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Crystal and Molecular Structure of Tris-acetylacetonate with Lanthanum (III) Metal Ion Complex

Kamaran Basheer Hussein [1]

[1] College of Education – Chemistry Department Salahaddin university , kamaran1963@gmail.com Erbil – Iraq

*Corresponding author email: kamaran1963@gmail.com.

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Abstract:

The used ligand Acetylacetone is often abbreviated (acac), complex was isolated as pale yellow crystals from the reaction of $La(NO_3)_3.6H_2O$ metal salt with Acetylacetone at room temperature .The molecular formula of tris(acetylacetonatodiaqua)lanthanum(III) complex elucidated by the XRD, i.r and UV-Visible techniques .The La^{3+} is linked by eight oxygen donor atoms of three acetylacetone anions that behaves as bidentate ligands, and two oxygen donor atoms of water molecules acting as monodentate ligand. In this research (NO_3^-) didn't participate in coordination despite the use of the La^{3+}nitrate salt type of the metal , while in other similar researches nitrate ion linked with two oxygen atoms acts as a bidentate ligand. The geometrical structure of the metal chelate was distorted cubic.

Keywords:

Crystal structure, lanthanum salt, acac, X-ray diffraction

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التركيب البلوري و الجزيئي لثلاثي – اسيتايل اسيتون مع معقد الأيون الفلزي لنثانيوم(III)

كاميران بشير حسين[1]

1 قسم الكيمياء ، كلية التربية ، جامعة صلاح الدين ، kamaran1963@gmail.com، اربيل ، العراق
Corresponding author email: kamaran1963@gmail.com

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الخلاصة

الليكاند المستخدم اسيتايل اسيتون غالبا يعبر عنه ب (acac), تم عزل المركب على شكل بلورات صفراء شاحبة من تفاعل الملح الفلزي $La(NO_3)_3.6H_2O$ مع (acac) في درجة حرارة الغرفة . الصيغة الجزيئية لمركب $[La(acac)_3(H_2O)_2]$ تم توضيحها بواسطة تقنيات حيود الأشعة السينية و طيف الأشعة تحت الحمراء و طيف الأشعة فوق البنفسجية المرئية .

يتناسق La(III) الأيون الفلزي مع ثماني ذرات أوكسجين مانحة من ثلاث جزيئات (acac) تتصرف كروابط ثنائية , وذرتان مانحتان للأوكسجين من جزيئات الماء تعمل كروابط أحادية .

في بحثنا هذا لم يشارك (NO_3^-) في التنسيق على الرغم من استخدام نترات اللانثانيوم كملح فلزي . بينما في ابحاث اخرى مماثلة أيون النترات مرتبطة بذرتين من الأكسجين مع الأيون الفلزي كليكاند ثنائي السن , ان العدد التناسقي لذرة La هي ثمانية , الشكل الهندسى للمعقد المخلبي مكعب مشوه .

الكلمات الدالة: التركيب البلوري , ملح اللانثانيوم , اسيتايل اسيتون acac , حيود الأشعة السينية .

Citation:

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Introduction

β-diketones are always used in complex formation that includes lanthanide elements because they make multi dentate oxygen complexes with lanthanide ions without difficulty. These days, lanthanide chemical compounds achieve application in many excellent machines such as chemical sensors , typically systems , emitting light accessories and deliquescent materials [1-10] . The Ln(III) is set in an eight binding arising from three bidentate acac molecules and two water monodentate ligands this behavior is called hypo dentate[11].Where acetylacetone, crystallized in the Triclinic, *P*1 crystal system, space group.It has been described that the binding character of the complexes rely on some factors, such as the geometric consistency, the nature of the giver-atoms and the planarity of ligands[12-14] .The sites of coordination is observed in the crystal structure of $(acac)_3$, La1-- O2 , 2.435(3) ,La1-O1 ,2.511(3) , La1-O3,2.498(3) , La1-O4, 2.515(2) , La1-O5 ,2.490(2) , La1-O6 ,2.523(3) which are electronically preferable coordination positions for the meta ion Ln^{3+}[15].

