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Mechanochemical Synthesis of Hydrazone Lanthanide Complexes to Overcome the Conventional Method Limitation

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ABSTRACT

The synthesis of lanthanide (III) Schiff base complexes will use a solvent-less reaction as a broad method of producing chemical products without the need for solvents. Mechanochemical synthesis produced pure products directly and demonstrated quantitative conversion without any byproducts. Schiff base ligand synthesis using lanthanides (III). The reaction of isatinmonohydrazone with salicylaldehyde, which then reacted with lanthanide (III) chloride for forming complexes of Ln (HISA)2Cl3 type, in which HISA= [(2-hydroxy-benzaldehyde)-3-isatin] bishydrazone and Ln = La (III), Sm (III), Eu (III), and Gd (III). In vibratory ball-mill conditions, all reactions have been conducted. Magnetic susceptibility measurement, molar conductance, UV spectral data, and proton NMR spectral data were used for characterizing the complexes and the ligand. X-ray diffraction (XRD) was used for characterizing the structure of ligand and lanthanides (III) complexes. XRD pattern of the ligand showed its crystalline nature, whereas that of lanthanum (II1) complex showed its amorphous nature. The ligand served as a neutral tridentate, which coordinated through neutral, azomethine, and tridentate. The goal of this study is to develop environmentally friendly as well as economic process for the synthesis of some lanthanide (III) complexes with heterocyclic hydrazone, that avoid the use of solvent, minimize the formation of byproduct, with high yield, and short reaction time.

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1- INTRODUCTION

Conventional synthesis through condensation regarding primary amines with product compounds in solution necessitates bulk solvent, product isolation, and generated water's removal. Since a lot of such reactions may be completed in a single step with quantitative yields through solid-state reactions, this is of great importance. This method embraces using bulk solvent while avoiding issues with solution-based chemistry, like low solubility of the solvent and hydrolysis or solvolysis of the products. Mechanochemical techniques have emerged as one of the most promising preparatory approaches for synthesizing new materials [1] Lanthanides have distinctive positions on the periodic table and a range of intriguing characteristics. The coordination chemistry of lanthanides and their complexes has garnered significant attention [2] due to the fact that Schiff bases could coordinate to various lanthanide systems due to their exceptional coordination nature to the rare earth ions and their capacity to sensitize the properties of lanthanide ions [3, 4]. The chemistry of lanthanides is a promising field of study that is stimulated by a wide range of applications.

The coordination chemistry regarding lanthanide Schiff base complexes, their intriguing structure, their function in medical and chemical diagnostics and treatments, and their potential applications in a wide range of fields as diagnostic tools in catalysis, biology, material sciences, luminescence, industry, and agriculture all serve to bolster chemists' interest in such fields of study [5,30] Because of their ability to coordinate with chelated Schiff-base ligands, low toxicity, and significant biological activity following ligand bonding, lanthanide-based metal complexes have been thoroughly studied [6] Green chemistry has been the subject of extensive investigation by chemists over the past few decades [7]. Their primary goal is to employ unconventional synthesis techniques that require no or less solvent, are simple to perform, are environmentally friendly [31], take less time to react, and provide high yields while reducing waste and the purity of the target molecules.

The majority of organic solvents are volatile and pose a threat to the environment through contaminating the atmosphere, but many are dangerous and could be harmful to human health [8,9]. Additionally, the solid-state reaction or solvent-free reaction are environmentally friendly techniques for organic synthesis that offer a number of benefits, including lower emissions, lower expenses, and easier handling and processing [10, 11, 12]. Mechanochemical synthesis, also known as mechanochemistry, is typically thought of as a solid-state synthetic approach. It could be as straightforward as grinding or shaking two reactants in a mortar and pestle or as complex as using commercially available ball mills [12, 13, 14]. The two main methods used to increase mechano-chemistry are mechanical milling and hand grinding. Mechanical milling is often carried out in a mixer/shaker mill or a planetary mill at a 5Hz–60Hz frequency, hand grinding, also referred to as the manual grinding, is typically carried out in a pestle and mortar [15, 16]. Vibratory ball mill, planetary ball mill, and mortar and pestle are the three main categories of mechanochemical apparati. Reagents and milling balls are shaken inside a milling vial in a vibratory ball mill. Compared to conventional solvent-based syntheses, mechanochemical approaches have the following key advantages: (1) eliminated or decreased solvent waste, (2) shortened reaction times, and/or (3) increased yield [17].

