Synthesis, spectroscopic, Thermal and antibacterial assay for Azothiobutricacidligand and Co (II), Ni (II) and Cu (II) complexes

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Abstract:

Inthepresentcommunicationasynthesizedligand[2,3-dimethylanilineazothiobarbutaricacid](DMAT)wasusedtopreparethreenewcomplexesof(Co(II)Ni(II)and Cu(II))Complexes.Theligandanditscomplexeswerecharacterizedbyelementalanalysis(CHN),UV-Vis,FTIRandHNMRspectroscopy, magnetic susceptibility measurement and molar conductance. The optimal condition (PHand concentration) and mole ratio for the preparing complexes were also studies. All data was showedthat the ligand acts as N,O- bidentate and all complexes have the composition of (1:2) (M:L) chelatestype and octahedral geometry. All prepared complexes are non-electrolytes. The pathogentic evaluationfortheligand (DMAT)and itscomplexes wereexperienced invitro againsttwo typeof bacteria.

Keywords: Spectralstudies,azo,thiobarbutaricacid,biologicalactivity.

Introduction:

The history of dyeing can be separated into two topic interval, the "pre-aniline," extending to 1856andthe "post-aniline" period. The former was characterized by a rather exclusive range of colors that werebasedon dye-producinganimals and plants[1]. Azo compoundscontain the–N=N–group: R_1 -N=N-R_2 In aromatic azo compounds, the R groups are arene rings; the structures of these are stablethaniftheRgroupsarealkylgroups,andit'sformedbyacouplingreactionbetweenadiazoniumsaltanda coupling agent. For the time being, synthetic azo compounds are vastly used in different applicationfieldssuch as food,cosmetics, medicines, paints,plastics, automobileindustry[3-5]. However, the classical application scope of the synthetic azo dyes still remains the textile industry andthe finishing of fibrous materials so as to impart together with coloration, antimicrobial properties is ofgreat inters [6]. In the present study a new azo ligand (DMAT) and its complexes with [Co(II), Ni(II),Cu(II)]werepreparedand identificationbyspectral study.Theantimicrobial studywasalsostudied.

Experimental:

1. MaterialsandInstruments:

All substances and solvent are of top purity and used as found from the productions.Microelementalanalysis (C.H.N) was gained on a(Eure EA 3000 Elemental analyzer). UV-Vis Spectra were performedin ethanol on a (Shimadz UV-160A) ultra violet-visible spectrophotometer. FTIR-spectra were recordedon a (Shimadz FTIR-8400s Fourier Transform Infrared) spectrophotometer (200-4000) cm^{-1} using CsIdiscs. The ^{1}HNMR spectra were gained on a (^{1}HNMR Spectrometer 400 MHz, Avance III 400 Bruker,Germany"usingDMSOasasolvent.Conductivitiesweredeterminedfor(10^{-3}M)ofcomplexesinDMSOat 25°C using (HANNA instruments

/ Conductivity Tester). pH measurement were performed using(HANNA instruments pH Tester / Pocket pH Tester). Melting points have been gained by using (StuartMeltingPoint Apparatus).

2. Synthesisof[2,3-dimethylanilineazothiobarbutaricacid](DMAT):

The Ligand (DMAT) was synthesized according to the general method [7] with some modification bydissolving(0.001M)(0.121g)of2,3-dimethylanilineinamixturecontainingof(2ml)ofsulphuricacid ,(10ml)ethanoland(10ml)ofdoublydistilleddeionizedwater.Thesolutionmixturewascooledto(5C°) .(10ml) of (10%) sodium nitrite solution was added drop wise with stirring in order to obtain thediazoniumsaltsolution.After20minthediazoniumsolutionwasslowlyaddedtoacooledbasicsolutionof (0.001M)(0.1661M) of thiobarbutaric acid. The read colored mixture was neutralized by sulphuricacid and the solid precipitate was filtered off and washed several times with (1:1) (ethanol : water)mixturethen left to dry[scheme (1)] . Thepercentageyield (80%).

Scheme 1 : Synthesis of Ligand
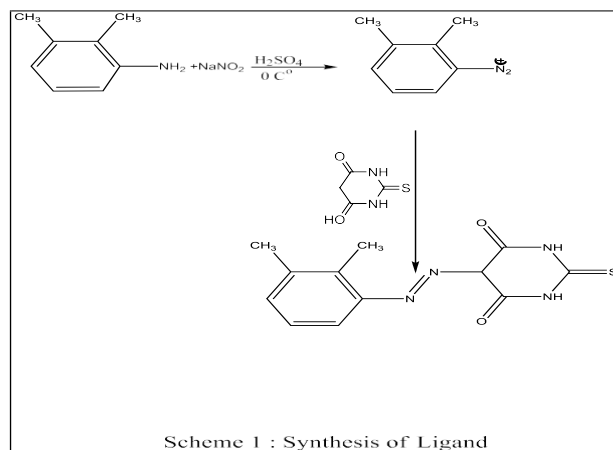
3. Preparationofthestandardsolution:

For preparation the (Co(II) Ni (II) and Cu (II)) Complexes. the metal chloride (0.001M) dissolved insuitable buffer solution was mixed with (0.002 mole) of (DMAT) in ethanol and was heated for(2hr.).AllthepreparedComplexes,whichprecipitatedwerecooledandthenfiltered,washedseveraltimeswith(1:1) (ETOH: H2O) and dried. The suggested stoichiometry structure of complexes is shown in scheme(2).

