A})_2(\text{P.I.C})_3]$,where H.P.I.C= $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, L.A = derived-alkaloid, $\text{C}_{17}\text{H}_9\text{NO}_3$

,and diagnosed using FT-IR, C.H.N.S and X-ray diffraction. Reaction of the samarium (iii) compound and (ct-DNA) was characterized by different methods, via UV-Vis, circular dichroism and fluorescence spectroscopy. The results displayed that the K_b (binding constant) of the samarium (iii) compound and (ct-DNA) was studied to be (5.03_103) L/mol using electronic spectra. The thermo-dynamic study proposed that the fluorescence strength of the samarium (iii) compound was little by (ct-DNA) essentially by a (dynamic quenching) mechanism. Also, this samarium (iii) complex showed important growing inhibition on the typical (three) (HepG₂, T-24, SK – OV-3) and tumor cell lines with the corresponding (IC₅₀) values. The *in vitro* anti-tumor action was similar with (cisplatin and LA), which proposed that it might be an original broad band anti-tumor factor with high substantial solubility, Fig. (8).

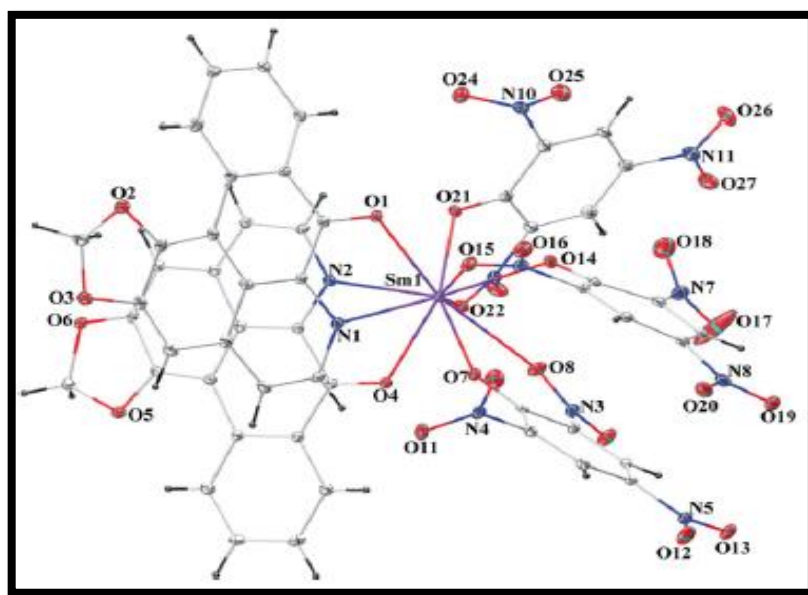


Fig.(8):The structure of complex .

In 2018, Yasuchika et al. [39] were synthesized of a new Terbium(iii), Europium (iii), and Samarium(iii) compounds shows an significant part in the plan of monochromatic (green, deep-red and red) luminescent materials for shows, sensing devices and lighting. The (4f–4f) radiation of Ytterbium(iii), neodymium(iii), and Europium(iii) compounds is detected in FT-IR for security applications and bio imaging. Organic molecular project elements, including (1) the energy transfer from metallic ions of effective photosensitized luminescence (2) the control of the excited triplet (T_1) state, the properties on the (C.T) band, are studied. The electroluminescence and triboluminescence of Ln(iii) complexes are also studied, Fig. (9).

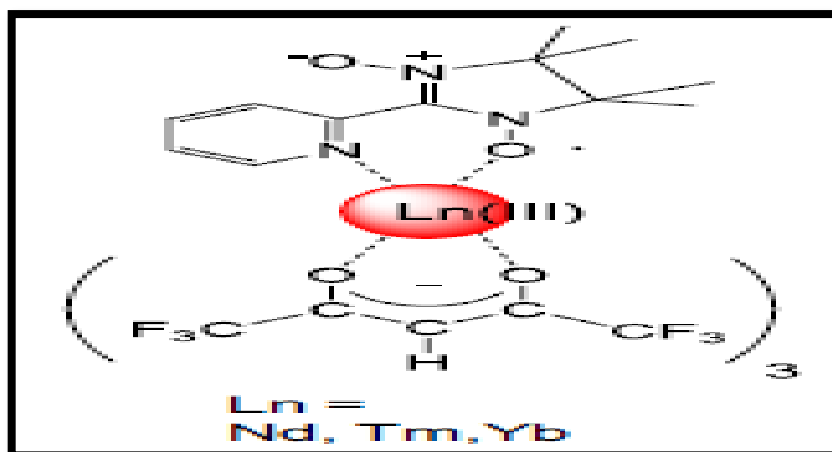


Fig. (9):The structures complexes.

