

Spectroscopic Studies of 3-(4-chlorophenylazo)- 4- hydroxyl acetophenone and Some of it's Metal Complexes

Kamran Basheer , Mohammad Karim and Wishyer Ali

Department of Chemistry , College of Science – Education , University of Salahaddine , Erbil , Iraq

دراسة طيفية ل 3-(4-chloro phenylazo)- 4- acetophenone ل hydroxyl و بعض معقداتها للأيونات الفلزية

كامران بشير حسين محمد كريم صمد وشيار علي أسماعيل
قسم الكيمياء – كلية التربية الأقسام العلمية – جامعة صلاح الدين – أربيل / العراق

المستخلص

تم تحضير صبغة الأزو 3-(4-chlorophenylazo)-4-hydroxyacetophenone L بواسطة تفاعل p-chloroaniline مع p-hydroxyacetophenone من خلال تفاعلات الأزوداج أحادية الأزو. لقد تم مفاعلة الصبغة الجديدة المحضرة مع أملاح La(III), Ce(III), Eu(III), Dy(III), Sm(III) والتي أعطت معقدات أحادية نواة العنصر. تظهر المعقدات نسبة مولية 1:3 الشكل الهندسي حول الأيونات الفلزية هي ثماني السطوح. كما تم تشخيص تراكيب كل من صبغة الأزو ومعقداتها بواسطة الأشعة تحت الحمراء والأشعة المرئية وفوق البنفسجية و قياسات التوصيلية المولارية ومطياف الرنين النووي المغناطيسي. بينت أطياف الأشعة تحت الحمراء بأن الليكاند يتناسق مع الأيونات الفلزية بشكل ثنائي السن من خلال ذرة أكسجين مجموعة الهيدروكسيل وذرة نايترودجين مجموعة أزو، لقد وجد بأن تناسق أيونات العناصر الانتقالية الداخلية هي تناسق سداسي. بيانات التحاليل لليكاند ومعقداتها في اتفاقية جيدة بصياغتهم.

Abstract

Azo dyes 3-(4-chlorophenylazo)-4-hydroxyacetophenone (L) were synthesized by reaction of p-chloroaniline to p-hydroxyacetophenone through mono azo-coupling reaction. Reaction of new azo-dye with La(III), Ce(III), Sm(III), Eu(III) and Dy(III) salts gave mono nuclear complexes, the complexes exhibited 1:3 M:L stoichiometry. Complexes showed octahedral geometry around metal ions.

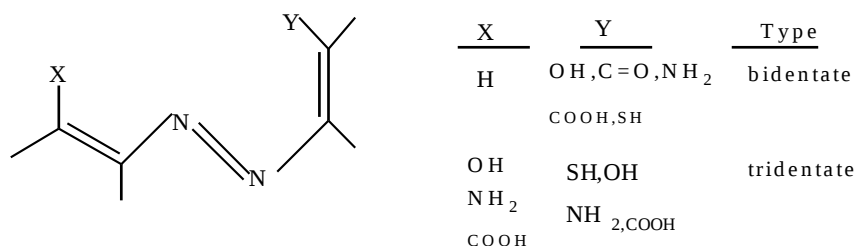
Their structures were identified by FTIR, UV-Visible, molar conductance and NMR spectran. IR spectra show that the ligand is coordinated to the metal ions in a bidentate manner and complexation with the ligand through the oxygen atom of hydroxyl group (OH) and azo nitrogen. It was found the inner transition metal ions was six-coordinated. Analytical data of the ligand and it's complexes are in good agreement with their formulation.

Keywords: trivalent metal ions, spectral studies , characterization , azo metal chelate dye.

Introduction

Lanthanides exhibit a number of features in their chemistry that differentiate them from the d-block metals. The reactivity of the elements is greater than that of the transition metals. The 4f orbitals in the Ln^{3+} ion do not participate directly in bonding, being well shielded by the $5s^2$ and $5p^6$ orbitals [1]. Their spectroscopic and magnetic properties are thus largely unaffected by the ligand. The versatile ligational behaviour of azo compounds had evoked considerable interest in the past.

Both the azo dyes and their metal complexes find applications in dye industry. In some cases the complexes assume more importance due to technical reasons[2-7], like better fiber affinity, and light fastness. Moreover, the presence of metals makes the dyes more specific and selective. Metal complexes of azo compounds are broadly divided into two categories, namely the ones in which the azo group is involved in bonding and the others in which it is not. The former are derived from azo compounds containing donor functions such as OH, NH_2 , COOH, SH, etc., in a congenial position so as to form six or five membered chelates (structure.1), azo groups show weak donor properties but in conjunction with other strong donors like OH, NH_2 or C=O they form very stable chelates[8,9].



structure.1- five or six membered ring chelates.

