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Synthesis and characterization of (novel heterocyclic) 3-amino-9-ethyl carbazole dithiocarbamate [AECZDTC] ligand and its metal complexes

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ABSTRACT

The growing interest in the chemistry of sulphur donor ligands are due to their encouraging anticancer, antibacterial and antifungal activities as well as their widespread industrial application. Dithiocarbamates belong to this class and much attention has been paid to them. A New series of bidentate ligand dithocarbamate of 3-amino-9-ethyl carbazole dithiocarbamate (AECZDTC) Ligand and its Metal complexes *(AECZDTC) have been synthesized by new synthetic methods as it's sodium salt. In the reaction of Copper Chloride and Ruthenium Chloride with* the AECZDTC *corresponding complexes were prepared. The complexes were characterized by elemental analysis, IR, ^{1}H NMR, UV, ESR, TGA – DTA and conductometric titrations. In addition the authors have been screened the compounds for biological activity of Cu, Ru complexes. It was found that the compounds have shown activity against bacteria.*

Keywords: Synthesis, Characterization, Dithiocarbamate metal complexes, 3-amino-9-ethyl carbazole dithiocarbamate

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INTRODUCTION

Dithiocarbamates are highly versatile mono-anionic chelating ligands which form stable complexes with all the transition elements and also the majority of main group, lanthanide and actinide elements. They are easily prepared from primary or secondary amines and depending upon the nature of the cation can show good solubility in water or organic solvents. They are related to the thiuram disulfides by a one-electron redox process (followed by dimerisation via sulfur sulfur bond formation). Dithiocarbamates are lipophilic and generally bind to metals in a symmetrical chelate fashion, but examples of other coordination modes are known, the monodentate and anisobidentate modes being most prevalent. They are planar sterically non-demanding ligands which can be electronically tuned by judicious choice of substituents. They stabilize metals in a wide range of oxidation states, this being attributed to the existence of soft dithiocarbamate and hard thioureide resonance forms, the latter formally resulting from delocalization of the nitrogen lone pair onto the sulfurs, and consequently their complexes tend to have a rich electrochemistry. Metal complexes of dithocarbamate and their applications have been widely investigated during the past years. Dithicarbamate metal complexes have been used as pesticides[1-3], as antiviral and antibacterial agents[4,5] and as catalysts[6-8]. The thermal behavior of transition metal complexes of dithiocarbamate has been widely investigated[9-13].The applications of such complexes depend to a large extent on their molecular structure. The author in the present study provides a new series of metal complexes of Cu (II) and Ru(II) with carbamate ligand derived from 3-amino- 9-ethyl carbazole. These complexes were characterized by elemental analysis, IR, NMR, UV- Vis Spectrometer, ESR, TGA-DTA and Conductometric measurements to determine the mode of bonding and geometry, biological and anticancer activities of the ligands and metal complexes were also carried out.

MATERIALS AND METHODS

All materials used in this investigation were purchased from Sigma/Aldrich and AR (Merck). Solvents used were of reagent grade and purified before use by the standard methods Cu[AECZDTC], Ru[AECZDTC] complexes were prepared by the procedures described in the literature. The percentage composition of the elements (CHNO) for the compounds was determined using an elemental analyzer CHNO model Fison EA 1108.The Infrared spectra were recorded as potassium bromide (KBr) discs using a JASCO FT/IR-5300.The 1H (400Hz) nuclear magnetic resonance spectra were recorded using the ACF200 Broker Germany Spectrometer. Ultraviolet Spectra were recorded using Prekin-Elmer lab India, UV-Vis Spectrometer. The Electron spin resonance spectra were recorded using the JES-FA Series and TG-DTA spectra were recorded using the SPTQ600 PA, Thermo gravimetric analyses of the metal complexes were carried out by using the Perkin Elmer system in thermal analysis center Stick Cochin and ethyl alcohol were used as solvent. All chemicals used in the present investigation were pure Aldrich chemicals.

Preparation of Sodium salt of dithiocarbamate ligands:

0.05mol of amine was dissolved in 10ml of absolute alcohol in a clean beaker which was placed in ice. To this cold solution 5ml of sodium hydroxide (10N) solution was added and then pure carbondisulphide (3.02ml, 0.05M) was added in drop wise through separating funnel with constant stirring. The components were stirred mechanically for about 30min, sodium salt of dithiocarbamate precipitated out. It was dried and recrystallised from methanol.

