Synthesis , Characterization and Biological Studies of Some New Mixed Nickel(II) Complexes Containing Dithiocarbamate and 1,10-phenanthroline Ligands

Atared . F . Hassan
Department of chemistry ,College of Science , Basrah University

Abstract

Complexes [Ni(dtc1)$_2$(phen)] (I) , [Ni(dtc1)(phen)$_2$]Cl (II) ,[Ni(dtc2)$_2$(phen)] (III) ,[Ni(dtc2)(phen)$_2$]Cl (IV) , [Ni(dtc1)(dtc2)(phen)] (V) and [Ni(dtc2)$_2$(H$_2$O)$_2$], where dtc1=Benzyl dithiocarbamate , dtc2 = p-chloro benzyl dithiocarbamate ,phen=1,10-phenanthroline were prepared by reaction of $NiCl_2.6H_2O$ with different mole ratio of phenanthroline and dithiocarbamate Ligands.All complexes were characterized by C H N analyses , IR ,UV-Vis. , ^{1}H NMR and XRD diffraction . The analytical data indicated that the dithiocarbamate ligands and phen are coordinated as bidentate ligands.The biological activities of these compounds shows that some promising activity against gram positive bacteria (*Staphylococcus aureus*) and gram negative bacteria (*Aeromonas*

Keywords : Mixed ligand ,dithiocarbamate ,phenanthroline , benzyl amine ,nickel Complexes.

INTRODUCTION

Diothiocarbamate metal complexes are of great interest due to their various applications in agriculture , pharmaceutical and medicine(Coucouvanis et al.,1976 and Boris Cvek et al.,2008). They have been used as a precursor for synthesis of metal sulfide nano particle (Thammakan et al.,2006 and Srinivasan et al., 2012) . Metal dithiocarbamate complexes have been reported to show de toxicant and immune pharmacological properties ,such as fungicidanal (Darain et al., 1999 and Patel et al., 1999) ,insecticidal (Daris A.G. 1997) and herbicidal (Caruso F. et al.,2004) properties . They have been act as anticancer agents (Ramalingam K . et al., 1987) . The synthesis of metal complexes of dithiocarbamate with nitrogenous bases such as pyridine ,picoline and 1,10-phenanthrpline have been previously reported (Ramalingam K. et al., 1987 , Manohar A. et al., 1977 , Manohar A. et al., 2006 , Srinivasan N. et al.,2009 and Srinivasan N . et al., 2010) .

In this work six nickel (II) mixed ligand complexes containing dithiocarbamate anion and 1,10-phenanthroline were prepared and characterized .The resulting complexes were screened for their anti bacterial activity.

MATERIAL AND METHODS

All reagents and solvents used in this work were of analytical reagent grade (Aldrich , Sigma Co. and British Drug House) and used as supplied .

Physical measurements

Elemental analysis for C, H and N was done by CE -440 ELEMENTAL ANLYZER .

FTIR spectra were recorded as KBr discs with a FT-IR 8400 Shimadzu instrument . Electronic spectra were recorded by Spectro Scan 80D U K . ^{1}H NMR spectra were recorded with a Bruker DPX- 300(300MHZ) and Bruker LA-250(250MHZ) using TMS as internal standard and d$_6$-DMSO as a solvent . Melting points were determined on a GallenKamp melting point apparatus and uncorrected . X-ray diffraction (XRD) was performed using Philips PW 1700 Series Diffract meter , Leiden ,Netherlands.

SYNTHESIS

Preparation of sodium benzyldithiocarbamate(dtc1)

Solution of amine 80 mmol in 70 ml ethanol was treated with sodium hydroxide (3.2 g ;80 mmol) in 10 ml deionized water ,cooling with stirring , then (6.08g ; 80 mmol)of carbon disulfide added gradually with continues cooling over (30 min.) and maintained the temperature below 10 ^{o}C .A white precipitate of the corresponding dithiocarbamate ligand was collected filtration then washed with methanol and dried.

Preparation of sodium p-chlorobenzyldithiocarbamate (dtc2)

This compound was prepared by the same method described ……etc

Equation of reaction

$$CS_2 + R-NH_2 + NaOH \rightarrow [R\text{-}NH\text{-}CS_2]^- Na^+$$

R= benzyl amine or p-chloro benzyl amine.

