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website:- www.journalofchemistry.org**Synthesis Characterization and Spectral studies Ru(III) and La(III) Dithiocarbamate complex molecule**D. BABA BASHA¹, G. RANJITH KUMAR^{2,2*} and R. MALLIKARJUNA RAO³¹Department of Physics, College of Computer and Information Science, Majmaah University, Al' Majmaah-11952, Kingdom of (Saudi Arabia)²Department of Physics, School of Applied Sciences, REVA University, Bangalore-560064 (India)^{2*}Department of Physics, Rayalaseema University, Kurnool, Andhra Pradesh (India)³Department of chemistry, Sri Chaitanya IIT academy, SPSR Nellore, Andhra Pradesh (India)Corresponding Author Email: b.dudekula@mu.edu.sa<http://dx.doi.org/10.22147/juc/140302>

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Abstract

Complexes of the type $[M(DTC)_2(H_2O)_2]$ where $M = Ru$ and La and $Nacs_2L =$ sodium salt of histamine dithiocarbamate ligands have been synthesised and characterised by physico chemical (elemental analysis, conductance magnetic susceptibility measurements) and spectral techniques Infrared spectroscopy, magnetic susceptibility, ultraviolet and Atomic absorption spectroscopy, ¹HNMR spectroscopy. The FT-IR spectra of the complex indicate that ligand behave as a bidentate manner coordinating via nitrogen and sulphur for their structures and studied for structure activity relationship with complexes the anionic metal ligand complexes exhibit octahedral geometry. Thermal behaviour of these complexes show hydrated complexes losses water molecules of hydration in the first step. In thermogravimetric analysis first step followed immediately by decomposition of the coordinated water, anions and ligands in the subsequent steps.

Key words: histamine, conductance, structure activity relationship, octahedral geometry.

Introduction

The vast development of sulphur containing dithiocarbamate metal complexes and their applications are in various fields and also these are used for the different regions due to structural properties of ligand

of dithiocarbamate, this type of enhancement property of metal complexes depend upon the nature of transition metal as well as ligand natures. The complexing ability of dithiocarbamates was well established due to the presence of lone pair of electrons in the sulphur atom and of the general electron

donating character of the double bond, more stable metal complexes will be formed by chelation with dithiocarbamate moiety¹⁻¹¹. Literature survey reveals that there are numerous references to the existence of dithiocarbamates, they act as monodentate, bidentate and polydentate ligands. Surveys have also revealed that the dithiocarbamates not only have very good complexing ability towards metal ions but also serve innumerable purposes of application in many regions of agriculture, industry medical technology polymer chemistry and used in environmental inorganic analysis. Main view of the above important applications the author in the present investigation was prone to prepare a new dithiocarbamate and its solid metal complexes with the hope that the new dithiocarbamates and its metal complexes may find a spectacular place in any of the fields cited above. The coordination ability of various transitional metal complexes of dithiocarbamates are investigated in the field of biological and pharmaceutical activity¹²⁻¹³ and also used for the determination of metal ions in different samples of analytical chemistry, these are also used to extract the metal ions from different solutions all above applications concern with molecular structure of the complexes. The present research program provides an in detailed interpretation about a series of dithiocarbamate ligands derived from Histamine and their Ru and La (III), metal complexes. These were evaluated of structures by using Elemental analysis, IR, ¹HNMR, Mass, absorption spectroscopy (UV), TGA-DTA, Electronic spectroscopy, Powdered X-RAY Spectroscopy studies¹⁴⁻²⁵, Conductometric measurements, Magnetic moments to predict the mode of bonding and geometry carried out in the present investigation. Solid state chemistry gives important conclusions like geometry, metal–ligand bond strength, oxidation state²⁶⁻²⁸, electronic configuration, structure and stability of the metal complexes. Solid dithiocarbamate complexes of transitional metal ions have been synthesized and characterized in order to ascertain the nature of bonding, oxidation state, stability and structure by using various studies like IR, ¹HNMR, ESR, Conductometric, VSM, TGA–DTA, and X Ray Diffraction analysis have been carried out.