Experimental

Chemicals

All employed chemicals were of AnalaR grade purchased from (Aldrich, Merk, BDH) and used without purification, including $\text{Sm}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Dy}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, p-chloroaniline, hydrochloric acid, p-hydroxyacetophenone, xylene, absolute ethanol, N,N-dimethyl formamide(DMF), methanol, NaNO_2 , diethylether, NaOH, distilled water was used through the experiment.

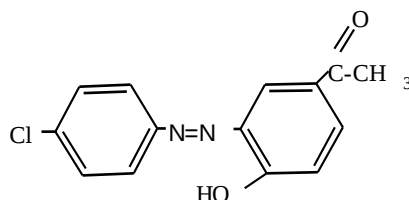
Preparation of the azo compound

Step 1: Formation of diazonium salt

p-chloroaniline (5.1g, 0.04mol) was dissolved by heating gently in a (32ml) of 3M HCl. After most of the solid has dissolved the solution was cooled in an ice bath to 0°C . While stirring, added slowly (40ml) of freshly prepared 1M of sodium nitrite solution, in which the temperature remains below 10°C . The solution kept in the ice bath and immediately proceeded to the next step.

Step 2: Coupling process: (addition of p-hydroxyacetophenone)

p-hydroxyacetophenone (5.44g , 0.04mol) was dissolved in 80ml of 1M sodium hydroxide then cooled with stirring in the ice bath and added slowly to the diazonium salt solution . The mixture allowed to stir for 15min. until crystallization is completed. The solid azo dye was collected by vacuum filtration , washed several times with water , dried and recrystallized from the mixture of (1:2) xylene :ethanol to obtain yellow crystals , of 3-(4-chlorophenylazo)-4-hydroxyacetophenone . The compound have the general structural formula .



3-(4-chlorophenylazo)-4-hydroxyacetophenone

Preparation of the metal complexes

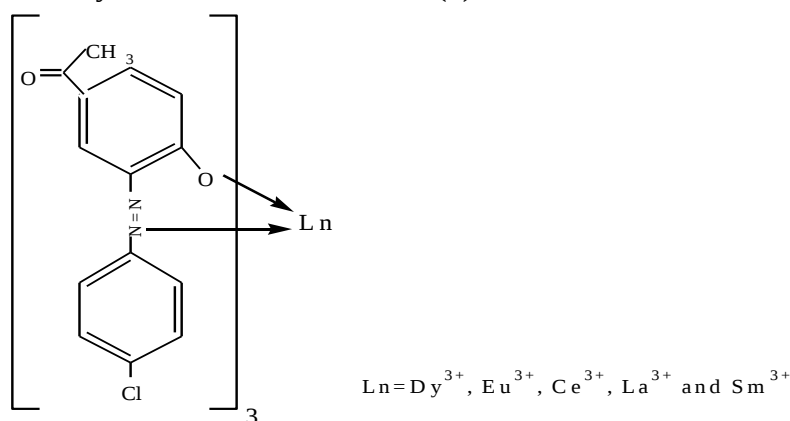
A solution of Ln^{3+} (1mmol) when $\text{Ln}^{3+} = \text{Dy}^{3+}$, La^{3+} , Ce^{3+} , Eu^{3+} & Sm^{3+} in ethanol was added to warm ethanolic solution (30ml) of the ligand (1mmol) . After 1h stirring the pH of the solution was adjusted to 8-10 and the resulting solution was then refluxed on a water-bath for about 2h . The solution was then concentrated and kept overnight . The powdery material thus separated was filtered . Washed successively with small amounts of EtOH and finally with diethylether and dried in oven .

Analytical methods

The analyses of the metal ions were carried out gravimetrically using the standard oxalate method [10] , in the college of education at scientific laboratory departments , Salahaddin University-Erbil . For determining the stoichiometry of the azo metal complex, the absorbance of a series of metal salt (in 85% EtOH + 15% H_2O) + ligand (in EtOH) mixtures which were prepared from their 10^{-3} mol/l solutions as 1+9ml, 2+8ml, 4+6ml, 5+5ml, 6+4ml, 6.7+3.3ml, 7+3ml, 8+2ml, 9+1ml, etc. were measured. The data were analyzed using Job's method [11,12]. Magnetic susceptibility measurements were made using Bruker Magnet BM6 at room temperature (25°C) . The conductivity of the complexes were measured in N,N-dimethylformamide using HANNA Instruments Quick Reference Guide (pH , $\mu\text{S}/\text{cm}$, mg/L , $^\circ\text{C}$). UV-Visible Spectrophotometer model Ce3021 was used for absorbance measurements using 1cm quartz cuvette , the study was conducted in the college of science education Salahaddin University-Erbil. Melting points were determined by a Electrothermal melting point apparatus 9100 LTD (UK) and are uncorrected . IR- Spectra were recorded on a Bio-Rad Merlin , FT-IR spectroscopy Mod FTS 3000 , in which solid materials were taken as a disc KBr special for spectroscopy . The ^1H -NMR , ^{13}C -NMR and ^{13}C -DEPT-135 were taken on a Bruker ultrashield 300 MHz with TMS as internal references , in Al-al-Bayt Central Labs (Jordan) .