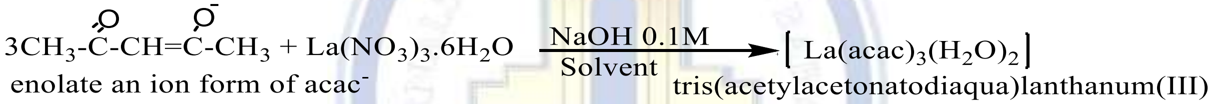
1-Experimental

1.1. Chemicals and Methods

All chemicals were commercially ready and used as they arrived. Acetylacetone (acac) and lanthanum nitrate hexahydrate $La(NO_3)_3.6H_2O$ salt were obtained from Aldrich and BDH chemical Co., acetonitrile and sodium hydroxide were obtained from Fluka., distilled water were used. Molar conductivity in DMSO (10^{-3}M) were measured at room temperature, using pH /conductivity meter. Should be in the result with a value of the complex conductivity indicting that the nature of the complex was non-electrolyte. Infrared spectra were measured using KBr discs in 4000-400 cm^{-1} range on IR Affinity -1- Shimadzn Spectro Photometer. Ultraviolet –Visible spectra were measured in DMF on Shimadzu 1800-UV-Visible Spectrophotometer double beam . The studies were conducted in the College of Education Salahaddin University –Erbil – Iraq. The XRD-diffraction studies were taken in Ondokus Mayis University, Department of Physics, Samsun, Turkey . Melting points were measured by an Electrothermal melting point apparatus 910 LTD (UK) and are uncorrected.

1.2. Synthesis of La(III) Complex

$La(NO_3)_3.6H_2O$ (1mmol, 0.433g) was dissolved in 20ml of a mixture (methanol + acetonitrile) and adding (1.9ml) acac , the reaction mixture was left to stir for 20min. at room temperature and it's pH was kept in the range of 9-10 by adding 0.1M NaOH dropwise . Then filtered the supernatant was conserved to slow evaporation from the solvent mixture, crystals were obtained after two weeks (m.p 110 °C) gave pale - yellow plated - like crystals. The structure of the complex formed in solutions has been determined by Job's method the results show 1:3 metal to ligand ratio, agreed with x-ray data as described in Fig.3. The chemical reaction was shown in the following form .



$$3CH_3-\overset{O}{C}-CH=\overset{O^-}{C}-CH_3 + La(NO_3)_3.6H_2O \xrightarrow[\text{Solvent}]{\text{NaOH 0.1M}} [La(acac)_3(H_2O)_2]$$

enolate an ion form of acac$^-$

tris(acetylacetonatodiaqua)lanthanum(III)

2-Result and Discussion

2.1-IR Spectra

The IR spectral data of $[La(acac)_3(H_2O)_2]$ complex, taken from of KBr disc , on an agreement with the formula fixed by the XRD technic . The wide strong band at 3381 cm^{-1} assigned to the hydroxyl group stretching of coordinated water molecule in coordination sphere [16] .The absorption band at 1620 cm^{-1} is due to the C-O stretching ; in which deprotonated and the enolate form of the ligand acac$^-$ coordinated with the Ln(III) central metal ion [17].C=C stretching at 1473 and 1413 cm^{-1} are also identical to the molecular structure . Medium and weak intensities bands observed in the range 486 cm^{-1} assigned to La-O stretching modes. IR data details are displayed in the Fig.1 .

2.2- Ultraviolet-Visible Measurements

The ultraviolet-visible absorption spectra of the $[La(acac)_3(H_2O)_2]$ and $acac^-$ ligand were recorded in DMF solution 10^{-3} M and are shown in Fig .2 .

The high – energy signal was fixed at 296 nm result from the π-π* of the C=O group of $acac^-$ .The other broad low energy signals at 390 nm due to the n- π* of the conjugated C=O group[18] . The red - shifted in the spectrum of the complex may be back to the coordination action between the acetylacetone and the Ln cation , with absorption bands at 410 , 366 and 334 nm .

2.3- XRD-data

XRD data and improvement are given in Table 1. The crystallographic studies show that (acac) ligand behaving as oxygen donor molecule . The binding of the donor compound to La^{3+} results in the pointing of three six membered chelating rings and two coordinated water molecules, complex didn't crystallize with any molecule of solvent.Unit cell parameters: a 9.0847(6), b 10.8658(7), c 11.5211 (8) P-1.

