Synthesis, Structural and Antibacterial Study of Some Metal Ion Dithiocarbamate-Azo Complexes

Thanaa J. Al-Hasani, Mustafa K. Al-Taie*
Department of Chemistry, College of Science, University of Baghdad, Baghdad-Iraq.
* Email: Mustafa5511@yahoo.com

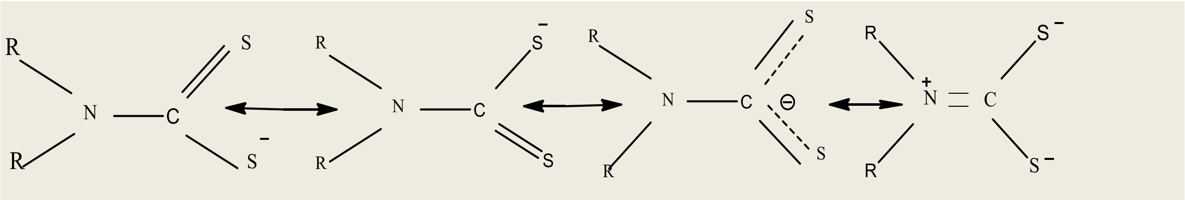
Abstract

Sodium diethyldithiocarbamate (DTC) forms stable colored [$M^{II}(DTC)_2$] complexes where M^{II} = Mn, Fe, Co, Ni, Cu and Zn. The characterization data suggested square planar geometrical structure for Co^{II}, Ni^{II} and Cu^{II} complexes and a tetrahedral structure for Mn^{II}, Fe^{II} and Zn^{II} complexes. Six new complexes of general formula [$M(DTC)_2PAN$] where PAN=1-(2-Pyridyl azo)-2-naphthol, were synthesized by using two different routes of preparation. The structures of the complexes are discussed in relation to the analytical, spectroscopic, magnetic and conductivity data. The DTC-ligand exhibits bidentate behavior acting as S,S`-donors in all complexes. PAN was also behave as bidentate N,N` ligand. The electronic spectra along with magnetic moment values suggested an octahedral structure for [$M(DTC)_2PAN$] complexes. The biological activity for ligands and the prepared complexes were studied against *Escherichia Coli*, *Pseudomonas* (G^-) and *Staphylococcus Aureus, Bacillus* (G^+) bacteria. Some of the complexes have a relatively strong deactivating capacity against the specimen of bacteria. The presence of PAN ligand increased the inhibition zone.

Keyword: Dithiocarbamate, azo complexes, PAN, magnetic moment, N,N` ligand.

1-Introduction

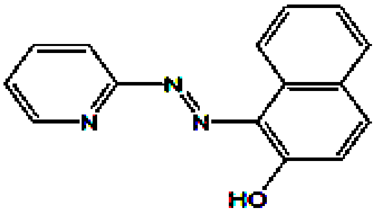
Dithiocarbamates (DTCs) are versatile chelating ligands with application in industry [1], agriculture [2] and biology [3]. Since the DTCs contain nitrogen and sulphur donor atoms they capable of forming complexes with most of the elements [4]. The ($R_2NCS_2^-$) are the semi-amides of dithiocarbonic acid [5]. The structure of these monoanionic 1,1-dithio ligands can described by four resonance structures [5], as shown below :



(a) (b) (c) (d)

Manganese dithiocarbamate complexes are known for all oxidation states 1 to 4, although the nature of manganese (II) complexes, [$Mn(S_2CNR_2)_2$], still remains a topic of some debate [5]. A mixed ligand manganese (II) complexes of the type [$Mn(S_2CNR_2)_2(L)$] (R =Et, C_5H_{10}, C_4H_8O; L = 2,2'-bpy, 1,10-phen), are described as adduct [6]. Iron (II) and iron (III) dithiocarbamate complexes, [$Fe(S_2CNR_2)_2$] and [$Fe(S_2CNR_2)_3$], react with NO to produce [$Fe(NO)(S_2CNR_2)_2$], which are used as trapping agents for the physiologically important molecule [5]. A large number of Co(II) DTCs are also known and have been prepared from a variety of amines [7]. A series of octahedral cobalt (II) dithiocarbamates with bi- and tetradentate N-donor ligands has been reported, these adducts are pyridine, isoquinoline, γ-picoline, 3,5-lutidine,1,10-phenanthroline and ethylenediamine [8]. Nickel (II) –DTC complexes can also form an octahedral arrangements with a series of N-donor ligands such as 1,10-phenanthroline [8]. The reaction has also been studied spectrophotometrically. Most copper (II) bis (dithiocarbamate) complexes contain a square planar copper (II) centre. A number of studies have shown that complexes can be built from simple monomeric units and centro-symmetric dimeric structures which assume the four and five-coordinate geometries with a magnetic moment value of 1.6-1.9 B.M [9]. Zinc (II)-bis (dithiocarbamates) adopt either a monomeric structure or a centro-symmetric dimeric structures in the solid state [5, 7]. The presence of bulky substituents favours monomeric structures.