Preparation of complex [Ni(dtc1)$_2$(phen)] (I)

An aqueous solution of $NiCl_2,6H_2O$ (0.238g;1mmol) and aqueous ethanol solution of sodium benzyldithiocarbamate(0.41g ; 2mmol)was mixed and stirred continuously,then aqueous solution of 1,10-phenanthroline (0.198g ;1mmol) was added drop wise with vigorous stirring and gentle heating for 1hr . An olive green precipitate was obtained and collected by filtration. The precipitate was washed several times with a hot mixture of water and ethanol solution and dried in vacuum.

This procedure was used for preparation of all nickel (II) mixed ligand complexes .See figure (1) .

Preparation of complex [Ni(dtc1)(dtc2)(phen)](V)

The complex were synthesized by mixing 1:1 mole ratio of sodium benzyldithiocarbamate (dtc1) and sodium p-chlorobenzyldithiocarbamate (dtc2) dissolved in a hot aqueous ethanol solution with $NiCl_2.6H_2O$ (1mmol)dissolved in minimum amount of distilled water with continuous stirring at the first step , above then an equimolar of 1,10-phenanthroline(phen) was added drop wise with continuous stirring and gentle heating for 1hr . An olive green precipitate were filtered off ,washed several times with a hot solution of ethanol and water and dried in vacuum.

Figures 1 and 2 should transfer to results and discution.

