

Photo degradation of Lanthanum (III) Complex with 1, 2 , 4-Thiadiazole in Dimethyl Sulfoxide (DMSO) Solvent

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التجزئة الضوئية لمعقد اللانثانوم (III) مع 1،2،4-الثياديازول في مذيب ثنائي ميثل سلفوكسايد

الخلاصة

تم تحضير المركب [5-اميلو -3- (4- اورثوهايديروكسي ثايوسيمي كاريازيدو) -1-2-4- ثياديازول] من خلال تفاعل (3- مركبتو -5- اميلو -1-2-4- ثياديازول) مع (اورثوهايديروكسي ثايوسيمي كاريازيد) بنسب مولية (1:1) شخص الليكند بالاعتماد على اطياف الاشعة تحت الحمراء واطياف الاشعة فوق البنفسجية والمرئية . تم تحضير معقد اللانثانوم ذات الصيغة $La[C_9H_{10}N_6S_2O)_2Cl_2]Cl$ من خلال تفاعل الليكند المحضر مع ملح كلوريد الانثانيوم بنسب مولية (2:1) على التوالي تم تشخيص المعقد والتوصل الى ترتيبه الهندسي بالاعتماد على الطرق الطيفية . تمت دراسة حركية التفكك الضوئي للمعقد المحضر ووجد ان تفاعل التجزئة الضوئية من الرتبة الاولى ومن ثم تم قياس ثابت سرعة التفكك (Kd) وبدرجة حرارة (25°C) . تضمنت الدراسة ايضا حساب ناتج الكم لتفاعل لتفاعل التجزئة الضوئية (Φ)

Abstract

5- Amino -3- [4- O- hydroxypheny Ithiosemi carbazido] -1,2,4-thiadiazole compound has been prepared by the reaction of (3-mercapto -5- ami,2,4- thiadiazole) with (O-hydroxyphenyl thiosemicarbazide) in mole ratios of (1:1) .The ligand has been characterized and its structure was elucidated depending upon the spectral data of IR and U.V-Vis spectra . Lanthanum complex of the formula $[La(C_9H_{10}N_6S_2O)_2Cl_2]Cl$ was prepared through the reaction of the prepared ligand with lanthanum chloride in mole ratios (2:1) respectively . The mode of bonding and overall geometry of the complex was determined through physicochemical and spectroscopic methods . The kinetic of the photo-degradation of the prepared complex was investigated and it was the first order and the rate constant (Kd) determined at (25°C) Further more primary quantum yields (Φ) has been also calculated.

Keyword : La(III) Complex , 1,2,4-Thiadiazole, irradiation, photo degradation.

Introduction:

The photochemistry of coordination compounds has become an increasingly popular technique for controlling and tuning the reactivity of transition metal complexes and organometallic compounds as well as rather uncommon reaction pathways can be initiated by electronic excitation of diverse spectroscopic states of these compounds besides stoichiometric electron-transfer dissociation substitution as well as rearrangement reactions induced by light [1]. Heterocyclic moieties can be found in a large number of compounds which display biological activity. The biological activity of the compounds is mainly dependent on their molecular structures. The synthesis of 1,2,4-thiadiazoles has attracted a great deal of interest through the years due to their biological activities. 1,2,4-thiadiazole derivatives are widely found in bioorganic and medicinal chemistry with application in drug discovery and development for treatment of human leukemia cell [2]. Thiadiazole are considered to be good coordinating ligands [3]. Because this ligand contains an S=C-N-N unit that allows for bidentate coordination to metal ions through amine and thio-substituted to form a stable five-member ring [4]. Lanthanum chloride manifests as anti-tumor. Genotoxicity of lanthanum (III) in human peripheral blood lymphocytes has also been reported [5]. La is the first element of the lanthanide series, and bone is one of the main sites where La accumulates, lanthanum (La) has been used for the treatment of hyperphosphatemia in end-stage renal failure and dialysis patients [6]. As well as a rollover many in the industry, it is the most important uses of compounds. Lanthanum is in lamps, arc carbon is usually used. Lanthanum chloride and lanthanum oxide in materials phosphorous which is why the colors that appear on your TV and is also used in the manufacture of fiber optics are used to transmit audio and video, and digital messages were dissolved. Fiber optic replaced copper wire for this purpose in 1974 [7-9]. The complexes of rare earth ions have aroused much interest. Lanthanides are a subject of increasing interest in bioinorganic and coordination chemistry [10].

In this work we used complex of Lanthanum for ligand [2-Chloro-2-bis {5-amino-3 [4'-o-hydroxy]-thiosemicarbazido]-1,2,4-thiadiazol} Lanthanum (III) chloride for study of the photodegradation in DMSO solvent. Photodecomposition of complexes with 1,2,4-Thiadiazole is similar to metal carbonyl complexes. The photodegradation of La complex in (DMSO) solvent was performed [La(C₉H₁₀N₆S₂O)₂ Cl₂] Cl.

Experimental techniques

Preparation (3-Mercapto-5-Amino 1,2,4-thiadiazole): the preparation of this article, as stated in the literature [11] dissolving (5.40 g 0.04 mole) of (2-dithiobiuret) in sodium hydroxide (20 ml) (2N) to dissolve completely, then cooled solution yellow mediated by the snow, with the addition (12 ml) of 35% hydrogen peroxide (H₂O₂) drop by drop, and after the completion of the process added stir for an hour and a half at a temperature of (0°C) then added HCl (36%) drop by drop, to read (pH=5) consists deposit lumpy white milky yellowish, precipitation is sucked off and returned crystallized in boiling water to get the required material to give yield (4.2 g 77.7%) , as shown in scheme (1).