$M^{+2} = Co$, Ni , Cu
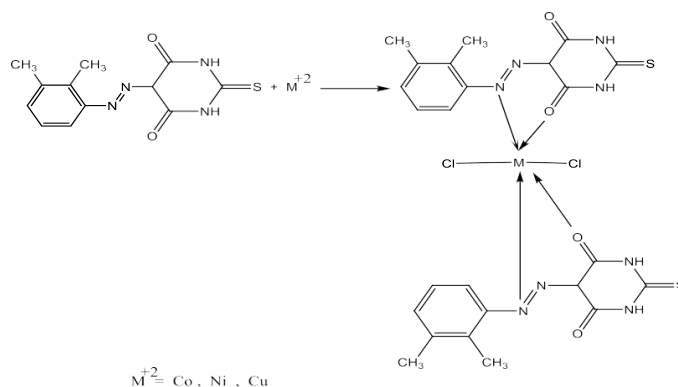
Scheme (2) : Preparation of Complex

3.ResultsandDiscussion:

Thereactionofthepreparedligand(DMAT)withselectedmetalions[Co(II)   Ni(II)andCu(II)] Whichleadstoformationcomplexwithformula[Co(DMAT)2Cl2],[Ni(DMAT)2Cl2]and[Cu(DMAT)2Cl2] thathave (1:2) stoichiometry. The ligand acts as N, O- chelator, where N (azo) and O (keto in acid). ThecompositionfortheligandanditcomplexesissupportedbymethodTable(1)wasshownthephysical _chemical properties , elemental analysis , molar conductance for the ligand and its complexes. All theprepared complexes were not hygroscopic, stable in air and soluble in most organic solvent like DMSO,DMF, ethanol and acetone. The molar conductivity measurements of (10^{-3}) in ethanol were explainednonelectrolyte properties for all complexes. The magnetic susceptibility measurement's data was alsolistedin Table (1):

Table(1):physical-

chemicalproperties,elementalanalysis,moleratio,molarconductanceforthel igand(DMAT) andselectedmetalions

Compound	color (Yield %)	λmax(nm)(m.p)	Elementalanalysis %Found %(Calculated)					Λm (S.mol⁻¹.cm²)	Mag B.M
			M	C	H	N	Cl		
DMAT	red (82)	448 (256)	_____	52.36 (52.33)	4.00 (3.98)	20.36 20.29	___	____	_____
[Co(DMAT)2Cl2]	purple bluish (72)	682 (328)	8.23 (8.20)	42.35 (42.29)	3.23 (3.21)	16.47 (16.39)	10.44 (10.19)	15	3.4
[Ni(DMAT)2Cl2]	deep red (68)	491 (312)	8.53 (8.49)	42.37 (42.33)	3.23 (3.20)	16.47 (16.41)	10.44 (10.40)	12	2.8
[Cu(DMAT)2Cl2]	purple (77)	570 (322)	9.32 (8.98)	42.63 (42.21)	3.25 (3.11)	16.57 (16.12)	10.50 (10.29)	14	1.6