Experimental section

Materials and Methods

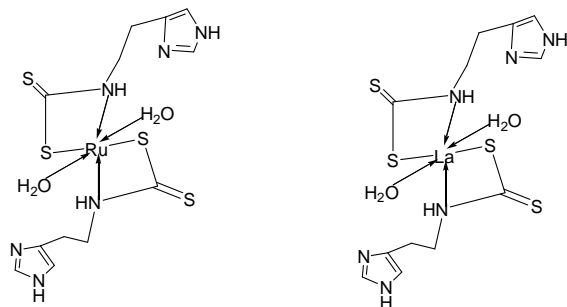
Lanthanum chloride and Ruthenium chloride used in present study were analytical grade chemicals ethanol and methanol, dioxane were purified by distillation. Ru(III)La(III) were estimated by using perkin – Elmer flame atomic absorption spectroscopy, ¹HNMR spectra of ligand and metal complexes were recorded as 400 MHz Nuclear magnetic resonance spectrometer HCU in Hyderabad HI in CDCl₃ solvent. UV-Spectra were recorded using Perkin-Elmer lab India. The IR were recorded as (KBr) discs using a JASCO FT/IR-5300. The ESR spectra were recorded using the JES-FA Series and TG-DTA spectra were recorded using the SPTQ600 PA, TGA–DTA Spectral analyses of the metal complexes were carried out by using the Perkin Elmer system in thermal analysis centre Stick Cochin and ethyl alcohol were used as solvent. All chemicals used in the present investigation were pure Aldrich chemicals.

Synthesis of Dithiocarbamate ligand and its metal complexes:

((2-(1H-imidazol-4-yl)ethyl) carbamodithioic acid dithiocarbamate and their metal complexes) 0.2 mol of heterocyclic amine was dissolved in 100 ml of ethyl alcohol taken in a 250ml of beaker which is placed in ice cubes resulting cold solution mixed with 10 ml of NaOH solution, and the solution followed by adding CS₂²⁷ (0.2mol) in drop wise through the separating funnel in about 40 min with constant stirring. To get brown colored solution is formed resulting solution slowly precipitated to form sodium salt of dithiocarbamate. It was placed in room and recrystallized from methanol and dried in desiccator over CaCl₂ crystals synthesized compound crystals was used in melting point.

For the Preparation of La (III) and Ru (III) metal chloride salts were used. Dissolve 3.2947g (0.01 Mole) of newly synthesized ligand in adequate of methanol. To this solution, aqueous solution of 0.01 moles of corresponding metal chlorides and 1 ml of trimethyl amine. The mixture was stirring 6 hours on magnetic stirrer in room temperature; dark colored (Ru complex), brown colored (La complex) precipitated

were separated out. The colored metal complexes were washed with water and then methanol and were recrystallized from ether.



Synthesized metal complexes

Results and Discussions

Infrared spectral analysis of $[Ru(HCDT)_2]$ Metal Complexes²⁹⁻³²

The IR Spectrum of $[Ru(HCDT)_2]$ complexes. A strong band appeared at 1406cm^{-1} in the region was assigned to the thiouroid bond, this peak is shifted to $1406\text{-}1440\text{cm}^{-1}$ indicate the complex of thiouroid N-CSS bond stretching frequency, this shifting of bond

to carbon nitrogen double bond character is not free in delocalize in the complex greater contribution in complexity formation. IR spectrum of histamine dithiocarbamate complex have different stretching frequencies in spectrum indicate at 3330cm^{-1} this peak shown NH and OH frequencies of coordinated water molecules. The peak observed at 2985cm^{-1} is aromatic C-H frequency is the bond appear at 1645 , 1154 , 1025M , 325Cm^{-1} indicate C=C, OH bending, C-N, C-S C=S bonding vibrations.

The Infrared spectrum of La (III) complex was compared the (HCDT) ligand. The typical IR Spectrum of $[La(HCDT)_2]$ complex. The bond observed at 1406cm^{-1} express the ligand thiouroid bond frequency in the I.R spectrum, shifted in the complex from 1406 to 1485 in higher energy region due to double bond character of CN is not freely delocalize with CNSS double bond greater contribution in the structure in the same few new bonds appear in the spectrum which are not observed in the isolated dithiocarbamate ligand, the new band in the region of $532\text{-}420\text{cm}^{-1}$ indicate metal sulphur bond in the complex (MS) Table 1. Aromatic ring Frequency appeared in the region of 1629cm^{-1} is stretching of Table-1.

Compound name	NCSS	-NH-	-C=C-	C-S	M-S	OH-(H ₂ O)
HCDT	1406.1	3338	1634.7	900.81	---	3596.2
$[Ru(HCDT)_2]$	1440.27	3447.65	1640.55	1025.58	403.55	3447.65
$[La(HCDT)_2]$	1485.83	3385.63	1629.72	950	532-420	3385.63

HCDT ring the appearance of broad band at 3385cm^{-1} can be assigned to the stretching vibrations of $\nu\text{-NH}$

and OH Co-ordinated water molecules present in their complete these are observed from graph fig 1 & 2.

