

SYNTHESIS, CHARACTERIZATION, BIOLOGICAL ACTIVITY AND THERMAL DEGRADATION OF (BENZYL -; P-CHLOROBENZYL-)DITHIOCARBAMATE AND 1,10-PHENANTHROLINE MIXED LIGANDS COMPLEXES.**Atared F. Hassan¹, Hayat H. Abass^{1*} and Nadhim A. Abdul-Hussein²**¹ Chemistry Department-College of Science -Basra University²Physics Department-College of Science-Basra University

ABSTRACT: A new Cobalt (II) and Copper (II) complexes with mixed ligands including [benzyl - (dtc1) ; p-Chlorobenzyl- (dtc2)] dithiocarbamate and 1,10- phenanthroline (phen) have been prepared by reacting $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with appropriate mole ratio of these ligands. These complexes have been characterized by elemental analysis, ¹H NMR, infrared, electronic spectra, X-ray diffraction (XRD), thermal analysis and tested for anti-bacterial activity against several bacterial strains, namely *Staphylococcus aureus* and *Escherichia coli*. The results suggest an octahedral structure for all the mixed ligands complexes with two nitrogen donor atoms of heterocyclic compound (1,10- phenanthroline) as well as sulphur of dithiocarbamate.

KEYWORDS: Dithiocarbamate, Phenanthroline, Mixed Ligand Complexes, Cobalt (II) Complexes, Copper (II) Complexes.

INTRODUCTION

Dithiocarbamates and their metal complexes play an important role in industries, agriculture, pharmacy, medicine and chemistry (Shalin et al. 2009). These compounds exhibit a wide range of biological properties. Metal dithiocarbamates are known to have biological activities such as anti-microbial, antifungal (Darian et al., 1999), insecticidal (Patel et al., 1999) and herbicidal properties (Daris, 1997) and they have been act as anticancer agents (Caruso et al., 2004). Most aliphatic and aromatic dithiocarbamate complexes synthesized have only dithio group as ligand, so they exhibit only uni- negative bi- dentate possibility (Perti C. et al., 1980, Ferberti A.C. et al., 1986 and Franchini G.C. et al., 1986). Metal complexes of dithiocarbamates with nitrogenous bases such as 1,10-phenanthroline, 2,2'-bipyridine and its derivatives have been reported (Serrano J L. Et al., 2003, Giovagnini Let al., 2005, Siddiqi K S. et al. 2005, Manhör A et al., 2006, Parkasam B A et al., 2006, Parkasam B A et al., 2007 and Pastorek R et al., 2007).

In this article we report the synthesis and characterization of benzyl and p-chlorobenzyl dithiocarbamate ligand and its Cu(II) and Co(II) complexes and their mixed ligand complexes of these with 1,10-phenanthroline. Anti microbial activities of the complexes were investigated in vitro.

MATERIAL AND METHODS

All materials and solvent used in this investigation were purchased from (Sigma, Aldrich and British Drug House) and used as supplied.

Physical measurements

Elemental analysis for C, H and N was done using CE-440 ELEMENTAL ANALYZER, FT-IR spectra were recorded as KBr pellets with a FT – IR 8400S Shimadzu instrument . Electronic spectra were recorded by Spectro Scan 80 D U K. ¹H NMR spectra was measured by using an NMR spectrometer (Bruker ,300 MHz) using TMS as internal standard and d₆–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. Thermo gravimetric measurements were carried out under nitrogen atmosphere using a TGA Q50 V20 ,13 Build39.

SYNTHESIS

Preparation of sodium benzyl- and sodium p-chlorobenzyl dithiocarbamate (dtc1&dtc2).
The method of synthesis these ligands has been reported in previous paper (Atared A.F. 2015).

Synthesis of Dithiocarbamate Metal complexes

An aqueous solution of 1mmol of metal salt and ethanolic solution of 2mmol of sodium dithiocarbamate ligand were mixed with constant stirring . The reaction mixture was stirred with gentle heating for 1hr. The colored precipitate was obtained and collected by filtration . The precipitate was washed several times with a hot mixture of water and ethanol and dried over calcium chloride in a desiccators . other complexes were prepared by the same procedure.