In 2019, Voskresenskayaa et al. [40] were synthesized of new Ce(IV) complexes by 1-phenyl-2,3-dimethyl-4-dimethylaminopyrazolone-5, 7-iodo -8 -hydroxyl -quinolone -5-sulfonic acid and 8-oxy quinolone, which are made at the step (first) of oxidation of these heterocyclic complexes with Ce(IV) and calculated by spectrophotometry, pH-metry and photometry at ionic strength ($I=2$) in H_2SO_4 solutions at (285.15–297.15) K, where pH 0.5–3.0. The conformation of the compounds and the formula in the organic ligand is found in them are studied. The constants of stability and constants of rate of their intra-molecular redox breakdown are studied. In chemistry coordination for the quantitative description of oxidation reactions of organic compounds with transition metal ions it is possible to use the type of linear correlations between thermodynamic stability and kinetic stability of the intermediate complexes discussed in this study, Fig. (10).

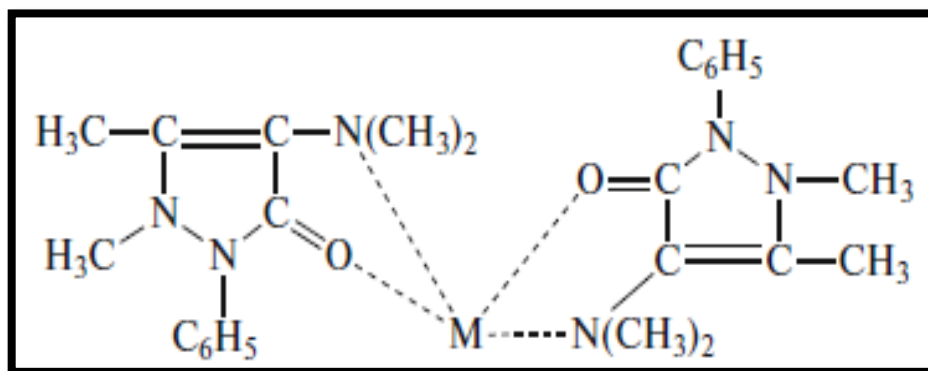


Fig.(10): Synthesis of complex (M=cerium(IV))

In 2019, Nagwa et al [41] were prepared samarium - 5-fluorouracil (5-FU) complex to enhance the effectiveness of the 5-FU drug. This complex was characterized by UV-Vis spectrometry high performance liquid chromatography and various calorimetric of scanning. Furthermore, the antitumor activity of the prepared complex was explored on the human colon cancer cell Caco₂ via evaluation of the cytotoxic activity of this complex through trypan blue cell viability. Apoptosis was also assessed through morphological changes, by Annexin V=PI flow cytometric analysis. The results revealed that the trivalent Sm enhance the 5-FU effect against the chemo-resistant colorectal carcinoma cell line, Fig. (11).