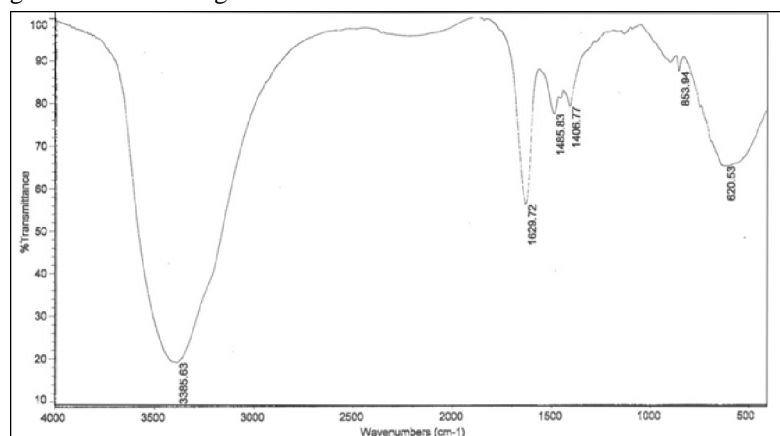


Figure-1

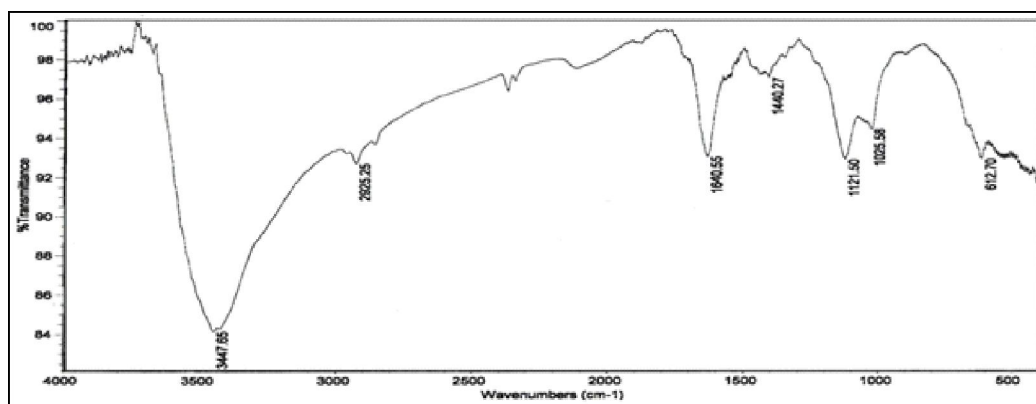


Figure-2

Ligond and metal complexes of Histamine Dithiocarbamate:

¹HNMR spectral analysis of Histamine Carbamodithiolate Ligand and its Metal complexes³³⁻³⁴

¹HNMR spectrum of the ligand HCDT. Three C-H protons of the pyridine ring of Carbamodithiolate forms a two doublet at the region of 7.26-7.38ppm. One multiplet is at 7.64-7.93ppm. The singlet appeared in the region 7.1 ppm was due to NH proton in thiouroid region of Carbamodithiolate ligand. In the complex signal shifted from 7.1 to 7.2 ppm. High chemical shift designates as increased C-N double bond strength attracted electrons towards C-N character shifted to down field. The broad signals in the range 7.2 to 7.95 ppm showed the CH protons aromatic rings of ligand

in metal complex and broad signals in the range 10.2 ppm is complexation of water molecule. Based on above data Spectrum of La metal complex, thiouroid bond shifted from 7.1-7.26 hence the signal shifted to down field regions as shown in Table-2.

¹H NMR spectral Data of Histamine Carbamodithiolate (HCDT) metal complexes

Table-2

Compound	H-N-C (thioureide bond)	(H ₂ O) Coordinated water
HCDT	7.1	----
[Ru(HCDT) ₂]	7.2	10.2
[La(HCDT) ₂]	7.26	10.4

