

Synthesis and Spectroscopic Study of Some Metal Transition Amino Organic Compounds with N-(2-Oxo-1,2-Dihydropyrimidin-4-ylcarbamoethyl) Acetamide (DPA)

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A New ligand, N-(2-oxo-1,2- Dihydropyrimidin-4- ylcarbamoethyl) Acetamide (DPA) was prepared by reaction of iso thiocyanate derivative with Cytosine. The ligand has been characterized through elemental analysis, H1 NMR, C13NMR, FT-IR, and UV Visible spectra, such ligand's transition metal complexes have been characterized through conductivity measurement, FT-IR, UV Visible spectra and magnetic susceptibility, all the complexes of this ligand are solid crystal and molar ratio (2:1) (ligand: metal). The form of molecular for these complexes octa hedral. The general formula $[M(DPA)_2Cl_2]$, where $M+2 = (Mn, Co, Ni, Cu, Zn, Cd, Hg)$.

Keywords: Cytosine, acetyl chloride, transition metals.

INTRODUCTION

Cytosine It is a pyrimidine derivative, and one of the nitrogenous bases found in ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) with a chemical formula of $C_4H_5N_3O$. Pyrimidine is an aromatic heterocyclic moiety containing nitrogen atom at 1st and 3rd positions and play an important role to forms the central core for different necessity of biological active compounds [1]. DNA base pairing in motifs other than the well-known Watson-Crick structure have been under thorough study in recent years, where in particular the G-quadruplex and i-motif structures have received considerable attention [2]. In Watson-Crick base pairing, it forms three hydrogen bonds with guanine [3]. In the cytosine-tetrad there is a very large central cavity suitable for cation recognition, but the complexes adopt a non-planar structure unsuitable for stacking, except possibly for ions with very large radii [2]. Were also studied synthesis and characterization of mixed Ligand complexes of cytosine, and thiocyanate with some transition metal ions Co (II), Ni(II), Cu(II), Zn(II) and Cd(II) [4]. A research took place where new Mixed-Ligand Complexes of Cytosine and Its Silver Nanoparticles: Spectral, Analytical, Theoretical and Biological Activity Studies were done [4] cv. Synthesis, structural characterization, DFT calculations, biological investigation, molecular docking and DNA binding of Co(II), Ni(II) and Cu(II) nanosized Schiff base complexes bearing pyrimidine moiety [5]. Ligand was prepared and characterized by elemental analysis, H1nmr, C13nmr, conductivity measurements, IR and UV-visible spectroscopy and cyclic voltametric [6] [7]. The aim of this work is prepare new ligand N-(2- oxo-1,2- Dihydropyrimidin-4- ylcarbamoethyl) Acetamide (DPA) and it's metal complexes with Mn^{+2} , Co^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} , and Hg^{+2} .

Experimental Chemicals: Metal salts ($HgCl_2$, $MnCl_2 \cdot 4H_2O$, $CdCl_2 \cdot H_2O$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, also $ZnCl_2$) have been acquired from fluka, Mercke, cytosine, Acetyl chloride and ammonium thiocyanate BHD, Merk and Fluka.

Preparation of the Ligand (DPA)

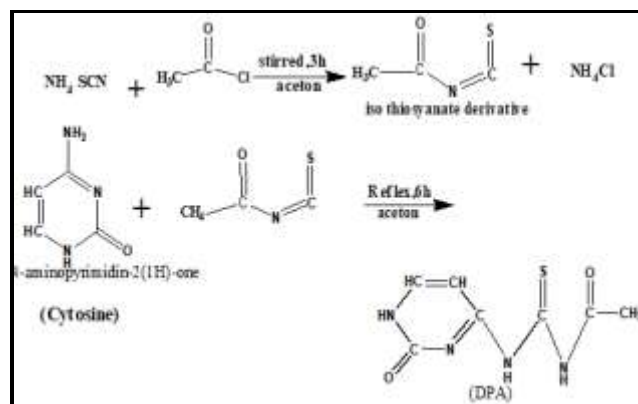
Preparation of the Acetyl Isothiocyanate: Mixture of acetyl

chloride (1.86ml, 26mmol) then dissolved ammonium thiocyanate (2g, 26mmol) in (25ml) of acetone mixed the two solution and stirred about 3 hours.