Results and Discussion

Metal Ln(III) salt reacts with azo ligand 3-(4-chlorophenylazo)-4-hydroxyacetophenone in 1:3 molar ratio in alcoholic medium to afford dark orange / yellow complexes. The ligand and its complexes are stable at room temperature and are nonhygroscopic. The ligand is soluble in common polar organic solvents, such as ethanol, methanol and chloroform but partially soluble in benzene. The azo complexes are relatively well soluble in DMF and DMSO. The formula of the complexes were determined by these peak wavelengths by the continuous variations method of Job. The metal / ligand ratio was found 1:3. The structure of the azo metal chelate dye was shown in structure (2).



Structure 2 - Suggested structural formulae of metal complexes.

The molar conductance value ($5\text{--}11\mu\text{S}/\text{cm}$) of the complexes which was carried out the chelates were dissolved in DMF the molar conductivities of 10^{-3}M of their solutions at $25\pm 2^{\circ}\text{C}$ were measured. Table(1) show the molar conductance values of the complexes. Further, the low molar conductance of the complexes might arise due to large size of the anionic coordination sphere, which might have low ionic mobility. The values of molar conductance, suggest that complexes are nonelectrolytes, so that no additional inorganic or organic counterions are needed to counter balance the electric charges of the complexes. The IR spectra of the complexes are similar. Table (2), gives the characteristic bands of ligand and its complexes.

Infrared spectra

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The main infrared bands and their assignments are listed in Table (2). In the ligand spectrum fig.(1) the appearance of a broad band at 3332cm^{-1} attributed to (OH) group [13]. The binding sites in these complexes are deduced from their infrared spectra, see fig.(2). The involvement of the deprotonated OH group in chelation is confirmed by the $\nu(\text{C-O})$ str. band, observed at 1274cm^{-1} in free ligand, to the 1246cm^{-1} in the $[\text{Sm}(\text{L})_3]$ complex. A strong absorption peaks have been noticed in ligand spectra at 1601cm^{-1} which can be due to $\nu(\text{N=N})$ str. mode of azo group. Now, shifting of peaks for N=N str. vibrations from its original peak frequencies in ligand spectra found to be characteristic supported the Sm(III) complex formation. In the far-IR spectra of all complexes, the non-ligand bands observed at $442\text{--}468\text{cm}^{-1}$ region can be assigned to the $\nu(\text{M-N})$ stretching vibration of

the azo nitrogen. Conclusive evidence regarding the bonding of oxygen to the metal ions is provided by the occurrence of bands at $510\text{--}520\text{cm}^{-1}$ as the result of $\nu(\text{M-O})$ [14].

¹H-NMR, ¹³C-NMR and ¹³C-DEPT data of azo ligand

3-(4-chlorophenylazo)-4-hydroxyacetophenone

¹H-NMR (fig.3) shows a singlet at (2.65)ppm for three protons CH₃ attached to the carbonyl group, four doublets at (7.08,7.50,7.81,and 8.01) and a singlet at (8.54)ppm for seven protons of the two phenyl rings. However, in the ¹H-NMR spectrum of the ligand a distinct singlet signal assigned to the hydroxyl group was found at (13.25)ppm.

¹³C-NMR (fig.4) shows twelve singlet signals corresponding to twelve types of carbon in different chemical shifts, two of them at (26.34 and 195.81)ppm belongs to carbon atom of (CH₃ and carbonyl)groups respectively, the other ten signals at (118.71,123.58,129.78,129.98,133.25,134.51,136.07,137.84,148.54 and 156.87)ppm were fitted to the (C₈,C_{10,14},C_{11,13},C₃,C₅,C₄,C₁₂,C₆,C₉ and C₇) respectively.