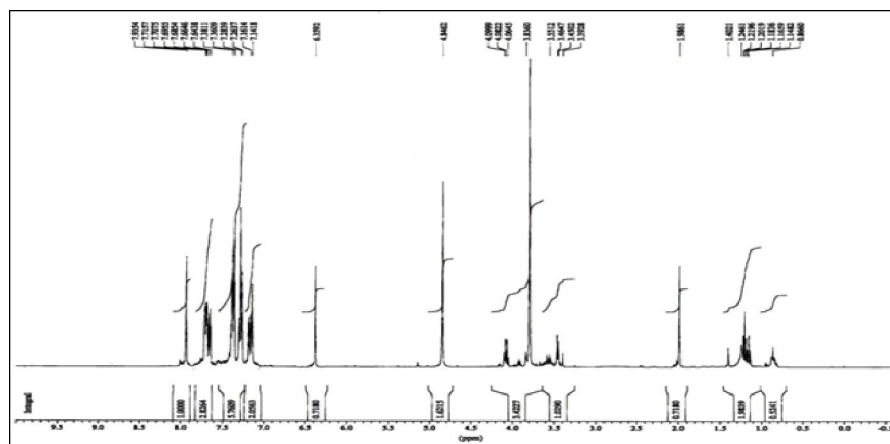


Figure-3

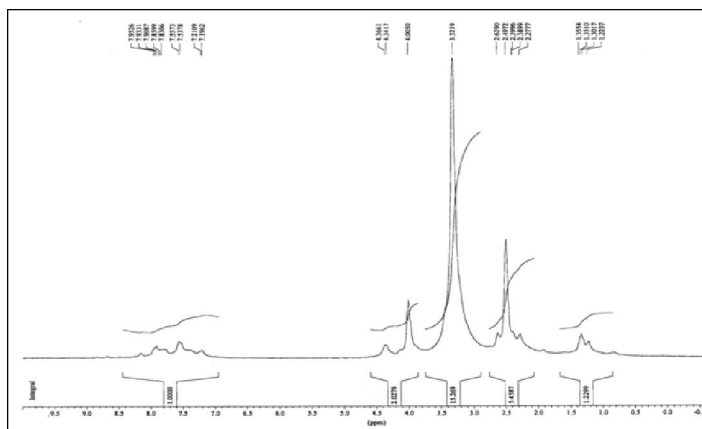


Figure-4

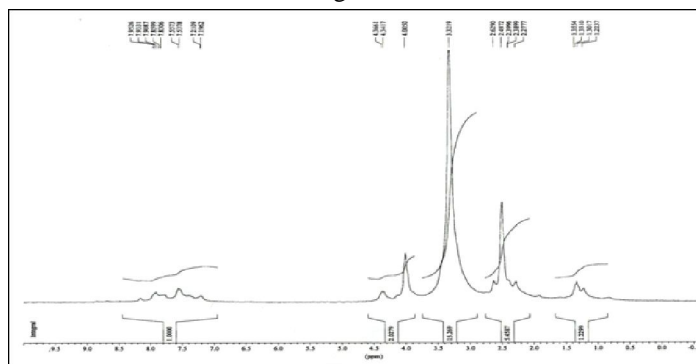


Figure-5

3.8.3. UV-Visible spectral elucidation of Histamine Dithiocarbamate metal complexes :

Electronic excitation of the ligand and metal complexes investigated by UV –Visible spectrometer this spectrometer was used for the identification of energy levels of the compound. The charge transfer may occur due to the migration of electrons from the ligand orbitals to metal orbitals vice versa. The Dimethyl formamide as a solvent used for the solution spectra of UV-Visible analysis.²⁹ The electronic spectra of the Sodium salt of Histamine dithiocarbamate ligand, it illustrates an intense absorption bands at 273.50 nm this band indicate to $\pi-\pi^*$ and $n-\pi^*$ transitions. Intra ligand transitions occur in the complexes below 300 nm. The intensive bands observed in the region at 251.21 nm and 276.80 nm in case of $[\text{Ru}(\text{HDTC})_2]$ complex, due to intra molecular charge transfer of ligand to metal and d-d(dx^2-y^2 dxy dyz) transfer of electrons

in the complex.

The Electronic spectrum of the $[\text{La}(\text{HDTC})_2]$ complex. In this complex observe two bands at 274.52 nm and 329.65 nm. as for the above intentions observed Table- 3.