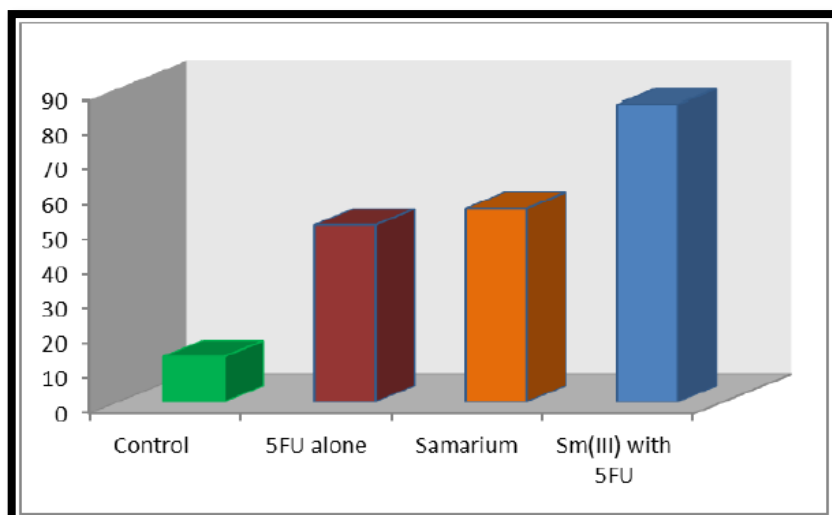
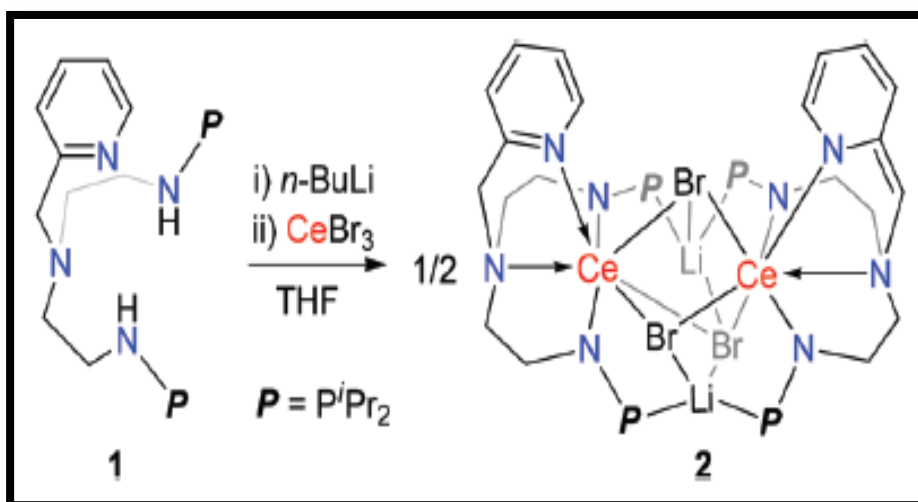


Fig.(11): Effects of Sm (III)-5-FU complex in Caco₂ cell line

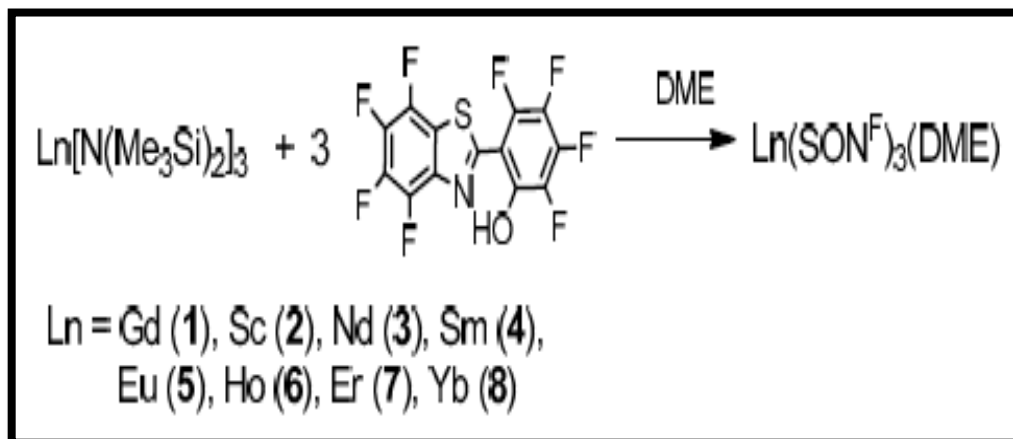
In 2019, Xiaoqing and Congqing [42] were syntheses chain of hetero - bimetallic compound of (Br) bridged Ce(iii)-alkali metal or group (9) metals by a multidentate N-P ligand. Hetero - metallic complexes show main role in activation and catalysis of small molecules because of the synergistic properties of various metals, Scheme (4).



Scheme (4): The synthesis of complex.