Preparation of N-(2-Oxo-1,2-Dihydropyrimidin-4-ylcarbamoethyl) Acetamide

Dissolved (2.93g, 26 mmol) of the cytosine in (25ml) acetone then filtered the former solution above cytosine solution, refluxed the mixture for (6 hours) and let it to dry. The product is yellow, and it was recycled with ethanol yield (65%), M. P°C (190-192), C % found (39.56) calc. (39.6), H % found (3.55) calc. (3.77), N % found (26.62) calc. (26.41), S % found (14.95) calc. (15.09) the suggested formula ($C_7H_8N_4O_2S$), as shown in scheme (1)

Preparation Of The Complexes: (0.43g, 2mmole) of the ligand (DPA) was dissolved in (25ml) of Ethanol and added to solution (10ml) of (1 mmole) metal salt ($MnCl_2 \cdot 4H_2O$, $ZnCl_2$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $CdCl_2 \cdot H_2O$ and $HgCl_2$) (0.2g, 0.14g, 0.24g, 0.24g, 0.17g, 0.20g and 0.27g) respectively. The mixture was at 25°C for 6 hours, the precipitate was collected by filtration, washed with water-ethanol



Scheme 1: synthesis of ligand (DPA)

Table 1: Some of properties of (DPA) and its metal complexes

Formula	Color	M.W g/mol	M.Pc°	Yield (%)	Elemental analysis (%) calc. (found)				
					C	H	N	S	M
$C_7H_8O_2N_4S$ (DPA)	Yellow	212.04	190-192	65	39.6 (39.56)	3.77 (3.55)	26.41 (26.62)	15.09 (14.95)	
$[Mn(DPA)_2 Cl_2]$	Brown	550.018	242 d	61	30.54 (30.50)	2.908 (2.73)	10.18 (10.075)	11.63 (11.48)	9.988 (10.12)
$[Co(DPA)_2 Cl_2]$	Deep Blue	554.01	235 d	78	30.324	2.88	10.11	11.55	10.636 (11.334)
$[Ni(DPA)_2 Cl_2]$	Deep Yellow	553.773	275 d	73	30.33	2.889	10.112	11.56	10.59 (10.71)
$[Cu(DPA)_2 Cl_2]$	brown	558.62	265 d	57	30.074 (29.56)	2.864 (2.466)	10.024 (9.745)	11.456 (11.12)	11.73 (12.02)

[Zn(DPA) ₂ Cl ₂]	Light yellow	560.45	220 d	55	29.975	2.854	9.99	11.419	11.66 (11.54)
[Cd(DPA) ₂ Cl ₂]	white	507.48	247 d	69	33.104 (32.56)	3.1528 (3.073)	11.034 (11.12)	12.611 (12.33)	22.15 (21.55)
[Hg(DPA) ₂ Cl ₂]	white	695.68	230 d	54	24.149	2.299	8.0496	9.199	28.84

RESULTS AND DISCUSSION

FT-ir spectral data for ligand (dpa): FT-IR spectrum of cytosine fig (1) detected the band at ν (3383) cm⁻¹ which due to ν (N-H) also another band at ν (3174) cm⁻¹ could be attributed to ν (N-H₂) group [8]. The FT-IR spectrum of ligand (DPA), Fig (2) showed a band at ν (3109) for ν (N-H), strong band at ν (1662) for ν (C=O amide) and another band at ν (1215) cm⁻¹ ν (C=S) (10) show in table (2)

Table 2: The characteristic infrared band in cm⁻¹ for cytosine and ligand (DPA)

Compound	ν (N-H)	ν (N-H ₂) Asym.	ν (C=O) Amide	ν (C=S)
cytosine	3383	3174		
DPA	3109		1662	1215

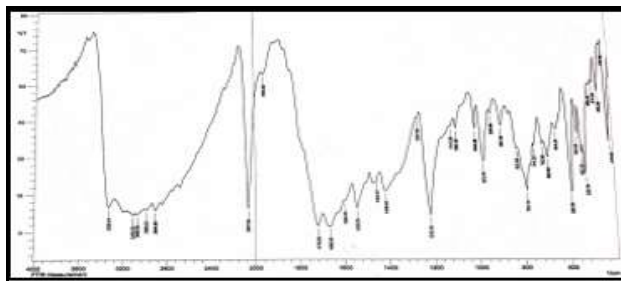


Figure 1: FT-IR for cytosine

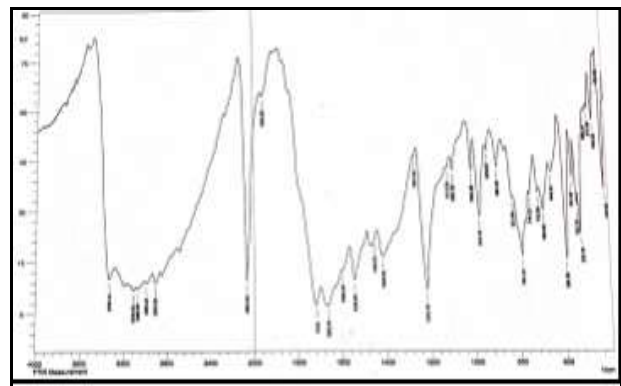


Figure 2: FT-IR for (DPA)