Synthesis of Dithiocarbamate Metal Complexes

The aqueous solution of 0.005mol of metal salts was added with constant stirring to an aqueous solution of 0.01 sodium dithiocarbamate ligand. The reaction mixture was stirred at room temperature for 8 hours. The colored precipitate was obtained. The precipitate was filtered and washed with water and then with methanol and dried over calcium chloride in a desiccator. All the complexes were prepared in 1:2 ratios of metal to ligand.

Table-1: Analytical data of the AECZDTC ligand and their metal complexes

Molecular Formula X =H_2O	Molecular Weight in GMs	Color	Yield in%	Elemental analysis											
				Carbon %		Hydrogen%		Nitrogen%		Sulphur%		Oxygen%		Metal%	
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Ligand $C_{15}H_{13}N_2S_2$	285.41	Yellow	68	63.12	63.11	4.59	4.52	9.81	9.80	22.47	22.43	----	----	----	----
[Cu.L_2]2X	384.98	Yellow	76	46.80	46.79	4.45	4.41	7.23	7.25	16.66	16.61	8.31	8.30	16.51	16.50
[Ru.L_2.X_2]	422.51	Black	77	42.64	42.63	4.06	4.00	6.61	6.61	15.18	15.12	7.57	7.54	23.92	23.90

RESULTS AND DISCUSSION

I.R. Analysis of the Ligand (AECZDTC)

Infrared spectra were recorded with a JASCO FT/IR-5300 Spectrometer (4000-400cm^{-1}) using KBr pellets. By utilizing this spectroscopy, the presence of important functional groups in the compound can be identified. Table-2 through light on the observation made in analyzing IR spectra of ligand and metal complexes.First, the (1450-1550 cm-1) region, which was primarily associated with υ (N-CSS) stretching vibrations. Second, the 950-1000 cm-1 region, which is associated with υ (C-S) stretching vibrations.

The characteristic band at 1444.79cm^{-1}, was assigned to υ (N-CSS); this band defines a carbon Nitrogen bond order between a single bond (υ =1250-1350cm-1) and a double bond (υ = 1640–1690cm-1). The appearance of a band in that region 1641 cm^{-1} indicates that, of the three possible resonance structures reported by Chart et al., characterized by a strong delocalization of electrons in the dithiocarbamate moiety.

A single sharp band at 1040.48 cm^{-1} was assigned to the stretching vibrations of the C-S bond. The band at 3373.03 cm^{-1} associated with the υ(N-H) stretching vibrations. Sharp band observed in the region of 2975.65 cm^{-1} and 2087 cm^{-1} indicate aromatic =C-H Stretching and NH- bending vibrations. The characteristic absorption band at

1609.15 cm^{-1} indicate aromatic stretching vibration. The absorption bands in appear in between the region of 1158.11–610.55 cm–1 (C–C ,C–O, C–N).

I.R. Characterization of AECZDTC-Cu Metal Complex.

The interpretation of IR spectra of dithiocarbmates complexes of Transition metals had arisen and considerable interest both diagnostically to determine the mode of co-ordination and as a mean of assessing the nature of bonding in these complexes. The Infrared spectrum of Cu (II) complexes was compared the [AECZDTC] lignad. The typical IR Sprectrum of [AECZDTC] complexes presented in Fig.

A strong band exhibited at 1444.79 cm-1 in the I.R spectrum of the ligand, which was assigned to the Thioureide bond was shifted to 1444.79-1466.09 cm^{-1} region[14-15]. On Passage from the free dithiocarbamate ligand to their complex, the υ(N–CSS) mode is shifted to higher energies, showing an increase of Carbon-Nitrogen double bond character and hence a greater contribution of the structure . The Infrared active υ (N–CSS) mode was sensitive to both chain length and the steric bulk of the substituents. As the double character was more pronounced in the complex it can be concluded that the ligand was co-ordinated through S, S atoms.

To discern the bonding type of the dithiocarbamate ligand in their complexes, the Bonati-Ugo method is, by far, the most popular one. It consists of tracing the 940-1060 cm-1 spectral region, where the υ (C-S) modes were thought to appear. In fact, the bands due to CSS moiety were usually coupled to other vibrations and are very sensitive to the environment around this group, but they were also useful to distinguish between Monodentate and Bidentate Co-ordination. The presence of only one band in the investigated region, commonly attributed to υ (SCS) mode, it indicates completely symmetrical bonding of the dithiocarbamate ligand to metal in bidentate mode where as a doublet was expected for the Monodendate coordination.