In 2019, Tatyana et al. were [43] synthesized of new a set of Scandium, Neodymium, Samarium, Europium, Holmium, Gadolinium, Erbium, Ytterbium compounds with per-fluorinated 2-(benzothiazol-2-yl)phenolate ligands $[\text{Ln}(\text{SONF})_3(\text{DME})]$ through interaction of silylamides $\{\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3\}$ with phenol $[\text{H}(\text{SONF})]$. By using the measurement of (X-ray analysis), the structure of the primary phenolic, Sc, and Er complexes was determined, which revealed that the resulting compounds are mononuclear, unlike their previously manufactured analogues as they are non-fluorinated binuclear $[\text{Ln}(\text{SON})_3]_2$. When excited by light of all the obtained complexes (in THF solutions or in the solid state) with (395 or 405) nm intense illumination of the bonds at (440-470) nm. The Neodymium, Ytterbium and Europium complexes display in the near high intensity (FT-IR region) while the Samarium lumines derivatives produce both in the (FT-IR and in the UV-Vis

region) and the Erbium complex also produce a weak metal-centered peak in the UV-Vis region, Scheme (5).



Scheme (5): Production of complexes 1–8

In same year, Sanjay et al. were [44] synthesized of lanthanide compounds, $[\text{Sm}(\text{HL})_2(\text{T.H.F})_2]$ (1), $[\text{Eu}(\text{HL})_2(\text{T.H.F})_2]$ (2) and $[\text{Yb}(\text{HL})_2(\text{T.H.F})_2]$ (3), where $\text{HL} = \{2\text{-N-(3-aminopropyl) benzimidoyl}\}$ -6-benzoyl-4-methylphenol and diagnosis by C.H.N.S, mass spectrometry, conductance, FT-IR, ^1H NMR and UV-Vis spectra and cyclic voltammetric. The spectral studies propose that the $[\text{Ln}_4\text{O}_4]$ co-ordination polyhedron is a distorted dodecahedral. The electrochemical performance of (1–3) display a reversible metal centered oxidation wave at (0.544–0.643) V and ligand centered reduction at (1.085–1.260) V versus Ag/Ag^+ . Reaction of (1), (2) and (3) with DNA proposes an inter-calative bonding model, Fig.(12).

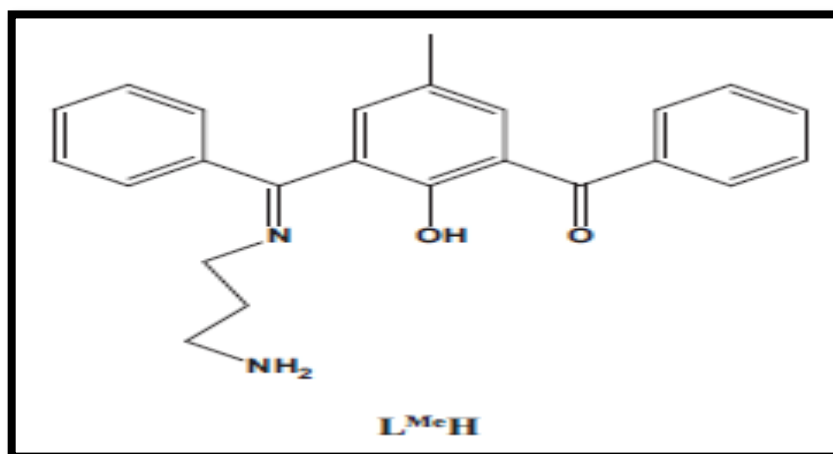


Fig.(12): Synthesis of compound (LMeH).

In 2020, Xiao-Tian et al. were [45] synthesized of three compounds, general formula $[\text{Ln}_3\text{Zn}_3(\text{Hvanox})_3(\text{vanox})_3(\text{NO}_3)_6(\text{H}_2\text{O})_5] \cdot n\text{EtOH}$, where $\text{Ln}^{\text{III}} = \text{Dysprosium}$, $n=3$ (1), $\text{Ln}^{\text{III}} = \text{Terbium}$, $n=5$ (2), $\text{Ln}^{\text{III}} = \text{Erbium}$, $n=5$ (3) through interaction of o-vanillin oxime (H_2L) and Zinc nitrate hexahydrate and Ln-nitrate hexahydrate salts in the found of triethylamine. Magnetic data reveal that (1), (2) shown (Field-induced dependence), shown (Single molecule-magnets) performances, whereas (3) displays slow magnetic re-laxation, Fig.(13).