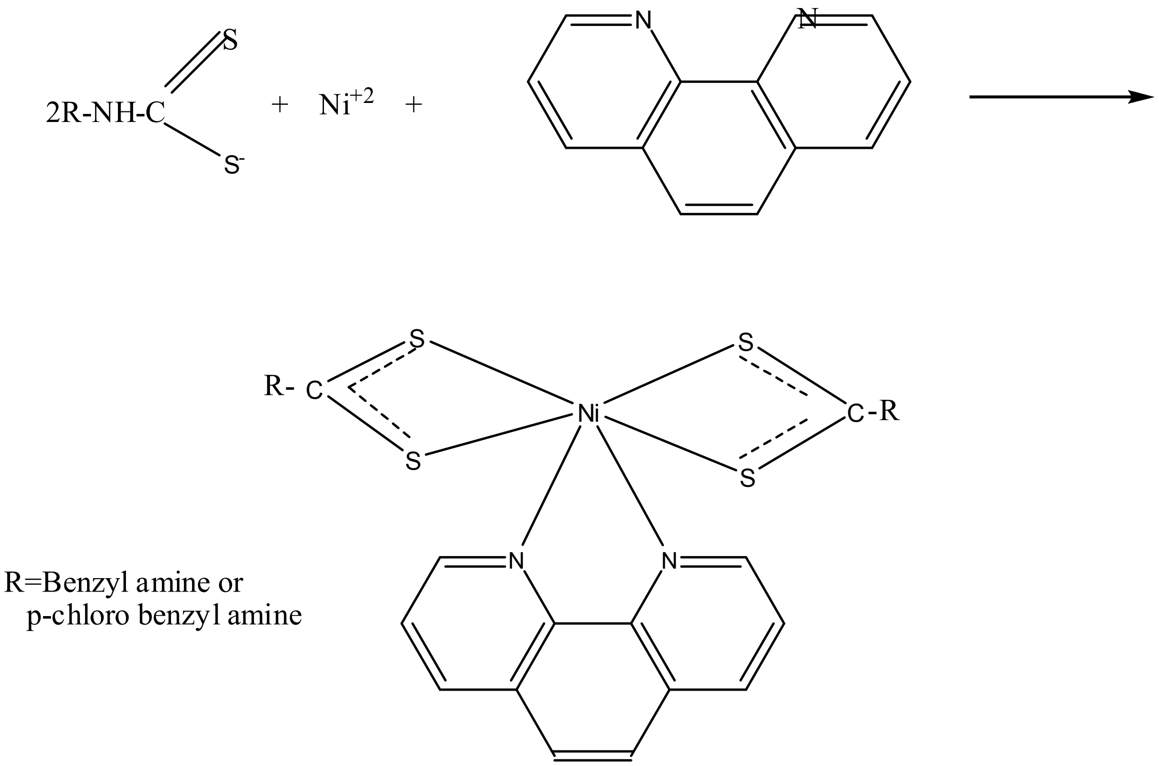
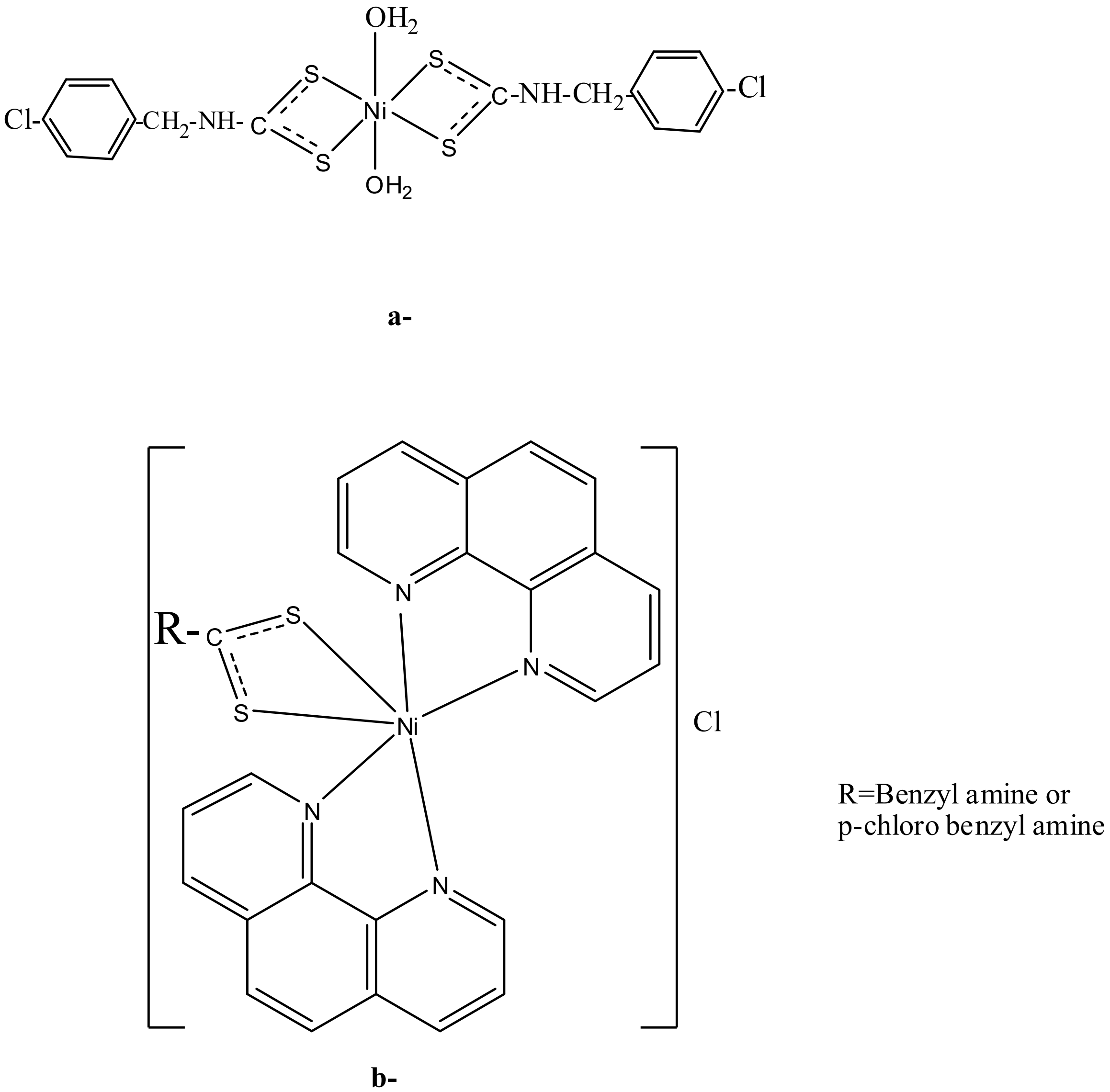


Figure 1. Proposed structure or the reaction mechanism for mixed ligand complexes Type [Ni(dtc)$_2$(phen)].



Figure(2):a- Proposed structure of complex (VI)$[Ni(dtc2)_2(H_2O)_2]$, b- Proposed structure of complexes type $[Ni(dtc)(phen)_2]Cl$.