Program(s) used to refine structure : SHELXL2018/3 (Sheldrick , 2018) [19] The binding sphere of the lanthanum La^{3+} in $[La(acac)_3(OH_2)_2]$ complex is saturated , whereas Ln ions prefer to be associate with eight or nine donor atoms [20] . The lanthanide ion can expand the outer shell its by forming adducts with neutral molecules containing oxygen or nitrogen donor atoms . Such a molecule can be OH_2 [21] ,tris-acetylacetonate complex with La(III) can easily coordinate with water molecules . The C.N of the Ln l ion in tris -acetyacetonato Ln(III) complex being eight. The eight donor atoms were six oxygen atoms from acac ligand and two oxygen atoms from water molecule are appropriate in a coordination sphere of the central Ln atom , forming a garbled square antiprism shape [22] . The structure was repeated on F^2 by a full-matrix least – squares procedure using anisotropic extraction variables for all non-hydrogen atoms. There are any oxygen atoms nearly Ln atom at distances among $2.435(3)^0$ - $2.607\ (3)^0$, metal oxygen (La-O) bonds in which six of them for three molecules of $acac^-$ each molecule acts as a bidentate oxygen donor ligand, and the other two oxygen atoms attributable to water molecules coordinated with La(III) central metal ion . The angles of O-La-O bonds vary in the range 68.24(9)^0 – 147.51 (9)^0 , the average distance from a lanthanum ion to a carbonyl oxygen atom is 2.506 A^0, while the average distance of lanthanum to coordinated water 2.587 A^0. The Carbon atoms of the six membered rings are in a flat form Fig.3, and the internal C-C-C angles change between 117.1(3)^0 and 124.9(4)^0 . The chosen bond distance and angles are presented in Table .2 and 3 respectively.

Hydrogen bonding in acac complex

Compounds containing the β-diketone contain two important types of hydrogen atoms in chemistry , proton transfer and hydrogen bonding[23-25]. Metal-ligand interactions cannot always be detected among the many intra-and intermolecular distance that due to the scattering[26] . Intramolecular O-H….O hydrogen bonds show between the protonated oxygen and the deprotonated oxygen atoms . The intra and intermolecular H-bonds of La(III) complex , distances are : O8-H8A…..O1= 0.85 ^{0}A , D-H it is the shortest interchain distance and the angle value for D-H….A = 141 (deg.) Table .4. Molecules are thus linked by hydrogen bonds in limp chains which are a ppear parallel in the direction Fig.5. show H-bonding geometry and molecular packing . Extra power in the crystal lattice increases stability of the compound , it is considered an additional force for binding .

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Many thanks to College of Education Chemistry Department Salahaddin University –Erbil – Iraq , for IR and UV-Vis. Facilities . Thanks to Prof.Dr.Necmi Dege for caring out the XRD crystal analysis of the Lanthanum complex at Faculty of Science Department of Physics Ondokuz Mayis University,Samsun- Turkey .

Conclusions

Based on the results of our investigations especially x-ray data it's confirmed that lanthanum complex with acac$^-$ ligand is coordinated by the Oxygen atom of the carbonyl group of acac$^-$ and the oxygen atoms of water molecule, thus a monodentate ligand. UV-Vis. and IR spectrophotometry analysis are in a perfect agreement with XRD data. The coordination polydentate composite of eight oxygen atoms six of them goes back to acac$^-$ ligand molecules and two oxygen donor atoms of the two neutral water molecules around a Ln $^{3+}$ may be qualified as an irregular cubic.

Conflict of interests.

There are non-conflicts of interest.