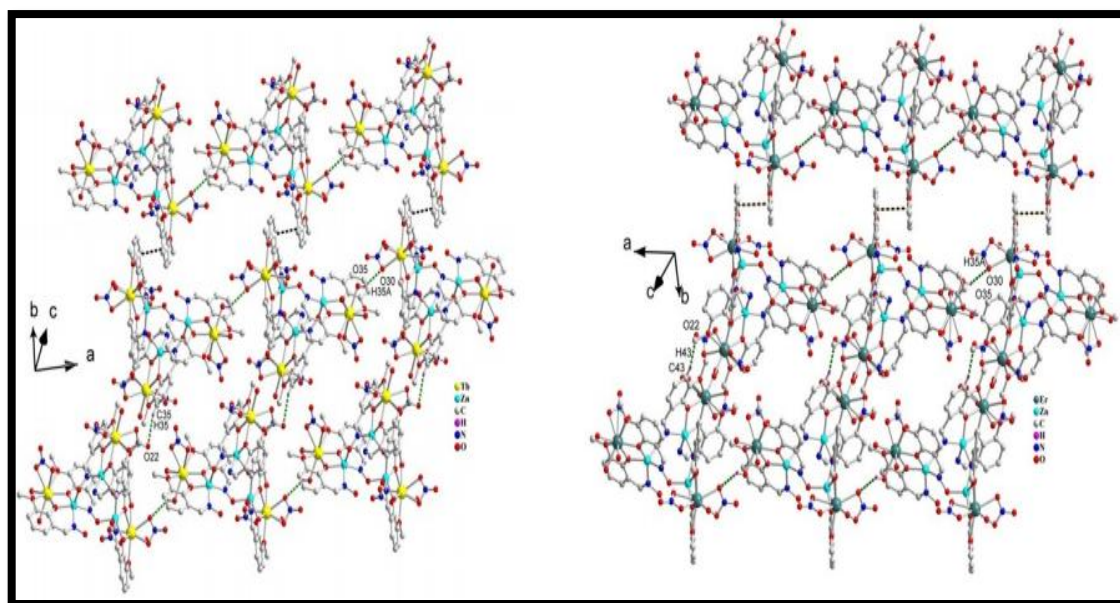
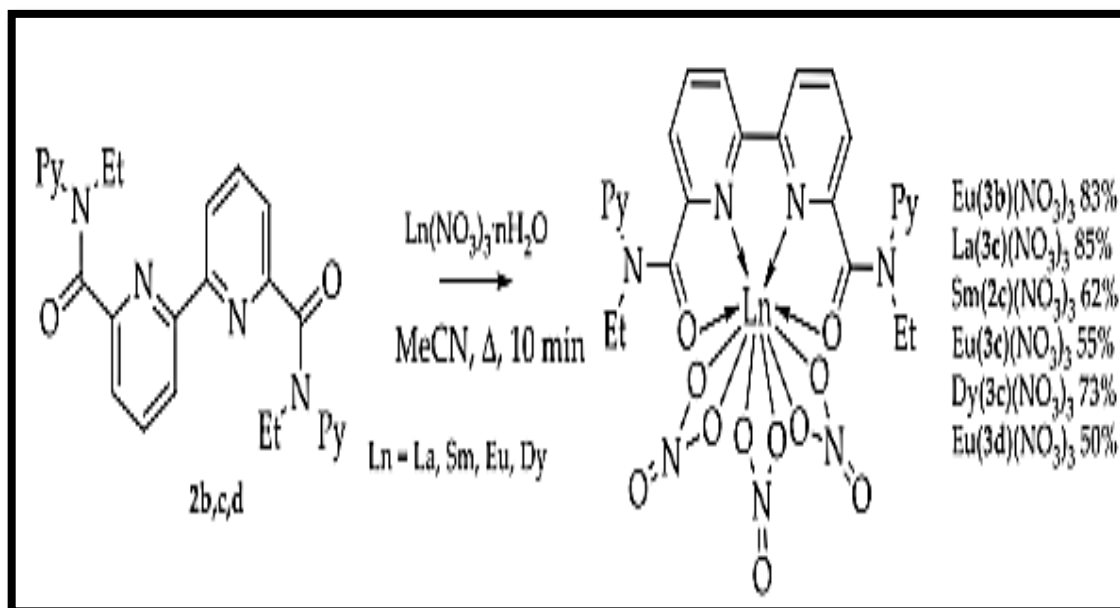


Fig.(13): The 2D supramolecular network of complex 2 (left) and 3 (right).