On the other hand azo compounds are very important class of chemical compounds receiving attention in scientific research. They are as highly colored and have been used as a dyes and pigments [10] and in various applications such medicines, cosmetics, food, paints, plastics and shipbuilding [10,11]. The characteristic feature of each dye in this class is the chromophoric azo group (-N = N-) which form part of the conjugated system and joins two or more aromatic rings [12]. N–heterocyclic azo compounds are among highly sensitive organic reagents, suitable for the spectrophotometric determination of transition metal ions in trace concentrations [10,13]. In this group of reagents, 1-(2-pyridyl azo)-2-naphthol (PAN) is the most sensitive and promising reagent for determination of many metal ions, including lanthanides [14].



PAN

In view of analysis above interesting survey, we report here the synthesis, spectral characterization and biological activity studies of new M^{II}-DTC-PAN complexes, where M^{II} = Mn, Fe, Co, Ni, Cu, Zn, and DTC =diethyldithiocarbamate. The preparation was held on either by the reaction of PAN with the previously prepared $[M(DTC)_2]$,or, by the direct reaction of the metal salt with DTC and PAN.

2- Experimental

2-1: Physical measurements

The C.H.N.S analysis were performed at Campbell Microanalytical Laboratory, University of Otago, New Zealand "PerkinElmer 2400 series II CHNS/O Elemental Analyzer". The molar conductivity measurements were obtained using "P.W – 9528" Digital Conductometer "HANA H19812 pH/EC/TDS Meter". Magnetic susceptibility was measured at room temperature on a Gouy balance using (Auto Magnetic Susceptibility Balance Sherwood Scientific). Melting point were measured using "Stuart Melting Point Apparatus". The percentage of metal in complexes were performed by flame (Nova AA – 350, Analytik Jena) Atomic Absorption Spectrophotometer. The UV–Vis spectra in ethanol as 10^{-4} or 10^{-3} M in the range 200-1100nm, were measured using (Shimadzue, UV–1800) Ultraviolet–Visible Spectrophotometer. The FTIR spectra were recorded as KBr disc in the range 4000-400cm^{-1} for the ligands and as CsI disc in the range 4000-200 cm^{-1}for the complexes using (Shimadzue, FTIR 8400 S).

2-2: Preparation of $[M(DTC)_2]$

An aqueous solution of (5ml) (0.001 mole) metal salt $MnCl_2.4H_2O$ 0.1979gm (BDH), $(NH_4)_2Fe(SO_4)_2.6H_2O$ 0.2924gm (Merck), $CoCl_2.6H_2O$ 0.2379gm (Merck), $NiCl_2.6H_2O$ 0.17049 gm (M & B), $CuCl_2.2H_2O$ 0.2377gm (Aldrich) or $ZnCl_2$ 0.1362gm (B.D.H), was added dropwise to an aqueous solution (35ml) of 0.450gm (0.002mole) of sodium diethyldithiocarbamate (Aldrich). The reaction mixture was stirred at room temperature for 2-3 hours. The formed colored precipitate was filtered, washed with water then with 1:1EtOH/ water mixture and dried at 50^0C.