Anti the bacterial screening

The biological activity test was done by Agar diffusion method by weighing 2gm of the extract and adding it to 20ml of DMSO ,then 50mL were taken from this mixture by micro syringe and was put in holes made by cork porer in petri dishes which contained the pathogenic bacteria.

Preparation of pathogenic bacterial petri dishes:

0.1ml of nutrient broth which inoculated with Staphylococcus aureus which is gram positive and Aeromonas hydrophila which is gram negative separately . The broth was spreaded by L-shape spreader .The petri dishes were incubated at 37 ^{o}C for 15 minutes then inocubated with bacterial broth and inocubated over night at 37^{o}C then the results were recorded.

RESULTS AND DISCUSSION

The complexes are stable ,non-hydroscopic and the color of complexes are dark green to olive green . The complexes were obtained in 59-69% yield .The C H N analyses agrees well with the theoretical values , suggestive of six coordinate geometry . Melting point , percentage yield and C H N elemental analysis are listed in table (1).

Table(1):Physical and analytical data of synthesized complexes.

No.	Emperical Formula	% yield	Color	m.p (^oC)	Elemental analysis Found(calcd)		
					C	H	N
(I)	$[Ni(dtc1)_2(phen)]$	66%	Olive green	*107	56.33(56.75)	4.01(4.12)	9.29(9.01)
(II)	$[Ni(dtc1)(phen)_2]Cl$	64%	Olive green	*115	57.11(57.33)	4.19(3.97)	10.41(9.68)
(III)	$[Ni(dtc2)_2(phen)]$	60%	Dark green	*165	50.01(50.11)	3.29(3.14)	8.34(8.06)
(IV)	$[Ni(dtc2)(phen)_2]Cl$	69%	Green	*130	57.24	3.45	10.437
(V)	$[Ni(dtc1)(dtc2)(phen)]$	59%	Olive green	*105	54.71(55.02)	3.63(3.93)	8.78(8.73)
(VI)	$[Ni(dtc2)_2(H_2O)_2]$	67%	Reddish green	132-134	36.32(35.76)	3.43(3.35)	5.30(5.52)

***Decomposition temperature .**

INFRARED SPECTRA

The assignment of infrared spectra bands of new complexes are listed in table (2). The dithiocarbamate complexes show two diagnostic bands in the infrared spectra ,the first is a sharp band between 1448- 1490 cm^{-1} which attributed to $V\ C{=}N$ stretching vibration(Aprakasm B. et al., 2007), This band lie between V C=N and V C-N in the 1640-1690 Cm^{-1} and 1250-1350 Cm^{-1} range respectively (Sovili S.P. et al ., 2000) which indicate a partial double band character of C=N group arising from mesomeric drift of electrons from the dithiocarbamate moiety toward the Ni (II) center (Manohar A. et al., 2006 and Aprakasam B. et al., 2007).

A second signal band appears in the region between 1012-1029 Cm^{-1} corresponds to V (CSS) vibration and indicates bidentate coordination mode of the dithiocarbamate moiety through the two sulfur donar atoms (Gavalheiro et al., 2000). The presence of single N(C-S) around 1000Cm^{-1}in agreement with previous published literature for dithiocarbamate complexes (Sovili S.P. et al., 2000 , Assat A.Y. et al., 2009 and Benedini V.D. et al., 2006) .

In complex(VI) a broad band appeared at 3300-3500 cm^{-1} and peak at 945cm^{-1} indicate presence of coordinated water molecule (Geary w. j. 1971).

Electronic spectra of complexes

The electronic spectra of the prepared complexes were recorded in the range 200-1100 nm using di methyl foramide (DMF) as a solvent .The electronic specta of Ni(II) six coordinate complexes showed an absorption below 350 nm are due to intra ligand $\pi - \pi *$ transition ,mainly associated with N-C=S and S-C=S groups in all complexes .The intense bands observed at 385-390 nm are due to either metal-ligand or ligand – metal charge transfer and weak bands at 600 -665 nm are due to d-d transition (Beck W. et al., 1978) . The electronic spectra data were tabulated and shown in Table (2).

