Syntheses new legend [4(-dimethylamino)benzaldehyde (5-phenyl-1.3.4-oxadiazole-2-yl)hydrazone] with some transition metal complexes

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Abstract: Anew ligand [4(-dimethylamino)benzaldehyde(5-phenyl-1.3.4-oxadiazole-2-yl)hydrazone] (L) and its Cr(III),Fe(III) Co(II), Ni(II)and Cu(II) complexes were synthesized. The authenticity of the ligand and its transition metal complexes were established by elemental analyses, conductance and magnetic susceptibility measurements, as well as spectroscopic (IR, 1HNMR, mass). . It may be concluded that the ligand coordinate through Nitrogen atoms as shown in figure (3). for all the complexes. The ligand acts as a didentate ligand coordinating through the oxadiazole nitrogen $[N^{11}]$ and the nitrogen atom of shiff bace $[N^{13}]$. This view is further supported by the appearance of a band corresponding to the metal-nitrogen stretching vibration at 503-597 cm⁻¹ in the complexes. The magnetic studies suggest an tetrahedral and octahedral geometry of the complexes .the Ni and Cu atoms leading to the formation geometry .Octahedral tetrahedral geometry proposed was for the(Cr(III),Fe(III)andCo(III)prepared complexes

1. Introduction

1, 3, 4-Oxadiazole derivative are the heterocyclic that have received considerable attention during the last two decades, They found in number of pharmaceutical applications [1-4] several compounds are known as antimicrobial agents [5–7], Some of these compounds have also analgesic, antiinflammatory, anticancer, anti-HIV agent, antiparkinsonian and antipriliferative agent [8,9,10,11,12]. Some material applications of 1,3,4-oxadiazole derivatives lie in the field of liquid crystals[13], PVC stabilizers [14-16]1,3,4-Oxadiazole derivatives are also among the most widely employed electron conducting and hole blocking (ECHB) materials in organic light-emitting diodes (LEDs).. Although some types of metal complexes have found to be good emitters and or excellent electron transporters with excellent thermal properties.

2.1 Preparation of the ligand

The new ligand [4(-dimethylamino)benzaldehyde(5-phenyl-1.3.4-oxadiazole-2-yl)hydrazone] (Scheme 1) was prepared as follows:

A mixture of methyl benzoate(13.6g, 0.1mole) and hydrazine hydrate (0.2mole, 10ml) dissolved in ethanol (50mL)[14] was refluxed on a water bath for 3 hr, The resultant mixture[A] was concentrated and the white solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 80 %, m. p. 147-149C.

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A mixture of [A](0.05mol, 6.8 g) ,KOH (0.05mol, 2.8 g) in 100ml ethanol and CS2 (0.05mol , 3mL)was refluxed on a water bath for 8 hr, until the evolution of H₂S gas ceased [17,18]. The excess CS₂ was removed under reduced pressure. The resultant mixture[B] was acidified with acetic acid and the white solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 80 %, m. p. 204-206 °C.

A mixture[B] (0.05mol, 8.9 g) and hydrazine hydrate (0.07mole, 3.8ml) dissolved in ethanol (50mL) was refluxed on a water bath for 3 hr ,until the evolution of H_2S gas ceased. The excess CS_2 was removed under reduced pressure. The resultant mixture[C] was concentrated and the light pink solid which separated was filtered and recrystallised from ethanol. The purity of the compound was followed by TLC on precoated silica gel. Yield: 73 %, m. p. 170-168C.

A mixture[C] (0.02mol, 3.52 g) and 4-(dimethylamino) benzaldehyde (0.02mole, 2.98ml) dissolved in ethanol (50mL) was refluxed on a water bath for 3 hr, . The resultant mixture[ligand] was concentrated and the yellow solid which separated was filtered and recrystallised from ethanol.



2.2 Preparation of complexes

The Cr(III), Co(III), Fe(III), Ni(II) and Cu(II) complexes were prepared by refluxing the respective hydrated metal chloride (1 mmol) in 15 mL ethanol with 50 ml of an ethanolic solution of the ligand (1 mmol,



0.3 g) for 4 hr. The resultant solids which separated were filtered, washed with ethanol and dried in air.