Synthesis 5-Amino-3-[4'-O-hydroxy phenyl Thio semi carbazido]-1, 2, 4-Thiadiazole (ligand):

Weighed (1.33g, 0.01 mol) of (3-Mercapto-5-Amino 1,2,4-thiadiazole) and dissolved in (25ml) of absolute ethanol and stir degree (70°C) until the completion of melting. Then add (0.01mole, 1.83g) of (O-hydroxyphenyl thiosemicarbazide) dissolved in a mixture of (15 ml Ethanol absolute+5ml Dioxane) being escalation reflux for 12 hrs., and then evaporated to half the original

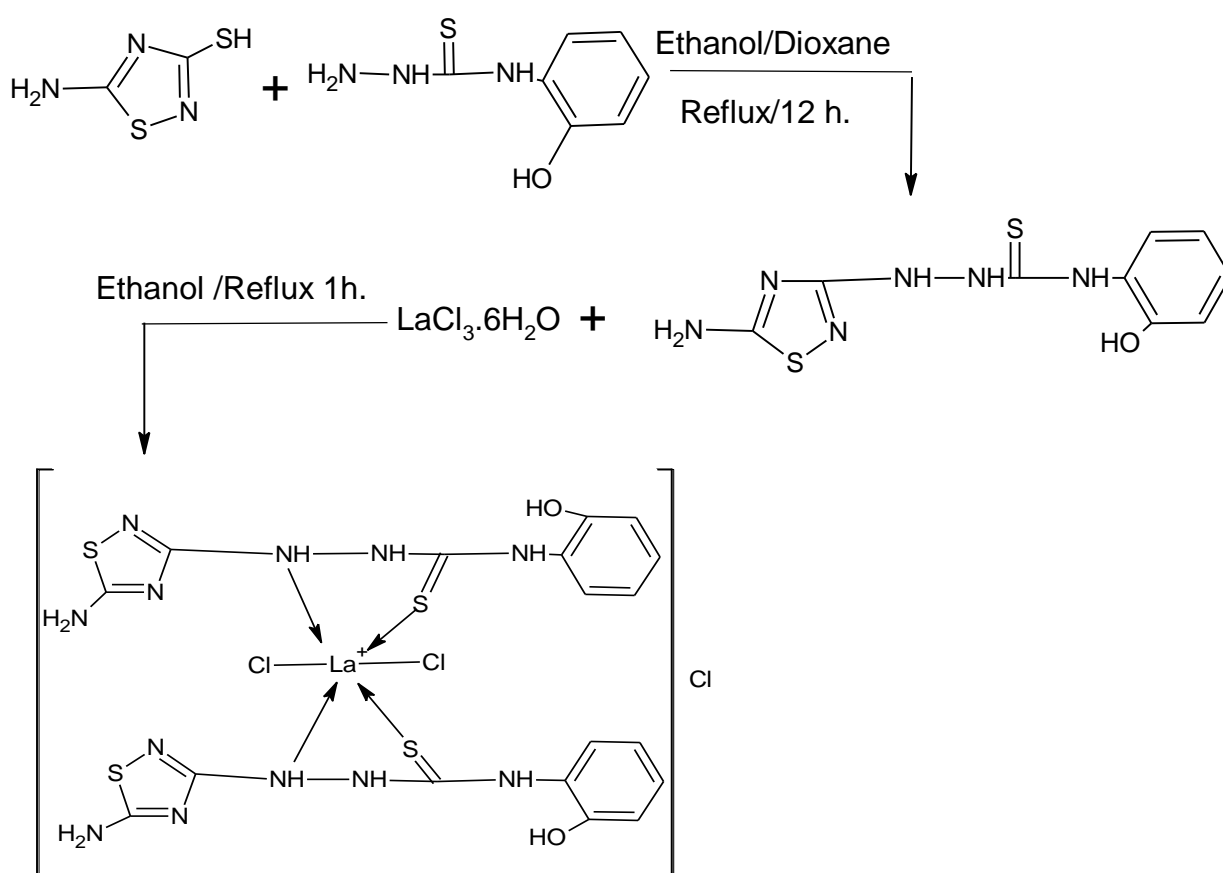
volume and cooled in snowy bath with constant stirring to an oily substance that consists returned washed absolute ethanol and dried to get the yellow precipitate to give good yield (70%, 1.9gm), elemental analysis(C.H.N) calc. (found)= C % 38.29 (37.39), H% 3.546 (3.28), N %29.78 (28.82), S% 22.7 (22.4), as shown in scheme (1).

Synthesis of [La(C₉H₁₀N₆S₂O)₂Cl₂]Cl : A solution of La(III) Chloride (0.001 mole, 0. 0.245 gm) in ethanol (5ml) was added to a solution of ligand (0.002 mole , 0.564 gm) in ethanol (10 ml) it has been noticed that the solution turned to a yellow color . The P^H of the solution was raised up to (7) by using 10% ammonia solution . the resulting mixture was stirred under reflux for 1 h and cooled . a colored precipitate was formed the product was then filtered and washed from hot absolute ethanol .

Table 1: Some of the physical properties and molar conductivity of the ligand (L) and it's complexes

Symbol	Molecular formula	Color	M.p (°C)	Yield % (gm)	Molar conductivity Ohm ⁻¹ cm ² .mole ⁻¹
L	C ₉ H ₁₀ N ₆ S ₂ O	yellow	258-256	70% (1.9gm)	–
La ^{III}	[La(C ₉ H ₁₀ N ₆ S ₂ O) ₂ Cl ₂]Cl	yellow	>300*	64 % (0.202gm)	22

d*: decomposition



scheme (1)

Chemical

[a] Potassium ferrioxalate hydrate $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ actinometer was prepared by the method reported by Hatchard and Parker [12].