Table (2): Electronic spectra (nm) of the mixed ligand complexes

No.	Complexes	Bands (nm)
(I)	$[Ni(dtc1)_2(phen)]$	255 , 325 , 390 , 600
(II)	$[Ni(dtc1)(phen)_2]Cl$	325 , 385 , 665
(V)	$[Ni(dtc1)(dtc2)(phen)]$	260 , 325 , 390 , 600

^{1}H NMR STUDY OF COMPLEXES

The ^{1}H NMR spectra of synthesized complexes show that the resonance of aromatic rings were observed in the region (7.15-7.48) ppm . The NH proton of amine dithiocarbamate exhibited signal in region (7.97-11.0)ppm. The signal observed in (4.67 – 4.47)ppm are due to methylene (CH_2) protons .The N M R data of synthesized complexes are listed in table(3).

Table (3) Imported IR bands(cm-^{1}) and ^{1}H NMR data for complexes.

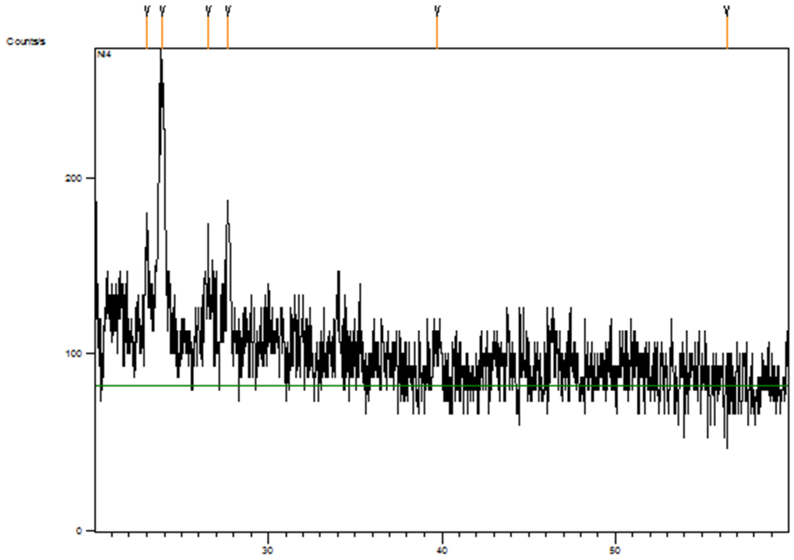
No.	*V C—Nstr.*	*V C—S str.*	*V N—H str.*	*V C=C str.*	^{1}H NMR (DMSO-d_6). Tms=0ppm
(I)	1450	1026	3288	1552	4.67(s,2H,CH_2); 7.97(s ,N—H); 7.21-7.42(m,Ar—H).
(II)	1452	1027	3290	1554	4.67(s,2H,CH_2) ; 7.97(s, N—H); 7.21-7.42(m , Ar—H).
(III)	1446	1014	3244	1580	4.48(s ,2H,CH_2) ; 11.-2(s ,N—H); 7.27-7.48(m , Ar—H) .
(IV)	1448	1027	3286	1554	
(V)	1452	1012	3292	1558	4.67(s , 2H,CH_2) ; 7.97(s , N—H); 7.15-7.47(m , Ar—H).
(VI)	1490	1012	3307	1560	4.65(s, 2H, CH_2) ; 8.06(s,N—H); 7.26-7.47(m, Ar—H).

X-RAY DIFRACTION STUDY (XRD)

Figure (3) show the XRD patterns of complex (III and VI).The patterns show that the complexes(III and IV) are poly crystalline with average crystallite sized of nano particles about 69 nm and 82.5 nm respectively according to the Deby-Scherrer formula (Cullity B. 1956):

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

a-XRD Pattern of complex (III)



b- XRD Pattern of complex (IV)