The synthesis of the Schiff's bases of isonicotinic acid hydrazide employing innovative, environmentally friendly methods involving stirring, sonication, and microwave irradiation, was reported by Wang, G. W., in 2013 [18]. High yields and reduced reaction times could be obtained by using greener techniques in aqueous conditions, according to preliminary studies [19]. Under microwave assisted synthesis, 2-cyano-N'-(1-(4-hydroxy-6-methyl-2oxo-2H-pyran-3yl) ethylidene) synthesis and its first transition metal complexes were described. To improve mixing in the solid-state reactions, the materials are ground into a fine powder. It would be more accurate to think of ball-milling chemistry as the modern, advanced form of conventional grinding chemistry [20]. One of the greatest solvent-free synthesis techniques is mechanochemistry. Because of its advantages over traditional solution-based methods, chemists are now very interested in this field. One of the main advantages of mechanochemistry may be the avoidance of traditional work-up, which is more significant. This advantage also contributed to the substantial advancement of green processes, which proved to be cost-effective, time-efficient, and ecologically safe. [21] The objective of this research is to provide a solvent-free, low-byproduct-formation, high-yield, quick-reaction method for the synthesis of certain lanthanide (III) complexes with heterocyclic hydrazone that is both economical and environmentally friendly.

2- METERIAL AND METHODS

2.1 Materials

Every chemical utilized was of AnalaR grade and came from Fluka and Sigma-Aldrich. E. Merck provided the metal salts, which were employed exactly as supplied.

2.2 Mechanochemical synthesis

In a semi-spherical vessel with a diameter of 9.5 cm, all of the reactions will be conducted in the vibratory ball-mill Pulverisette 0 (Fritsch, Germany), which is outfitted with a single stainless-steel ball weighing 500 g and 50 mm in diameter. The plate vibrates at amplitude of 2.0 mm and a frequency of 50 Hz. A Carbolite PF60 oven set to 80 °C will be used to dry the products.

2.3 Synthesis of Schiff base ligands.

2.3.1 Synthesis of monohydrazone

For 30 minutes at room temperature, a single-ball vibratory ball mill will be used to combine the solid reactants, hydrazine hydrate (10 mmol) and isatin monohydrazone (10 mmol) , in a 1:1 ratio. Following the reaction period, a solvent wash and vacuum drying will be performed on the powder mixture.

2.3.2 Synthesis of bishydrazone

For three to forty-five minutes at room temperature, a vibratory ball mill with a single ball will be used to grind 10 mmol of salicylaldehyde and 10 mmol of isatin monohydrazone (1:1). After being washed with a solvent, the powder mixture will be vacuum-dried will be vacuum-dried.

2.3.4 Synthesis of metal complexes

For one to two hours at room temperature, 0.005 of lanthanide (III) chloride and 0.01 of the ligands were combined and put in vibratory ball mill. Following the reaction period, powder combination will be washed and vacuum-dried.

3- RESULTS AND DISCUSSION

Because of their antitumor and antimicrobial properties, lanthanide (III) complexes with the heterocyclic hydrazone Schiff base ligand are essential in biological applications [22]. The most popular technique to prepare Ln (III) complexes involves harsh reaction conditions and high temperatures, which takes a long time. Furthermore, volatile organic solvents like CHCl3 and CH3Cl2, which are regarded as environmentally hazardous solvents, were utilized in significant quantities in conventional procedures. The mechanochemical synthesis holds great potential as an alternative environmentally and economically viable method for the synthesis of lanthanide (III) complexes, according to recent advancements in green chemistry [23, 24]. The reaction time was found to have been reduced from hours to minutes due to Mechano Chemical technique. The synthesis was repeated multiple times to verify the repeatability of the product, and TLC (silica gel) was used to verify the ligand's purity. Rotating the reaction platform reduced the reaction mixture's inhomogeneity.

The mechano chemical synthesis approach overcame the limitations of traditional technologies and increased product yield in a shorter amount of time. It was discovered that the complexes have been sparingly soluble in DMF and DMSO, yet nonhygroscopic as well as insoluble in common organic solvents like the acetonitrile, methanol, carbon tetrachloride, and chloroform. The complexes' formulation as shown in Table 1 and their analytical data were in good agreement. Their nonelectrolytic nature was sufficiently validated by measurements of molar conductance in various solvents. The overall formula for all complexes is [Ln (HISA)2Cl3], and they all showed a 1:2 metal to the stoichiometry of the ligand.