2.3 Measurements

Elemental C, H and N analysis were carried out on a Thermofinigan flash analyzer, the FTIR spectra in the range (4000-200) cm-1 were recorded as CsI discs using a Shimadzu FTIR spectrophotometer, molar conductance measurements were made in anhydrous DMSO at 25 °C using Inolabcond 720,.The 1H nuclear magnetic resonance spectra were recorded on a Mercury-300BB NMR 300 spectrometer, relative to the internal standard tetramethylsilane (TMS) , DOSO-d6 used as solvent. Melting points were determined in open capillary tubes using an electro thermal melting point /SMP3I apparatus. Mass spectra were recorded in the range (0-800) m/e on a 5973 network mass selective detector .

3. RESULTS & DISCUSSION

The purity of the ligand and its complexes were checked by TLC using silica gel-G as adsorbent., elemental analysis tabulated in Table (1), Melting point ,magnetic susceptibility, physical properties and molar conductance of all the compounds studied are tabulated in Table (2).. The calculated values were in a good agreement with the experimental values.

Experimental			Theoretical			
C%	H%	N%	C%	H%	N%	
65.97	5.2	22.1	66.34	5.5	22.79	

Table 1. Analitical data for the ligand

Table 2. conductance, physical properties and magnetic data of the ligand and its complexes

	Compound	Molecular	Color		Melting	µef f
No	-	formula		Scm ²	Point	B
				mol ⁻¹		
1	Ligand	$C_{17}H_{17}N_5O$	Yellow			
			pale			
2	[Cr(L)2Cl2]Cl	CrC ₁₇ H ₁₇ N ₅ OCl ₃	brown	33.4	200-202	3.5
3	[Fe(L)2Cl2]Cl	FeC ₁₇ H ₁₇ N ₅ OCl ₃	Pale rose	25.6	177-179	5.9
4	[Co(L)2Cl2]Cl	CoC ₁₇ H ₁₇ N ₅ OCl ₃	Pale	27.9	18189	4.6
			brown			
5	[Ni(L) Cl2]	NiC ₁₇ H ₁₇ N ₅ OCl ₂	Dark	10.2	199-201	2.7
			yellow			
6	[Cu(L) Br2]	CuC ₁₇ H ₁₇ N ₅ OBr ₂	Pale rose	11.8	222-223	1.6



3.1 Infra-Red Spectroscopy

The FTIR spectrum for L shows a characteristic stretching absorption bands at 3238cm^{-1} , 1647 cm^{-1} , 1307 cm^{-1} and 1452 assigned to (N-H) group ,C=N of the oxadiazole ring, asymmetrical C-O-C, symmetrical C-O-C stretching respectively. The C=N and N-N stretching vibrations are important to predict the bonding mode of the ligand ,these bands shift lower wavelength in the spectra of complexes compare with ligand, observed changes are the evidences of complexion had happened . The IR data of the complexes are shown in Table (3) and figure(1-2). The Table lists the stretching frequency () for some of the characteristics groups exhibited by the ligand and complexes.

NO	Compound	N-H	C=N	C-O- C Asy	C-O- C sy	M-N	M- Br	M-Cl
L	$C_{17}H_{17}N_5O$	3238	1647	1307	1452			
1	[Cr(L)2Cl2]Cl	3290	1446	1363	1466	567		231
2	[Fe(L)2Cl2]Cl	3280	1620	1389	1498	505		314
3	[Co(L)2Cl2]Cl	3268	1605	1319	1492	503		304
4	[Ni(L) Cl2]	3292	1621	1319	1489	599		300
5	[Cu(L) Br2]	3286	1639	1386	1492	597	290	

Table 3: Characteristic absorption bands of ligand and its complexes

3.2 Nuclear Magnetic Resonance

The data of proton NMR of the ligand [4(dimethylamino)benzaldehyde

(5-phenyl-1.3.4-oxadiazole-2-yl)hydrazone] displayed good solubility in DMSO. The proton nuclear magnetic resonance spectral data gave additional support for the composition of the ligand. The spectra also exhibit a singlet $-CH_3$ peaks at 3.3 ppm due to methyl group, anther peaks exhibit at 5.3 ppm due to singlet -NH. the aromatic ring exhibit peaks at (8.7-6.8)ppm .the proton NMR of the ligand shown in figure(6)

3.3 Mass spectra:-

The mass spectrum of the ligand exhibits a molecular ion peak [M0] at m/z 307,the ligand spectra shows fragment ion peak at m/z 77 due to phenyl ring ,the spectra shows another peaks at m/z(119,145,160,187 and 204) due to(C7H5NO),(C8H5N2O),C8H6N3O),(C9H7N4O)and (C10H12N4O) respectively as shown in(Fig.7).