Synthesis of mixed ligand complexes

An aqueous solution of metal salt (1mmol) and ,aqueous solution of 1,10-phenanthroline (2mmol) were mixed with stirring . The ethanolic solution sodium dithiocarbamate ligand (1mmol) was added drop wise with vigorous stirring about 1hr.with gentle heating. The mixture cooled to room temperature , the precipitated complexes were filtered off, washed several times with a hot mixture of water and ethanol and dried. Other complexes were prepared by the same procedure.

Anti-bacterial test

Anti-bacterial test was performed on gram negative bacterial (*Escherichia coli*) and gram positive bacterial (*staphylococcus aureus*) by Agar diffusion method by weighing 2 gm of the extract and adding it to 20 ml of DMSO , then 50ml were taken from this mixture by micro syringe and was put it 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* and *Escherichia coli* separately . The broth was spreaded by L-shape spreader . The petri dishes were incubated at 37⁰C for 15 minutes then incubated with bacterial broth and incubated over night at 37⁰C then the result were recorded. After wards , the zones of inhibition of bacterial growth that appeared around the wells of compounds were examined and the diameters measured and recorded in millimeters (mm).

RESULTS AND DISCUSSION

All the metal complexes are stable and non-hygroscopic in nature, the complexes are generally soluble in water, ethanol, fairly soluble in DMSO, DMF and THF, the Co(II) complexes slightly soluble in dichloromethane. The color of Co(II) complexes are dark brown and the Cu(II) complexes are either green or pale blue.

The analytical data and physical characteristics of metal complexes are listed in table 1.

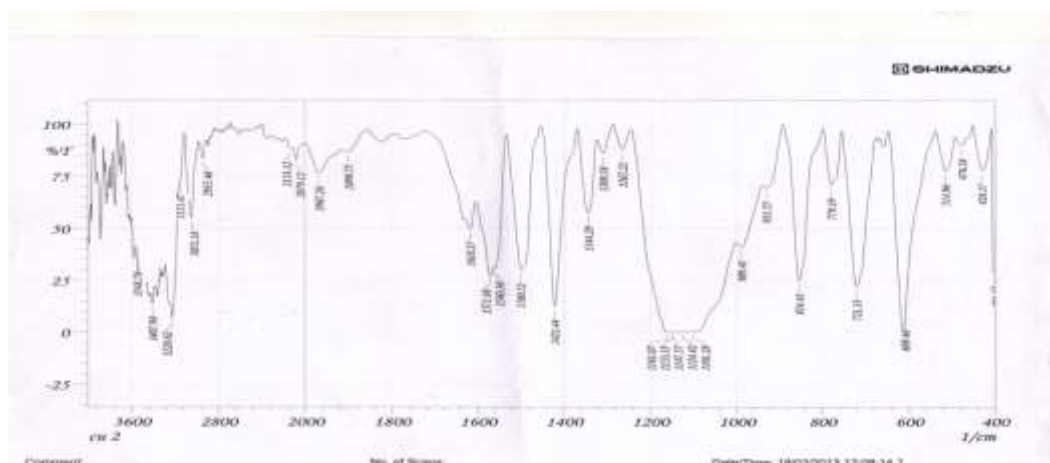
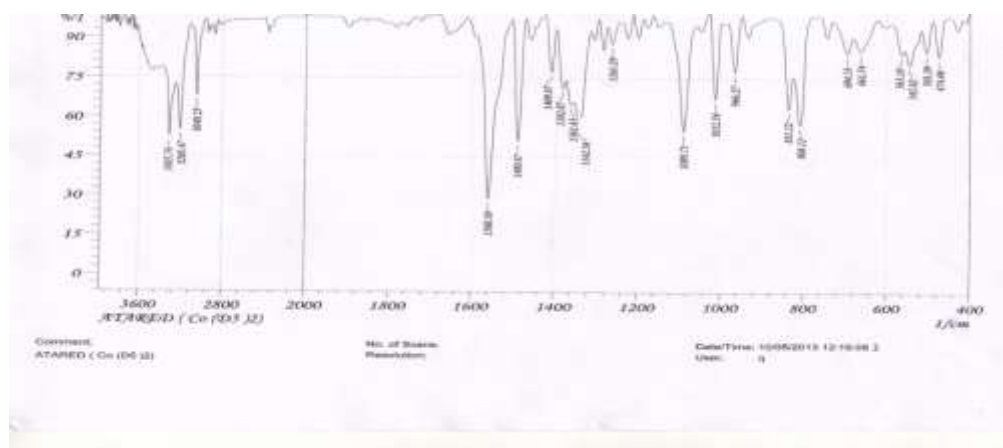
Table (1): Physical and analytical data of synthesized complexes.