3.1. ElectronicSpectra andMagneticmeasurementforsolidcomplexes:

Theelectronicspectralresultsoftheligand(DMAT)anditscomple

xesare tabulatedinthetable(2)andfigure (1-4). The electronic spectra were recorded in absolute ethyl alcohol as a solvent within range(200-1100)nmandat(10^{-4}M).Theelectronicspectraoftheligandshowthreebands,thefirstandsecondbands at (278 nm, 35971 cm^{-1}) and (318 nm, 31446 cm^{-1}) attributed to ($\pi \rightarrow \pi*$) for aromatic system.The third band at (420 nm, 23809 cm-1) attributed to (n $\rightarrow\pi*$) for intraelectronic transition through (-N=N-) [4]. The electronic spectra of [Co(DMAT)^{2}Cl^2] was gave three bands at (918 nm (108932 cm^{-1}),754 nm(132625 cm^{-1}) and 535(186915 cm^{-1}) which may be assigned to (^{4}T1g $\rightarrow$ ^{4}T2g(F)υ1, ^{4}T1g $\rightarrow$^{4}A2g(F) υ2 and ^{4}T1g $\rightarrow$ ^{4}T1g(F) υ3 respectively. The position of these bands are in a good agreement withan octahedral geometry [11]. The magnetic susceptibility and polar conductivity measurement indicatedthat the Co-DMAT complex to be paramagnetic (3.4 B.M) and non-conductivity for [Ni (DMAT)2Cl2]complexrevealedthreebands.Thefirstappearedat(857nm,11668cm^{-1})belongstotransition(^{3}A2g$\rightarrow$^{3}T2g(F) υ1), while the second band at (747nm, 13386 cm^{-1}) assignable to (^{3}A2g (F) $\rightarrow$ ^{3}T1g(F) υ2) transitionand the third is a broad band at (571nm, 17513cm^{-1}). These bands indicated an octahedral geometryaroundNi(II)ion.Thecalculatedvalueofmagneticsusceptibility(2.8B.M),thisconfirmtheparamag neticpropertiesandnon-conductivitybehavior[4].Theelectronicspectrumof[Cu(DMAT)2Cl2]showssplitbandtheaverage(529nm, 18903cm^{-1})whichwasassignedto^{2}B1g$\rightarrow$^{2}Egtransition.Whichthebandat(976nm,102459cm^{-1})attributedto^{2}B1g$\rightarrow$^{2}A2gtransition.ThesetransitionsfallswithintheJhan- Teller deformation, thus the octahedral takes D4h form. In addition the value of magnetic moment(1.6 B.M), which agree with distorted octahedral geometry. The conductance measurement indicate thenon-conductance[4].
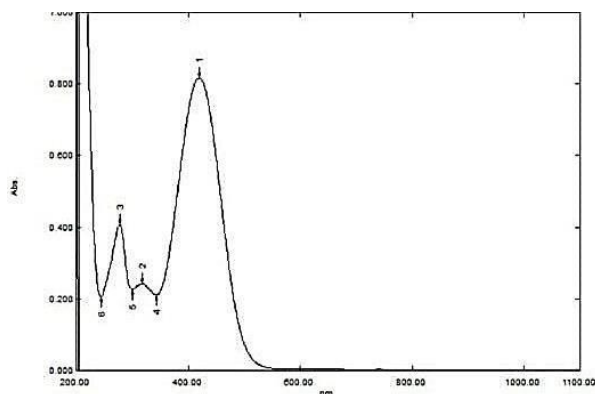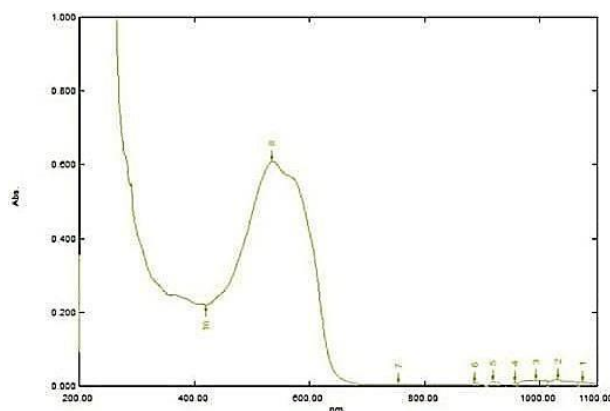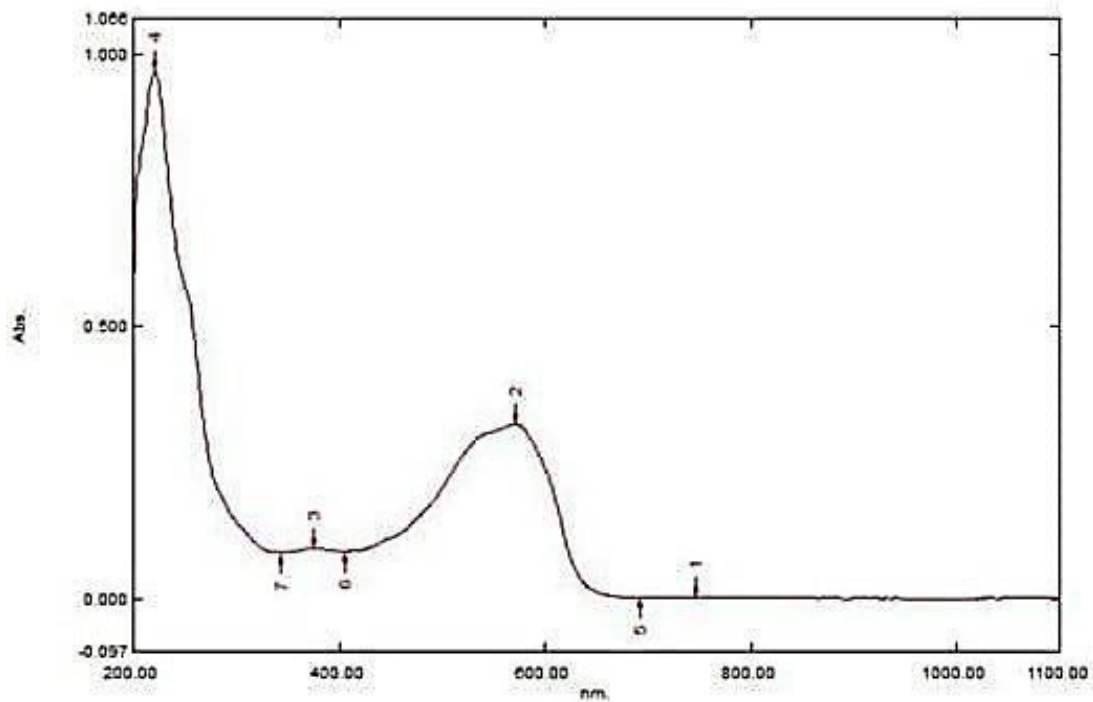

Figure (1):UV-Vis spectrumofthe ligand

Figure(2):UV-Visspectrumof the(Co)complex

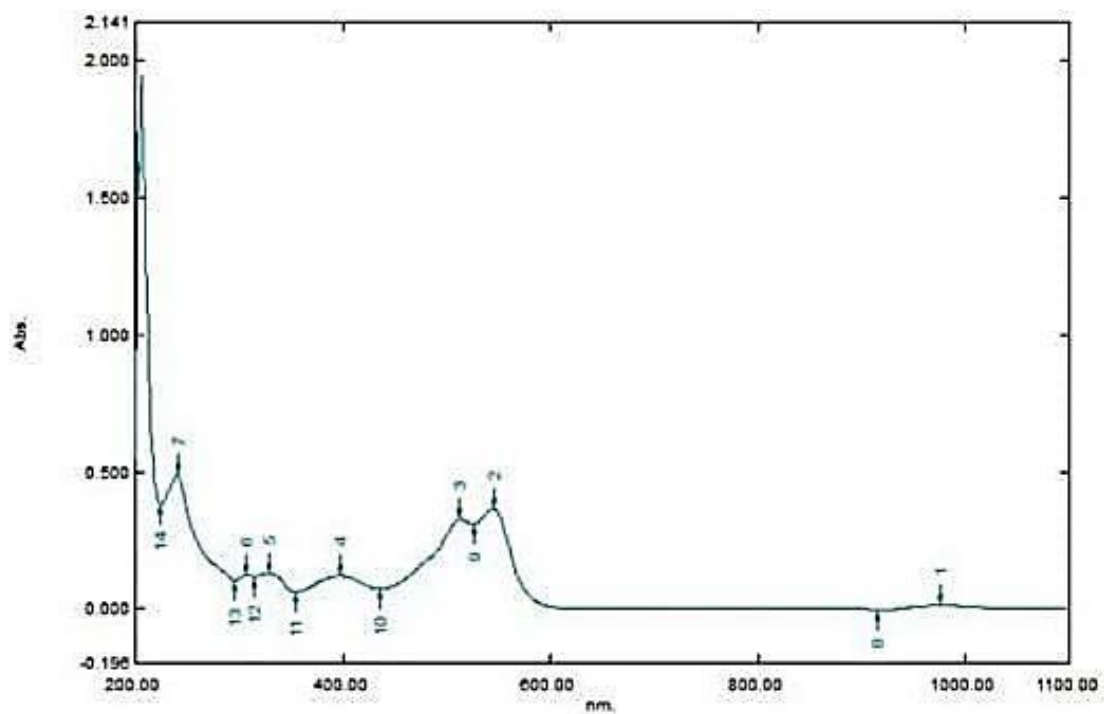**Figure(3):UV-Visspectrumof the(Ni)complex**