Basing on the above concept the presence of single band at 1008 cm^{-1} region was assumed to υ (C-S) stretching vibrational mode and it indicates the symmetric bidentate behavior of the ligand that means the AECZDTC ligand was co-ordinated through both the sulphur atoms[16].

Along with new bands these bands were formed which are not observed in the spectrum of the ligand, the band in the resin 546-449 cm^{-1} was assigned to the υ (M-S) metal ligand bond of the complex. The appearance of band at 1440 Cm^{-1} indicate C=C Stretching of two aromatic rings the appearance of broadband at 3435.50 cm^{-1}can be assigned to the stretching vibrations of υ- NH and co-ordinated water molecules present in their complexes[17]. Two sharp peaks observed at in the region of 2975.17 and 2888.07 indicate =C-H and C-H of CH_3, In the spectra of both ligand and complex, significant change were observed, for molecular vibrational stretching mode. The two weaker bands at 866-745 cm^{-1} were assigned respectively to –OH is rocking and wagging vibrations of co-ordinated water in the complex.

Characterization of. AECZDTC-Ru Metal Complex.

The interpretation of IR spectra of dithiocarbmates comples of Transition metals had arise and considerable interest both diagnostically to determine the mode of co-ordination and as a mean of assessing the nature of bonding in these complexes. The Infrared spectrum of Ru (III) complexes was compared the [AECZDTC] lignad. A strong band exhibited at 1444.79 cm-1 in the I.R spectrum of the ligand, which was assigned to the Thioureide bond was shifted to 1444.79-1466.35 cm^{-1} region. On Passage from the free dithiocarbamate ligand to their complex, the υ(N–CSS) mode is shifted to higher energies, showing an increase of Carbon-Nitrogen double bond character and hence a greater contribution of the structure . The Infrared active υ (N–CSS) mode was sensitive to both chain length and the steric bulk of the substituents. As the double character was more pronounced in the complex it can be concluded that the ligand was co-ordinated through S, S atoms.

To discern the bonding type of the dithiocarbamate ligand in their complexes, the Bonati-Ugo method is, by far, the most popular one. It consists of tracing the 940-1060 cm-1 spectral region, where the υ (C-S) modes were thought to appear. In fact, the bands due to CSS moiety were usually coupled to other vibrations and are very sensitive to the environment around this group, but they were also useful to distinguish between Monodentate and Bidentate Co-ordination. The presence of only one band in the investigated region, commonly attributed to υ (SCS) mode, it indicates completely symmetrical bonding of the dithiocarbamate ligand to metal in bidentate mode where as a doublet was expected for the Monodendate coordination.

Basing on the above concept the presence of single band at 1027 cm^{-1} region was assumed to υ (C-S) stretching vibrational mode and it indicates the symmetric bidentate behavior of the ligand that means the AECZDTC ligand was co-ordinated through both the sulphur atoms.

Along with new bands these bands were formed which are not observed in the spectrum of the ligand, the band in the resin 641-473 cm^{-1} was assigned to the υ (M-S) metal ligand bond of the complex. The appearance of the band at 1600 Cm^{-1} indicate C=C Stretching of two aromatic rings the appearance of broadband at 3422.18 cm-1 can be assigned to the stretching vibrations of υ- NH and co-ordinated water molecules present in their complexes. Single sharp peaks observed at in the region of 2976.87 indicate =C-H vibration of aromatic rings. In the spectra of both ligand and complex, significant change were observed, for molecular vibrational stretching mode. The two weaker bands at 866-745 cm-1 were assigned respectively to –OH rocking and wagging vibrations of co-ordinated water in the complex.

TABLE-2 IR CHARECTERIZATION OF LIGAND AND ITS METAL COMPLEXES

Compound name	Thiouroid bond	-NH-	C=C-H	-C=C-	C-S	M-S	OH-(H_2O)
AECZDTC	1444.79	3373	2987	1609	1048.48	---	----
AECZDTC-Cu	1466.09	-------	2975.17	1440	1008	546-449	3435.50
AECZDTC-Ru	1466.35	-------	2976.87	1600	1027	641-473	3422.18

^{1}HNMR Spectral Studies of 3-amino 9-Ethyle Carbazole Dithiocarbomate [AECZDTC] Ligand and its Metal complexes.