3.1 Ligand Structure

The ligand's analytical data showed that isatin monohydrazone as well as salicylaldehyde formed in 1:1 ratio, and the ligand's spectral characteristics supported isatin bishydrazone formation. The salicylidene moiety's hydrogen-bonded OH group was responsible for the ligand's broad band infrared spectrum, which was centered around 3300 cm-1. In the indole ring system, NH group's vibrational characteristics appeared as medium-intense band at 3280cm-1. The isatin moiety's v (C=O) can be attributed to a strong band that appears at 1718cm-1. At 1283 and 994cm-1, respectively, phenolic ν(C-0) and hydrazinic ν(N-N) bands have been detected. At 1593 and 1615cm-1, respectively, vibration properties of aldimine and ketimine groups have been detected. This observation was strongly supported by the electronic spectrum, which contributed two bands of absorption at 360nm and 345nm that were attributed to ketimine and aldimine groups' n-π* transitions, respectively. The ligand's proton NMR spectrum has been collected and displayed a signal at 11.45 that was consistent with the infra-red and ultraviolet pectral data. -NH- proton of indole ring and the proton that is connected to azomethine group are responsible for peaks at 9.91 and 8.81 σ, respectively. Aromatic protons have been seen as singlets in 6.91–7.96 σ range. The bishydrazone was given an internally hydrogen bonded structure based on the spectral data above (Fig.1).

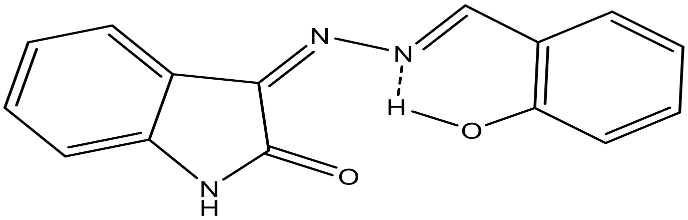

Figure 1. Structure of bishydrazone

3.2 Metal complex structure

The lanthanide complexes' infra-red spectral bands are displayed in Table2 along with their tentative tasks. Although complexes' spectral characteristics differ from the ligand's, they're comparable to one another. The band caused by aldimine moiety ν(C=N) has been moved to a lower level of frequency by 15–20cm-1 in the metal complexes' spectra, suggesting that it was involved in chelation with the metal ion. The band that corresponds to the moiety of ketimine, on the other hand, was essentially unaffected, suggesting that this group did not participate in the formation of bonds with the metal ion. Its coordination with metal ion was suggested by the metal complexes' shift of ν(C=O) band to a lower frequency of around 3040 cm-1. The phenolic OH group's coordination, however, was a completely different phenomenon. Without deprotonation, phenolic oxygen has been linked to the metal ion. According to some reports, the lanthanide ion interaction with phenolic oxygen in lanthanide complexes of specific bases of salicylidene does not raise acidity sufficiently for proton ionization.

As a result, the lanthanide ion coordinates the phenolic oxygen without deprotonation. This causes ν(C-0) stretching frequency to shift positively by 15–25 cm-1 and the OH band to become less broad in the metal complexes, exhibiting a peak that is centered at 3393cm-1. This is unmistakable proof of phenolic oxygen coordination with no de-protonation. There have previously been reports of this kind of coordination by phenolic oxygen without deprotonation [25]. Non-ligand bands in 430cm-1 -440cm-1, 350cm-1 -360cm-1, and 310cm-1 -320cm-1 regions of the complexes' far infrared spectra were identified as belonging to the ν(M-0), ν(M-N), and ν(M-Cl) vibrations, respectively [26]. Proton NMR spectrum of [La (HISA)2C13] that has been recorded in DMSO-d6 showed a signal for OH proton at 11.15ơ, which is consistent with UV and IR spectral data. This suggests that OH group was coordinated to metal ion with no de-protonation. The other proton's signals had been detected in the expected range and just moved slightly by 0.20 to 0.25 σ in the metal complex's spectrum [27].