2-3: Preparation of $[M(DTC)_2PAN]$ Complexes

These complexes were synthesized by two ways:-

2-3-1: By the Addition of DTC and PAN solutions to Metal Salts Solution (Direct method)

A solution mixture of 0.450 gm (0.002 mole) DTC dissolved in distilled water (35ml) and ethanolic solution (45ml) of 0.24927gm (0.001mole) PAN (Fluka) was added to an aqueous solution (5ml) of (0.001mole) metal salts, $MnCl_2.4H_2O$ 0.197gm, $(NH_4)_2Fe(SO_4)_2.6H_2O$ 0.292gm, $CoCl_2.6H_2O$ 0.23793gm, $NiCl_2.6H_2O$ 0.2771gm or $ZnCl_2$ 0.1362gm. The reaction mixture was stirred at room temperature, the formed colored precipitate, filtered off, washed with water, then with 1:1 EtOH /water mixture and dried at 50 ^{0}C.

2-3-2 By the Reaction of $[M(DTC)_2]$ complex with PAN(Indirect method)

An ethanolic solution (45ml) of 0.24627gm (0.001 mole) PAN was added to ethanolic solution (45ml) of (0.001mole) $[Mn(DTC)_2]$ 0.351gm, $[Fe(DTC)_2]$ 0.3523gm, $[Co(DTC)_2]$ 0.3555gm, $[Ni(DTC)_2]$ 0.3553gm or $[Zn(DTC)_2]$ 0.3619gm as a 1:1 $[M(DTC)_2]$: PAN ratio. The solution mixture was stirred for (1-2) hours. Colored precipitate was formed, filtered off, washed several times with water then with ethanol and dried at 50^{0}C.

2-4: Antibacterial activity

Biological activity of compounds in 10^{-4} DMSO were measured using four types of bacteria *Escherichia Coli*, *Pseudomonas* (G^-) and *Staphylococcus Aureus* ,*Bacillus* (G^+) bacteria.

3-Results and discussion

The reaction of the metal salts with the ligands may be depicted by the following equations

$MCl_2.nH_2O + 2NaDTC \rightarrow M(DTC)_2 + 2NaCl + nH_2O$

M^{II} = Mn, Co, Ni, Cu, Zn, n= 4,6,6,2,0 respectively.

$(NH_4)_2Fe(SO_4)_2.6H_2O + 2NaDTC \rightarrow Fe(DTC)_2 + Na_2SO_4 + (NH_4)_2SO_4 + 6H_2O$

All the complexes were stable in air and not hygroscopic, soluble in most organic solvents. The analytical and spectral studied data, suggest a molecular formula $[M(DTC)_2]$ for all prepared complexes. The CHNS elemental analyses were in a good agreement with the above suggested formula. The molar conductivity measurements of 10^{-4} M in ethanol and DMF displayed zero or low values for Λm supporting the neutral behavior of these complexes, Table (1).

There is a wide spread controversial about the geometrical structure of M-DTC complexes in the literature, especially for Mn^{II}, Fe^{II} and Cu^{II} complexes [9] the suggested structures were not confirmed by convincing analytical data. The investigation data obtained in this work has revealed that all the prepared M^{II}-DTC complexes have four coordination geometrical structure, they are either square planar or tetrahedral, thus, these complexes are capable to extend their coordination number.

New complexes of M^{II}-DTC-PAN have been obtained by two different methods, the direct method which was represented by the direct reaction of the metal salts with both ligands in a mole ratio of 1:2:1 M:DTC:PAN.

$MCl_2.nH_2O + 2NaDTC + PAN \rightarrow [M(DTC)_2PAN] + nH_2O + 2NaCl$

M^{II}= Mn, Co, Ni, Zn n= 4,6,6,0 respectively.

$(NH_4)_2Fe(SO_4)_2.6H_2O + 2NaDTC + PAN \rightarrow [Fe(DTC)_2PAN] + 6H_2O + Na_2SO_4 + (NH_4)_2SO_4$

and the indirect method which was represented by the addition of PAN to the previously prepared $[M(DTC)_2]$ complexes in a 1:1 ratio according to the following reaction equation.$[M(DTC)_2] + PAN \rightarrow [M(DTC)_2PAN]$

Many attempts have been made for the reaction of Cu^{II}-DTC with the PAN. No reaction was obtained by the two methods. This is may be due to the disability of Cu^{II} ion to extend its coordination number with these type of ligands or because of the polymeric structure of the $[Cu(DTC)_2]$.