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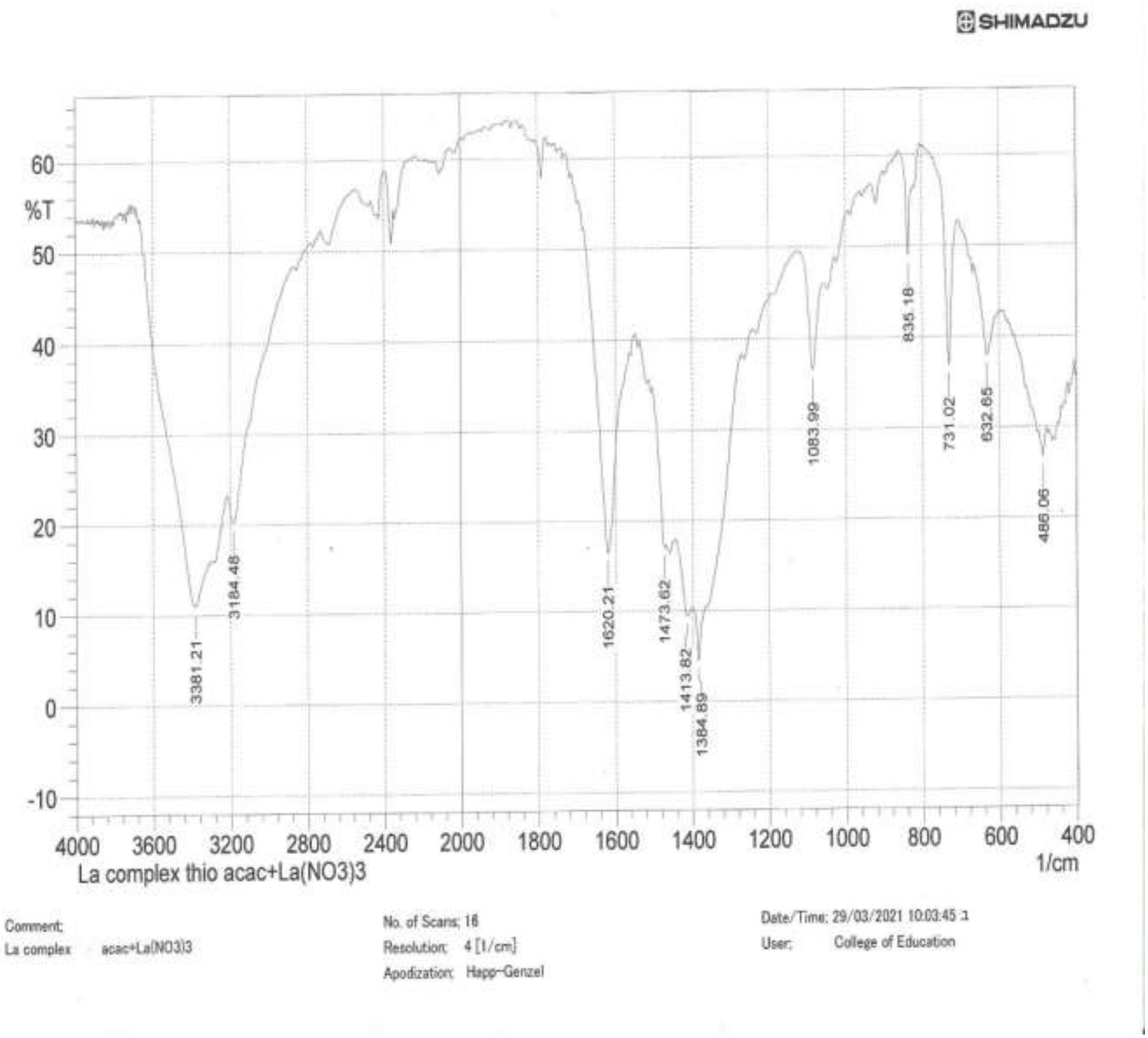

Fig.(1). IR spectrum of La^{3+} complex .