In 2020, Nataliya et al. [46] were synthesized of some compounds of lanthanides with di-amides of [2,20 – bipyridyl-6,60-dicarboxylic acid] behavior different heterocycle-based side series for the clarification of the result of the heterocycle on the properties and structure of the ligands. The multigram scale ways for the synthesis of different [N-alkyl-heterocycles] and their di-amides were established. The complexes of novel ligands were created and X-Ray and ^1H -NMR calculated their structure in solid state and solution. The luminescence of novel Erbium compounds was meaningfully greater than for all before [2,20 – bipyridyl-6,60 – dicarboxamides] and (QY) ranges (18%). Irregularity ratios of Erbium compound were (25%) greater when associated other compounds with [2,20 – bipyridyl-6,60 – dicarboxamides], which shows large deviance from the contrary center, Scheme (6).



Scheme (6): Preparation of Ln(III) complexes

To protect against corrosion of aluminum alloy (AA2024), widely used cerium has been used for this purpose. The introduction of synergistic inhibition has been studied by using different oxidation states of cerium (Ce^{3+} and Ce^{4+}) with other compounds. However, the mechanism of inhibitory corrosion is still unclear when (Ce^{4+}) is used with organic compounds. In 2020, Mohamed et al [47] studied inhibition action of melamine (M) and (Ce^{4+}) on aluminum alloy (AA2024) corrosion in (3.5% Sodium chloride) solution. In order to study the synergistic effect of various (Ce^{4+} - M) ratios on (AA2024) corrosion, Electrochemical Impedance Spectroscopy and Potentiodynamic Polarization techniques were used. The Potentiodynamic Polarization method displayed that a grouping of (Ce^{4+} 50% and M 50%) result the lower most rates of corrosion, together action as cathodic inhibitors. The role of the compounds (organic) is to increase the reduction of Ce^{4+} were studied by a original mechanism of corrosion synergistic inhibition using Ce^{4+} and compounds (organic), Fig. (14).

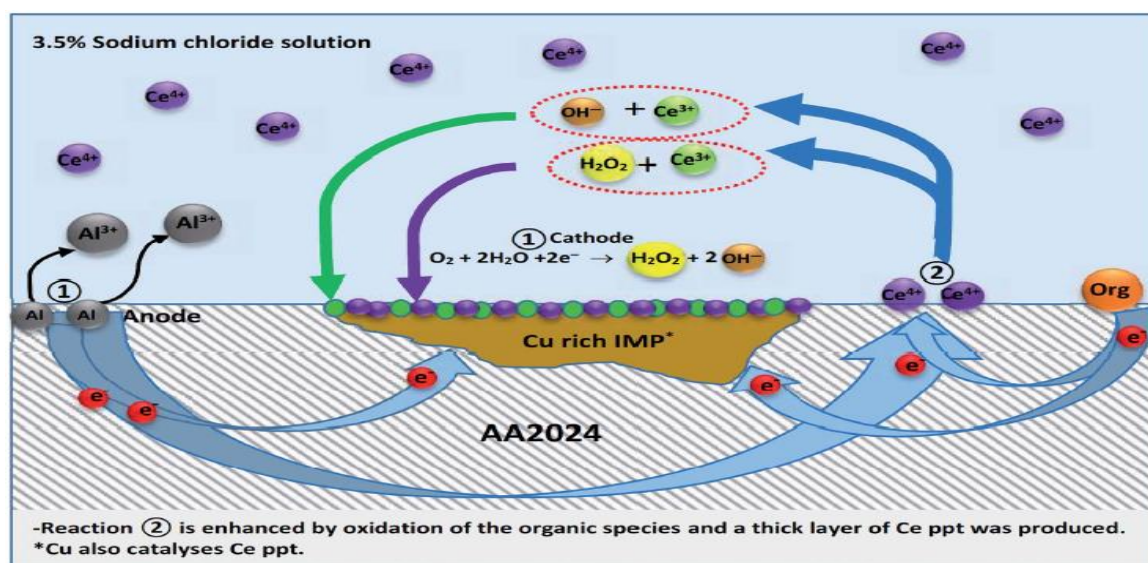


Fig.(14): The role of inhibitor (Ce^{4+} /organic) in protecting corrosion (AA2024)