No.	Empirical Formula	%yield	Color	m.p (°C)	<i>Elemental analysis found(calcd)</i>		
					<i>C</i>	<i>H</i>	<i>N</i>
(I)	[Co(dtc1)(phen) ₂] Cl.2H ₂ O	50%	dark brown	*112	57.10(57.16)	3.94(4.19)	9.02(10.4)
(II)	[Co(dtc1) ₂ (phen)] 2H ₂ O	53%	dark brown	150-153	52.59	4.41	8.76
(III)	[Co(dtc1) ₂ (H ₂ O) ₂]	55%	dark brown	142-144	41.85(41.84)	3.74(4.18)	6.10(6.08)
(IV)	[Co(dtc2)(phen) (H ₂ O) ₂]Cl	53%	dark brown	122	42.66(42.66)	3.50(4.11)	6.98(7.45)
(V)	[Co(dtc2)(phen) ₂] Cl.2H ₂ O	55%	dark brown	*197	54.20	3.84	9.88
(VI)	[Co(dtc2) ₂]	60%	dark brown	143-145	39.52(39.04)	2.73(2.86)	5.83(5.68)
(VII)	[Co(dtc2)(H ₂ O) ₄] Cl.2H ₂ O	58%	dark brown	93-95	22.65(22.92)	3.91(4.56)	3.13(3.34)
(VIII)	[Cu(dtc1) ₂ (H ₂ O) ₂]	70%	Pale green	*170	41.61(41.40)	3.97(4.34)	6.44(6.04)
(IX)	[Cu(dtc2)(H ₂ O) ₂] 2H ₂ O	66%	Green	*162	34.02(33.78)	3.29(3.89)	5.39(4.96)
(X)	[Cu(dtc2) ₂ (phen)] 2H ₂ O	68%	Green	*263	46.64(47.16)	3.78(3.67)	8.21(7.85)
(XI)	[Cu(dtc1)(dtc2) (H ₂ O) ₂]2H ₂ O	73%	Pale blue	*174	37.08(37.21)	3.92(4.09)	5.81(5.42)

*Decomposition temperature

INFRARED SPECTRA

The relevant bands of sodium dithiocarbamate ligands and their metal complexes are listed in table 2. The dithiocarbamate ligands (dtc1) and (dtc2) exhibited two characteristic bands in the infrared spectra, the first band is due to VC ---N thioureide vibration which is observed at 1502 -1490 cm⁻¹ respectively.

Fig.2(a) IR spectrum of complex $[\text{Cu}(\text{dtc}1)_2(\text{H}_2\text{O})_2]$.Fig.2(b) IR spectrum of complex $[\text{Co}(\text{dtc}2)_2]$

While for all complexes this band appear as a strong band which in the region $1490\text{--}1537\text{ cm}^{-1}$. The shift in VC –N vibration to higher wave numbers is due to mesomeric drift of electron from the dithiocarbamate moiety towards the metal center, increasing the contribution of the thioureid form (Bonati F et al .1967, Manohar A et al. 2006, Aprakasam B A et al 2007 and Nakamoto, 1986).