Electronic excitations (UV-Visible) of ligand and its metal complexes :

Table-3

Molecule	Wavelengths in nm	Electronic transitions
L= AHPDTC	273.50	$\pi-\pi^*$
	293	$n-\pi^*$
$[\text{Ru}(\text{L})_2(\text{H}_2\text{O})_2]$	251.21	$\pi-\pi^*$
	276.80	$n-\pi^*$
$[\text{La}(\text{L})_2(\text{H}_2\text{O})_2]$	274.52	$\pi-\pi^*$
	329.65	$n-\pi^*$

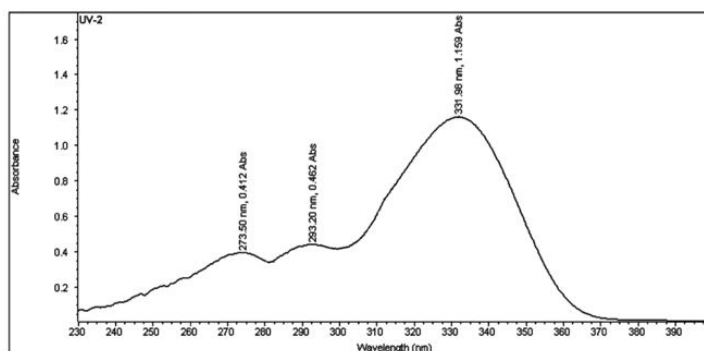


Figure-6

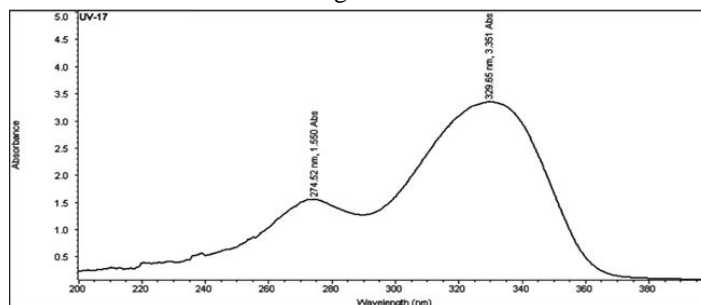


Figure-7

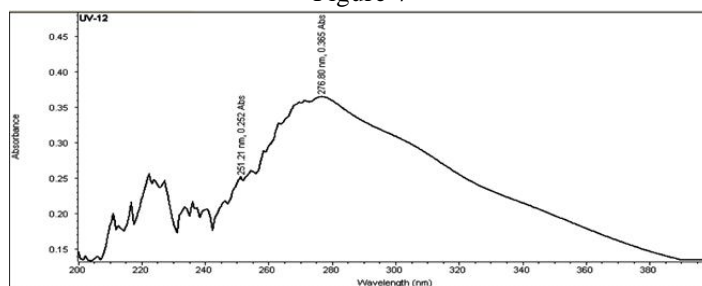


Figure-8

*Thermal studies of Histamine Dithiocarbamate (HDTc) Metal complexes*³⁵⁻³⁶

Thermo gravity analysis was used for the analysis of complex thermal behaviour some of the complexes are stable in presence of temperature some of the unstable complexes with temperature this information carried out by thermogravimetric analysis, TG analysis and also used for the hydration power of the complex means no of water molecule present in the complex. The typical TGA is used for the structure of the complex conformation formula is it having water molecule or not decomposition temperature of the metal complexes has followed up to 600°C. This decomposition analysis was observed in the absence

of nitrogen atmosphere. Present experimental analysis of Ru complexes the first stage of decomposition 93.29 to 185.79°C this is specifying the coordinated water molecule, and this indicate endothermic dehydration of the metal complex, the next stage of decomposition corresponding to exothermic decomposition the temperature ranges from 203.29°C to 238.29°C forming the compound of metal ligand decomposition $M(SCN)_2$ again, this is followed by the third stage of decomposition of occur due to formation of RuS temperature range above 365.79-420.79°C. Same as for the above procedure varies temperature ranges in case of La metal complex submitted in below the table.

Table-4 TGA-DTA –Analysis of Histamine metal complexes

COMPLE-XES	Decompo-sition Temparat-ure	Molecular change	Loss of Mass (%)	Total loss mass of (%)
RuL ₂ X ₂ L= C ₆ H ₅ N ₂ S ₂ O	93.29-185.79	Loss of 2H ₂ O molecules	6.54	83.31
	203.29-238.29	Decomposition of L	54.55	
	365.79-420.79	Formation of RuS	22.22	
LaL ₂ X ₂ L= C ₆ H ₅ N ₂ S ₂ O	86.13-146.13	Loss of 2H ₂ O molecules	7.56	87
	186.13-421.13	Decomposition of L	54.55	
	543.63-591.13	Formation of LaS	24.89	