In 2020, Khaled et al [48] were syntheses new complexes by reaction metals ion U(VI), Sm(III) and Ce(III) with (A.P.D.B), where A.P.D.B = [2-((4-(N-acetylsulfamoyl) phenyl) diazenyl)-3,4,5-tri hydroxyl benzoic acid]. The compounds were made in alkaline medium by (borate buffer) at pH=9 of U(VI) and Sm(III) and at pH=8 of U(VI) and Sm(III)-A.P.D.B compound was improved in the founds of (C.T.A.B) via a cationic micellar media while that of Ce(III)-A.P.D.B compound was enhanced through used aerosol (G.P.G) surfactant. The suggested ways were also enhanced through used DMF and acetone as (organic solvents) for only Sm(III) and U(VI)-APDB compounds, respectively. The compounds were made by (1:2) (M : L) ratio. The interference action of different diverse ions was also studied. The suggested ways were positively applied of the determination micro-amounts of the carefully chosen metallic ions in plant samples, bio-logical and industrial, Fig.(15).

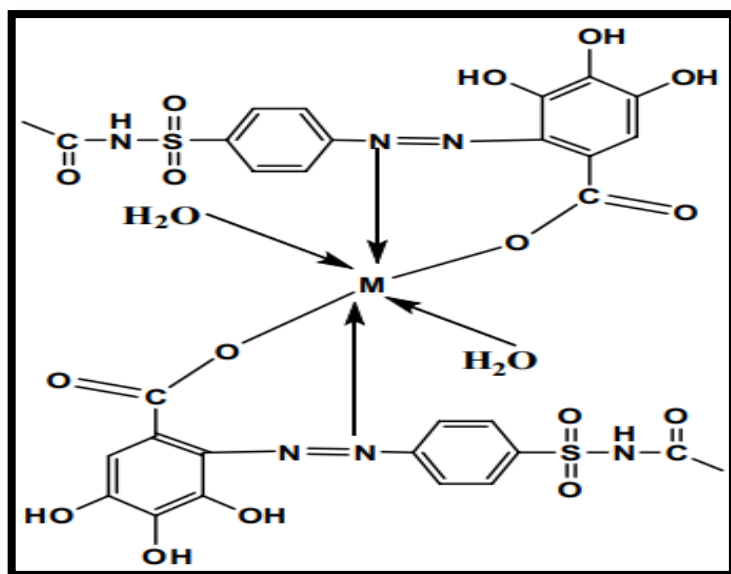


Fig.(15): The structure of complexes
M= Ce(III) , Sm(III) and U(VI)

In 2020 Rafael et al [49] were prepared of new (Ru(II)–Nd(III)) heterobimetallic compounds with silyl (alkoxy) active groups. Infrared emission due to visual excitation leading to energy transfers from the ruthenium (II) donor to the neodymium (III) acceptor. Activity of energy transfer (η_{EnT}) and Rates of energy transfer (k_{EnT}) are, respectively, 44% and $0.61 \times 10^7 \text{ s}^{-1}$ for $\text{RuL}_1\text{--NdL}_3$ complex. η_{EnT} (84%) and greater values of k_{EnT} ($3.04 \times 10^7 \text{ s}^{-1}$) were noticed of $\text{RuL}_2\text{--NdL}_4$ compound. ($\text{RuL}_1\text{--NdL}_3$ and $\text{RuL}_2\text{--NdL}_4$) compounds were diagnosis using C.H.N.S, mass spectrometry, ^1H -NMR and FT-IR. For the purpose of obtaining applications as biosensors or new biomarkers near infrared (NIR) the presence of trialkoxysilyl-substituted ligands will allow grafting on any silica or silicate surface, Fig.(16).