Figure (4) :UV-Vis spectrum of the (Cu) complex

Table(2):UV-Visfor DMATandits Complexes

Compounds	λnm	Wave Numbercm^{-1}	Assignment	Geometry
[Co(DMAT)2Cl2]	918	108932	$^4T_{1g}\rightarrow\,^4T_{2g}(F)\upsilon1$,	Octahedral
	754	132625	$^4T_{1g}\rightarrow\,^4A_{2g}(F)\upsilon2$	
	535	186915	$^4T_{1g}\rightarrow\,^4T_{1g}(F)\upsilon3$	
[Ni(DMAT)2Cl2]	857	11668	$^3A_{2g}\rightarrow\,^3T_{2g}(F)\upsilon1$	Octahedral
	747	13386	$^3A_{2g}(F)\rightarrow\,^3T_{1g}(F)\upsilon2$	
	571	17513	$^3A_{2g}(F)\rightarrow\,^3T_{1g}(P)\upsilon3$	
[Cu(DMAT)2Cl2]	529	18903	$^2B_{1g}\rightarrow\,^2E_g$	Distortedoctahedral
	976	102459	$^2B_{1g}\rightarrow\,^2A_{2g}$	

3.2. IRSpectraof preparedLigandsanditsComplexes:-

Foridentificationanddetectthecoordinationsitethatmaybeinvolvedincomplexation[showsinFigures(5-7)]werecarriedintherange(200-4000)cm^{-1}inCsI.Thesespectrawassuggestedthemodeofbondinginthecomplexes.   Thespectra   revealed thefollowingphenomena:

a. A broad band at (3456 cm-1) in the spectrum of the ligand (DMAT) was related to enolichydroxyl(OH)duetotautomericformfortheligandhaveastrongintramolecularhydrogenbond between (C$_6$=O) and (-N=N-) [11]. On complexes this band was changed in the shape andpositionso this assignable to thebrokingof hydrogen bond byeffect of metal ion.
b. The bond was attributed to U (N-H) in pyrimidine moiety is observed at (3166 cm-1) don'teffected on coordination when compared the spectra of all complexes with the spectrum of thefreeligand [4].
c. The strong triplet bond appeared in the (DMAT) spectrum at (1693, 1649, 1625) cm"

wereassignedtoꓴC-0)ofketoform.Thegreatshiftofthe(C-O)stretchingfrequencyinthespectrumcoordination [10] (Table 2). of the prepared complexes which indicates the (C-0) group one oftheparties to coordination [10][Table 2].

d. Anothersiteofchelationisazogroup.thisbondwasappearedascheletbandsat(1413,1361)cm^{-1} in the spectrum of the (DMAT) belong to ꓴ(N=N), the shape of this band were changed andshifted to low frequency as was shown in Table (2) Change in the stretching frequencies of theazogroup suggestinginvdement ofthisgroupincoordination with metalions[4,9].

e. A band was attributed to ꓴ(C=S) was appeared at (1217) cm^{-1} in the spectrum at the free ligandandthisbandappeared atapproximatelyinthesamerange,which willindicatingthatdiol notenterin complexation[11].

f. Anumberofnewbandnotpresentinthespectrumoffreeligandwereseen,however,themostnoticeable change are in the range (450-200) cm^{-1} region the weak band were appeared in thisregion may belogs to ꓴ(M-O), ꓴ(M-N) and ꓴ(M-Cl) . This will supporter result about thecoordinationsites ofligand (DMAT)with metal ion [4,9].

Table(3): FTIRforDMATanditsComplexes

compound	ꓴ(OH)	ꓴ(C=O)	ꓴ(N=N)	ꓴ(N-H)	ꓴ(C=S)	ꓴ(M-O)	ꓴ(M-N)	ꓴ(M-CL)
DMAT	34565s	1693 1649 T,S 1625	1413d,w 1361	3166w	1217w	___	___	___
Co-comp	3460s	17031 d,s 1604	1404 m	3178w	1213w	543w	466w	235 m
Ni-comp	3465s	1652d,s 1616	1386 m	3180w	1193w	541w	457w	233 m
Cu-comp	34445s	17013 d,s	1392	3175w	1217w	549	412w	228 m
		1679						