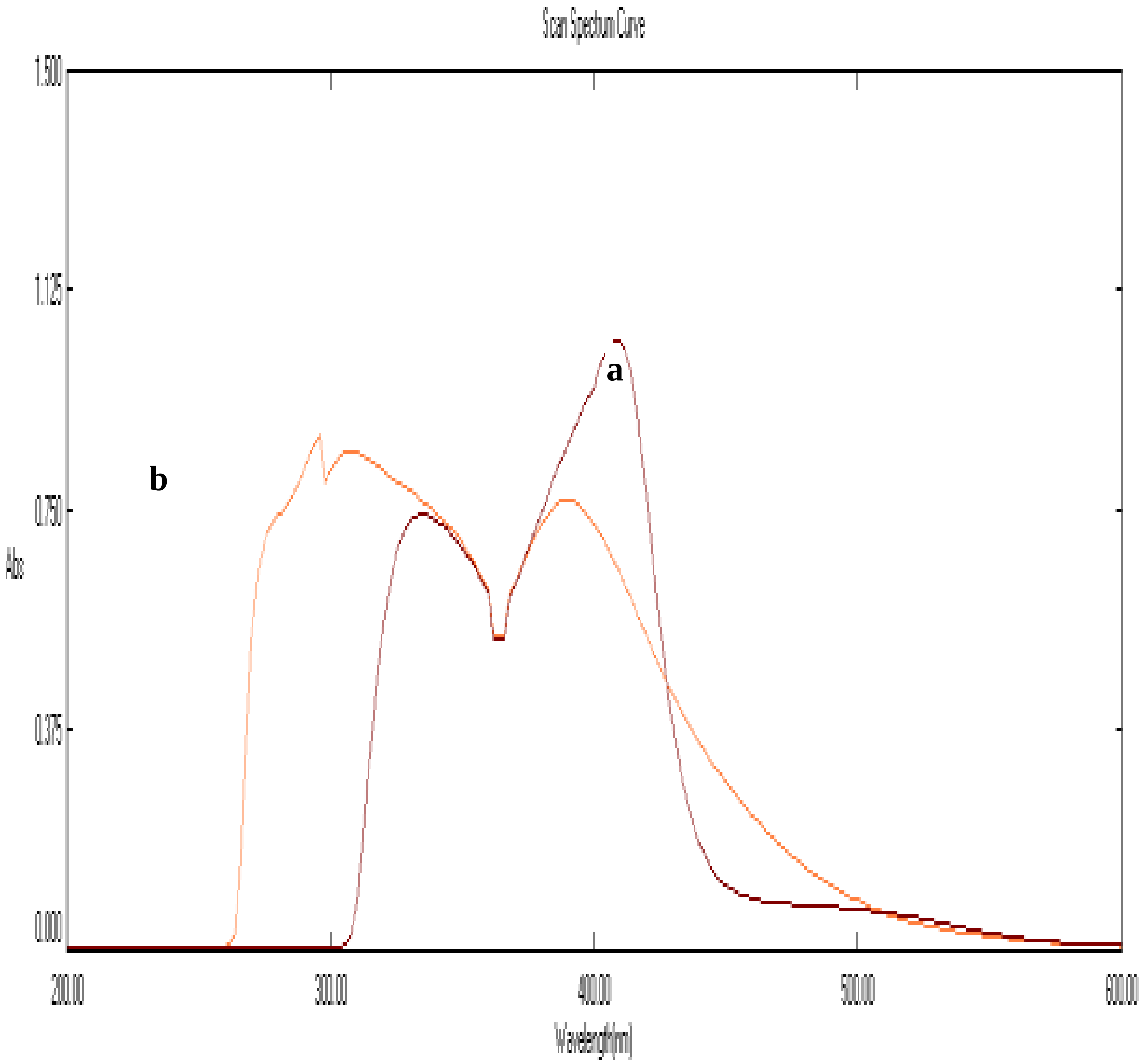

Fig.(2). UV-Vis. spectrum of (a) La(III) complex (b) acac Ligand.