The final study results suggests that each complex prepared by the two methods has the same properties and formula. All the prepared complexes are dark colored, air-stable, insoluble in water and soluble or partially soluble in most organic solvents. Fair solubility was achieved in DMF and DMSO. Some of physical and analytical data were tabulated in Table 1. The elemental analysis support the chemical formula $[M(DTC)_2PAN]$ for all complexes. The low values of Λ_m for 10^{-4}M DMF solution of these complexes at 25^{0}C indicate the non-electrolyte behavior of these complexes.

3-1: Electronic spectra

The UV-Vis spectra of the ligands and their complexes of 10^{-4} M solution in ethanol were recorded. The DTC spectrum showed three peaks at 205nm (48780cm^{-1}), 258nm (38760cm^{-1}) and 291nm (34364cm^{-1}). These peaks assigned to the intra-molecular intra-ligand transitions corresponding to ($\pi \rightarrow \pi^*$) of the N– C=S system, ($\pi \rightarrow \pi^*$) of the S–C=S group and ($n\rightarrow \pi^*$) located on sulphur respectively [15]. On the other hand PAN ligand spectrum exhibits two peaks at 225nm (44444cm^{-1}) and 304nm (32895cm^{-1}) which assigned to the moderate ($\pi \rightarrow \pi^*$) transitions of the aromatic rings. A third high intense λmax peak was observed at 464nm (21552cm^{-1}) which was related to the ($\pi \rightarrow \pi^*$) transition of intermolecular charge-transfer taken place through the azo group (-N=N-). Another peak was also observed as a shoulder at (410-415) nm may be attributed to ($n \rightarrow \pi^*$) transition.

The electronic spectrum of [Mn(DTC)$_2$] complex showed peak at 351nm (28490 cm^{-1}) belong to charge transfer, another two weak peaks were observed at 909nm(11001cm^{-1}) and 487nm (20534cm^{-1}) assigned to the $^6A_1\rightarrow{}^4T_{1(G)}$ and $^6A_1\rightarrow{}^4T_{2(G)}$ transitions respectively support the tetrahedral structure of this complex. The magnetic moment of 5.693B.M. confirm the tetrahedral structure of [Mn(DTC)$_2$] [16]. The UV–Vis spectra for the prepared [Mn(DTC)$_2$PAN] complex showed three peaks at 552nm (18115cm^{-1}), 520nm (19230cm^{-1}) and 398nm (25125cm^{-1}) assignable to $^6A_1g \rightarrow {}^4T_1g$ (G), $^6A_2g \rightarrow {}^3T_1g$ (G) and $^6A_2g \rightarrow {}^3T_2g$ (P) transitions, respectively,[17]. The magnetic moment of the complex, 5.897 B.M is an additional evidence for an octahedral structure.

The UV-Vis spectrum of the [Fe(DTC)$_2$] complex represented by the presence of a weak split peak at 583nm (17153cm^{-1}) and 505nm (19802cm^{-1}) which belongs to $^5E_{(D)}\rightarrow{}^5T_{2\ (D)}$ transition[16]. The magnetic moment 4.782B.M. is within the range of high- spin tetrahedral Fe(II) complexes. The magnetic moment of [Fe(DTC)$_2$PAN] complex has been found to be 4.753 B.M, which is within the range of values corresponding to high-spin octahedral complexes of iron(II). The λmax which belongs to the ($\pi \rightarrow \pi^*$) transition of PAN ligand,465nm (21505cm^1), was shifted by about 40nm to higher wave length and appeared at 504 nm (19841cm^{-1}) the other peak at 769 nm(13003cm^{-1}) was assigned to the electronic transition type $^5T_2g \rightarrow {}^5E_1g$ [18].

The electronic spectrum of [Co(DTC)$_2$] complex showed only one peak at 634 nm(15773cm^{-1}) which is a result of the typical $^4A_2g\rightarrow{}^4T_1g$ transition for square planar complexes [19]. The magnetic moment of 1.82B.M support the presence of one unpaired electron in the outer shell of Co(II) ion in complex and this confirm the suggested square planar geometry of [Co(DTC)$_2$]complex. The magnetic moment of [Co(DTC)$_2$PAN] complex was found to be 3.30 B.M which indicate a high-spin d^7 octahedral geometry. The electronic spectra also support the octahedral symmetry around Co(II) and this represent by presence of the split peak at 624nm (16025cm^{-1})and 581nm (17211cm^{-1}) which are tentatively assigned to ^4T_1g (F) $\rightarrow {}^4T_2g$ (F) and ^4T_1g (F) $\rightarrow {}^4A_2g$ (F) transitions respectively [18].