Table1. Analytical data as well as other ligand and metal complex details

Complexes	Yield	Analytical data/%				Molar conductance/(cm^2/Ω/mol			$μ_{eff}$
	%	M	C	H	N	$C_6H_5NO_2$	DMF	DMSO	BM
[La(HISA)$_2$Cl$_3$]	65	16.52(16.23)	42.66(42.13)	2.52(2.590)	14.690(14.740)	3.50	12.20	6.50	D
[Pr(HISA)$_2$Cl$_3$]	63	6.37(6.41)	42.52(42.02)	2.56(2.590)	14.750(14.700)	2.20	13.50	5.30	3.550
[Ce(HISA)$_2$Cl$_3$]	70	16.48(16.35)	42.37(42.07)	2.44(2.590)	14.650(14.720)	2.40	13.20	5.80	2.480
[Sm(HISA)$_2$Cl$_3$]	68	17.42(17.34)	41.49(41.57)	2.49(2.560)	14.460(14.540)	3.70	11.50	7.30	1.580
[Nd(HISA)$_2$Cl$_3$]	60	16.70(16.75)	41.93(41.85)	2.62(2.580)	14.580(14.640)	2.70	11.10	6.70	3.600
[Gd(HISA)$_2$Cl$_3$]	64	19.75(19.75)	45.46(45.37)	2.66(2.700)	10.630(10.580)	3.50	11.40	6.20	7.650
[Eu(HISA)$_2$Cl$_3$]	65	17.40(17.48)	41.37(41.48)	2.61(2.530)	14.590(14.510)	2.80	12.60	6.40	3.520

Table 2. Infrared and far infrared spectral data of the metal complexes (cm-1)

Complex	ν(OH)	ν(N-H) indole ring	ν(C=O) indole ring	ν(C=N) ketimine	ν(C=N) aldirnine	ν(C-O) phenolic	ν(N-N)	ν(M-N)	ν(M-O)	ν(M-Cl)
HISA	3,330	3,280	1,718	1,615	1,593	1,282	994	-		
[La(HISA)$_2$Cl$_3$]	3,390	3,280	1,685	1,616	1,568	1,310	1,007	355	430	316
[Pr(HISA)$_2$Cl$_3$]	3,384	3,281	1,684	1,614	1,569	1,305	1,008	350	431	318
[Ce(HISA)$_2$Cl$_3$]	3,394	3,283	1,686	1,614	1,570	1,312	1,009	360	435	320
[Sm(HISA)$_2$Cl$_3$]	3,385	3,282	1,690	1,617	1,571	1,308	1,008	352	436	313
[Nd(HISA)$_2$Cl$_3$]	3,386	3,280	1,689	1,616	1,570	1,307	1,010	354	438	310
[Gd(HISA)$_2$Cl$_3$]	3,393	3,283	1,688	1,613	1,569	1,306	1,010	358	440	315
[Eu(HISA)$_2$Cl$_3$]	3,388	3,279	1,688	1,615	1,568	1,307	1,007	350	435	320

3.3 Electronic spectra

The ligand's UV spectrum showed a slight redshift in characteristic absorption maxima at 360nm and 345nm, which correspond to n-π* transition of ketimine and aldimine moieties. It is abundantly evident that the ligand's coordination with the metal ion has not resulted in any structural changes. Lanthanide complexes with visible spectral bands are extremely sensitive to stereochemistry [28]. For the praseodymium (III) complex, it was observed that some hyper-sensitive bands are more intense than those of aquated ions. Due to inhomogeneous electro-static field and alterations in symmetry surrounding lanthanide (III) ion, this could be attributed to quadrupolar effects [29]. Ligands have been discovered in order to generate a slight red shift of these bands when the aqua ion was used as a standard. This was observed in a number of lanthanides complexes and provides indirect evidence for ligand and lanthanide ion coordination. Changes in the complexes' interelectronic repulsion parameters may be the cause of those red shifts, which are ascribed to the nephelauxetic impacts. It seemed that coordination number was also unchanged in solid state because the spectrum of each complex was similar to that in solution. A coordination number of nine has been suggested based on all of the spectral evidence mentioned above (Fig.2).