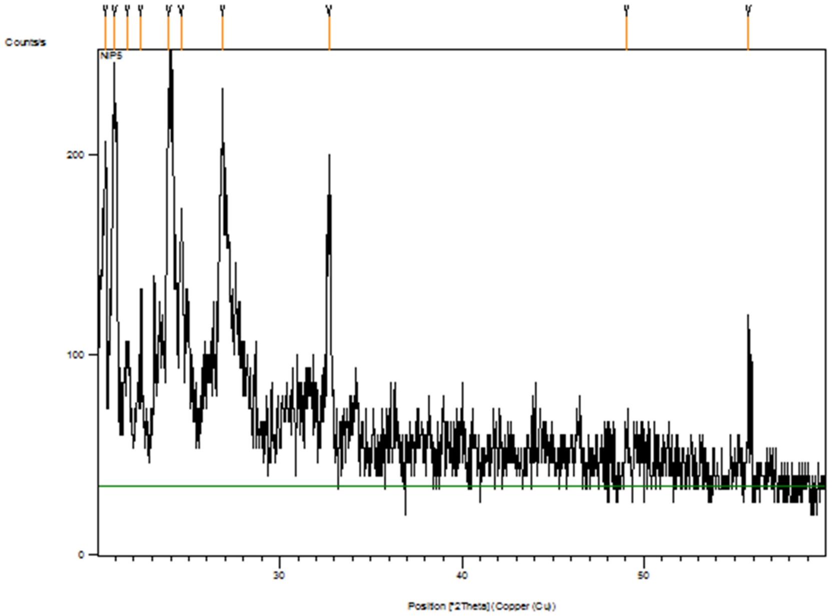
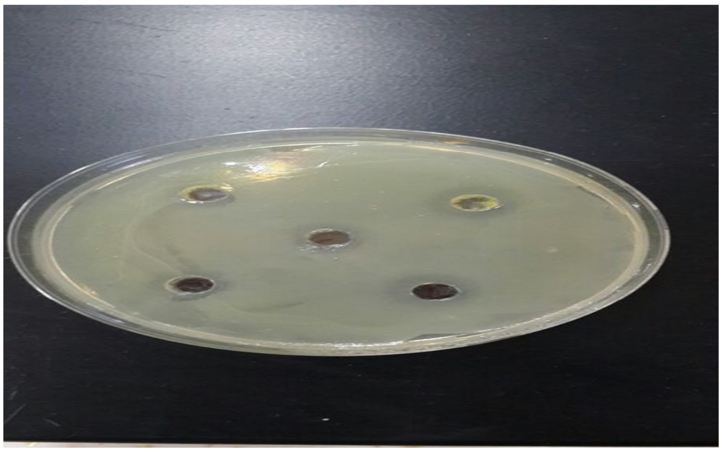
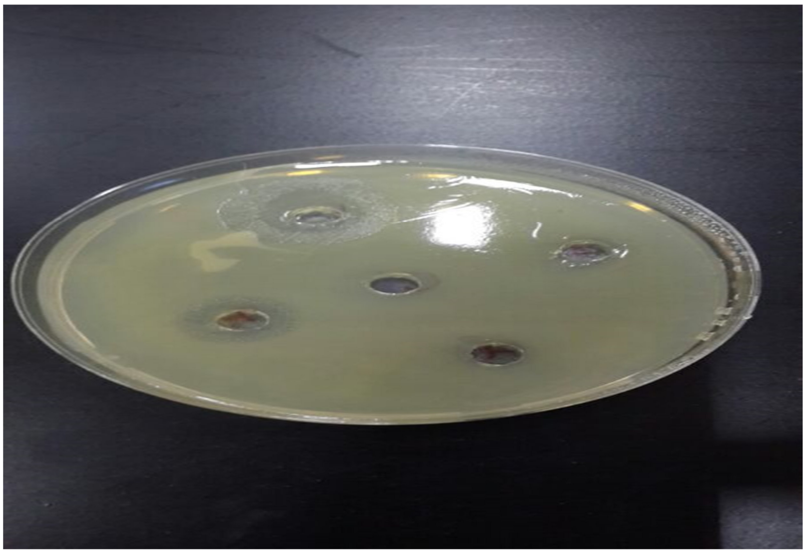


Figure (3) : XRD PATTERN For Complex (III) &(IV).



Staphylococcus aureus



Aeromonas hydrophila

Fig (4): Anti bacterial activities of the complexes.

ANTIBACTERIAL SCREENING

The complexes $[Ni(dtc1)(phen)_2]Cl$ (II) and $[Ni(dtc2)_2(phen)]$ (III) had moderate activity against Aeromomas hydrophila (gram negative bacterial), while complexes $[Ni(dtc2)(phen)_2]Cl$ (IV) and $[Ni(dtc2)_2(H_2O)_2]$ (VI) had low to moderate activity against Staphylococcus aureus (gram positive bacterial).

Table (4): Antibacterial screening for synthesized complexes.