The UV-Vis spectrum of [Ni (DTC)$_2$] complex exhibited two d-d transition peaks at 552nm (18116cm^{-1}) and 627nm (15949cm^{-1}) which were ascribed to the $^1A_1g\rightarrow{}^1B_2g$ and $^1A_1g\rightarrow{}^1A_2g$ transitions. The appearance of two d-d transition peaks in addition to the diamagnetic character of this complex, which was represented by zero value of the magnetic moment will verify the square planar structure of this complex [20]. The electronic spectrum of [Ni(DTC)$_2$PAN] complex revealed three absorptions appeared at 917nm (10905cm^{-1}) belongs to the ^3A_2g (F) $\xrightarrow{\upsilon_1}$ ^3T_2g , 608nm (16447cm^{-1}) assignable to ^3A_2g (F) $\xrightarrow{\upsilon_2}$ ^3T_1g (F) and 390 nm (25641cm^{-1}) assigned to^3A_2g (F) $\xrightarrow{\upsilon_3}$ ^3T_1g (P) transition. In this spectrum, Figure 1, it is clear that the ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) of PAN ligand are shifted to higher wave length and appeared at 524 nm (19083cm^{-1}) and 562nm (17794cm^{-1}) respectively. The peak at 324 nm (30864cm^{-1}) was related to charge transfer transition. The magnetic moment value of 2.743 and 2.941B.M. for Ni^{II} complexes ,prepared by the two methods, is in a good agreement for the suggested high-spin octahedral symmetry [21].The UV-Vis spectrum of [Cu(DTC)$_2$] complex exhibited two d-d transition bands at

433nm (23095cm^{-1}) and 653nm (15314cm^{-1}) which were ascribed to the $^2B_1g \rightarrow {}^2A_1g$ and $^2B_1g \rightarrow {}^2E_2g$. These two transitions are belongs to a square planar structure. The magnetic moment of this complex was 1.923B.M [5], which can be discussed in terms of C.F.T.

The UV-Vis spectrum of [Zn(DTC)$_2$] complex showed no d-d bands as expected for d^{10} complexes because of no empty d-orbitals. In the spectrum of the [Zn(DTC)$_2$PAN] complex, the shift of the λmax peak of PAN ligand, which belongs to ($\pi \rightarrow \pi^*$) transition, is very clear. The peak suffered bathocromic shift with splitting by about (50-80)nm the complex is diamagnetic and likely to be octahedral [18].

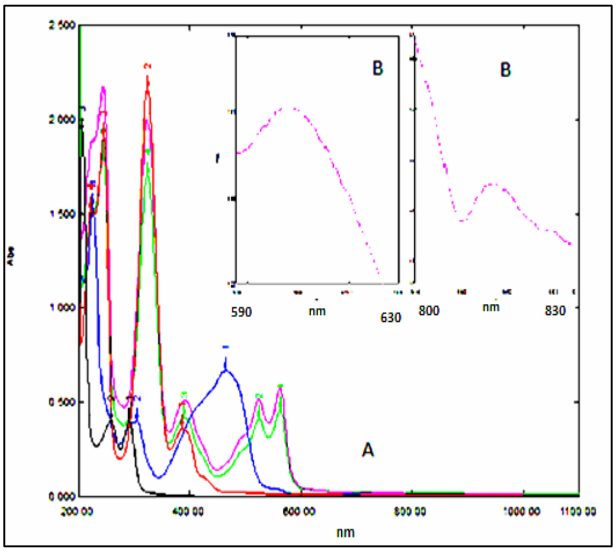


Fig.(1) UV-Vis spectra of (A) 10^{-4} M ethanolic solution of DTC (---), PAN (---), [Ni(DTC)$_2$] (---),[Ni(DTC)$_2$PAN] method(1) (---), [Ni(DTC)$_2$PAN] method (2) (---), (B) 10^{-3} M ethanolic solution of [Ni(DTC)$_2$PAN].