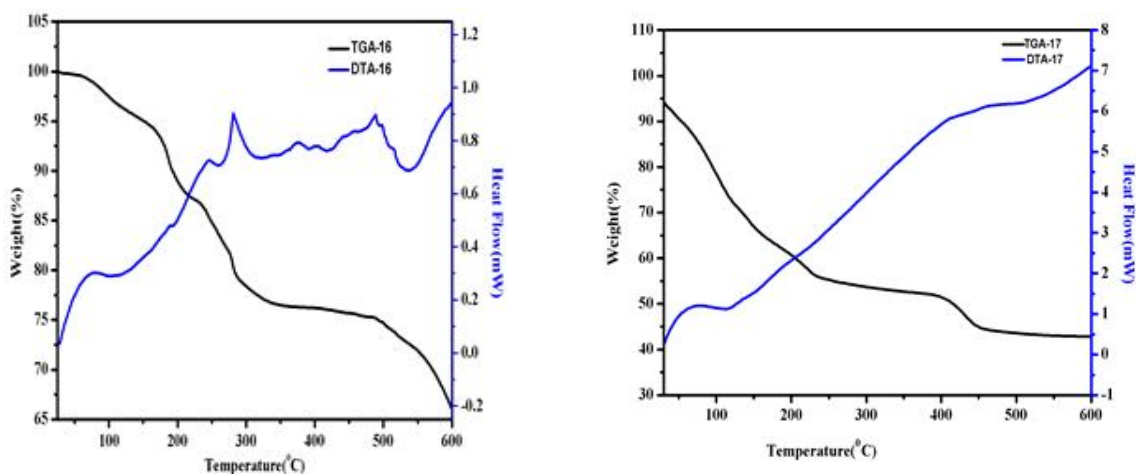


Figure 9 & 10

ESR Spectral Analysis of Histamine Dithiocarbamate (HDTC) metal Complexes³⁷⁻³⁸

Electron spin resonance spectroscopy give the information about electronic excitation of the complex in DMF at liquid nitrogen temperature. Electronic spin resonance spectroscopy is low temperature spectrum. Cu have three speaks of small intensity have been identified these are considered $g_{||} > g_{ave} > g_{\perp} > 2.0023$ to originate from $g_{||}$ /component. $g_{||}$ /value is less than 2.3 for Covalent character greater the value of $g_{||}$ / 2.3 indicate ionic character could predicted metal –ligand bond in the complex's. The lower P and a^2 values for [Ru(HDTC)₂] complex and [La(HDTC)₂] suggest the presence of strong in-plane FI bonding which in agreement with the higher ligand field. Spectral data suggest octahedral geometry for Ruthenium and Lanthanum complexes values indicated in Table-V

Orbital reduction -Spin hemiltonian Parameters of Ruthenium complex in dimethylformaamide solution:

Table 5

PARAMETERS	[Ru(HDTC) ₂]
$g_{ }$	2.5245
g_{\perp}	2.09862
g_{ave}	2.1179
G	4.4117
$A_{ }^*$	0,02333
A_{\perp}^*	0.0187
A_{ave}^*	0.0207
$K_{ }$	0.0245
K_{\perp}	0.0264
P*	0,0064
α^2	0,2384

* Values are given as cm⁻¹ units.

Orbital reduction -Spin hemiltonian Parameters of Lanthanum complex in dimethyl formaamide solution:

Table 6	
Parameters	[La(HDTC) ₂]
$g_{ }$	2.0498
g_{\perp}	2.01235
g_{ave}	2.01425
G	4.75
$A_{ }^*$	0.02354
A_{\perp}^*	0.0197
A_{ave}^*	0.0217
$K_{ }$	0.02222
K_{\perp}	0.0210
P^*	0.0054
α^2	0.4324

* Values are given as cm^{-1} units.