The Distortionless Enhancement by Polarization Transfers [15], summarized by ¹³C-DEPT is the most commonly used method to determine the multiplicity of ¹³C-signals. The resulting of ¹³C-DEPT spectrum containing only signals arising from protonated carbons and the non-protonated carbons don't give signals in the ¹³C-DEPT. The peaks arise by (-CH₃ and -CH-) groups appear oppositely phased from those of (-CH₂-) group, so signals of (-CH₃ and -CH-) groups pointed upwards (+) while signals of (-CH₂-) group pointed downwards (-). The ¹³C-DEPT-135 of azo compound (fig.5) shows upward signal at (26.37) for tri-protonated carbon atom of (-CH₃) group, also showed five different upward signals at (118.71,123.58,129.78,133.25 and according to the mono-protonated carbon atoms (-CH-) in two aromatic rings (C₈, C_{10,14}, C_{11,13}, C₅ and C₄) respectively, the disappearance of non-protonated carbons (C₃, C₁₂, C₆, C₉, C₇, and C₂) which appeared in the normal ¹³C-NMR is good evidence for determine the structure[16]. ¹H-NMR, ¹³C-NMR and ¹³C-DEPT data are illustrated in Tabel (3).

Magnetic susceptibility

The values of the magnetic moments of the complexes are summarized in Tabel (1). These values compare very well with those measured for other simple compounds. Moments of the complexes, which were corrected for diamagnetism, showed very little deviation from the van Vleck values [17]. Unlike the d-electrons of the transition metal ions, the f-electrons of the lanthanide ions are almost unaffected by the chemical environment and the energy levels are the same as in the free ion, due to very effective shielding by the overlying 5s² and 5p shells. The magnetic moment values of the complexes showed that the lanthanum(III) complex is diamagnetic, while all others are paramagnetic [18].

Electronic spectra

The lanthanum (III) complex has no significant absorption in the visible region, owing to the absence of 4f orbital electrons. The visible spectral bands of the lanthanide complexes were hypersensitive to stereochemistry. An enhancement of the

intensity of certain hypersensitive bands of the Eu(III), Dy(III), Ce(III) & Sm(III) complexes compared to the respective aquated ions was observed. These variations can be attributed to the action of an inhomogeneous electromagnetic field and by changes in the symmetry of the field on the lanthanide ion [19]. The sharp bands due to f-f transitions originating within the $4f^n$ configuration of the lanthanide ions are only slightly affected by the immediate surroundings of the metal ion, and this is commonly attributed to the shielded nature of the 4f orbitals by the overlying $5s^2$ and $5p^6$ orbitals. However, a shift to a lower frequency can be considered as being due to complex formation [20,21].

Acknowledgement

I would like to thank chemistry department at University Salahaddine – Erbil, for their technical assistance. Additional thanks are also due to Dr. Mohammad Salim and Mr. Yousif Taha for his kind help.

References

- 1- **Sulekh Chandra, Smriti Raizada and Soni Rani**., (2008), Lanthanide Complexes of tetradentate macrocyclic ligand: Synthesis and Spectroscopic investigation, J. Indian Chem. Soc., Vol.85, pp. 783-791.
- 2- **Crina Valentina Turcas Ion Sebe**., (2012), Azo dyes Complexes, Synthesis and Tinctorial Properties, U.P.B. Sci. Bull., Series B, Vol.74, No.1, pp.52-58.
- 3- **Divyesh R. Patel and Keshav C. Patel**, (2011) Novel 2-phenyl-3-[4-[N-(4-aminophenyl)carbamoyl]-phenyl]-quinazoline-4(3H)-one-6-sulphonic acid based mono azo reactive dyes., J. Serb. Chem. Soc., Vol.76, No.2, pp.177-188.
- 4- **Elena Ouskova, Jaana Vapaavuori and Mattikaivola**., (2011). Self-orienting liquid Crystal doped with polymer-azo-dye complex., Optical Materials Express, Vol.1, No.8, pp.1463-1470.
- 5- **V.A. Modhavadiya**, (2011), Synthesis, Characterization and Antimicrobial Activity of Metal Complexes containing Azo Dye Ligand of Sulfa Drugs., Asian Journal of Biochemical and pharmaceutical research, Vol.1, No.1, pp.114-120.
- 6- **Ali A.I. Abdul Zahra**., (2011), Synthesis, Characterization and Spectroscopic Properties of new azo-dyes and azo-metal complexes derived from 8-hydroxyquinoline., Basrah Journal of Science, Vol.28, No.1, pp.15-36.
- 7- **A. Emandi, I.C. Vasiliu**, (2010), Solvatochromic Properties of Azo and Azomethine Tridentate Ligands in Coordinative Compounds with [Er(ONO)] Chromophores, Digest Journal of Nanomaterials and Biostructures, Vol.5, No.4, pp.851-858.
- 8- **Chempakam Janardhanan Athira**, (2011), Synthesis and Spectroscopic Characterization of Some lanthanide(III) nitrate Complexes of ethyl 2-[2-(1-acetyl-2-oxopropyl)azo]-4,5-dimethyl-3-thiophene carboxylate, J. Serb. Chem. Soc., Vol.76, No.2, pp.249-261.
- 9- **Ales Ruzicka and Jaroslav Holecek**., (2003)., Structure of Azo Dye Organotin(IV) Compounds containing a C,N-Chelating Ligand., Appl. Organometal. Chem., Vol.17, pp. 168-174.