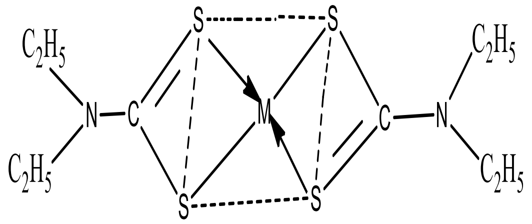
3-2: FTIR Spectra

The important IR bands of the ligands and their complexes are listed in Table (3). The stretching frequency of the υ(C – N) band for the free dithiocarbamates was intermediate between the stretching frequencies associated with typical single and double-bonded carbon and nitrogen atoms [22]. The υ(**C**⎓**N**) was appeared in the diethyldithiocarbamate spectrum as a doublet at 1477 and 1456 cm^{-1} and it was shifted toward higher frequencies in all $[M(DTC)_2]$ complexes and in all $[M(DTC)_2PAN]$ complexes. Another characteristic stretching frequency in DTCs spectra is the ν(**C**⎓**S**) which usually appear in the range 950-1050cm^{-1} [22], this band appeared in the IR spectrum of diethyl dithiocarbamate as a very strong band at 985cm^{-1} and it appears as a singlet and it suffers a high shift in all complexes spectra. A single strong absorption band in this region is indicative of the symmetrical bidentate coordination of the ligands as mention in introduction (structure c and d in page 1).

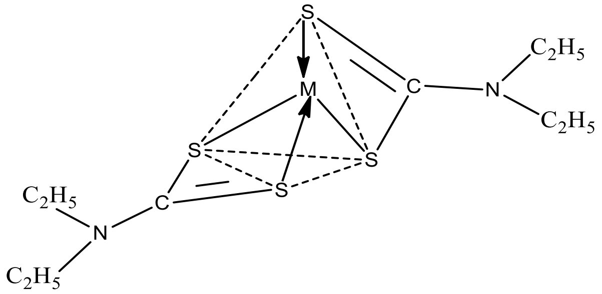
The spectra of all $[M(DTC)_2PAN]$ complexes show band in the region 3404-3470 cm^{-1}this band was assigned to the uncoordinated protonated OH group frequency. This band was not existed in the vibrational spectra of free PAN ligand which must be appeared in the range (3570-3450)cm^{-1} [23]. The absence of this band in the free ligand spectra is due to the azo- hydrazo tautomeric form in this molecule[14].

The most characteristic band in the PAN spectrum is the ν (**N**=**N**) which appeared at 1402 cm^{-1}. This band was shifted to lower frequency by (~29cm^{-1}) on complexation giving a good indication for the participation of this group in the coordination with metal ion. Many other bands belongs to azo stretching modes such as the ν (**C-N=N-C**), δ(C-**N=N**) and ν (**N**=**N**) were showed many changes in the complexes spectra Table 3. Far IR spectra of the complexes revealed new bands assignable to ν (**M-S**), ν (**M-N$_{py}$**) and ν (**M-N$_{azo}$**) modes.

Thus, on the basis aforesaid arguments the following tentative structures may be assigned for the prepared complexes.



M^{II}= Ni, Co, Cu



M^{II}= Mn, Fe, Zn

Fig.(2) The suggested square planar and tetrahedral geometrical structures of the $[M^{II}(DTC)_2]$ complexes.

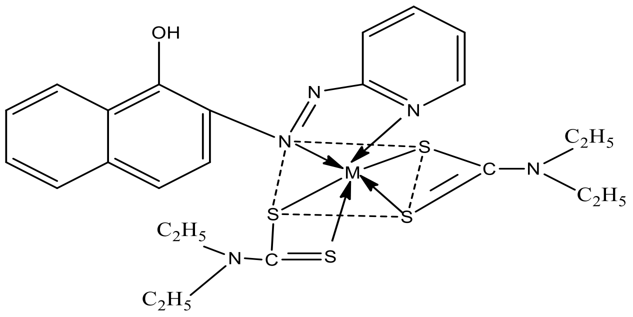


Fig.(3) The suggested Octahedral structures of $[M^{II}(DTC)_2PAN]$ complexes. M^{II}=Mn,Fe,Ni,Co,Zn.