The mass spectrum of the complex [Cr(L)2.Cl2]Cl shows a molecular ion peak at m/z [M0] 773 which is equivalent to molecular mass of the complex. This complex shows another a fragment ion peak with loss of chlorine atom at m/z 738. the ligand spectra shows fragment ion peak with loss two chlorine atom at m/z (767,702) due to (Cr(L)2Cl)and (Cr(L)2) respectively. the ligand spectra shows fragment ion peak at

m/z (512,272) due to (CrC6H4N8 O2)and CrC22H24N10 O2) respectively .

The mass spectrum of the complex [Cr(L)2.Cl2]Cl shows a molecular ion peak at m/z [M0] 780,the spectrum shows another peaks at m/z 747,646,407 and 240.

The mass spectrum of the complex [NiLCl2] shows a molecular ion peak at m/z [M0] 436, This complex shows another a fragment ion peak with loss of chlorine atom at m/z 401, the spectrum shows another peaks at m/z 203,191 and 168.

On the basis of the preceding discussion, the structure of the complexes suggested as follows in scheme(2)below.



Analytical and spectra data (1H NMR,IR, mass spectra) of all synthesized compounds were in full agreement with the proposed structure.

4.conclution.

The ligand [4(-dimethylamino)benzaldehyde(5-phenyl-1.3.4hydrazone] was successfully synthesized. The ligand oxadiazole-2-yl) was treated to different transition metal salt to afford the corresponding

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complexes. It may be concluded that the ligand coordinate through Nitrogen atoms as shown in figure (3). This view is further supported by the appearance of a band corresponding to the metal–nitrogen stretching vibrationat 503–597 cm⁻¹ in the complexes[19]. the Ni and Cu atoms leading to the formation tetrahedral geometry .Octahedral geometry was proposed for the(Cr(III),Fe(III)and Co(III) prepared complexes.

تم تحضير بعض معقدات العناصر الانتقالية (Cr(III), Co(III), Ni(II) and Cu(II) العناصر الانتقالية (Cr(III), Fe(III), Co(III), Ni(II) and Cu(II) مع اليكاند

[4(-dimethylamino)benzaldehyde(5-phenyl-1.3.4-oxadiazole-2-

yl)hydrazone]. حست الصيغ التركيبية لليكاند ومعقداته باستخدام تقنية تحليل الحساسية المغناطيسية والتوصيل المولاري بالاظافة ا

إلى استخدام أطياف الأشعة تحت الحمراء,أطياف الرنين النووي المغناطيسي وطيف الكتلة. الاستنتاج بان اليكاند هو ثنائي السن ويحصل التناسق من خلال ذرة النيتروجين لحلقة الاوكسادايازول وذرة النيتروجين لمجموعة(C=N) وهذا الاستنتاج يؤكد من خلال تشخيص حزم (503-503) عائدة إلى تناسق الذرة المركزية مع ذرة النيتروجين.

المغناطيسية ساهمت في تأكيد الهيئة الفراغية لكل من النيكل الثنائي والنحاس الثنائي بانها رباعي السطوح بينما اظهر الحديد الثلاثي,

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Figure (2) Electrostatic potential 2D and total charge density fo the ligan



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Figure (4) IR spectrum of the ligand cm^{-1} [Cr(L)₂Cl₂]Cl

Figure(5) IR spectra of



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Figure(6) NMR spectra of the ligand



Figure (7) mass spectra of ligand



Figure (8)mass spectra of ligand-Fe



Figure (8) mass spectra of [Cr(L)₂Cl₂]Cl





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