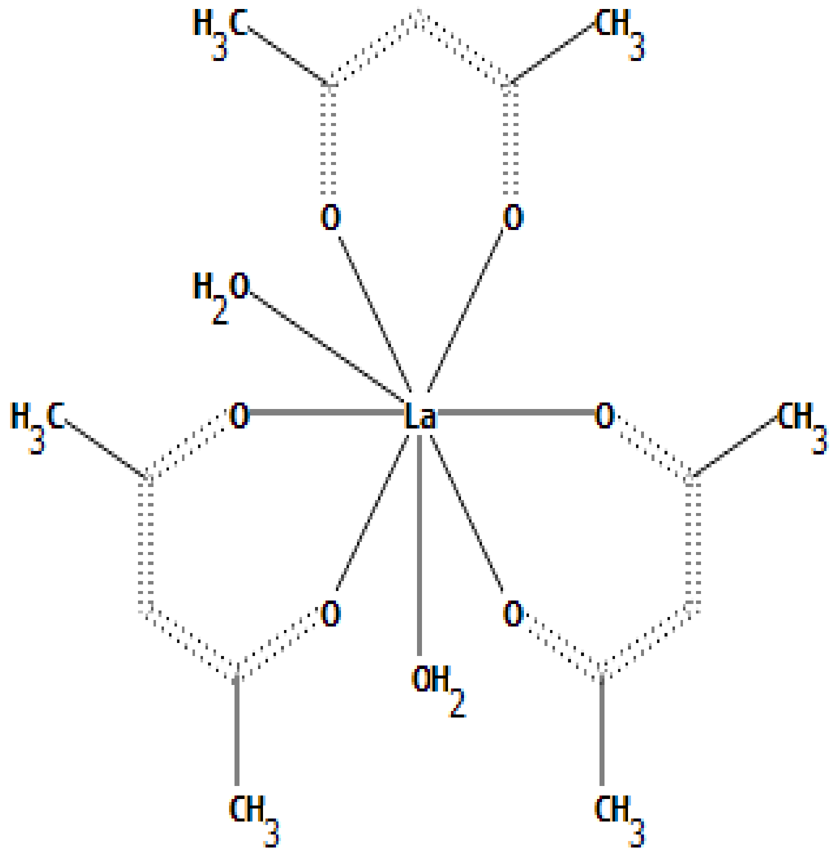

Fig.(3). Squar antiprismatic geometry (distorted cubic) of La^{3+}complex .

Datablock shelx - ellipsoid plot

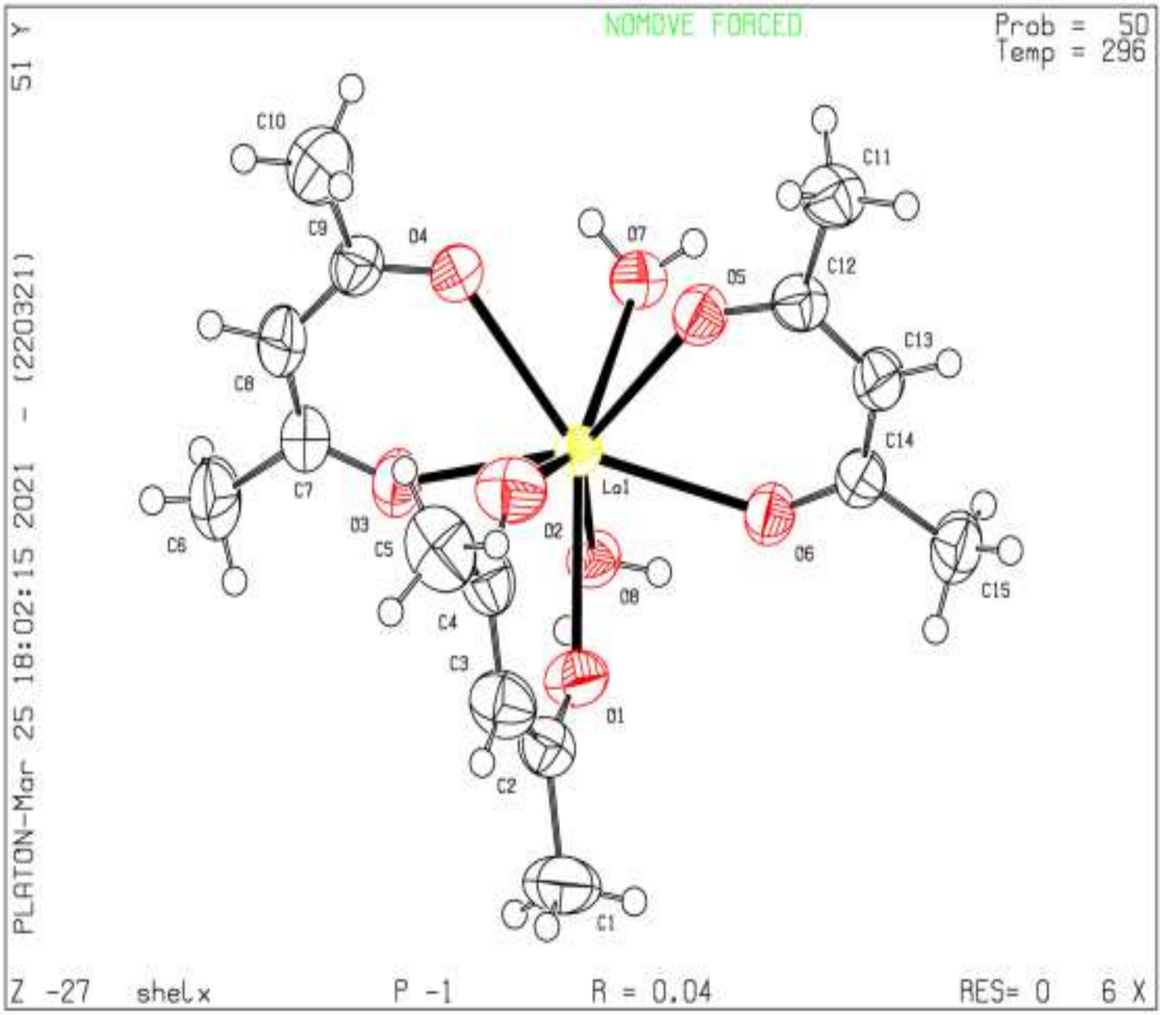

Fig. (4). Labeled diagram of the Ln^{3+} complex.