3-3: Antibacterial Activity

The biological activity for the ligands and all the prepared complexes were studied against four selected types of bacteria *Escherichia Coli, Pseudomonas* (Gram negative) and *Staphylococcus Aureus* and *Bacillus* (Gram positive). DMSO was used as a solvent and as a control. The concentrations of the compounds in this solvent were (1×10^{-4} M). The Disc Sensitivity Test method was used, The incubated was held for 24hr at 37^0C. Table 4 listed the deactivation capacity against the bacteria specimen of the prepared compounds under study. The results revealed that most of the metal complexes are potentially more active in comparison with the ligands. The improved activity of metal complexes can be explained on basis of chelation theory. This theory explains that a decrease in the polarizability of the metal could enhance the lipophilicity of the complexes, which leads to a breakdown of the permeability of cells, resulting in interference with normal cell processes [3]. In general, the presence of PAN ligand in the DTC-complexes increase the inhibition zone.

Table (4) Diameters (cm) of bacteria deactivation of the ligands and their complexes.

Compound	*E.Coli*	*Pseudomonas*	*Bacillus cereus*	*Staphylococcus aureus*
DMSO	-	-	-	-
DTC	1.2	1.1	-	-
PAN	1.3	1.2	1.4	1.7
$[Mn(DTC)_2]$	1.6	1.6	-	-
$[Fe(DTC)_2]$	1.4	1.7	1.3	-
$[Co(DTC)_2]$	1.2	1.2	1.3	-
$[Ni(DTC)_2]$	1.4	1.3	-	-
$[Zn(DTC)_2]$	1.3	1.4	1.2	-
$[Cu(DTC)_2]$	-	-	-	-
$[Mn(DTC)_2PAN]$	1.6	1.7	-	-
$[Fe(DTC)_2PAN]$	1.9	1.8	-	1.2
$[Co(DTC)_2PAN]$	1.5	1.5	1.3	1.3
$[Ni(DTC)_2PAN]$	1.9	1.4	1.3	-
$[Zn(DTC)_2PAN]$	1.8	1.8	1.3	1.3

Conclusion

All the $[M(DTC)_2]$ complexes responded to the increasing of their coordination number except Cu^{II}-DTC complex. Stable, colored, non-electrolyte complexes has been obtained by reaction of S,S and N,N ligands . The Uv-Vis and the magnetic susceptibility measurements suggested high-spin octahedral structure for the MII-DTC-PAN complexes, while the IR spectral data indicate the existence of the protonated OH in the PAN ligand which strongly verify the neutral bidentate behavior of the PAN ligand. The inhibition zone of Gram (+) and Gram (-) bacteria recorded increasing by the addition of PAN to the M-DTC complexes

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الخلاصة

إن ليكاند ثنائي ثايوكاربامات الصوديوم (DTC) كون معقدات ملونة مستقرة من نوع $[M^{II}(DTC)_2]$. حيث ان M(II)= Mn ، Fe، Co ، Ni، Cu ، Zn. نتائج التشخيص لهذه المعقدات اقترحت الشكل المربع المستوي لمعقدات Co^{II} ، Ni^{II}، Cu^{II} شكل رباعي السطوح لمعقدات Mn^{II} ، Fe^{II} ، Zn^{II}. ستة معقدات جديدة تمتلك الصيغة العامة $[M^{II}(DTC)_2PAN]$، حيث PAN = 1-(2-بريديل ازو)-2- نفثول، حضرت باستخدام طريقتين مختلفتين للتحضير. ان الصيغة المقترحة لهذه المعقدات تمت

بالاعتماد على النتائج التحليلية والطيفية فضلا عن قياسات الحساسية المغناطيسية والتوصلية الكهربائية. لقد سلك ليكاند DTC سلوكا ثنائي السن مانح من نوع S,S` في جميع المعقدات، كذلك فان PAN ايضا سلك سلوكا ثنائي السن مانح من النوع N,N. إن الاطياف الالكترونية وقيم العزم المغناطيسي اقترحت الشكل ثماني السطوح للمعقدات المحضرة. لقد درست فعالية المضادات البكتريولوجية لليكاندات والمعقدات المحضرة ضد اربع انواع من البكتريا ايشريشيا كولاي *Escherichia Coli* و بسيدوموناس *Pseudomonas* موجب الغرام ستافيلاكوكوس اوريوس *Staphylococcus Aureus* و باسيلاس *Bacillus* سالب الغرام البعض من المعقدات كانت استجابته واضحة وبشكل فعال ضد البكتريا كما ان وجود الـ PAN اسهمت في زيادة الفعالية لهذه المعقدات.