The ^{1}H NMR spectra of ligand and metal complexes in DMSO-d_6 as solvent were given in the spectral technique The chemical shift values of the ligand and metal complexes were shown in Table-3.Eight C-H protons of the two aromatic rings of Dithiocarbamate ligand forms a multiplet at different regions in between 7.36-8.1ppm. .The singlet appeared in the region 7.27 ppm was due to NH proton in thiouroid region of dithiocarbomate ligand. 3-amino 9-Ethylecarbazole contain ethyl group of methelene exhibit quartet at 2.63p.m. and methyl appeared as a triplet at 1.59-1.47ppm.

Shows the typical NMR spectrum of Cu metal complex. In the complex signal due to proton bonded to Nitrogen in the Thiouraide bound was observed in the 7.27 to 7.4 ppm. The down field shift of the complex may attributed to an increase of the - bond character and the delocalization of electrons along the C-N bond contributed by the substituents and also by the bidentate nature of the dithiocarbamate ligand[18]. On complexation, the electron density on – NH decreases, the precession frequency of proton bonded to nitrogen increases, hence the signal in shifts to down field regions[19]. High NH stretching indicates as increased C-N double bond character which is due to a greater electron density on the – NCCS moiety.

The broad signals in the range 7.27 to 8,08 ppm in the case of copper, Metal complex indicate the eight CH protons of fused aromatic benzene rings and broad signals in the range 10.5ppm in the case complexation of water molecule to metal ion, it was not observed in the case of free ligand .

The typical NMR spectrum of Ru metel complex. In the complex signal due to proton bonded to Nitrogen in the Thioureide bound was observed in the 7.27 to 7.28 ppm. The down field shift of the complex may attributed to an increase of the bond character and the delocalization of electrons along the C-N bond contributed by the substitutes and also by the bidentate nature of the dithiocarbamate ligand. On complexation, the electron density on – NH decreases, the precessional frequency of proton bonded to Nigrogen increases, hence the singal in shifts to down field regions. High NH stretching indicates as increased C-N double bond character which is due to a greater electron density on the – NCCS moiety.

Table-3 NMR CHARECTERIZATION OF LIGAND AND ITS METAL COMPLEXES

Compound	**H–N–C (thiureide bond)**	**(H_2O) Coordinated water**
AECZDTC	7.27	------
$(AECZDTC)_2Cu$	7.4	10.5
$(AECZDTC)_2Ru$	7.28	10.4

The broad signals in the range 7.4 to 7.87 ppm in the case of Ru Metal complex indicate the eight CH protons of fused aromatic benzene rings and broad signals in the range 10.4ppm in the case complexation of water molecule to metal ion, it was not observed in the case of free ligand .

UV-Visible spectral elucidation of 3-Amino-9-Ethyle Dithicarbamate(AECZDTC) metal complexes

The solution electronic spectra of the ligand and the complexes were recorded in DMF as solvent in the UV-Visible region. The electronic transition data was given in the Table-4

The electronic spectra of the Sodium salt of 3-Amino-9-ethyl carbazole dithiocarbomate ligand , it shows an one intense absorption bands at 310.47 nm These band may be due to * and n* transitions of N $\overset{\text{''''''}}{\text{——}}$ C $\overset{\text{''''''}}{\text{——}}$ S group and S $\overset{\text{''''''}}{\text{——}}$ C $\overset{\text{''''''}}{\text{——}}$ S[21]. On complexatin these bands were shifted. In all the complexes, bands below 300 nm were attributed to the intra ligand transitions.

The Copper complex shows one intense bands observed at 275.73nm were assigned to the intramolecular charge transfer of ligand (* and n* in the N-C = S group). The complex shows two less intense broad bands in the high wave length region corresponding to intraligand d d metal orbital's transitions. In particular this broad band can be assigned to the d_{xy} $d_{x^2-y^2}$ and $d_{xz,yz}$ $d_{x^2-y^2}$ transitions. A Moderately intense peak observed at 404.75 nm may be due to the ligand-metal charge transfer [LMCT][21].

The Ruthenium complex shows three intense bands observed at 222.66, 245.56 nm and 274.56 nm were assigned to the intramolecular charge transfer of ligand (* and n* in the N-C = S group). The complex shows two less intense broad bands in the high wavelength region corresponding to intraligand d d metal orbital's transitions. In particular, this broad band can be assigned to the d_{xy} $d_{x^2-y^2}$ and $d_{xz,yz}$ $d_{x^2-y^2}$ transitions. A Moderately intense peak observed at 390 nm may be due to the ligand-metal charge transfer [LMCT].