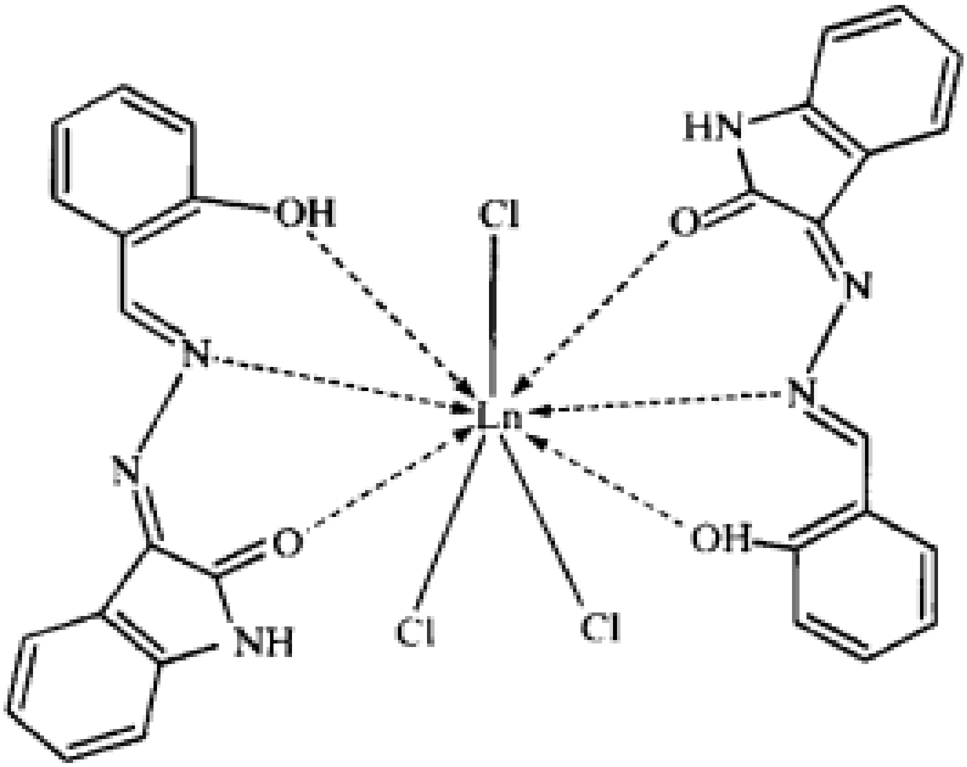

Figure 2. Structure of the metal complex

3.4 Magnetic properties

Table 1 displays the values of the complexes' magnetic moments. All other complexes have been found to be paramagnetic, whereas the lanthanum (III) complex was discovered to be diamagnetic. The results were comparable to those reported for complexes of a comparable type and showed good agreement with expected values.

3.5 XRD study

The high level of crystallinity of the ligand was demonstrated by its XRD pattern (Fig. 3). There were 14 reflections for 28 in the range of 80 to 550 on the diffractogram. After comparing calculated and obtained sin2Θ values, the ligand has been effectively indexed to the tetragonal crystal system [24], with the unit cell volume of 0.647nm3 and lattice parameters a=b=0.71518nm, c=1.26686nm. The amorphous nature of lanthanum (III) complex was revealed by the XRD analysis. This demonstrates unequivocally that the ligand's crystallinity was totally lost upon complexation with the metal ion.