The second single band which appears at 1026 cm^{-1} and at 1012 cm^{-1} corresponds to VC = S vibration in the dtc1 and dtc2 respectively. The shift to lower frequency in the VC = S band indicating the involvement of sulphur atoms of the ligand in the coordination with Co(II) or Cu(II) metal ions (Singh and Prased, 1998).

In all complexes except (VI) appearance of broad band at $3300\text{--}3500\text{ cm}^{-1}$ and a peak at $948\text{--}956\text{ cm}^{-1}$ indicates the presence of coordinated water molecules (Geary W J, 1971).

Electronic spectral

The electronic spectra of the prepared complexes were recorded in the UV- Visible region using DMF as a solvent. The electronic spectrum of Co(II) complexes exhibit an intense band closed to 325 nm were assigned to the intermolecular charge transfer of the ligand ($\pi - \pi^*$) in the $N - C = S$ group. A moderately intense and broad peak observed at 360 nm may be

due to either metal – ligand or ligand – metal charge transfer and weak bands at 420 and 665 nm are due to d-d transition metal (Ekennia A.C. et al., 2013, Venu G.K. et al., 2013, and Nicholls D., 1975).

The electronic spectrum of Cu(II) complexes showed a strong absorption band at 296nm and moderate band at 315 nm are due to intra ligand $\pi - \pi^*$ and $n - \pi^*$ transition associated with $N - C = S$ and $S - C = S$ groups. A weak bands with a higher wave length region at 448 and 600 nm can be attributed to d- d metal orbital transition.

^1H NMR SPECTRAL STUDIES

Fig (3 a,b) gives the typical NMR spectrum of $[\text{Co}(\text{dtc}2)_2]$ and $[\text{Co}(\text{dtc}1)(\text{phen})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ respectively.

In Co(II) complexes, signal due to N in thioureide band was observed in the region 7.96 - 8.37 ppm. On complexation, the electron density on $-NH$ decreases, the precessional frequency of proton bonded to nitrogen increases, then the signal was shifted to down field region. The multiple signals around 7.08 – 7.66 ppm are ascribed to aromatic protons. The signal observed in the region 4.65 – 4.95 ppm are due to methylene (CH_2) protons. The ^1H NMR data of synthesized Co(II) complexes are listed in table(2).

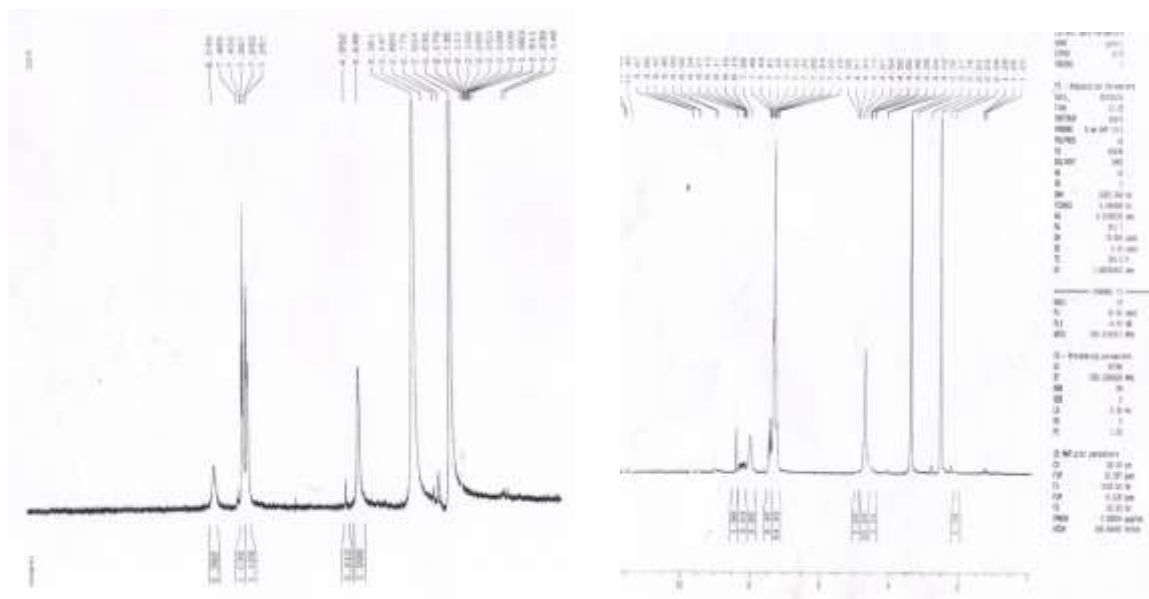


Fig.3(a). ^1H NMR spectrum of complex (VI) Fig.3(b). ^1H NMR spectrum of complex (I)