The photolysis apparatus used is shown in Figure (1).

[b] [2-Chloro-2-bis {5-amino-3[4'-o-hydroxyl-thiosemicarbazido]-1,2,4-thiadiazol} Lanthanum (III) chloride was prepared as reported earlier [13].

[c] The DMSO used was of spectroscopic grade apparatus.

- 1) The photolysis apparatus shown in figure (1). consist of medium pressure mercury lamp (150) (tz 365 nm) supplied by PH YWE ltd. was used light source.
- 2) UV-Vis spectral absorption bands were obtained using pye-unicam (8800) spectrophotometer at 25°C. using dimethyl sulfoxide (DMSO) as a solvent in quartz photochemical cell.
- 3) IR spectra were obtained using pye – unicom SP3-300 infrared spectrophotometer for the range (4000–200) cm^{-1} .
- 4) The acidity (PH) of the solution before and after irradiation was measured by (multi 740/PH–meter) procedures.

The photo experiments were carried out in (100ml) Pyrex cell with two holes in its upper section for the passage of gas and for sampling processes. 1500 w medium pressure mercury lamp was used as a radiation source – A known concentration ($1 \times 10^{-4} M$) of the complex was introduced in to the cell after treatment with oxygen for 30 min. the cell has closed tightly and the absorption spectra were recorded between 200-800 nm.

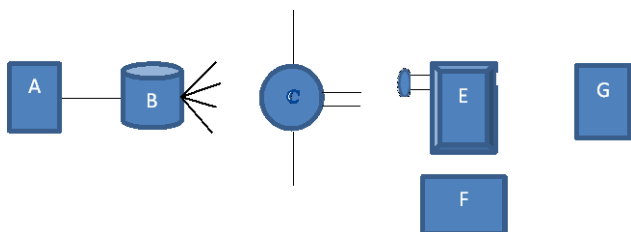


Figure 1: Schematic diagram of the experimental apparatus for photolysis of complex

- A) Power supply unit.
- B) Medium pressure mercury lamp MPML.
- C) Lenses ; (D) filter (365 nm) ; (E) quartz cell.
- D) Magnetic stirrer (G) circulating water thermostat.

Result and discussion

The spectra of Lanthanum complex UV-Vis spectra for the named complex have been found contain absorption bands around (360 nm) as shown in figure (2) as arepresentive example.

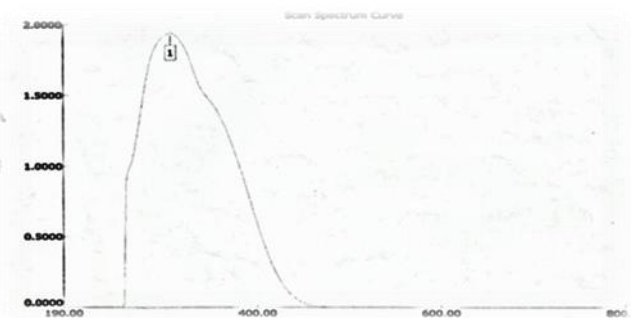


Figure (2) Electronic spectra of $[\text{La}(\text{C}_9\text{H}_{10}\text{N}_6\text{S}_2\text{O})_2\text{Cl}_2]\text{Cl}$.

Determination of molar absorbance for the complex taken several concentrations between $(1 \times 10^{-5} - 12 \times 10^{-5} \text{ M})$ and the λ_{max} in 280 nm as show in figure (3).

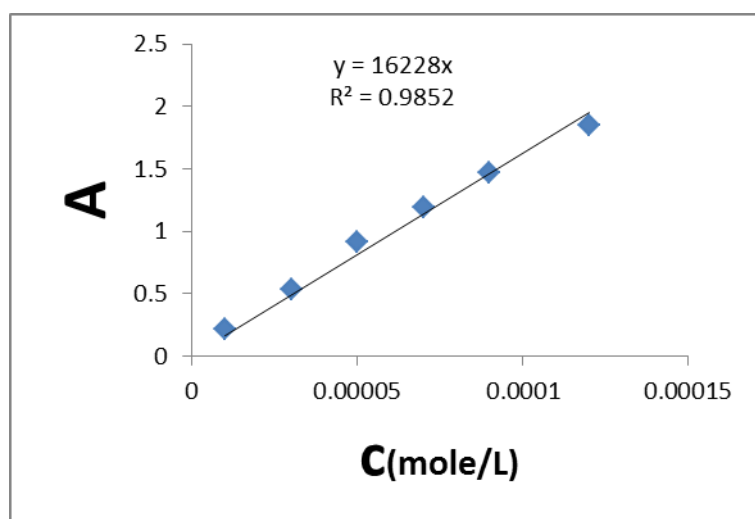


Figure 3: Calibration curve between concentration and absorption of the complex $[\text{La}(\text{C}_9\text{H}_{10}\text{N}_6\text{S}_2\text{O})_2\text{Cl}_2]\text{Cl}$

After photolysis of the complex was observed that the wave length of the complex shifts to lower wave length at 280nm. The changes in absorbance during photolysis were measured for different irradiation period of time at (280 nm) for complex in order to study the kinetics of the photo decay of complex in solution figure (4) .