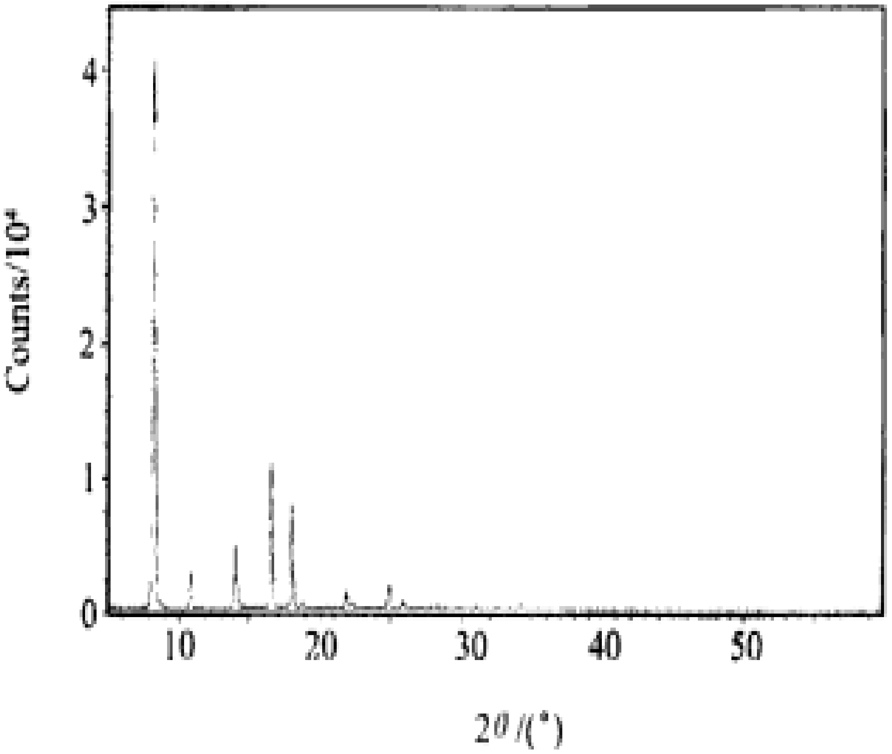

Figure 3. XRD pattern of the ligand

3.6 Thermal analyses

Using DTG, TG, and DTA methods, thermal behavior of [La (HISA) 2Cl3] in non-isothermal conditions has been examined. All of the curves have a qualitative correspondence and show a four-stage weight reduction, which is explained below. Analysis and IR spectral data analysis were used to identify the decomposition products. One salicylaldehyde moiety molecule lost weight during the first step of decomposition, which took place between 200 and 250 0C. It was discovered that the peak temperature that corresponded to this was 241 0C. With high temperatures of 384 and 458 0C, respectively, the 2nd and 3rd stages of decomposition took place in a 310o–400o and 410o–450o C temperature range. The second stage involved the removal of 3 chloride atoms and 1 salicylaldehyde molecule, whereas the third stage involved the elimination of one isatin molecule. Ultimately, the metal oxidized to La2O3 and the remaining isatin moiety was lost during the fourth stage of decomposition, which took place between 540 and 620 0C. This investigation was helpful in defining the metal complex in addition to offering important information about its thermal stability.

4- CONCLUSIONS

Conventional synthesis for the synthesized compounds through the condensation of primary amines with carbonyl compounds in solution typically requires acid catalysis, removal of the water byproduct, and evaporation of the solvent to isolate the final product. As a result, there is a significant interest in preforming these reactions in a single step using solid-state technique which can yield products in quantitative amounts. This approach eliminates the need for bulk solvents and avoids common issues seen in solution-based chemistry, such as low solubility of reactants and unwanted solvolysis or hydrolysis of the products. Among these solid-state approaches, mechanochemical methods have emerged as a highly effective and promising route for creating new materials.

The mechanochemical synthesis approach overcame the limitations of traditional technologies and increased product yield in a shorter amount of time. The results were comparable to those reported for complexes of a comparable type and showed good agreement with expected values.

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التخليق الميكانيكي لمجمعات لانثانيدات الهيدرازون للتغلب على قيود الطريقة التقليدية

الخلاصة

تم استخدام تفاعل معقدات قواعد شيف اللانثانيدية (III) بدون مذيبات كطريقة عامة لانتاج مواد كيميائية دون الحاجة الى مذيبات. تم عمل التفاعل بمواد نقية مباشرة واظهرا تحولا كميا دون نواتج ثانوية. تم تفاعل قواعد شيف باستخدام اللانثانيدات (III) حيث تفاعل احادي الهيدرازون مع السالسيل الديهايد, والذي بدوره تفاعل مع كلوريد اللانثانيد (III) لتكوين معقدات من نوع $Ln\ (HISA)_2Cl_3$, حيث ان HISA = [(٢-هيدروكسي بنزالدهيد)-٣-إيزاتين] بيهيدرازون و Ln = La (III)، Sm (III)، Eu (III)، وGd (III). اجريت جميع الفاعلات بظروف اهتزازية. حيث تم استخدام قياسات القابلية المغناطيسية, والموصلية المولية, وبيانات طيف الاشعة فوق البنفسجية وبيانات طيف الرنين النووي المغناطيسي للبروتون لوصف العقدات. تم استخدام (XRD) لوصف مركبات اللانثانيدات (III). حيث اظهرت النتائج نمط حيود (XRD) طبيعته البلورية, بينما اظهر مركب اللانثانوم (II1) طبيعة غير متبلورة.

تهدف هذه الدراسة الى تطوير عملية صديقة للبيئة واقتصادية لتفاعل بعض مركبات اللانثانيدات (III) مع الهيدرازون الحلقة غير المتجانس, والتي تتجنب استخدام المذيبات, وتقلل من تكوين النواتج الثانوية, حيث تتميز بنواتج مرتفعة ووقت تفاعل قليل.