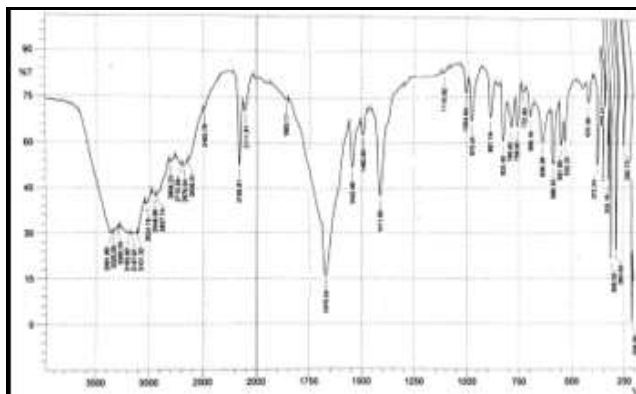


Figure 3: FT-IR spectrum for complex [Ni(DPA)₂Cl₂].

The spectra of all prepared complexes exhibited marks difference between bands belonging to the stretching vibration of ν (C=O amide) in the range between (1542-1656)cm⁻¹ shifted to lower frequencies by ν (138-24)cm⁻¹ suggesting of the possibility of the coordination of ligand through oxygen atom at the carbonyl group [9], while the band caused by ν (C=S) appeared between (1002-1652) cm⁻¹ shifted to lower frequencies by (213-437)cm⁻¹ which indicates to the coordination ligand through the (S) atom at the thion group to the central ion(8081). The stretching vibration band ν (N-H) either show change in their frequencies between (3093-3118)cm⁻¹ there for indicating do not coordinate to the metal ion [10]. M-O, M-S and M-Cl bonds are confirmed by the presence of the stretching vibration of around (422-470) cm⁻¹, (329-393)cm⁻¹ and (235-293)cm⁻¹ respectively [11-14].) show in table (3)

Table 4 1: H-NMR data for the ligand (DPA) in DMSO-d₆ and chemical

Symbol	PPM	Signal	No.Of Protons	Group
a	2.03	Duoblet	3H	CH ₃ , Methyl
b	2.12	Singlet	1H	NH, Amine
c	5.95	Singlet	1H	CH, Ethylene
d, d'	7.94	Singlet	1H	NH, secamide
e	8.46	Singlet	1H	CH, Ethylene

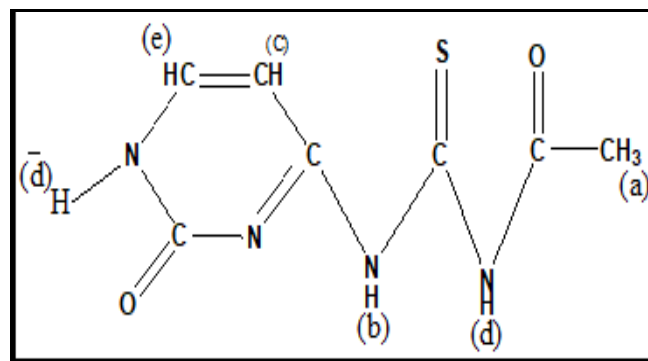


Figure 4: Structure of ligand (DPA)

¹H-NMR Spectral of ligand(DPA):-¹H-NMR Spectral of ligand (DPA) Fig (5) in (DMSO - d₆)

Showed the following signals, doublet peak at δ (2.03) ppm singlet peak at δ (5.95) ppm for (1H ,CH ,Ethylene) , singles peak at δ (7.94) ppm for (1H , NH , secamide) , singles peak at δ (8.46) ppm for (CH , Ethylene) table(4)

for (3H , CH₃ , Methyl) singlet peak at δ (2.12) ppm for (NH (Amide) singles peak at δ (2.51) ppm for (DMSO)

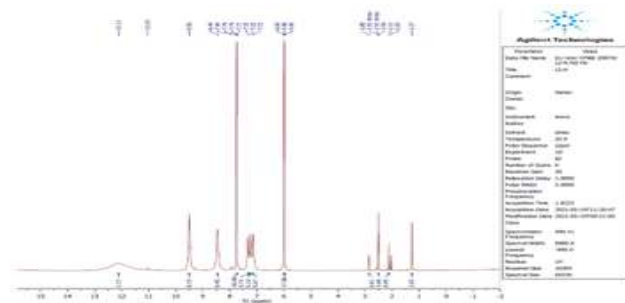


Figure 5: ¹H-NMR spectrum for ligand (DPA)

Table 3: The characteristic infrared band for free ligand (DPA) and its metal complexes.