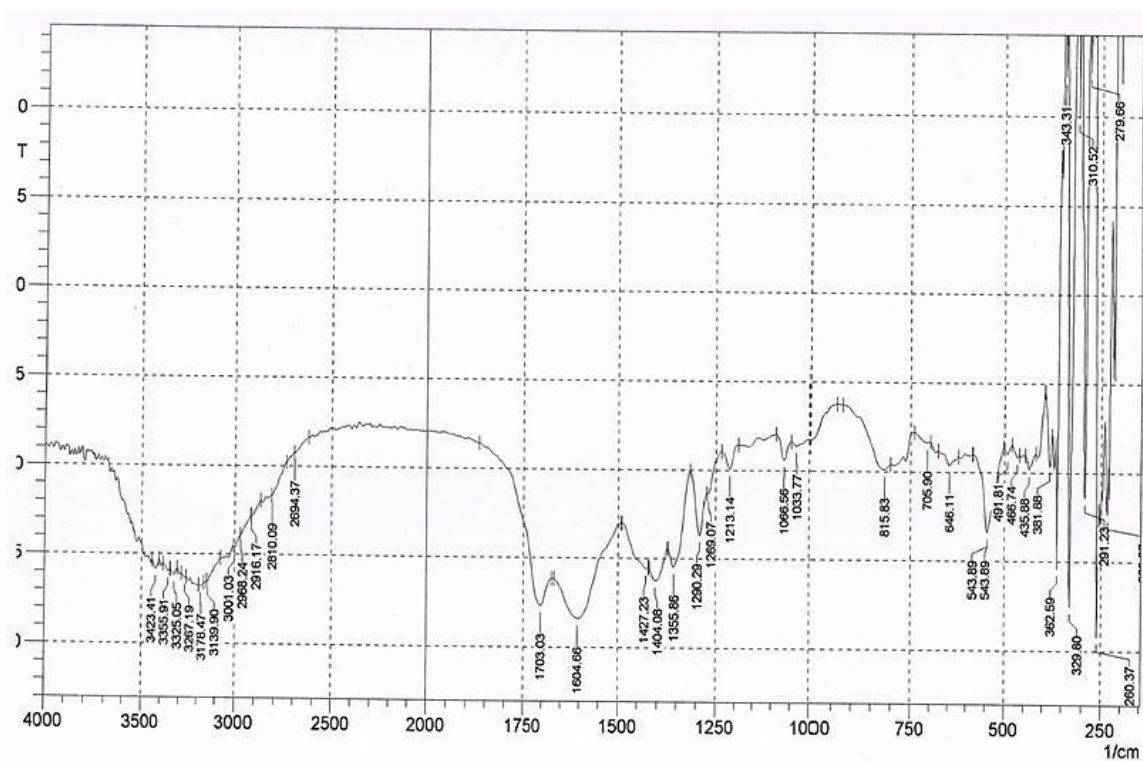T=triplet , d = doblet, s=strong, m=medum ,w =weak
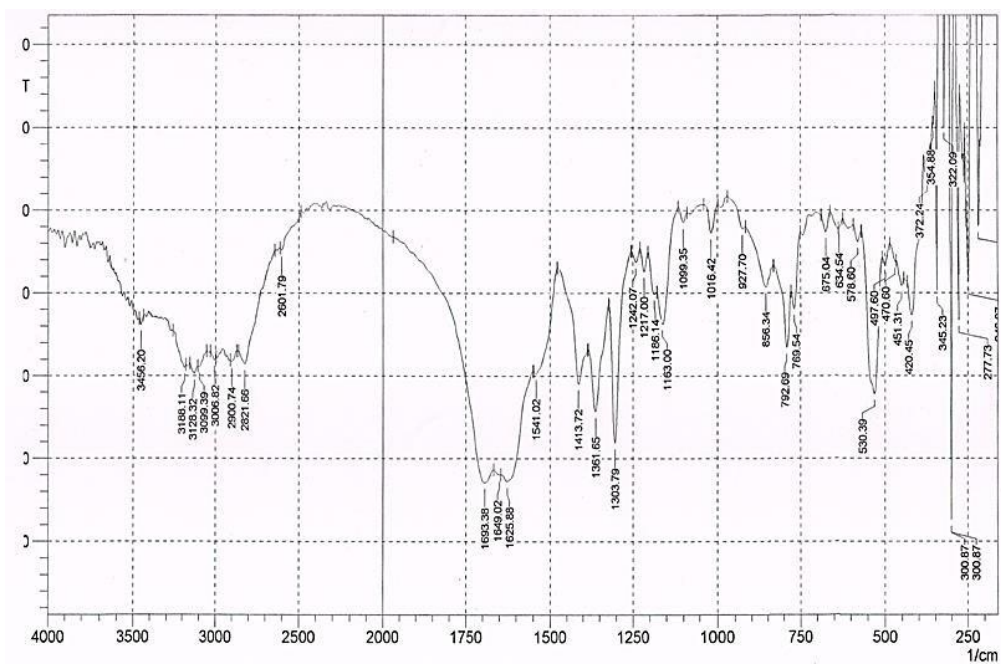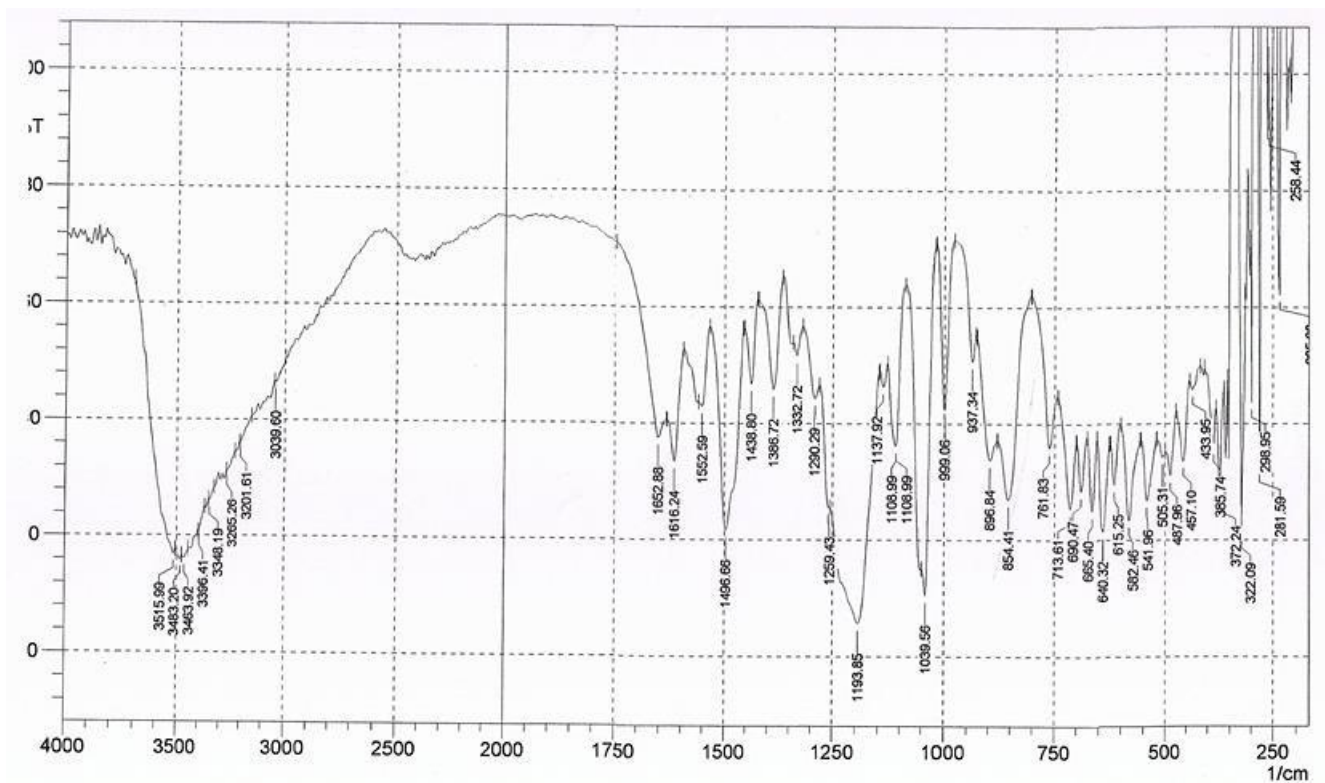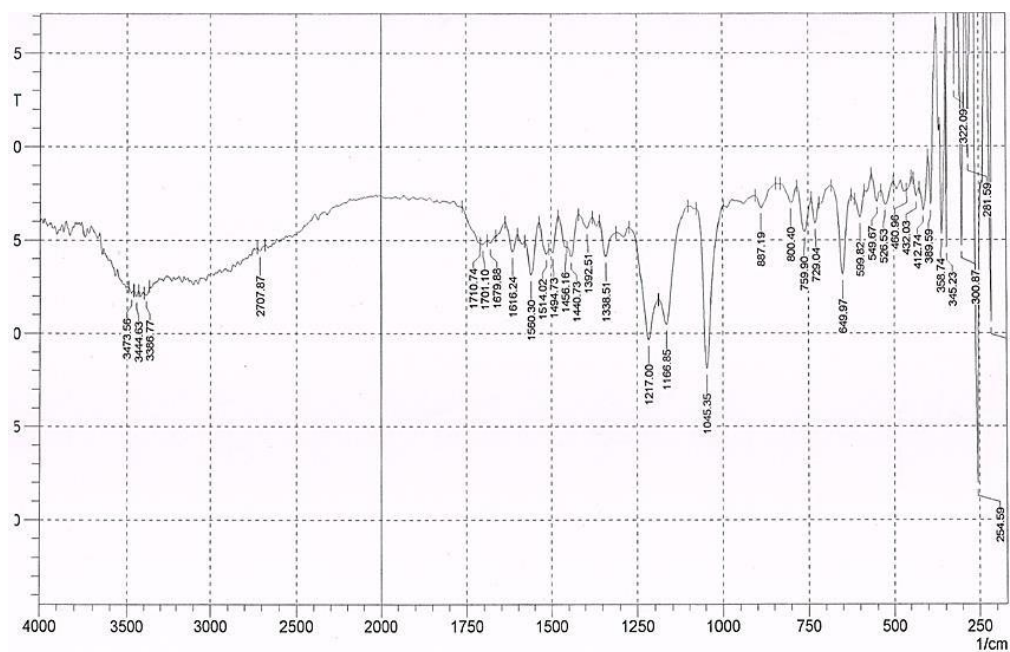
Figure(5): FTIRspectrumof theligand