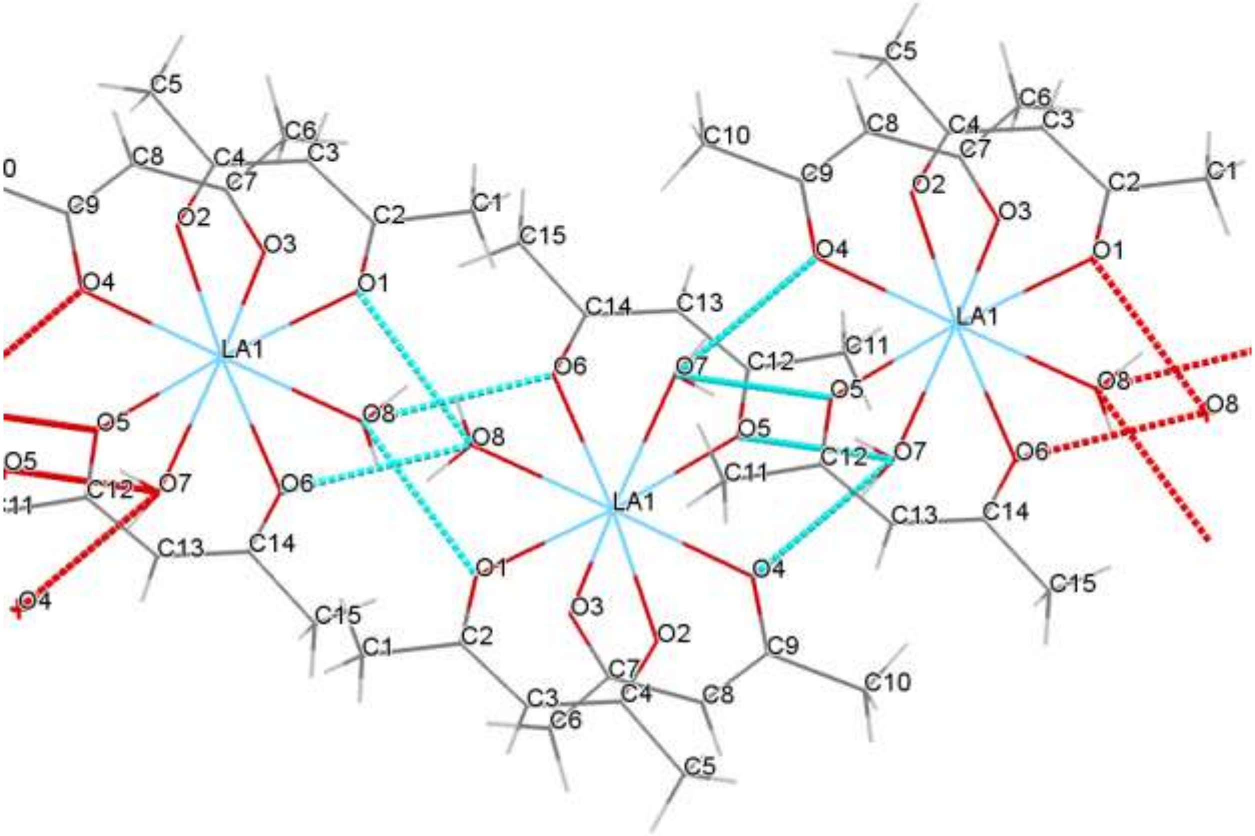

Fig.(5). Both intra , intermolecular hydrogen bonds in crystal lattice

Table.(1). Crystallographic details of the crystal .