The broad signal in the range (9.47-10.59) ppm is due to water molecules coordinated to metal ion.

Table (2):IR bands(cm^{-1}) and ^1H NMR data for complexes.

No.	VC $\nu_{\text{Nstr.}}$	VC $\nu_{\text{Sstr.}}$	VN $\nu_{\text{Hstr.}}$	^1H NMR (DMSO- d_6). Tms=0ppm
dtc1	1502	1026	3321	
dtc2	1490	1012	3305	
(I)	1537	1027	3290	4.67(s,2H,CH ₂) ;7.19-7.46(m, Ar-H) ; 7.99(s, N-H).
(II)	1504	1025	3290	4.66(s,2H,CH ₂) ;7.2-7.9(m, Ar-H) ; 8.38(s, N-H).
(III)	1506	1027	3328	4.67(s,2H,CH ₂) ;7.29-7.31(m, Ar-H) ; 7.96(s, N-H).
(IV)	1499	1008	3363	4.95(s,2H,CH ₂) ;7.31-7.66(m, Ar-H) ; 8.37(s, N-H).
(V)	1492	1014	3377	4.95(s,2H,CH ₂) ;7.2-7.5(m, Ar-H) ; 8.38(s, N-H).
(VI)	1490	1012	3305	4.64(s,2H,CH ₂) ;7.26-7.48(m, Ar-H) ; 8.04(s, N-H).
(VII)	1508	989	3325	
(VIII)	1490	1000	3228	
(IX)	1494	995	3309	
(X)	1519	1000	3361	
(XI)	1516	1050	3290	

X-RAY STUDIES OF THE CRYSTAL STRUCTURE OF COMPLEXES:

The crystalline structure of Co(II) complexes [I , III , V and VI] was investigated by using diffraction techniques . The results from the X-ray analysis showed that the precipitated powder of Co(III)complexes which prepared by Sol-gel techniques were poly crystalline . Fig. 4(a and b) shows typical diffraction pattern for [Co(dtc1)(phen)₂]Cl.2H₂O (I) and [Co(dtc1)₂(H₂O)₂] (III) complexes. The average crystallite size of nano- particle calculated using the Deby –Scherrer formula (Cullity B. 1956) are represented in table (3):