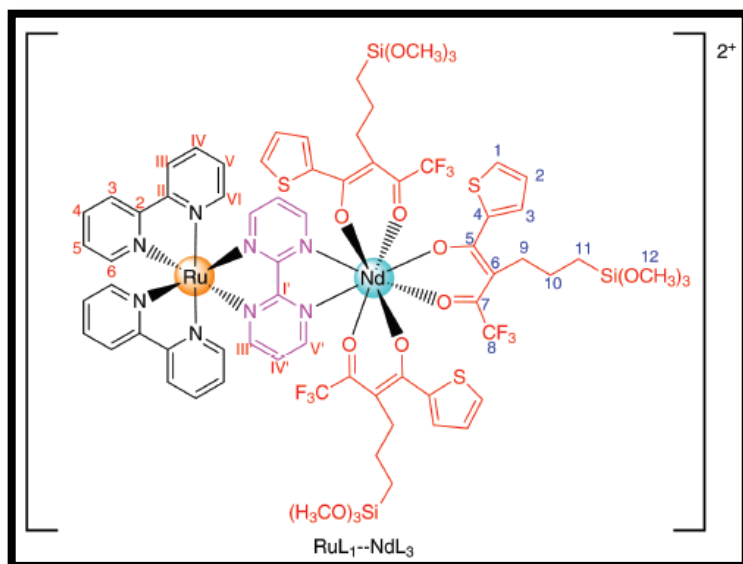


Fig. (16): Synthesis of the heterobimetallic complexes, $\text{RuL}_1\text{--NdL}_3$.

In 2020 Rong-fanget al [50] were synthesized of new Three lanthanide compounds , general formula, $\{[\text{Dy}_2(\text{bpda})_3(\text{H}_2\text{O})_3]_4 \cdot 2\text{H}_2\text{O}\}(\text{Dy-1})$, $\{[\text{Sm}(\text{bpda})_2(\text{H}_2\text{O})]_n\}$

(Sm-2) and $\{[\text{Tb}_2(\text{bpda})_3(\text{H}_2\text{O})_3]4\text{H}_2\text{O}\}$ (Tb-3) (H_2bpda $\frac{1}{4}$ 2,20 -bipyridine-6,60-dicarboxylic acid). Their buildings were studied using X-ray diffraction and diagnosis using C.H.N.S, FT-IR and thermo-gravimetric analysis. Dysprosium-1 and Terbium-3 are isostructural with a combine bi-molecular- four-metal cluster build with intra-molecular (H-bond) and they method a 3D supra-molecular structure with intermolecular (H-bond). Samarium-2 is a 1D series structure and is further linked by complicated (H-bond) into a 3D supramolecular structure. These three types display important typical luminescence from the ligand - the central Ln(III) ion, which is created by solid-state photo-luminescence data. Samarium-2 displays a long luminescence lifetime and great fluorescence quantum produce, Fig.(17).

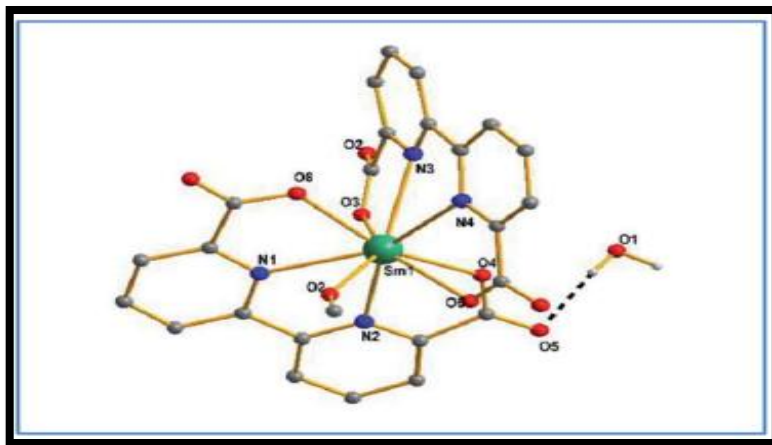


Fig.(17): The coordinated environment of Sm(III) .

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