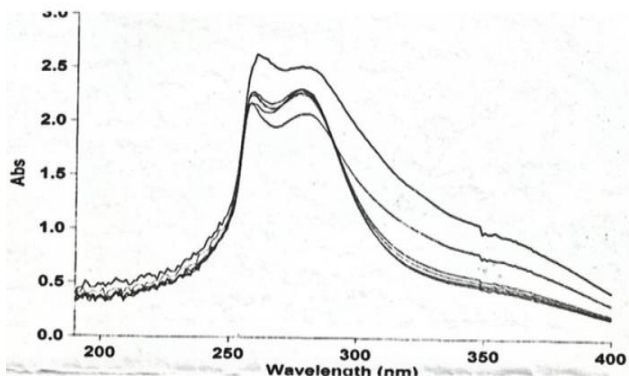


Figure -4- : Electronic spectra of [La (C₉H₁₀N₆S₂O) Cl₂] Cl spectra changes at 280 nm accompany changes in irradiation on time in dimethyl sulphoxide solvent at 298 k°
 (1) o : (2) 3 hr.

Effect changes the concentration of the rate reaction :

The use of different concentration for the complex for photolysis to study the effect concentration for rate reaction and calculate the order of reaction. Table (2) and figure (5) show the relationship between concentration the reaction of [La (C₉H₁₀N₆S₂O) Cl₂] Cl and time.

Table (2): Absorption of complex different time.

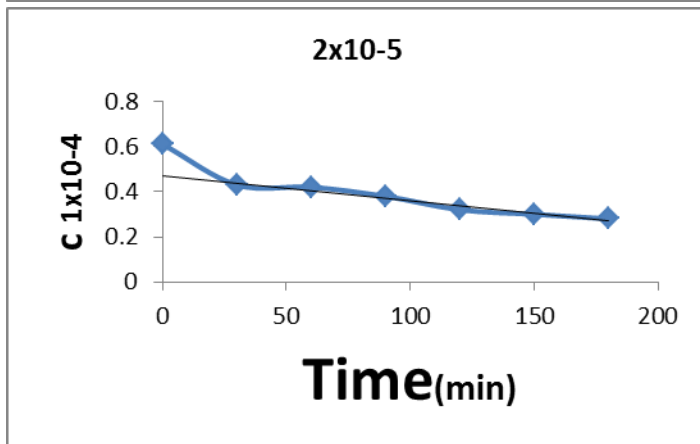
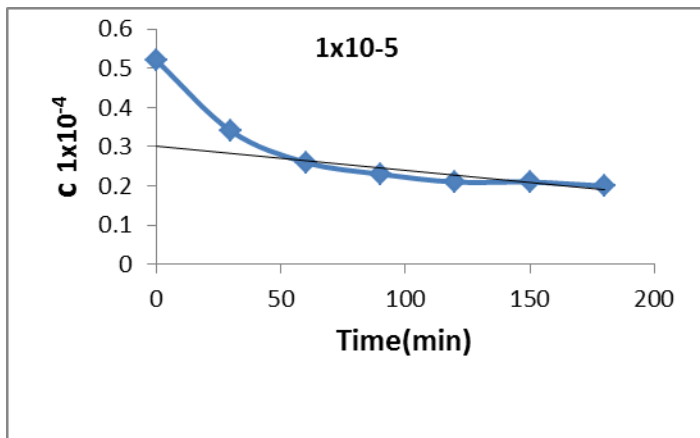
1×10^{-5}					2×10^{-5}				
Time (min)	Abs	Ct x10 ⁻⁴	(C ₀ -C _t) x10 ⁻⁴	Ln C ₀ -C _t	Time (min)	Abs	Ct x10 ⁻⁴	(C ₀ -C _t) x10 ⁻⁴	Ln C ₀ -C _t
0	0.85	0.52	0	0	0	1.001	0.61	0	0
30	0.86	0.34	0.18	-10.92	30	0.705	0.43	0.18	-10.98
60	0.87	0.26	0.26	-10.48	60	0.689	0.42	0.19	-10.87
90	0.86	0.23	0.29	-10.44	90	0.617	0.38	0.23	-10.68
120	0.86	0.21	0.31	-10.38	120	0.533	0.32	0.29	-10.44
150	0.85	0.21	0.31	-10.38	150	0.502	0.30	0.31	-10.38
180	0.86	0.20	0.32	-10.34	180	0.468	0.28	0.33	-10.31

5×10^{-5}

Time (min)	Abs	Ct $\times 10^{-4}$	$(C_0 - C_t) \times 10^{-4}$	Ln $C_0 - C_t$
0	1.379	0.84	0	0
30	1.217	0.75	0.09	-11.61
60	1.152	0.70	0.14	-11.17
90	1.005	0.61	0.23	-10.68
120	0.996	0.62	0.22	-10.72
150	0.901	0.56	0.28	-10.48
180	0.873	0.53	0.31	-10.38

1×10^{-4}

Time (min)	Abs	Ct $\times 10^{-4}$	$(C_0 - C_t) \times 10^{-4}$	Ln $C_0 - C_t$
0	2.285	1.4	0	0
30	1.728	1.06	0.34	-10.28
60	1.710	1.05	0.35	-10.26
90	1.598	0.98	0.42	-10.07
120	1.504	0.92	0.48	-9.94
150	1.463	0.90	0.5	-9.90
180	1.380	0.85	0.55	-9.80