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

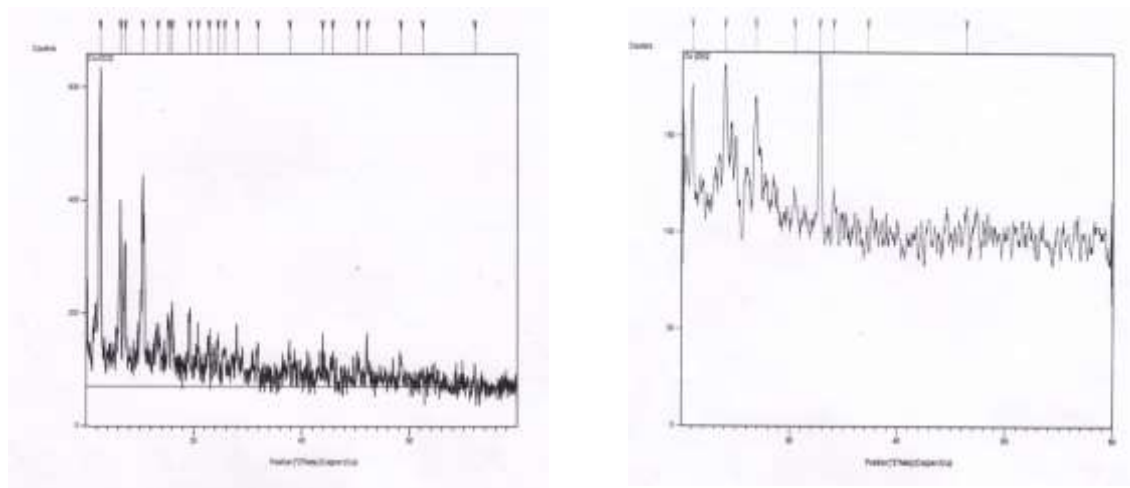


Fig.4(a).X-ray diffraction of $[Co(dtc1)_2(H_2O)_2]$. Fig.4(b).X-ray diffraction of $[Co(dtc2)_2]$

Table (3): The average crystallite size of synthesized Co(II) complexes.

No.	Complexes	Average crystallite size(nm)
I	$[Co(dtc1)(phen)_2]Cl \cdot 2H_2O$	116.53
III	$[Co(dtc1)_2(H_2O)_2]$	121.49
V	$[Co(dtc2)_2]$	88.51
VI	$[Co(dtc2)(H_2O)_4]Cl \cdot (H_2O)_2$	189.21

ANTI BACTERIAL ACTIVITY

The anti-bacterial activity results of metal complexes against Escherichia Coli and Staphylococcus aureus were given in the table (3) .

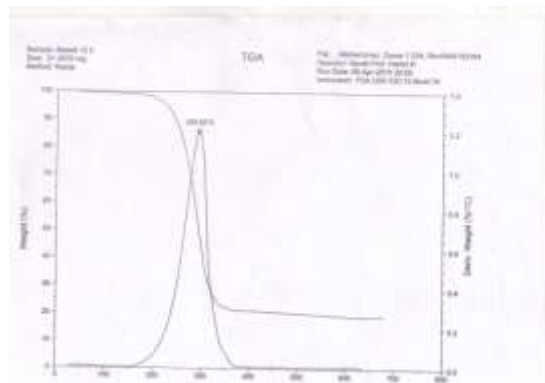
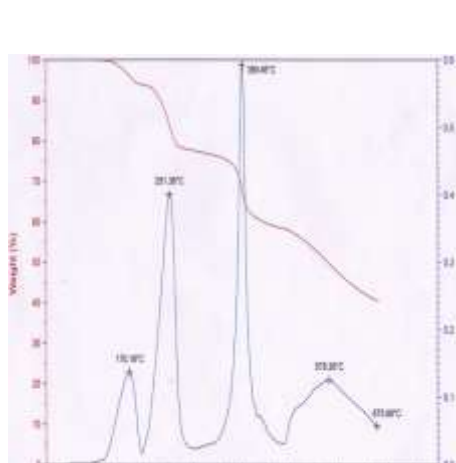
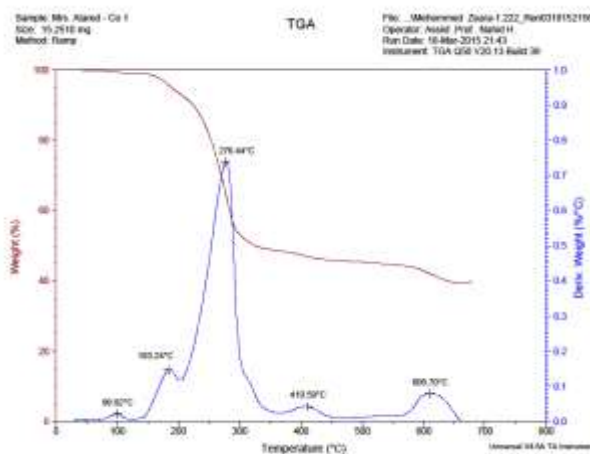
All complexes show selective activity against gram negative bacteria (Escherichia Coli) except complex $[Co(dtc2)(phen)(H_2O)_2]Cl$ (IV) and selective inactivity against gram positive bacteria (Staphylococcus aureus) except complex $[Co(dtc1)(phen)_2]Cl \cdot 2H_2O$ (I), the complexes (II , IV , XI) show very weak activity.