Compound	$\nu(\text{N-H})$	$\nu(\text{C=O})$ Amide	$\nu(\text{C=S})$	$\nu(\text{M-O})$	$\nu(\text{M-S})$	$\nu(\text{MCl})$
DPA	3109	1662	1215			
[Mn(DPA) ₂ Cl ₂]	3118(m)	1625(w)	1002(w)	472(w)	393(w)	235(w)
[Co(DPA) ₂ Cl ₂]	3093(m)	1656(m)	1110(w)	470(w)	366(m)	235(w)
[Ni(DPA) ₂ Cl ₂]	3101(m)	1542(m)	1110(w)	422(w)	372 (w)	283(w)
[Cu(DPA) ₂ Cl ₂]	3101(m)	1575(w)	1080	422(w)	372(w)	287(w)
[Zn(DPA) ₂ Cl ₂]	3109(w)	1649(s)	1103(m)	424(w)	351(w)	283(w)
[Cd(DPA) ₂ Cl ₂]	3100(m)	1652(s)	1137(m)	460(w)	366(w)	252(w)
[Hg(DPA) ₂ Cl ₂]	3109(w)	1649(s)	1103(s)	424(w)	329(m)	293(w)

¹³C - NMR Spectral of ligand (DPA): ¹³C - NMR Spectral of ligand (DPA) Fig (7) in (DMSO - d₆) Showed the following , signal peak at δ (25.57) ppm for (CH₃) signals peak at δ (39.38 - 40.38) ppm for (DMSO) , signal peak at δ (93.27) ppm for (CH₂, Ethylene) and signals peak at δ (147.09) ppm for (CH₂, Ethylene) , signal peak at δ (148.74) ppm for (C=O, Amide) , signals peak at δ (161.20) ppm for (C=N , I mine) , signal peak at δ (168) ppm for (C=O , Amide) and signal peak at δ (177.01) ppm for (C=S) table(5)

Table 5: ¹³C-NMR data for the ligand (DPA)

Symbol	PPM	Group
a	25.57	CH ₃
b	93.27	CH ₂ , Ethylene
c	147.09	CH ₂ , Ethylene
d	148.74	C=O , Amide
e	161.20	C=N, I mine
f	168	C=O , Amide
g	177.01	C=S

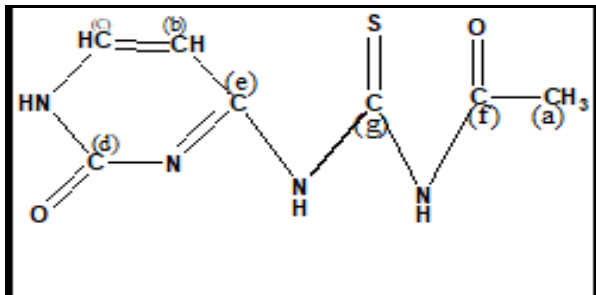


Figure 6: Structure of ligand (DPA)

Magnetic Properties for the Metal Complexes: Magnetic moment (M_{eff}) with regard to complexes related to Mn⁺²(d⁵), also Co⁺²(d⁷) have been indicated (5.87) B.M, also (4.97)B.M, that in anticipated spin-only values Higher value related to μ_{eff} of Ni⁺²(d⁸) complex (2.89) B.M because of orbital contributions. Magnetic moment μ_{eff} related to Cu⁺²(d⁹) complex indicated (1.74)B.M in expected value to one electro [15]

Molar Conductivity (DPA): Molar conductivity of the ligand (DPA) with some their metal complexe

Table 6:

Compound	Molar conductivity (sec.cm ² .mol ⁻¹)
DPA	1.12
[Mn(DPA) ₂ Cl ₂]	5.81
[Co(DPA) ₂ Cl ₂]	5.34
[Ni(DPA) ₂ Cl ₂]	3.12
[Cu(DPA) ₂ Cl ₂]	3.89
[Zn(DPA) ₂ Cl ₂]	11.74
[Cd(DPA) ₂ Cl ₂]	10.33
[Hg(DPA) ₂ Cl ₂]	12.11

in DMSO solvent, the non-electrolyte behavior of these complexes. And some of properties shown in table (5)

Spectra for Ligand (DPA): The UV-Vis Spectra yellow of ligand

(DPA) and its complexes recorded in the table (6), the ligand (DPA) in (DMSO) exhibits two peak, Fig (8) at (36231) and (27700) which are retunes to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition.