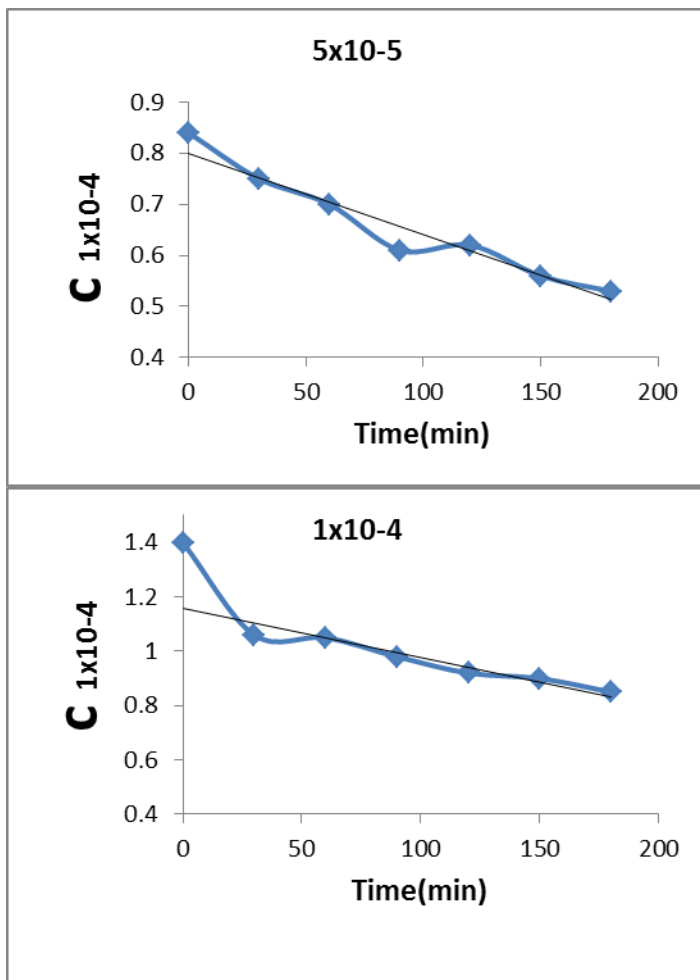


Figure (5): Relationship between concentration the reaction $[\text{La}(\text{C}_9\text{H}_{10}\text{N}_6\text{S}_2\text{O})_2\text{Cl}_2]\text{Cl}$ and time.

It is noted that the above figures of the average speed increases with initial concentration. And to calculate the order of reaction use the equation that $\ln R = \ln K + n \ln C_0$ and find the reaction is the first order reaction (0.86) show the figure (6).

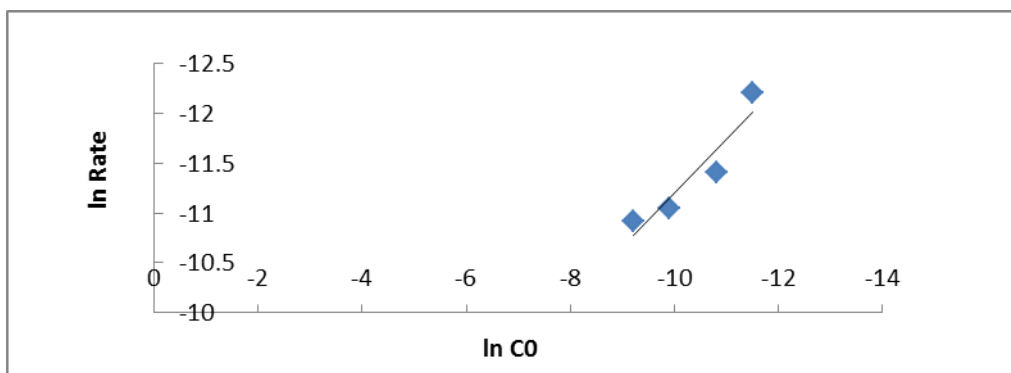


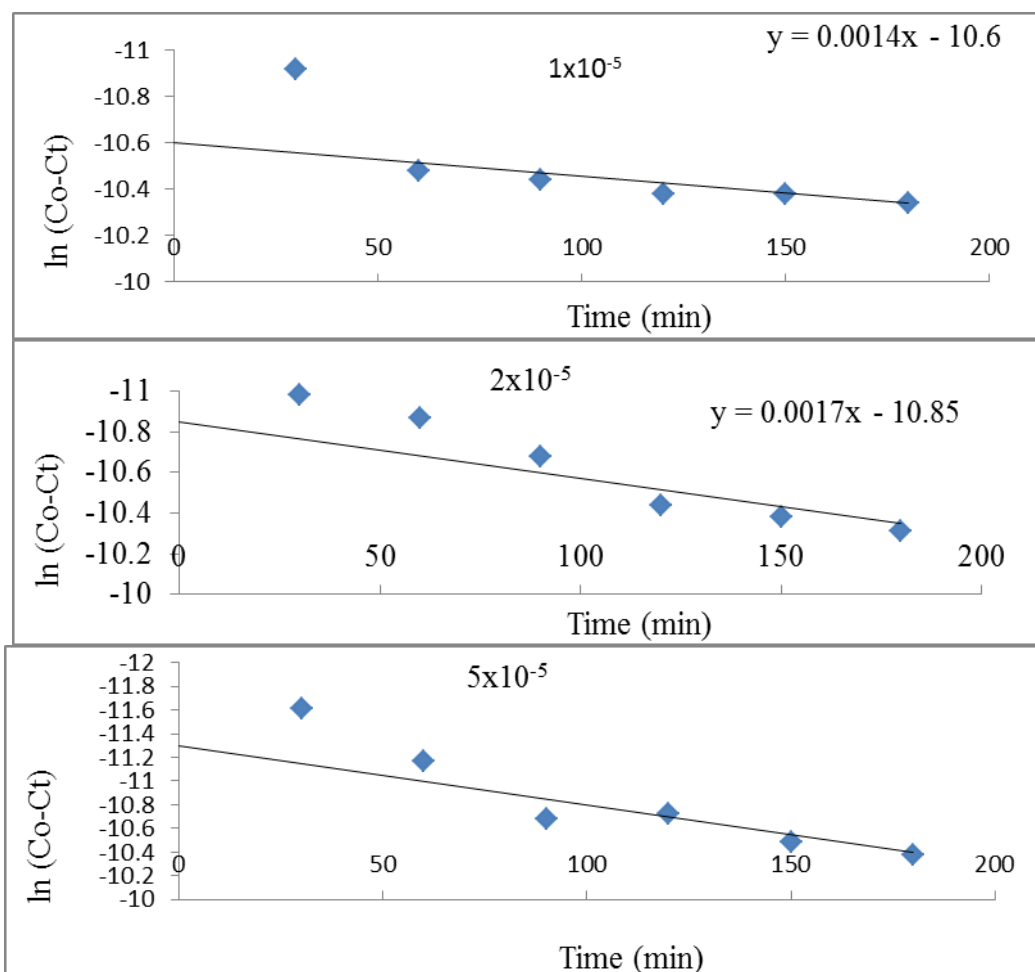
Figure (6) : Finding illustrates the rank of reaction