Table -4 UV-Vis spectral data of the ligand and its metal complexes

Compound	λ_{max}/nm	Possible assignment
L = AECZDTC	310.47	*, n*
$[Cu(L)_2(H_2O)_2]$	275.73	*
$[Ru(L)_2(H_2O)_2]$	226.66,245.56	*
	274.56	n*

Thermal Analysis of 3-Amino-9-Ethyl Carbazole Dithiocarnamate (AECZDTC) Metal complexes.

TG techniques were employed to follow the thermal behavior of complexes. According to the results obtained, the complexes are not volatile and their decomposition occurs in more than one step.Thermogravimetric studies on the complexes confirmed their proposed molecular formulae. The thermal decomposition of metal complexes has been followed up to 1000°. The decomposition behavior of the complexes was observed in nitrogen atmosphere. The experimental mass losses were in good agreement with the calculated mass loss values which were summarized in the Table-5.

The Copper complex of AECZDTC shows three main decomposition stages, and the first stage with a small endothermic dehydration step in the range of 88.678°C to 123.678°C was due to the loss of two water molecules coordinated to the metal[2, 11]. The Second step involves two sub steps which involve decomposition of the ligand moiety, Exothermic decomposition of the ligand moiety takes place around 173.678–213.678°C, to give the stable intermediate $M(SCN)_2$ and this was stable up to 401.178°C, which on further undergoes exothermic decomposition in the region 401.178–576.178°C in the third stage forming Copper sulphides (CuS) as final residual product[22].

The thermogram of the Cu complex AECZDTC shows First stage of decomposition around 81.179°C to 126.179°C, which indicates the presence of coordinated water molecules and this decomposition corresponds to small endothermic dehydration of the complex and gives anhydrous complex. The second decomposition stage with one broad exothermic peak corresponds to the degradation of ligand moiety in the region 183.679°C to 233.679°C forming $M(SCN)_2$ intermediate. This on subsequent stages undergoes exothermic decomposition to give the corresponding CuS as the final decomposition product at a high temperature above 348.679-571.679°C

The thermogram of the Ru complex of AECZDTC shows First stage of decomposition around 85.198°C to 130.198°C, which indicates the presence of coordinated water molecules and this decomposition corresponds to small endothermic dehydration of the complex and gives anhydrous complex. The second decomposition stage with one broad exothermic peak corresponds to the degradation of ligand moiety in the region 157.698°C to 212.698°C forming $M(SCN)_2$ intermediate. This on subsequent stages undergoes exothermic decomposition to give the corresponding RuS as the final decomposition product at a high temperature above 257.698-337.698°C.

Table-5: Thermal analysis of 3-Amino-9-Ethyle Carbazole Dithiocarnamate (AECZDTC) Metal complexes.

Complex X=H_2O	Temperature range in °C	Probable assignment	Mass loss (%)	Total mass loss (%)
CuL_2X_2 L= $C_{15}H_{14}N_2S_2$	81.17-126.17 183.67-233.67 348.67-571.67	Loss of $2H_20$ molecules Decomposition of L Formation of CuS	6.712 55.54 19.21	81.47
RuL_2X_2 L=$C_{15}H_{14}N_2S_2$	85.19-130.19 157.69-212.69 257.69-337.69	Loss of $2H_2O$ molecules Decomposition of L Formation of RuS	9.98 57.87 22.56	90.41

ESR Spectral Studies of 3-amino-9-ethyl carbazole dithiocarbamate (AECZDTC) Cu-metal complex

ESR spectra obtained for (AECZDTC) Copper complex in DMF at liquid nitrogen temperature and representative ESR spectrum was presented in Fig. In this low temperature spectrum, the three peaks of small intensity have been identified which are considered to originate from g|| component. The spin Hamiltonian, orbital reduction and bonding parameters of the complex were given in Table-6.

Kivelson & Neiman[23] have reported that g|| value is less than 2.3 for covalent character and it is greater than 2.3 for the ionic character of the metal–ligand bond in complex, applying this criterion, the covalent bond character can be predicted to exist between the metal and the ligand for complex[24].