Table (4): Anti-bacterial activities of complexes (zone formation in mm).

No.	Test compounds	Escherichia coli	Staphylococcus aureus
(I)	$[Co(dtc1)(phen)_2]Cl \cdot 2H_2O$	12	10
(II)	$[Co(dtc1)_2(phen)]2H_2O$	20	very weak
(III)	$[Co(dtc1)_2(H_2O)_2]$	10	-ve
(IV)	$[Co(dtc2)(phen)(H_2O)_2]Cl$	-ve	very weak
(V)	$[Co(dtc2)(phen)_2]Cl$	12	-ve
(VI)	$[Co(dtc2)_2]$	14	-ve
(VII)	$[Co(dtc2)(H_2O)_4]Cl \cdot 2H_2O$	12	-ve
(VIII)	$[Cu(dtc1)_2(H_2O)_2]$	14	-ve
(IX)	$[Cu(dtc2)_2(H_2O)_2]2H_2O$	14	-ve
(X)	$[Cu(dtc2)_2(phen)]2H_2O$	14	-ve
(XI)	$[Cu(dtc1)(dtc2)(H_2O)_2]2H_2O$	20	very weak

THERMAL STUDIES OF METAL COMPLEXE

The thermo grams in Figs.5(a & b) were analyzed and several thermal stability parameters were evaluated from TGA and DTG curves for the prepared compounds are listed in table (5).

**a****b****c**

(Fig.5) The thermo gram of **a-** (dtc1) ligand , **b-**complex $[\text{Cu}(\text{dtc}1)_2(\text{H}_2\text{O})_2]$ and **C-** complex $[\text{Co}(\text{dtc}1)(\text{phen})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$.

Table (5):TG/DTG characterization parameters of the thermal decomposition of synthesized complexes:

Complexes	Decomposition Temp. °C	Chare Residue At 600 °C	Temp.of 50% Weight loss °C	Rate of decomp. % / min.
Dtc1	293 one D.T	19%	324	13
Dtc2	262 , 296 two D.T	42%	330	13
[Co(dtc1)(phen) ₂]Cl.2H ₂ O	183,276,410,609 Four D.T	44%	323	19.5
[Co(dtc1) ₂ (H ₂ O) ₂]	280 , 595 Two D.T	29%	288	16
[Co(dtc2)(phen)(H ₂ O) ₂]Cl	215,306, Two D.T	53%	629	9.25
[Co(dtc2)(H ₂ O) ₄]Cl.2H ₂ O	126,194,626 Three D.T	32	312	13.5
[Cu(dtc1) ₂ (H ₂ O) ₂]	170,251,399, 578 Four D.T	47%	580	12
[Cu(dtc2) ₂ (H ₂ O) ₂]2H ₂ O	162,254,395, 418 Four D.T	45%	550	13
[Cu(dtc2) ₂ (phen)]2H ₂ O	161,401,464 Three D.T		<700	20
[Cu(dtc1)(dtc2)(H ₂ O) ₂]2H ₂ O	174,399,483 Three D.T	62%	<700	25

The thermo gram results, show that some of these compounds have two decomposition temperature while the others have three . On the other hand the chare residue of these compounds at 600 °C were more than 30% and some of it has more than 60% , This indicate the thermal stability of these compounds.

Also from the above results there is a good agreement between the theoretical and practical loss of molecules through the stages of decomposition. This phenomena leads to prove the chemical structure of the prepared compounds, Table (6) .

In all complexes the first stage of decomposition is due to loss of coordinated water molecules or the water of crystallization .The second step of mixed ligand complexes involves sub steps which involves loss of phen Molecule and is followed by dithiocarbamate moiety to give M(SCN)₂ and in the final stage forming metal sulphide (MS) as a residue . (Venu K. et al , 2013).