- 10- **Kolthoff-Sandell and Meehan-Bruckenstein.(1969).** Quantitative Chemical Analysis , the Macmillan Company, **1969** .
- 11- **W.J.Geary , G.Nickless and F.H.Pollard ,(1962),** The Metal Complexes of Some Azo and Azomethine Dyestuffs, Anal.Chim.Acta, Vol.26, pp.575-582.
- 12- **Shuangqing wang, Shuyinshen, HuijunXu., (2000) .,** Synthesis, spectroscopic and thermal properties of a series of azo metal chelate dyes, Dyes and Pigments, Vol.(44), pp.195-198.
- 13- **K.Nakamoto;(1978),**"Infrared Spectra of Inorganic and Coordination Compounds" New york , Ny: John wiley and Sons.
- 14- **M.Silverstein,G. ClaytonBassler Terence C.Morrill; (1981) ,** "Spectrometric Identification of Organic Compounds" Joha Wiley and Sons, Inc. New york, pp.130 .
- 15- **J.Legendziewicz, V. Tsaryuk, and M.Karbowiak, (2001).,** "Optical Spectroscopy and magnetic studies of dimeric europium capronate with 1,10-phennanthroline", New Journal of Chemistry, Vol.25,No.8 , pp. 1037-1042 .
- 16- **V.M. Parikh , (1985) ,** Absorption Spectroscopy of Organic Molecules ., Baghdad , Iraq , pp.225 .
- 17-**Cotton F.A, Wilkinson G.Murillo, C.A., Bochmann, M;(1999),** "Advanced Inorganic Chemistry" 6th Ed., Wiley and Sons, New york .
- 18- **Coordination Chemistry Reviews.,** Vol.7, No.1, **1971** .
- 19- **Greay, W.J., Nickless, G., F.H.,(1962),** The metal complexes of some azo and azomethine dyestuffs; Anal.Chim.Acta, Vol.27, pp.71.73.
- 20- **A.K.El-Qisairi,(2006),** Several Trivalent Rare Earth Complexes with 2,6-Diaminopyridine , Polish J.Chem., Vol.80 , pp.1593-1599.
- 21-**Man Singh and Sushma Anant, (2012),** Synthesis and Spectral Characterization of Praseodymium(III) Complex with New Amino Acid-Based Azo Dye, International Journal of Inorganic Chemistry ,Vol.12, pp.1-6.

Table(1): Analytical , conductance and magnetic moment data for Ln(III) complexes of azo ligand .

Complexes/Ligand	Colour	Yield%	M.P ⁰ C	Λ_m $\mu\text{S}/\text{cm}$ In DMF	$\mu_{\text{eff}}^a/\text{BM}$	M% Practical Teoretical
$\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2\text{Cl}$ (L)	yellow	97.99	158	270	-----	-----
$[(\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{Cl})_3\text{La}]$	Dark yellow	79	187	5	Diamag.	(14.79) (14.47)
$[(\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{Cl})_3\text{Dy}]$	Pale yellow	78	184	10	10.38	(16.65) (16.53)
$[(\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{Cl})_3\text{Ce}]$	Dark Brown	73	198	11	2.53	(14.89) (14.58)
$[(\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{Cl})_3\text{Eu}]$	Light yellow	70	195	10	3.30	(15.33) (15.62)
$[(\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{Cl})_3\text{Sm}]$	Orang	69	190	8	1.61	(15.66) (15.48)

Table (2): Selected IR data (400-4000) cm^{-1} of azo dye and their complexes .
 (s=strong , m=medium , w=weak , br=broad) L= $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2\text{Cl}$

Compound	$\nu(\text{N}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})_{\text{azo}}$	$\nu(\text{C}-\text{O})$
$\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2\text{Cl}$, ligand	1492(s)	1601(s)	-----	-----	1274(s)
$[\text{Sm}(\text{L})_3]$	1435(m)	1594(m)	510(m)	442(m)	1246(s)
$[\text{La}(\text{L})_3]$	1448(s)	1590(m)	500(m)	430(m)	1212(s)
$[\text{Ce}(\text{L})_3]$	1453(m)	1585(s)	510(m)	425(w)	1210(s)
$[\text{Eu}(\text{L})_3]$	1450(m)	1580(m)	495(m)	468(w)	1230(s)
$[\text{Dy}(\text{L})_3]$	1445(m)	1596(m)	520(m)	432(m)	1233(s)

Table-3: The ^{13}C -NMR, ^{13}C -DEPT & ^1H -NMR data for the prepared 3-(4-Chlorophenylazo)-4-hydroxyacetophenone : Solvent CDCl_3 .