[Mn (DPA)₂Cl₂] complex: The deep yellow complex of Mn (II), shows bands at (36101) cm⁻¹, (27855) cm⁻¹ and (11261) cm⁻¹ which are retunes to the electronic transition intra- ligand L.F, 6A_{1g}→4T_{2g}(G) and 6A_{1g}→4T_{1g}(G) respectively [16,17] .

[Co (DPA)₂Cl₂] complex: The deep green complex of Co (II), shows bands at (35842) cm⁻¹, (27777) cm⁻¹, (14771) cm⁻¹ and (10604) cm⁻¹ retunes to the electronic transition intra- ligand L.F, 4T_{1g}(F)→4T_{1g}(g) with mix C.T, 4T_{1g}→4A_{2g} and 4T_{1g}→4T_{2g} respectively, the repulsion parameter (B-) value is found to be (715.7) cm⁻¹, while β is equal to (0.74) [18].

[Ni (DPA)₂Cl₂] complex: The green complex of Ni (II), Fig (9) shows bands at (35971) cm⁻¹, (27700) cm⁻¹, (12674) cm⁻¹ and (10593) cm⁻¹ retunes to the electronic transition intra- ligand L.F, 3A_{2g}→3T_{1g}(p) with mix C.T, 3A_{2g}→3T_{1g}, and 3A_{2g}→3T_{2g} respectively, the repulsion parameter (B-) value is found to be (573) cm⁻¹, while β is equal to (0.55) [19].

[Cu (DPA)₂Cl₂] complex: The brown complex of Cu (II), Fig (10) shows bands at (35842) cm⁻¹, (25905) cm⁻¹ and (11286) cm⁻¹ retunes to the electronic transtion intra- ligand L.F, C.T and 2E_g→3T_{2g} respectively [20, 21].

[Zn (DPA)₂Cl₂] complex: The light yellow complex of Zn (II), shows bands at (35842) cm⁻¹, and (27700) cm⁻¹ retunes to the electronic transtion intra- ligand L.F and C.T respectively [22].

[Cd (DPA)₂Cl₂] complex: The white complex of Cd (II), shows bands at (35971) cm⁻¹ and (27777) cm⁻¹ retunes to the electronic transtion intra- ligand L.F and C.T respectively [22].

[Hg (DPA)₂Cl₂] complex: The white complex of Hg (II), show band at (36101) cm⁻¹ and (27855) cm⁻¹ retunes to the electronic transtion intra- ligand L.F and C.T respectively [22]

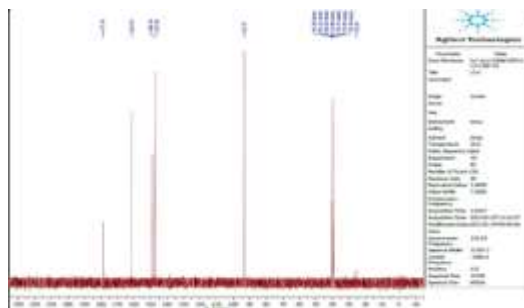
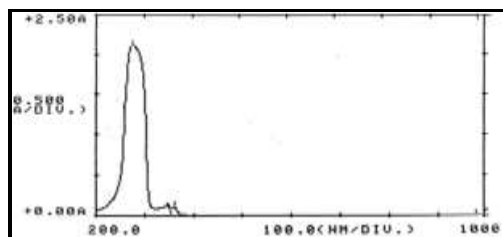
Figure 7: C¹³-NMR spectrum for ligand (DPA)

Figure 8: UV-Visible spectrum for ligand (DPA)