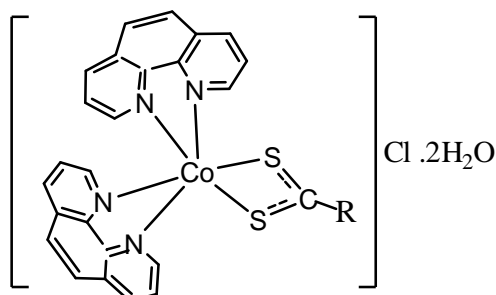
Table (6): Thermo analytical data of metal complexes

Compounds	<i>stage of decomposition</i> <i>type of molecules loss</i>		calculated %	founds%
[Co(dtc1)(phen) ₂]Cl.H ₂ O	Stage one	2H ₂ O+Cl	10.6	9.00
	Stage two	2phen+2H ₂ O	36.00	39.00
[Co(dtc2)(phen)(H ₂ O) ₂]Cl.2H ₂ O	Stage two	4H ₂ O+Cl + Phen	54.00	58.00
[Co(dtc2)(H ₂ O) ₄]Cl.2H ₂ O	Stage one	2H ₂ O	8.5	9.00
	Last stage	formation of CoS	21.5	25.00
[Cu(dtc1) ₂ (H ₂ O) ₂]	Stage one	2H ₂ O	7.7	7.00
			38.00	40.00

	Last stage formation of $\text{Cu}(\text{SCN})_2$			
$[\text{Cu}(\text{dtc}2)_2(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	Stage one	$2\text{H}_2\text{O}$	6.00	6.37
	Stage two	$4\text{H}_2\text{O}$	18.00	15.00
$[\text{Cu}(\text{dtc}2)_2(\text{phen})]2\text{H}_2\text{O}$	Stage one	$2\text{H}_2\text{O}$	5.00	7.50
	Stage two	$2\text{Cl}+2\text{H}_2\text{O}+\text{phen}$	42.77	42.00
$[\text{Cu}(\text{dtc}1)(\text{dtc}2)(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	Stage one	$2\text{H}_2\text{O}$	6.37	8.16
	Stage two	$4\text{H}_2\text{O}+\text{C}_7\text{H}_8$	30.00	25.00

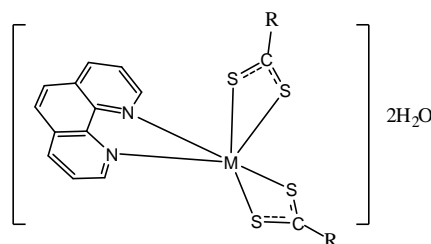
CONCLUSION

$\text{Co}(\text{II})$ and $\text{Cu}(\text{II})$ mixed ligand complexes have been prepared and studied. From the result of chemical analysis an octahedral geometry have been proposed for the mixed ligand complexes which presented in Figs 6(a ,b and c) . These mixed ligand complexes were thermally stable than their parent ligand and than the metal dithiocarbamate complexes , based on thermal gravimetric experiment analysis , in which the ligand decomposed either in a single or two steps whereas the mixed ligand complexes decomposed in two to four steps .



R=benzyl amine or p-Cl benzyl amine

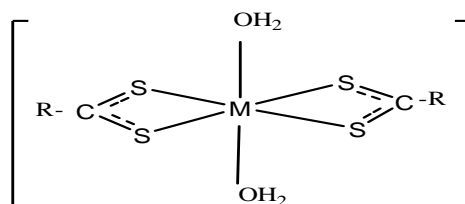
a



M= Co or Cu

R= benzyl amin or p-chloro benzyl amine

b



M=Co or Cu

R=benzyl amine or p-Cl benzylamine

c

Fig.6: The proposed structure of **a**- complex $[\text{Co}(\text{dtc})(\text{phen})_2]\text{Cl}.2\text{H}_2\text{O}$,

b- complex $[\text{M}(\text{dtc})_2(\text{phen})]2\text{H}_2\text{O}$ and **c**- complex $[\text{M}(\text{dtc})_2(\text{H}_2\text{O})_2]$.

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