^{13}C -NMR		^{13}C -DEPT		^1H -NMR			
δ/ppm	Assign.	δ/ppm	Assign.	δ/ppm	Multip.	Intens.	Assign.
26.34	C_1	26.34	C_1	2.65	S	3H	COCH_3
118.71	C_8	118.71	C_8	7.08	D	1H	Ar-H- C_5
123.58	$\text{C}_{10,14}$	123.58	$\text{C}_{10,14}$	7.50	D	2H	Ar-H- $\text{C}_{11,13}$
129.78	$\text{C}_{11,13}$	129.78	$\text{C}_{11,13}$	7.81	D	2H	Ar-H- $\text{C}_{10,14}$
129.98	C_3	133.25	C_5	8.01	D	1H	Ar-H- C_4
133.25	C_5	134.51	C_4	8.54	S	1H	Ar-H- C_8
134.51	C_4			13.25	S	1H	OH

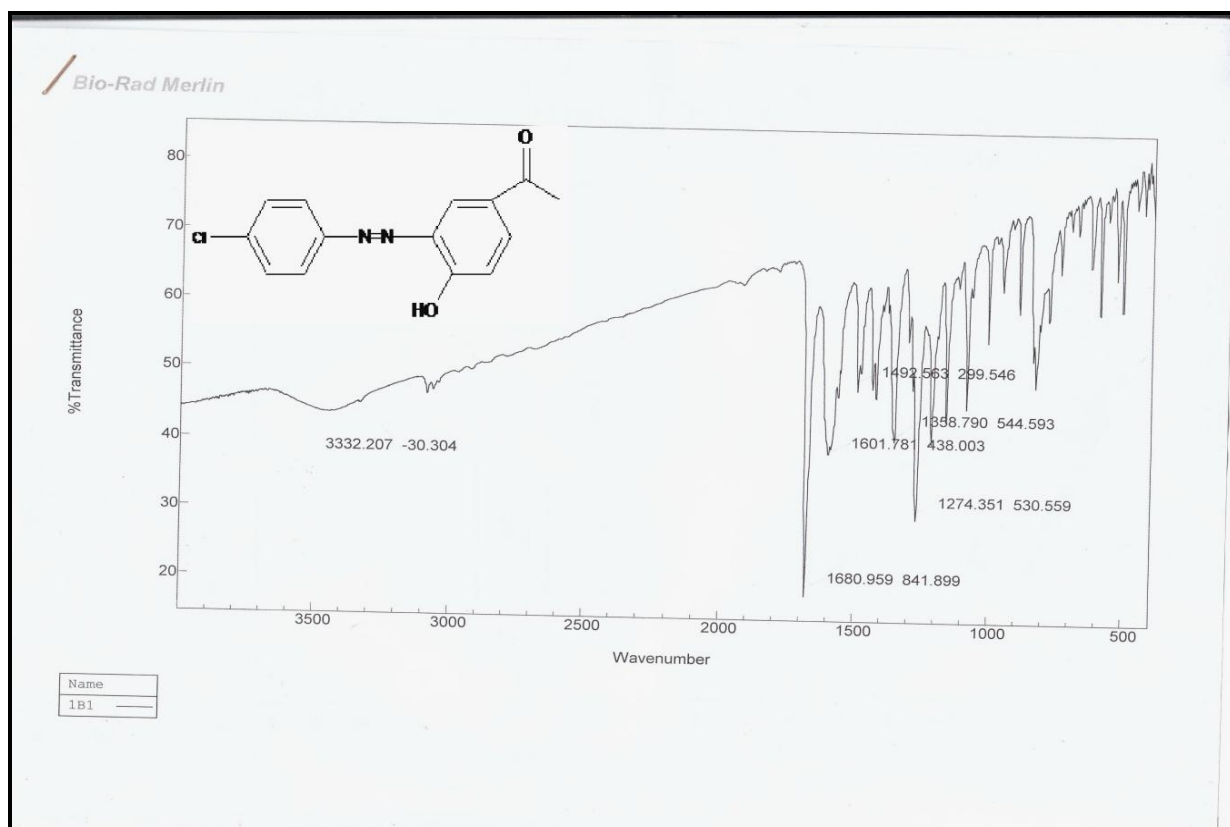


Figure (1): IR spectrum of azo compound