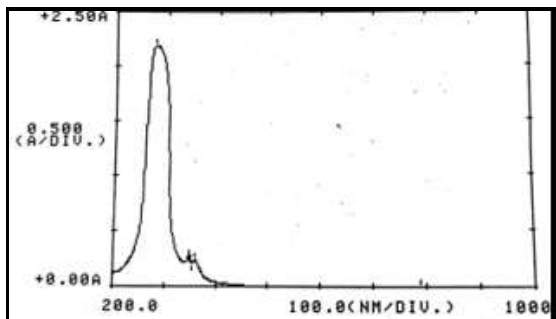
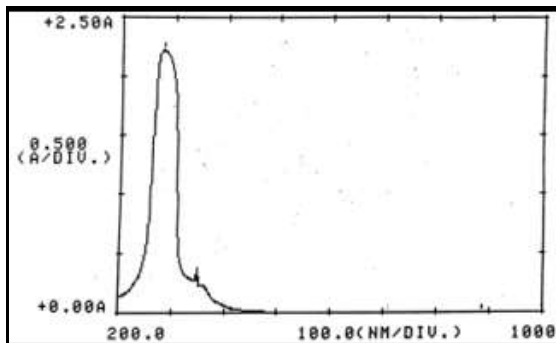
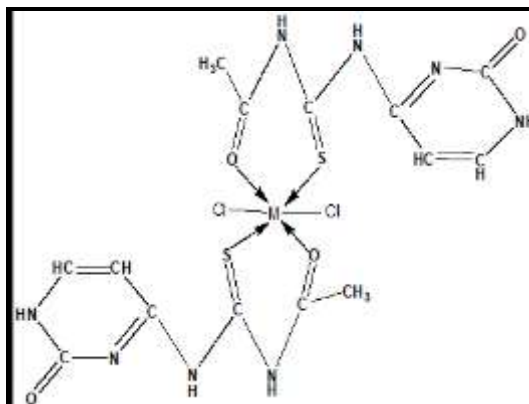

 Figure 9: UV-Visible spectrum for [Ni (DPA)₂Cl₂]

 Figure 10: UV-Visible spectrum for [Cu (DPA)₂Cl₂]


Figure 11: 3D The proposed molecular structure of (DPA)

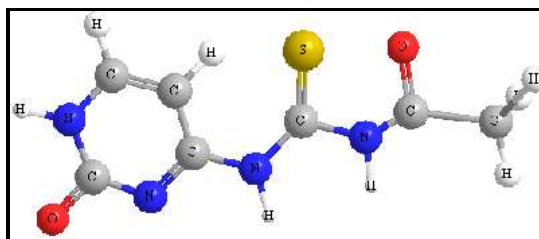

 Scheme 2: General suggested geometry of the complexes [M (DPA)₂Cl₂].

Table 6: The electronic transitions and structure geometries of (DPA) and its complexes

Compounds	(nm)	ABC	v-(cm ⁻¹)	E _{max}	Transitions
DPA	276	2.117	3621	2117	π→π*
	361	0.112	27700	112	n→π*
[Mn(DPA) ₂ Cl ₂]	277	2.230	36101	2230	L.F
	359	0.322	27855	322	C.T
	888	0.030	11261	30	6A1g→4T2g(G) 6A1g→4T1(G)
[Co(DPA) ₂ Cl ₂]	279	2.205	35842	2205	L.F
	360	0.176	27777	176	4T1g(f)→4T1g(p)
	677	0.143	14771	143	4T1g→4A2g
	943	0.030	10604	30	4T1g→4T2g
[Ni(DPA) ₂ Cl ₂]	278	2.192	35971	2192	L.F
	361	0.225	27700	225	C.TMix
	789	0.025	12674	25	3A2g → T1g (P)
	944	0.018	10593	18	3A2g→3T1g(F) 3A2g→3T2g(F)
[Cu(DPA) ₂ Cl ₂]	279	2.222	35842	2222	L.F
	386	0.354	25905	250	C.T
	886	0.018	11286	18	2Eg→2T2g
[Zn(DPA) ₂ Cl ₂]	279	2.205	35842	2205	L.F
	361	0.294	27700	294	C.T
[Cd(DPA) ₂ Cl ₂]	278	2.205	35971	2205	L.F
	360	0.294	27777	294	C.T
[Hg(DPA) ₂ Cl ₂]	277	2.247	36101	2247	L.F
	359	0.411	27855	411	C.T

CONCLUSION

A new ligand in the presented study was prepared through reaction from the Acetyl isothiocyanate with Cytosine, ligand has been characterized through elemental micro analysis C.H.N.S., FTIR, UV Vis also ¹H, ¹³C-NMR spectra. Ligand's metal complexes have been prepared, also characterized through FT-IR, UV Vis spectra, magnetic measurements, conductivity measurements, the suggested geometrical structure with regard to complexes have been octahedral geometry.

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