Figure (6):LFTIRspectrumof the(Co)complex

Figure(7):FTIRspectrumofthe(Ni)complex

Figure(8):FTIRspectrumofthe(Cu)complex

3.3. ¹HNMRSpectrum:

¹H NMR spectrum of the freeligand (DMAT) inDMSO has showen proton signals at 3.04, 9.63 and(7.45-7.81) ppm corresponding to the methyl moiety benzene ring, (N-H) on pyrimidine moiety forthiobarbituricacid and toprotons in benzeneringrespectively[14]
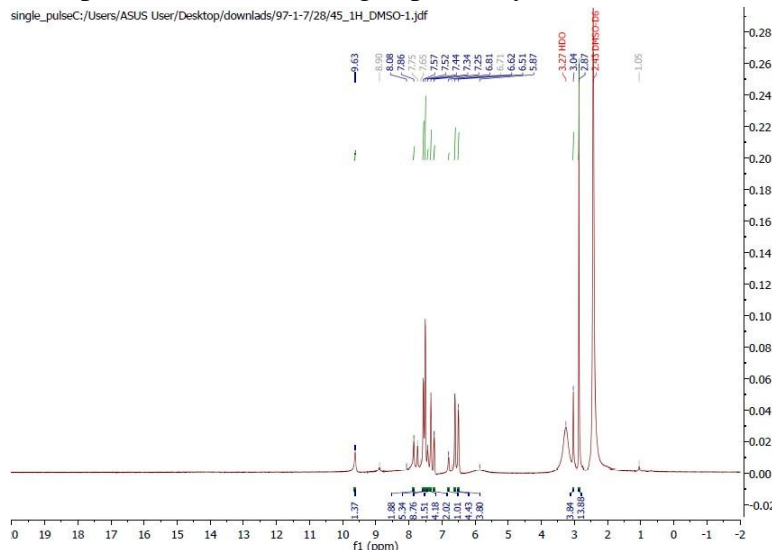
Fig(9): ¹HNMRspectrumofDMATligand.