The g tensor value of the copper complex can be used to derive the ground state. The trend $g_{||} > g_{ave} > g_{\perp} > 2.0023$ observed in the complex suggests that the unpaired electron was localized in $d_{x^2-y^2}$ orbital of the copper (II) complex. The lowest g value (>2.0027) also consistent with the $d_{x^2-y^2}$ ground state. The g||/A|| quotient value was 97.78 cm^{-1}, evidence in support of the octahedral geometry with no appreciable distortion.

The Axial symmetry parameter, G value was calculated by using the expression, $G = g_{||}–2/g_{\perp}–2$ and related to the exchange interactions between metal –metal centers, according to Heathway for the present complex the G=6.0223, indicates the formation of monomeric complexes. The ESR parameters g||, g⊥, $A_{||}^{*}$, and $A_{\perp}^{*}$ of the complex and the energies of d–d transitions were used to evaluate the orbital reduction parameters (K||, K⊥). According to Hath way the observed K|| < K⊥ indicates the presence of significant in plane Π–bonding. The molecular orbital coefficients or the bonding parameters a^2 (in plane a–bonding) and b^2 (in plane π–bonding) were calculated. The observed $ά^2$ value for the present chelate 0.5468 indicates that the complex was having some covalent character.

Table -6 Spin Hamiltonian and orbital reduction parameters of Copper complex in DMF solution

Parameters	Cu (AECZDTC)
g||	2..0812
g⊥	2.0154
g_{ave}	2.0232
G	6.0223
$A_{\|\|}^{*}$	0.0213
$A_{\perp}^{*}$	0.0324
A^{*}_{ave}	0.0311
K||	0.0357
K⊥	0.0349
P*	0.0048
$α^2$	0.5468

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

The reduction of P value of the free ion value ($0.036cm^{-1}$) might be attributed to the strong covalent bonding. The Fermi constant interaction term (K) indicates the interaction between the electronic and the nuclear spins given by the expression K=Ao/(P–Ago), where (Ago= g_e–g_o), it represents the amount of unpaired electron density at the nucleus. The lower P and a^2 values for Cu [AECZDTC] complex suggest the presence of strong in–plane FI bonding which in agreement with the higher ligand field. The shape of ESR lines, ESR data together with the electronic spectral data suggest octahedral geometry for copper complex

ESR Spectral Studies of 3-amino-9-ethyle carbazole dithiocarbamate (AECZDTC) Ru metal complex

ESR spectra obtained for Ruthenium complex in DMF at liquid nitrogen temperature and representative ESR spectrum was presented in Fig. In this low temperature spectrum, the three peaks of small intensity have been identified which are considered to originate from g|| component. The spin Hamiltonian, orbital reduction and bonding parameters of the complex were given in Table-7.

Kivelson & Neiman have reported that g|| value is less than 2.3 for covalent character and it is greater than 2.3 for the ionic character of the metal–ligand bond in complex, applying this criterion, the covalent bond character can be predicted to exist between the metal and the ligand for complex.

The g tensor value of the copper complex can be used to derive the ground state. The trend $g_{||} > g_{ave} > g_{\perp} > 2.0023$ observed in the complex suggests that the unpaired electron was localized in $d_{x^2-y^2}$ orbital of the Ruthenium (III) complex. The lowest g value (>2.0027) also consistent with the $d_{x^2-y^2}$ ground state. The g||/A|| quotient value was 108.18 cm^{-1}, evidence in support of the octahedral geometry with no appreciable distortion.

The Axial symmetry parameter, G value was calculated by using the expression, G = g||–2/g⊥–2 and related to the exchange interactions between metal-metal centers, according to Heathway, for the present complex the G=4.7211, indicates the formation of monomeric complexes. The ESR parameters g||, g⊥, $A_{||}^*$, and $A_{\perp}^*$ of the complex and the energies of d–d transitions were used to evaluate the orbital reduction parameters (K||, K⊥). According to Hath way the observed K|| < K⊥ indicates the presence of significant in plane Π–bonding. The molecular orbital coefficients or the bonding parameters a^2 (in plane a–bonding) and b^2 (in plane π–bonding) were calculated. The observed $\acute{\alpha}^2$ value for the present chelate 0.8654 indicates that the complex was having some covalent character.