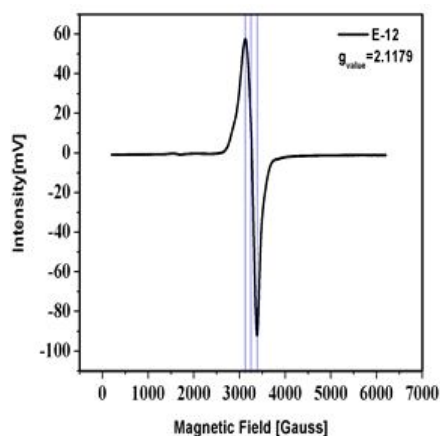


Figure-11

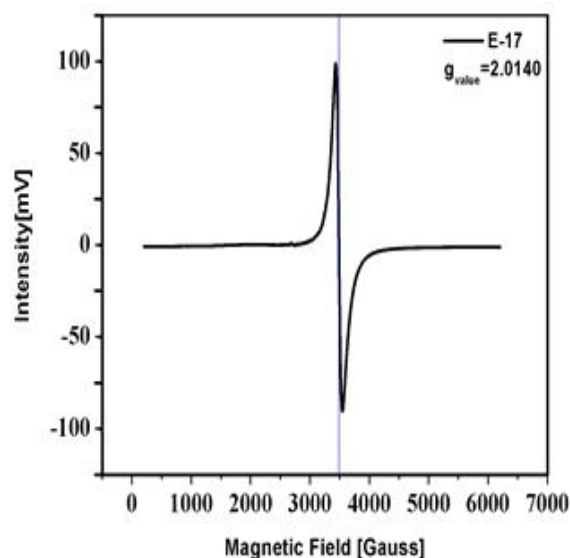


Figure-12

Powder X-Ray Diffraction Analysis of Histamine dithiocarbamate (AHPDTC) Metal Complexes :

The X-Ray diffractogram of $[M(\text{HDTC})_2]$ Complexes which range 2 between 3-50 where θ is the Bragg's angle²⁻⁵. Calculated values of miller indices (h k l) along with observed d-specified and 2θ were specified in the Table-7 All the peaks have been indexed and 2θ values compared in graph. Comparison values reveal that there was good agreement between the 2θ and d values observed in

Powder X-ray analysis of Histmine dithiocarbamate metal complexes Table 7

Exp-d	Cal-d	Exp- 2θ	Cal- 2θ	H	K	L
9.7715	9.7711	9.0392	9.0391	6	5	1
7.77149	7.77148	11.3725	11.3722	4	3	2
5.1477	5.1476	17.2057	17.2055	6	2	1
4.3130	4.3129	20.5686	20.5684	5	4	3
4.03373	4.03371	22.0096	22.0093	4	3	2
4.02130	4.02123	22.0783	22.0782	6	2	1
3.8220	3.8219	23.2449	23.2444	4	1	0
3.5159	3.5154	25.3037	25.3035	5	2	0
3.08246	3.08243	28.9409	28.9405	3	2	2
2.3287	2.3282	38.6173	38.6171	7	4	2

Table 8. Powder X Ray Diffraction Analysis data of Histamine dithiocarbamate

[La(HDTC) ₂] Metal Complex						
Exp-d	Cal - d	Exp - 2 θ	Cal - 2 θ	H	k	l
7.4540	7.4538	11.8542	11.8541	8	5	5
7.3613	7.3611	12.0095	12.0092	6	4	2
4.3183	4.3177	20.5427	20.5421	8	6	5
4.2532	4.2529	20.8647	20.8640	9	7	5
4.1258	4.1245	21.5132	21.5131	6	5	4
3.9780	3.9776	22.3214	22.3212	7	4	3
2.8345	2.8342	31.5254	31.5248	5	3	2
2.8336	2.8333	31.5325	31.5321	3	2	1