Test compounds	Results(Inhibition zone)(mm) Aerom0mas hydrophila Gram $^-$ bacterial	Staphylococcu aureus Gram $^+$ bacterial
(II)$[Ni(dtc1)(phen)_2]Cl$	Zero	24
(III)$[Ni(dtc2)_2(phen)]$	Zero	15
(IV)$[Ni(dtc2)(phen)_2]Cl$	7	Zero
(VI)$[Ni(dtc2)_2(H_2O)_2]$	10	Zero

CONCLUSSION

Nickel (II) mixed ligand complexes of dtc1 and dtc2 with 1,10-phenanthroline have been synthesized and characterized .The two ligands moieties exhibit a bidentate coordination mode in the complexes .

The complexes (II) &(III) exhibit mild in vitro antibacterial activities against Aeromomas hydrophila ,While complexes (IV)&(VI) had activity against Staphylococcus aureus .

REFERANCES

Assat A.Y. , Alyass I.M. and Mohammed A.S. , Tikrit Journal of pure Science , 2009 , 14(2),280.

Aprakasam B. ,Ramalingam K. ,Bocelli G. , Canfon A. , J. Polyhedron ,2007 , 26 ,1133-1138.

Beck W. , Giunth M. , Castilo M. ,Zippel H. , N-Dithiocarboxy-α-amino saure-komplexe Von Nickel,Palladium and Platin (II)Chem. Ber.1978 , 111 , 1246-1252.

Benedini V.D. ,Antunes P.A., Eder J.G. and Chierice G.O. , J. Bras. Chem. Soc. 2006,17 , MO. 4 , 680.

Boris Cvek , Vesna Milacic , Jan Taraba and Ping Dou Q., J.Med. Chem. ,2008 ,51 , 6256-6258.

Caruso F. ,Ross M. , Opazo C. and Pettinani C. , 2004 .Structural features of antitumor gold(I) Phospine derivatives analyzed with theoretical method, J . Argentine Cjem.Soc .,92, (1),pp.119-124.

Coucouvanis D. and Fackler ***J .*** P . Jr ., Square planer sulphur complexes . , Inorg . chem. , 1976 , 6 ,2047 – 2053 .

CULLITY B. ELEMENTS OF X-RAY DIFRACTION: ADDISION-WESLEY PUBLISHING COMPANY 1956.

Darain F. ,Banu L.A., Ahmed S. and Islam M.S., 1999,Antimicrobial and toxicological Studies of mixed ligand complexes of Cu(II) metal ions , Oriental , J.Chem., 15 (2), pp.269-274.

Daris A.G.(1997).Organotin Chemistry, VCH,Weinheim Germany.

Gavalheiro ETG., Ionashiro M., Marion GS. , Breviglieri T. , Chierice GO. , J.Transition Met. Chem. ,2000 , 25, 69-72.

Geary w. J., The use of conductivity measurement inorganic solvent for the characterization Coordination compound Coord. Chem. Rev. 7, 81 (1971).

Manohar A., Ramalingam K., Venkatachalam V. , Casellato U. and Graziani R. ,J. Polyhedron, 1997 , 16,1971-1977.

Manohar A. ,Ramalingam K. , Thiruneelakandan R. , Bocelli G. ,and Righi L. (2006) N-(2- Hydroxyethyl)-N-methyl dithiocarbamato complexes of nickel(II) wiyh phosphorus Donor ligands .Anorg.Allg. Chem., 632 , 461-464.

Patel L. K. , Chiklia K.H. , and Desai P.S. , 1999.Synyhesis of disperse dyes based on Thiazolidinone styryl system , their application on polyester fiber and their Antimicrobial activities. Oriental ,J. Chem. , 15 (2) pp. 363-365.

Ramalingam K. , Aravamudau G. and Seshasayee M. , J. Inorg. Chem. Acta,1987,128, 231-237.

Srinivasan N., Sathyaselvabala V., Kuppulekshmy K., Valarmathi P. and Thirumaran S., Monatsh Chem , 2009 , 140 , 1431 -1436.

Srinivasan N., Valarmathi P., Thirumaran S. and Ciattini S., Trans . Metal Chem., 2010, 35, 815 -819 .

Srinivasan N. , and Thirumaran S. , Super Lattices and Microstructures , 2012 , 51 ,912-920.

Thammakan N. , Somsook E. , Mater . Lett. ,2006 , 60, 1161-1165. MO. 4 , 680 .

CALL FOR JOURNAL PAPERS

MORE RESOURCES

IISTE Knowledge Sharing Partners