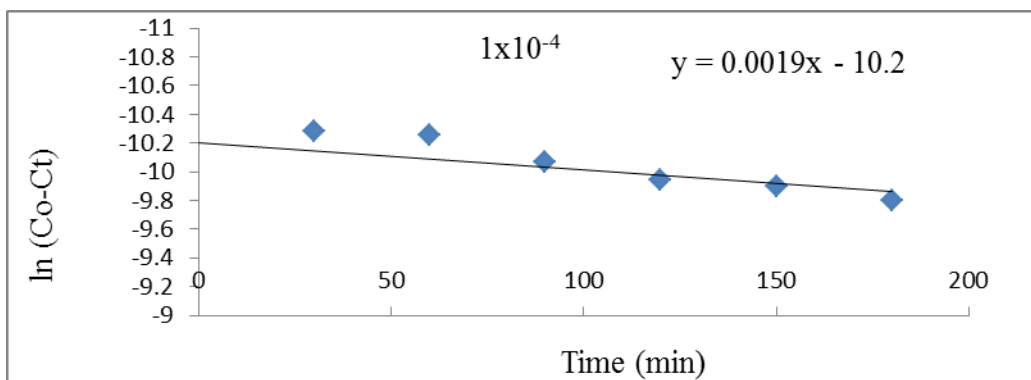
The specific decomposition rate constant of complex (kd) was determined after examining the order of reaction of these compounds [14] . The spectra of the complex [La (C₉H₁₀N₆S₂O)₂ Cl₂] Cl treated kinetically by plotting the curve between ln (C₀-C_t) versus irradiation time table (1) Only the plot of ln (C₀-C_t) with indication time gives straight line figure (4) which indicates that the reaction is first – order .

The (kd) of decomposition of this complex was determined by the following first – order equation .

$$\ln C_0 / C_0 - C_t = - k_d \dots\dots\dots(1)$$

The value of kd for this complex is (20x10⁻⁴ min⁻¹) on irradiation of the complex in dimethyl sulphoxide the [La (C₉H₁₀N₆S₂O)₂ Cl₂] Cl color changes gradually form yellow to light yellow and the absorbance intensity of all bands is decrease with time of irradiation in the region 200 -800 . S.Alsalch found that the hydrolysis of carbonyl at different PH solution follow first –order reaction kinetic [15] and S.m.Aliwifound that the photo oxidation reaction of CN ion on Tioz Surface follow first order relationship . the specific rate constants and then photo oxidation rate were measured [16]. Show table (2) and figure (7).





Figure(7): Variation of neutral of Absorbance with irradiation of complex $[La(C_9H_{10}N_6S_2O)_2 Cl_2] Cl$ in (DMSO) solvent using (MPML) At 298K°

6- ACTIVITY ENERGY:

To calculate the activation energy that need for the complex by use Arenuse equation

$$\ln K = \ln A - E_a / RT \dots\dots(2)$$

And the value to (Ea) equal 0.33KJ that refer the value is low because the photolysis not depend of changes the temperature and the show in the table(3)and figure (8).

Table (3): temperature and rate constant

T (K)	1/ T	K	Ln k
298	0.0030	0.0019	-6.265
308	0.0031	0.0027	-5.914
318	0.0032	0.0033	-5.713
323	0.0033	0.0041	-5.496

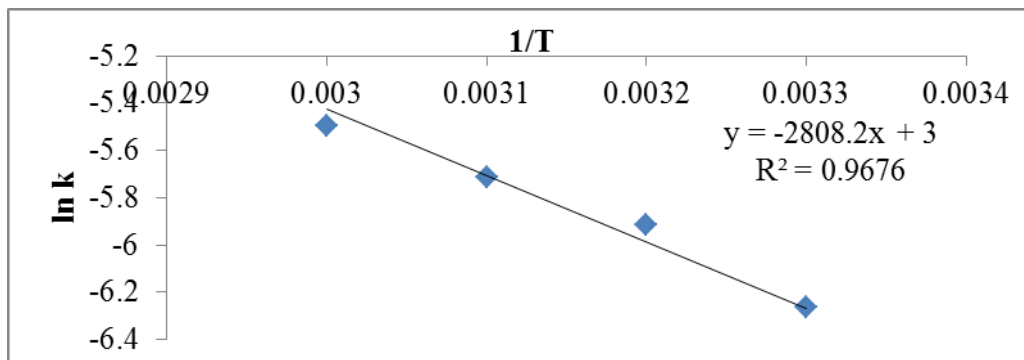


Figure (8) : Show the calculated energy of activation

The measurement of the incident light (I_0) was carried out by using standard method of potassium ferrioxalate actinometry [12].