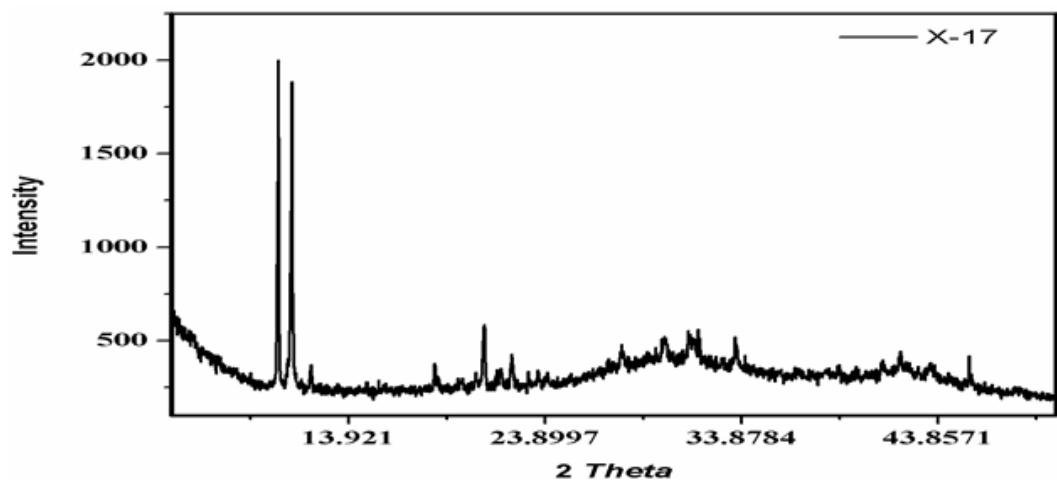


Figure-13

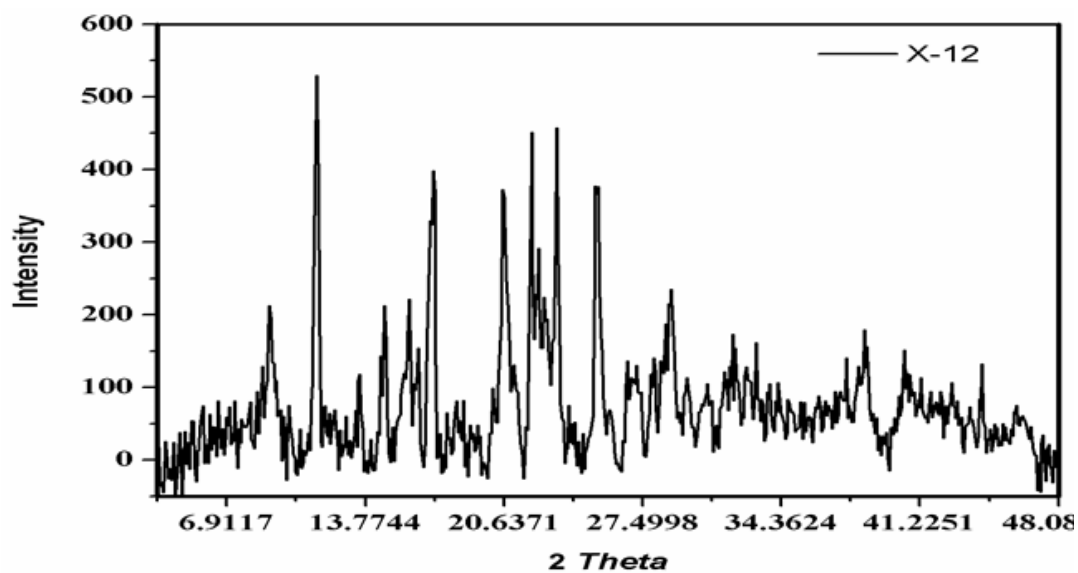


Figure-14

Conductivity measurement of Histamine metal complexes :

DMF Solvent used for the solvent for the identification of molar conductance of complex in DMF (0.001) was determined at 27±2°C using systronic 303 used in reading conductivity of the bridge. The specific and molar conductance of the complex was find out If molar conductance value is more than 20 Ohm⁻¹ cm⁻¹ the metal complexes is said to be electrolytic in nature values are indicated in Table 9.

Table 9.

Complexes	Conduc-tance	Specific conducta-nce (Ohm ⁻¹ Cm ⁻¹)	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
[Ru(AHPDT C) ₂ (H ₂ O) ₂]	0.86	0.86	860
[La(AHPDT C) ₂ (H ₂ O) ₂]	0.98	0.98	980

Conductivity measurements data of Histamine dithiocarbamate metal complexes :

Magnetic susceptibility measurements of Histamine Dithiocarbamate Metal complexes :

The magnetic susceptibility of histamine complex gives the effective magnetic moment values presented in below the table this magnetic values of ruthenium and lanthanum complexes show the considerable values of magnetic moment 5.67, 6.72 B.M. observed in Table 10.

Magnetic susceptibility measurements data of Histamine dithiocarbamate Metal complex :

Table 10.

Metal Complex	Magnetic moment (B.M)
[Ru(AHPDTC) ₂ (H ₂ O) ₂]	5.67
[La(AHPDTC) ₂ (H ₂ O) ₂]	6.72

Conclusion

This brief survey covers to determine the complete structures of above discussed organic molecules by using different spectroscopic techniques such as Infrared, Nuclear magnetic resonance, Electron Spin Resonance, TG-DTA, and X Ray Diffraction analysis have been carried out. Synthesized compounds indicate potent cytotoxic agents that might become potent antimicrobial for anti-cancer activity.

The newly synthesized dithiocarbamate metal complex behaves as didentate NcS₂ donar and forms the complexes of type [mL₂] with the help of various physicochemical and spectroscopic methods such as IR, H-NMR, UV-visible and ESR. The octahedral geometry of La, Ru complexes have been proposed.

Scope of Study: Chelating functional groups were prepared by different magnets in this way dithiocarbamate and primary, secondary amines and their dithiocarbamate groups were prepared. These materials were easily prepared and have reasonable stability except for hypholysis in concentrated acids and basis most of the studies were performed by direct determination structure of the complex using IR, H-NMR, (JGA-DJA) and X Ray Diffraction. These studies demonstrate that these materials have potentials for the future.

Acknowledgement

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