The reduction of P value of the free ion value ($0.036\ cm^{-1}$) might be attributed to the strong covalent bonding. The Fermi constant interaction term (K) indicates the interaction between the electronic and the nuclear spins given by the expression K=Ao/(P–Ago), where (Ago= g_e–g_o), it represents the amount of unpaired electron density at the nucleus . The lower P and a^2 values for Ru [AECDTC] complex suggest the presence of strong in–plane FI bonding which in agreement with the higher ligand field. The shape of ESR lines, ESR data together with the electronic spectral data suggest octahedral geometry for Ruthenium complex.

Table-7. Spin Hamiltonian and orbital reduction parameters of Ruthenium complex in DMF solution

Parameters	Ru (AECZDTC)
g||	2.4234
g⊥	2.09344
g_{ave}	2.1232
G	4.7211
$A_{\|\|}^*$	0.0224
$A_{\perp}^*$	0.0217
A^*_{ave}	0.02085
K||	0.0253
K⊥	0.0266
P*	0.0043
α^2	0.8654

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

Conductivity Measurements of 3- Amino 9-methyl carbazole (AECZDTC)Metal complexes.

The molar conductance of the complex in DMF ($3X10^{-3}$ M) was determined at $27+2^0C$ using systronic 303 direct reading conductivity bridge.

The specific and molar conductance value was calculated. If molar conductance value is more than 20 Ohm^{-1},cm^{-1}the metal complex is said to be electrolytic in nature .if the k value is less 20 Ohm^{-1} Cm^{-1} the metal complex is said to be non electrolytic in nature.

The conductance values of all metal complexes were given in the table-8. Molar conductance value for all the newly synthesized complexes were in the range 333-747 Ohm^{-1} Cm^{2}, Mol^{-1} the molar conductance of all metal complexes shows them to be electrolytic in nature.[26-27]

Table-8. Conductance data for M [AECZDTC] complexes (With cell constant 1.01)

Metal Complex	Conductance (Ohm's)	Specific conductance (Ohm^{-1}. Cm^{-1})	Molar conductance (Ohm^{-1}. cm^{2}. Mol^{-1})
[(AECDTC)$_2$ (H$_2$O)$_2$] Cu	0.33	0.33	333
[(AECDTC)$_2$ (H$_2$O)$_2$] Ru	0.56	0.56	565

Magnetic susceptibility measurements 3-Amino 9-Ehyle Carbazole and its of Metal complexes

The effective magnetic moment values for the complexes were presented in the Table-9. The magnetic moment of the Cu complex was 1.90 B.M. This value suggests the formation of octahedral complex. The present synthesized Cu, and Ru complexes show magnetic moment 1.85, and 6.67 B.M.

Table-9. Magnetic moments of Metal complexes

Metal Complex	Magnetic moment(B.M)
[(AECZDTC)$_2$ (H$_2$O)$_2$] Cu	1.85
[(AECZDTC)$_2$ (H$_2$O)$_2$] Ru	6.67

Biological activity:

The author in this present investigation attempted to find out the antibacterial activity of ligand and their metal complexes against Salmonella typhi, Enterococcus faecails and Escherichia coli choosing serial paper disc method Table 10. The results of the biological activity of the metal complexes indicated the following facts. A comparative study of the ligand and their complexes indicates that the metal chelates exhibited higher antibacterial activity than that of the free ligand. The increase in the antibacterial activity of metal chelates was found due to the effect of metal ion on the metal chelates which could be explained on the basis of overtones concept and chelation theory. On chelation the polarity of the metal ion reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charges of metal ion with donor groups. It was further noted that the delocalization of electrons over the whole chelate ring enhanced the lipophillicity of the complexes. This increased lipophillicity[28] enhanced the penetration of the complexes into lipid membrane and blocking the metal sites on enzymes of microorganism. The zones of inhibition of the ligand metal complexes were in the Table-10. The activity was compared with a zone of inhibition was measured in mm and reported in of Cu (II) and Ru(II)Complexes of Swift, is found to be more.

Table 10 Antibacterial Activity of the Metal complexes Total Area of Zone of clearance in mm

S.No.	Compound	Salmonella Typhi	Enterococcus Faecails	Escherichia coli
1	AECZDTC	22	23	20
2	(AECZDTC)$_2$Cu	24	26	21
3	(AECZDTC)$_2$Ru	22	28	21

CONCLUSION

The above study results reveals that, it can be concluded that Dithiocarbamate metal complex is so as a very good complexing agent towards many transition metal ions. By using above spectral studies, these behave bidentate ligands during complexation. All the metal complexes carry no change and are thermally stable. As such no single technique is independent of predicting final structures of the complexes.

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