$$I_0 = AV_1 / \epsilon \phi V_2 T$$

Where (I_0) is the incident light intensity; A the absorption at 510 nm; V_1 the final volume (25 ml); ϵ the extinction coefficient = slope of calibration curve ϕ ; the quantum yield = 1.12 at 365 nm; V_2 the volume taken from irradiation solution (1ml) and t the time of irradiation of actinometer solution (s). Determination of apparent quantum yield (ϕ)

The determination of apparent quantum yield (ϕ) has been done for lanthanum complex after the determination of absorbed light intensity I_{abs} and incidence light intensity I_0 as follows :-

$$\begin{aligned} I_{abs} &= I_0(1 - e^{-\Sigma \epsilon c l}) \\ &= 11.45 \times 10^{-5} (1 - e^{-16228 \times 1 \times 0.0001 \times 1}) \\ &= 11.45 \times 10^{-5} (1 - e^{-0.1622}) \\ &= 0.000406 \quad \text{Ein. l}^{-1} \cdot \text{s}^{-1} \end{aligned}$$

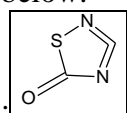
$$\phi = \text{Rate} / I_{abs} = K_d / I_{abs}$$

$$\phi = 2 \times 10^{-4} \times 1 \times 10^{-4} / 0.000406$$

The value of ϕ for complex = 0.4×10^{-4}

Qualitative analysis of photolysis products it is essential to examine the final products of photolysis in order to set up the mechanism.

Infrared (IR) spectra have been recorded for the final photoproducts of reaction. Figure (5) shows there is 3246 cm^{-1} (NH), 1541 cm^{-1} (C=N), 1473 cm^{-1} (C-N), 1076 cm^{-1} (C=S), 574 cm^{-1} (La-N), 451 cm^{-1} (La-S) the difference between (Figure 6) before irradiation and (Figure 5) after irradiation for complex $[\text{La}(\text{C}_9\text{H}_{10}\text{N}_6\text{S}_2\text{O})\text{Cl}_2]\text{Cl}$ shows that there is complete degradation of this the peaks are same put in ($1741, 1768, 1791 \text{ cm}^{-1}$) this refer to include (C=O) in complex that produce form conversion (NH₂) in episode Five to C=O and in benzene circle, as shown below.



The acidity of the final photolysis which was decreased with time of irradiation. The initial acidity was at (PH = 6.2) and the final was at (8.1). All these final photoreaction have been suggested without proposing the exact primary process.

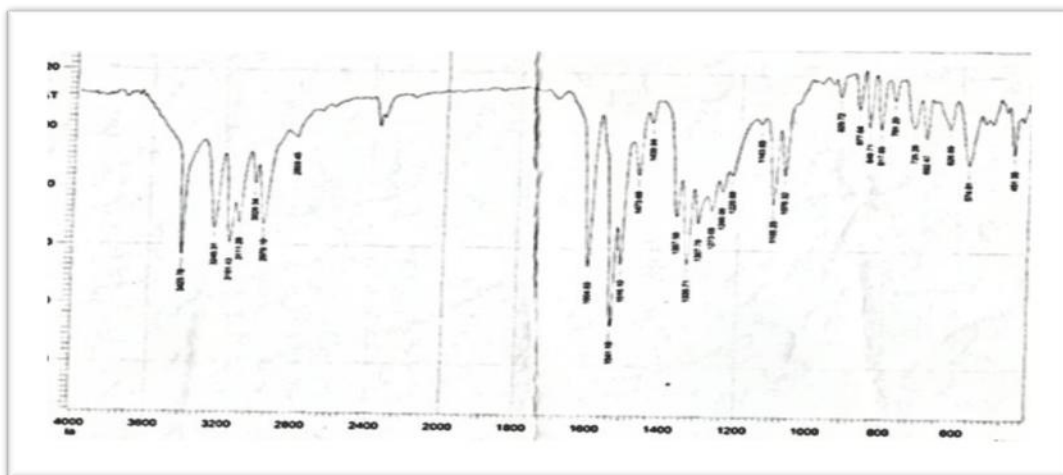


Figure (9): FTIR spectrum of complex $[La (C_9H_{10}N_6S_2O)_2 Cl_2] Cl$ at 298 K after photolysis