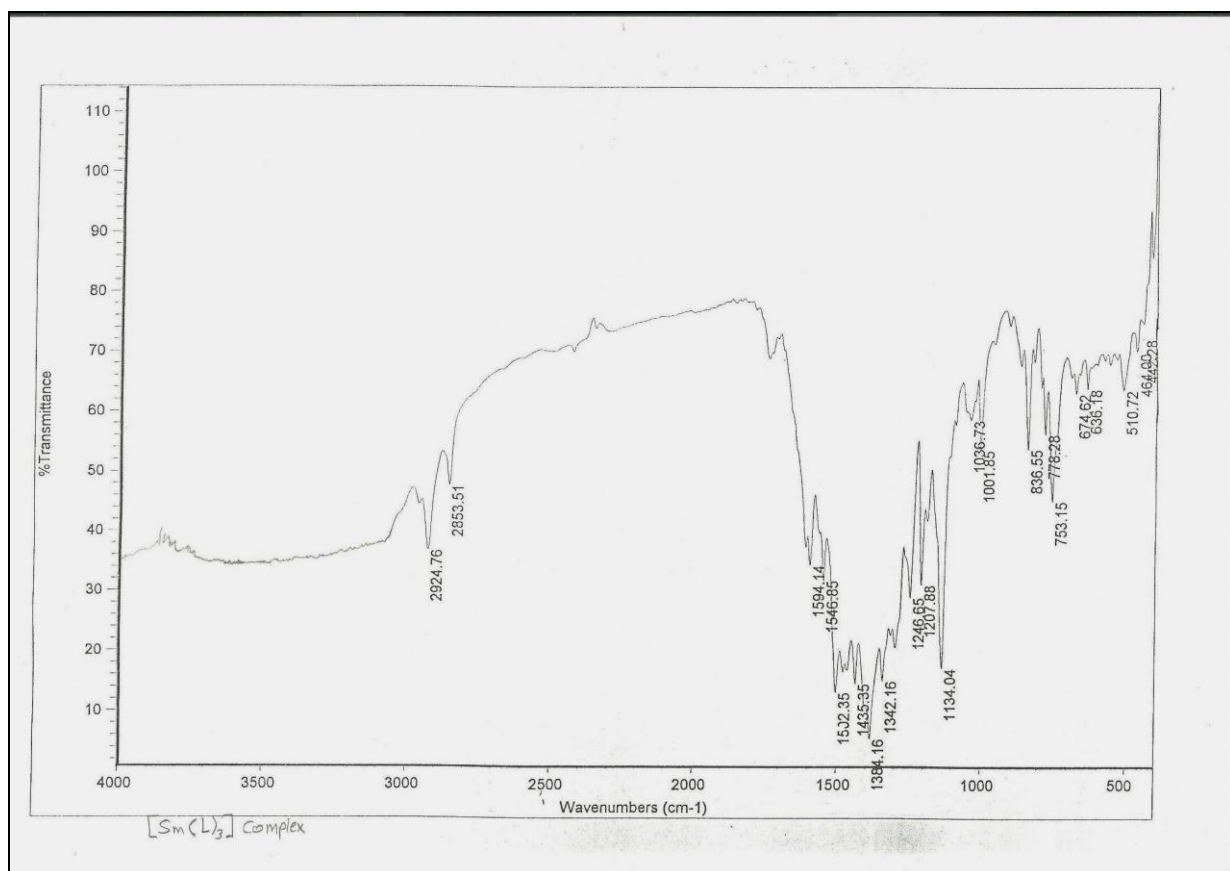
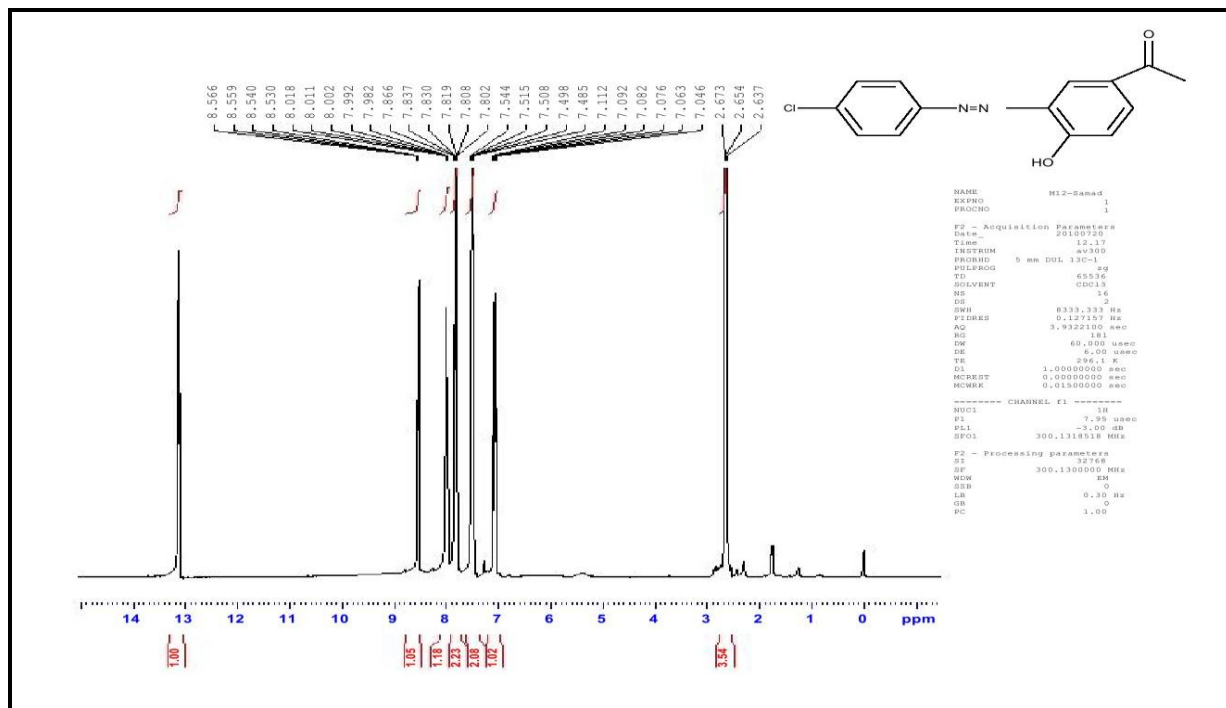
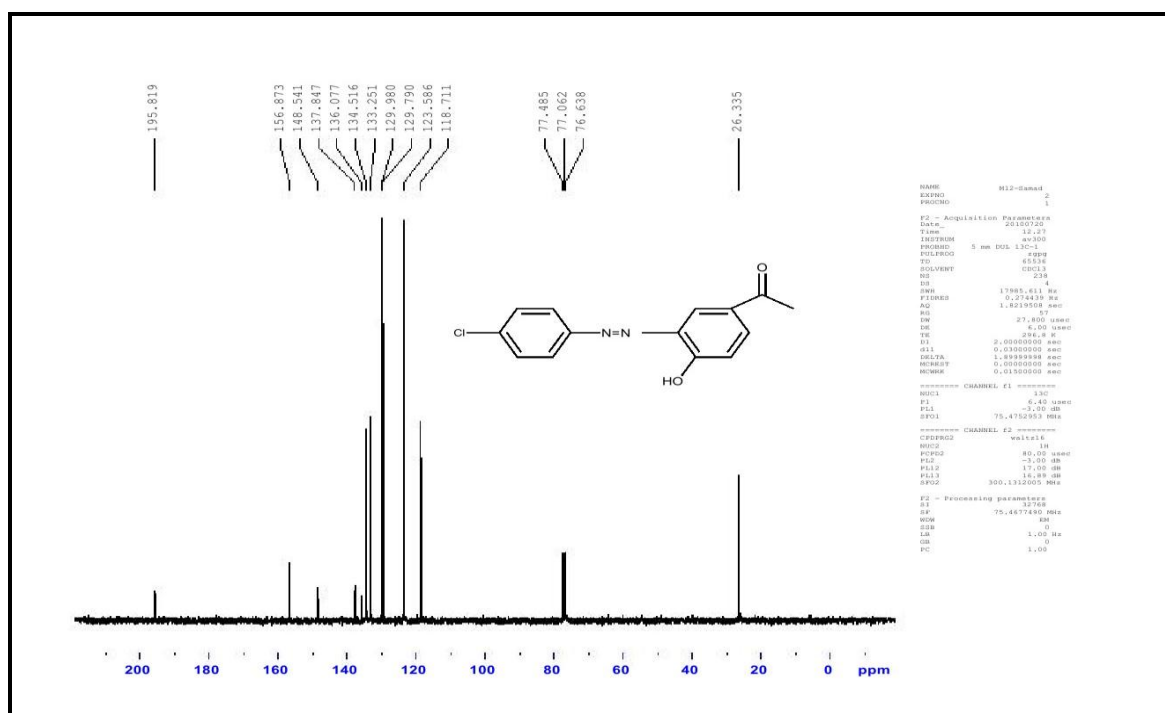


Figure (2): IR spectra of Sm(III) complex .

Figure (3): ¹H-NMR spectrum of azo compoundFigure (4): ¹³C-NMR spectrum of azo compound