AntibacterialEffect:

The capacity of antibacterial activity of the four newly synthesized compounds against four types ofbacteria (*Staphylococcus bacteria, Escherichia coli, Proteus Mirabillus and Bacillus*). The results ofantibacterial activities of the extracts are shown in Table 4. The result shows that the synthetizedcompounds showed higher antimicrobial activities than those of standard except *Bacillus*. Therefore, inthepresentworkallsynthesizedcompoundspossessedstrong,moderate,and strongactivitiesagainstalltestbacteria.

Table4:AntibacterialEffectofDMATanditscomplexes

Compound	GramPositive		GramNegative	
	Staph.	Ba.	E-coli	Pro.
DMAT	1.4	1.6	1.5	2.0
[Co(DMAT)2Cl2]	1.9	1.2	2.3	2.9
[Ni(DMAT)2Cl2]	2	1.8	2.5	2.2

[Cu(DMAT)2Cl2]	1.9	1.7	2.4	2.9
Melronidasul	0.7	3.5	0.8	0.8

Thermalanalysis:

For assessing the thermal decomposition process, the effect of the structural properties of chelatingfactor and type of the metal on the thermal properties of complexes. The ligand (DMAT) and itscomplexes were deliberated by thermo gravimetric analysis in the temperature range (25-1000)C°inargon atmosphere. The number of stages, temperature ranges, stages of degradation, degradationproductloss,thecalculatedandtheobtainedweightlosspercentagesandtheresiduesofallsynthesized complexes and ligand them are tabulated in table (4) and thermo gramcurves are shownin figure (10-13). They were appeared an agreement in weight loss betweentheir data was obtainedfrom the thermal decomposition and calculated, which backup the data of elemental analysis andaffirmsthesuggestedformula[15Z].FromdataofTGAcurvesitwasfoundthatthermaldegradationforthe ligand (DMAT) and its complexes were got in (2-4) steps, while the thermal stability is increased asinthefollowingorderligand(DMBT)<[Cu(DMAT)2Cl2]<[Co(DMAT)2Cl2]<[Ni(DMAT)2Cl2]depend ingonthepercentageoftheresidue.

Table5:Thermogravimetricanalysisdatafortheligand(DMAT)anditscomplexes.

Compound molecular(gm/mole)	TG range ofdegradation(c°)	Step	Mass lossobtained(calc.)%	assignment	Dsc(C°)
DMAT(C12H12N4O2S)(276)	25-450	1	89.02(88.40)	C12H12N4O2S(1.9)O0.1O	345.72 (EXO)750(EXO)
	450-1000	2	10.30(11.01)		
	>1000	residue	0.68(0.57)		
[Co(DMAT)2Cl2]CoC24H24N8O4S2Cl2(681.93)	25-250	1	11.44(11.43)	H7Cl2C24H17N8S2O3.5Co(0.5)O(0.5)	
	250-410	2	78.61(78.74)		354.2(EXO)
	410-1000	3	5.97(5.49)		
	>1000	Residue	3.98(4.32)	Co(0.5)	

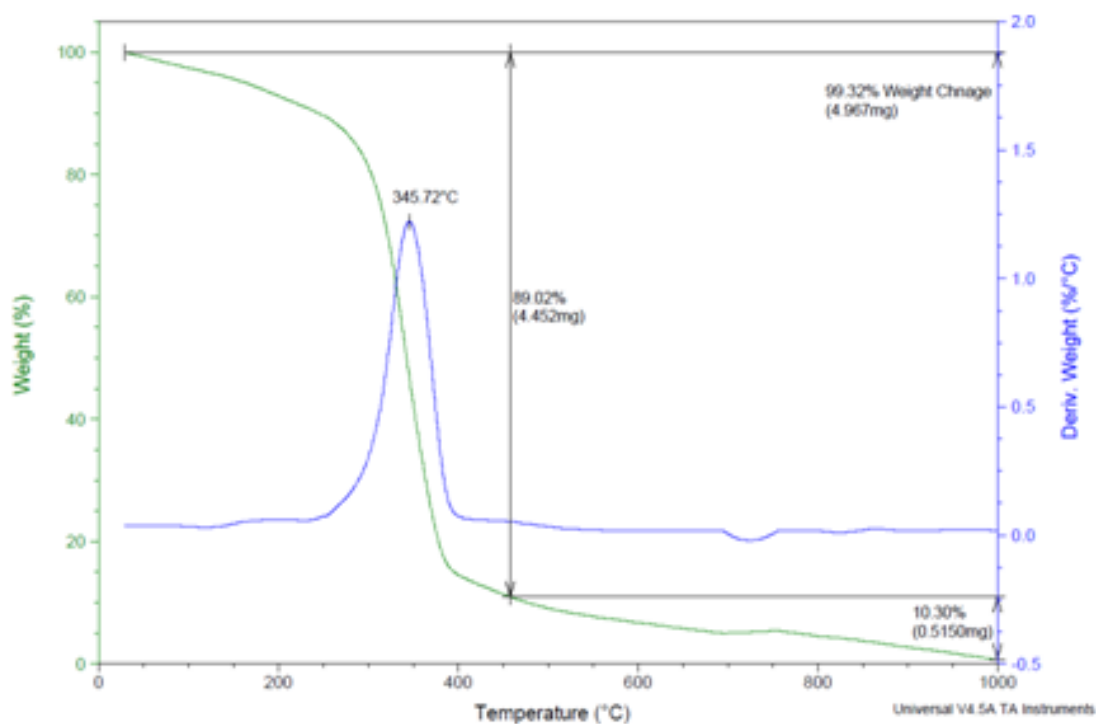|					
[Ni(DMAT)2Cl2]NiC24H24N8O4S2Cl2(681.69)	25-240	1	9.946(9.90)	CH2ClC23H4ClN3N5O3.5O(0.5)S(1,4)NiS(0.6)	314.48(EXO)
	240-430	2	53.24(52.41)		576.15(EXO)
	430-660	3	18.73(18.48)		
	660-1000	4	7.63(7.74)		
	>1000C°	Residue	10.46(11.32)		
[Cu(DMAT)2Cl2]CuC24H24N8O4S2Cl2(686.546)	25-250	1	6.5(6.48)	H9ClC24H15N8ClS2OCu(0.92)O30.08Cu	331.34(EXO)
	250-570	2	77.07(77.27)		619.7(EXO)
	570-1000	3	15.70(15.50)		
	>1000	residue	0.73(0.74)		