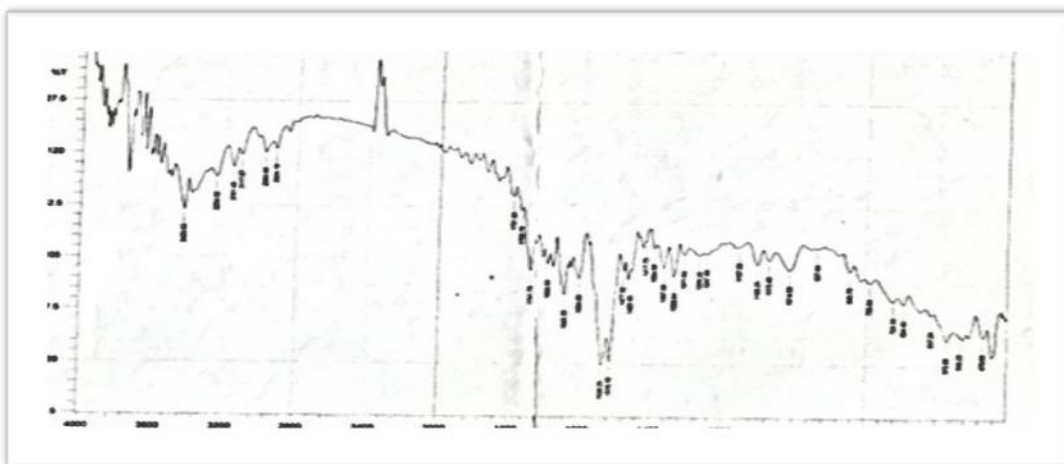
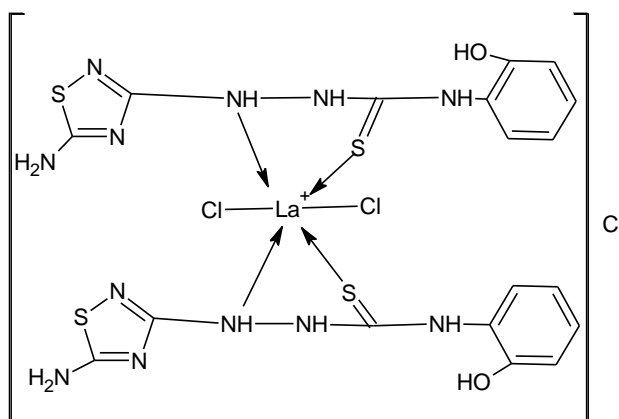


Figure (10) : FTIR spectrum of complex $[La (C_9H_{10}N_6S_2O)_2 Cl_2] Cl$ before photolysis

Conclusion

The condensation reaction of (3-Mercapto-5-Amino 1,2,4-thiadiazole) and O-hydroxyphenyl thiosemicarbazide) afford a new bidentate ligand. Transition metal complex of the thiadiazole derivative was obtained and analytical data confirmed a molar ratio (2:1) M:L. The suggested chemical configuration of the prepared complex was as shown below.



This complex has been formed photodergradation led to the disintegration of the compound was following up the progress of the reaction by the rank and found that the interaction of the first rank, and was equal to the dissociation constant ($20 \times 10^{-4} \text{min}^{-1}$) and also were calculated activation energy have found that the activation energy does not depend on temperature change .

References

- [1] Hennig H., "Homogeneous photo catalysis by transition metal complexes", *Coord. Chem. Rev.* 182:10123, 1999.
- [2] Sinan M., "Synthesis and Characterization of some transition metal complexes with 1,2,4-thiadiazole derivatives", M. Sc. Thesis , Mustansiriy univ., 2009.
- [3] Al-Maydama H., Al-Ansi T. , Jamil Y. and Ali A. "Biheterocyclic ligands: synthesis, characterization and coordinating properties of bis(4-amino-5-mercapto-1,2,4-triazol-3-yl) alkanes with transition metal ions and their thermokinetic and biological studies", *Ecl . Quim.* 33(3):29-42 ,2008.
- [4] McCarrick R, Eltzroth M. and Squattrito P., "Coordination geometries of bis(4-amino-3-alkyl-1,2,4-triazole-5-thione) complexes of first-row transition metals: crystal structures of complexes with propyl and hydrogen in the 3-position. Relationship to the 3-methyl and 3-ethyl analogs", *Inorg. Chim. Acta.*, 311(1-2):95-105, 2000.
- [5] Mohammad Reza G.,* Hamed G., Bagher L. and Parviz N., "Lanthanide Recognition: an Asymmetric Lanthanum (III) Microsensor Based on a New Schiff's Base" *Int. J. Electrochem. Sci.*, 4, 914-922, 2009.
- [6] J. Huang, 1 T.-L. Zhang, 2 S.-J. Xu, 1 R.-C. Li, 1 K. Wang, 1 J. Zhang, 3 Y.-N. Xie Effects of Lanthanum on Composition, Crystal Size, and Lattice Structure of Femur Bone Mineral of Wistar Rats. *Calcif Tissue Int* 78:241-24, 2006.
- [7] C. R. Hammond, "The Elements", in *Handbook of Chemistry and Physics* 81st edition. CRC press, 2000.
- [8] Kim, K; Shim, Kwang Bo. "The effect of lanthanum on the fabrication of ZrB₂-ZrC composites by spark plasma sintering" *Materials characterization* **50** :31, 2003.
- [9] C. K. Gupta and Nagaiyar Krishnamurthy, "Extractive metallurgy of rare earths", CRC Press. p. 441, 2004.
- [10] Irena K., Georgi M., Tzvetomira T. and Margarita K., "Synthesis, Characterization and Cytotoxic Activity of New Lanthanum(III) Complexes of Bis-Coumarins", *Chemistry and Applications*, Article ID 25651:1-9, 2006.
- [11] C Parkányi, H.L.Yuan and N. Sook Cho, *Heterocyclic Chem.*, 26, 1331, 1989.
- [12] C. G. Hatchard and C. A. Parker, "A new sensitive chemical actinometer II. potassium ferrioxalate a standard chemical actinometer ", *proc. Roy .Soc.*, 235, 1956.
- [13] A. K. Ayal, "Synthesis and spectrophotometris study of some metal ions complexes....", M.Sc. Thesis, Mustansiriyah univ., 2005.
- [14] M. F. Alias, Ph. D. thesis, Baghdad univ., Baghdad 2000.
- [15] S. S. Abdul Kadir and A. J. AL-Lami, "Study the chemical kinetics of insecticide carbaryl in aqueous solution", No. 1, 2008.

- [16] S. M. Aliwi, S. S. AL-Saleh, "Photo catalytic oxidation of cyanide ion aqueous TiO₂ suspension", Vol. 19, No. 3, 2008.