Chemical formula	$C_{15}H_{25}LaO_8$
Color / shape	Pale yellow / plate
Mr	472.26
Crystal system , space group	Triclinic , *PI*
Temperature(K)	296
A,b,c (A^0)	9.0847 (6), 10.8658(7), 11.5211(8)
A,β,γ (^{0})	75.361 (5) ,79.448(65.221(5)
Volume ($^0A^3$)	995.18,12
Z	2
Radiation type	Mo *Ka* , λ= 0.71073A^0
μ(mm^{-1})	2.18
Crystal size (mm)	0.65 x 0.44 x 0.28
R/WR2	0.042 , 0.123 , 1.07
No.of reflections	9749
$\Delta\rho_{max.}$, $\Delta\rho_{min}$ (e^0A^{-3})	1.44, -1.98
Θ range , deg.	3.2-37.3
Number of reflections I > 2δ (11)	9749
μ mm^{-1}	2.18
Refinement method	Full – matrix least squares of F^2
S	1.07
Rint	0.064

Table (2). Selected bond distances (A^0) for [La(acac)$_3$(H$_2$O)$_2$] .

La1-O2	2.435(3)	C14-C13	1.400(5)
La1-O5	2.490(2)	C14-C15	1.511(5)
La1-O3	2.498(3)	C9--C8	1.390(6)
La1-O1	2.511(3)	C9-C10	1.514(6)
La1-O4	2.515(2)	C8-C7	1.407(6)
La1-O6	2.523(3)	C8-H8	0.9300
La1-O8	2.567(2)	C7-C6	1.516(6)
La1-O7	2.607(3)	C13-H13	0.9300
O5-C12	1.276(4)	C15-H15A	0.9600
O7-H7B	0.8587	C15-H15B	0.9600
O1-C2	1.276(5)	C15-H15C	0.9600
O4-C9	1.275(5)	C2-C3	1.392(6)
O3-C7	1.260(5)	C2-C1	1.516(6)
O2-C4	1.255(5)	C3-H3	0.9300

Table (3) .Selected bond angles (deg) for $[La(acac)_3(H_2O)_2]$.

O2-La1-O5	80.76(11)	O4-La1-O6	144.24(8)
O2-La1-O3	90.93(12)	O2-La1-O8	140.11(11)
O5-La1-O3	147.51(9)	O5-La1-O8	132.94(9)
O2-La1-O1	68.89(9)	O3-La1-O8	70.39(9)
O5-La1-O1	118.78(10)	O1-La1-O8	74.84(9)
O3-La1-O1	86.34(10)	O4-La1-O8	124.99(9)
O2-La1-O4	74.71(10)	O6-La1-O8	72.30(8)
O5-La1-O4	79.28(9)	O2-La1-O7	144.30(9)
O3-La1-O4	68.24(9)	O5-La1-O7	74.15(9)
O1-La1-O4	134.88(9)	O3-La1-O7	96.74(10)
O2-La1-O6	113.48(11)	O1-La1-O7	146.16(9)
O5-La1-O6	68.55(8)	O4-La1-O7	75.99(9)
O3-La1-O6	141.90(9)	O6-La1-O7	80.47(9)
O1-La1-O6	76.75(10)	O8-La1-O7	74.58(8)
C12-O5-La1	138.6(2)	C14-O6-La1	137.6(2)
C2-O1-La1	136.7(2)	C9-O4-La1	132.6(2)
C7-O3-La1	136.8(3)	C4-O2-La1	139.5(3)
O6-C14-C13	125.1(3)	O6-C14-C15	117.1(3)
C13-C14-C15	117.9(3)	O4-C9-C8	124.7(3)
O4-C9-C10	116.2(4)	C8-C9-C10	119.2(4)
O5-C12-C13	124.9(3)	C9-C8-C7	124.9(4)
C9-C8-118	117.5	C7-C8-H8	117.5
O3-C7-C6	116.9(4)	C8-C7-C6	118.6(4)

Table.(4) Hydrogen bonding among donor (D) and acceptor (A) atoms in $[La(acac)_3(H_2O)_2]$ complex .

D-H…A	D-H (^{0}A)	H…A (^{0}A)	D…A(^{0}A)	D-H….A (deg)
O8-H8A…O1^{i}	0.85	2.07	2.783(4)	141
O8-H8B…O6^{i}	0.85	2.12	2.857(3)	145
O7-H7A..O4^{ii}	0.86	1.99	2.768(4)	151
O7-H7B…O5^{ii}	0.86	2.03	2.843(4)	157

-Symmetry codes: (i) $^-$x+1 , -y+1 , - z+1 ; (ii) – x+1 , - y+2 ,-z+1 .