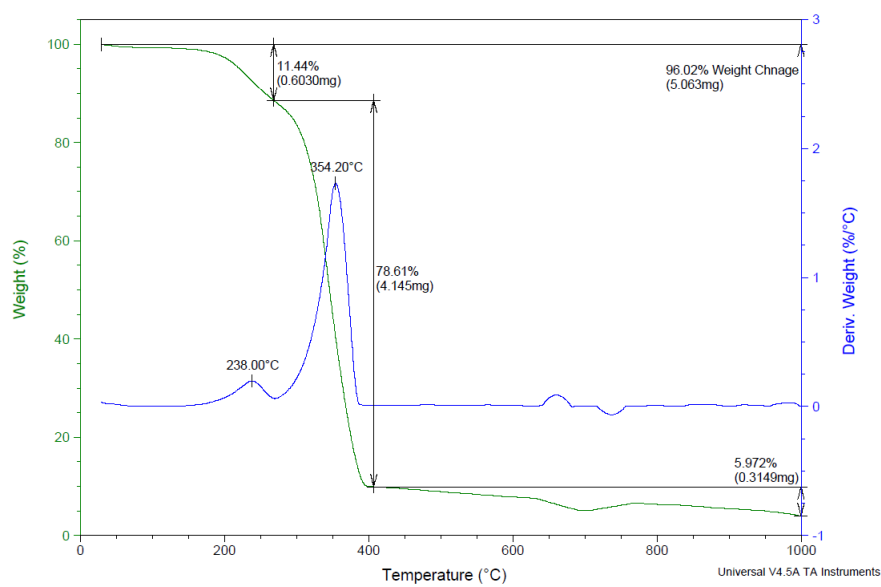**Figure10:DSC-TGA fortheDMAT**

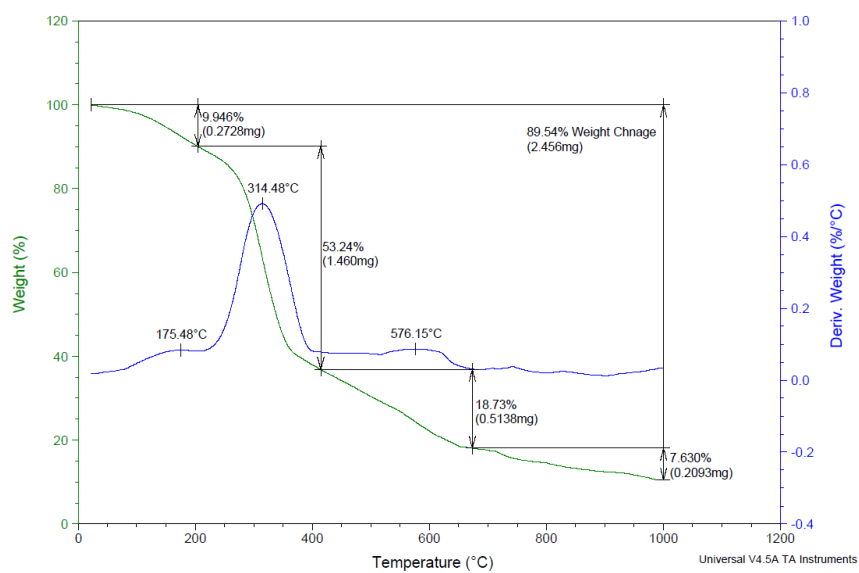**Figure11:DSC-TGA fortheCo-Complex**
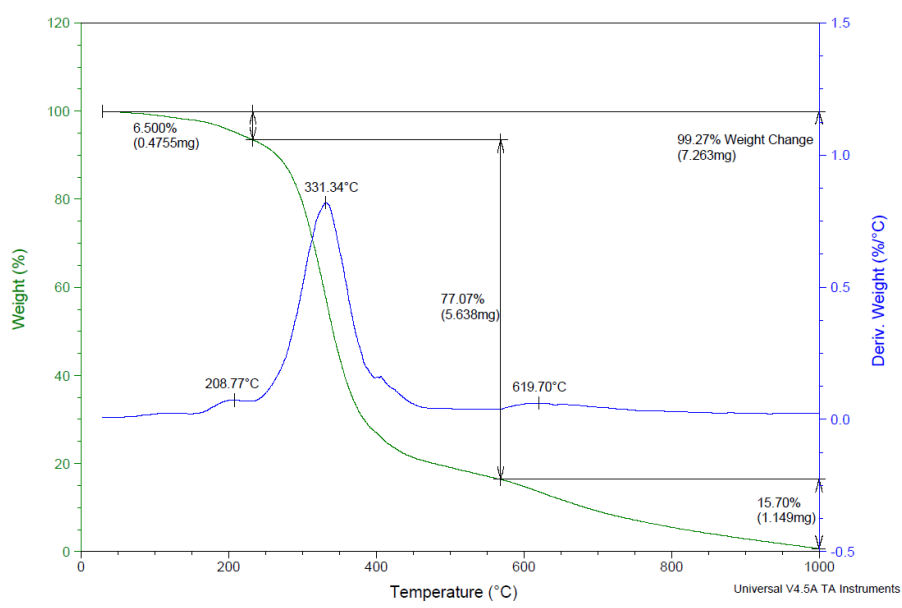

Figure12:DSC-TGA fortheNi-Complex

Figure13:DSC-TGA fortheCu-Complex

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