Synthesis and characterization of p-phenylenediamine N,N-butan-3- one oxime ligand and its complexes with some transition metals ions Ni (II) , Pd(II) , Pt(II) , Cu(II) and Co(II)

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Abstract

A new ligand incorporating a dioxime moiety, p-phenylenediamine-N N-butane-3-one oxime, (H_2L) has been prepared by reacting 1,4- phenylenediamine with 2,3- butanedionemono oxime. The ligand has been characterized by elemental analysis , i.r. ,u.v.-vis. , ^{1}H n.m.r and EI mass spectroscopies . The ligand reacted with some metal ions to give complexes of the general formulae : $[M(HL)]^+$, where M= Ni(II) ,Pd(II) Pt(II) ,Cu(II) and Co(II) . The complexes were characterized by elemental analysis (C.H.N and A.A) along with i.r. u.v.- vis , spectroscopies , molar conductance and magnetic moment measurements , indicating a 1:1 metal : ligand ratio , and the metal ions are coordinated with ligand via N atoms of oxime and imine nitrogen atoms (C= N) .

According to the above measurements , we concluded :

A square planar geometry was proposed for Ni () , Pd () , and Pt() complexes and a distorted tetrahedral geometry is proposed for Cu() , and Co(complexes .

Keywords: dioxime , phenylenediamine , new ligands.

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Introduction

The complexes of transition metals with oxime ligands have been extensively studied in recent years [1,2] . Chelating ligands containing oxime group have been the subject of many investigations during the last three decades[3,4] . The biological importance of oximes and their complexes is of great interest [5-10]. Different oximes and their metal complexes have shown notable bioactivity as chelating therapeutics , drugs , inhibitors of enzymes and as intermediates in the biosynthesis of nitrogen oxides [11,12]. The aim of this work is to study the coordination of metal ions with more than one oxime group ligands which may give stable chelate complexes that may may be used in pharmaceutical application [13-15] .

Experimental

^{1}H-n.m.r spectrum of the ligand was recorded on a Jeol EX270 MHz spectrometer . DMSO-d6 was used as solvent . Chemical shifts () are reported in (ppm) relative to Me4Si, using the solvent signal as internal reference . C,H and N contents were determined micro analytically on a Hewlett Packard 85 CHN analyzer , and metal contents of the complexes were determined by atomic absorption (A.A) technique using a shimadzu AA680G atomic absorption spectrophotometer .I.r. spectra were recorded as (KBr) discs using a Pyeunicom SP3-3005 and a Perkin-Elmer 1720 X series, FTIR spectrophotometer . Electronic spectra were recorded in the region (200-1100) nm for 10^{-3} M solutions in DMF AT 25 using a shimadzu , 160 spectrophotometer. Mass spectrum of the ligand were obtained by Electron-Impact (EI) on a shimadzu GC MS QPA spectrometer. Magnetic measurements were recorded on a Bruker BM6 instrument at 298 K following the Faradys method . Electrical conductivity measurements of the complexes were recorded at 25 for 10^{-3} M solutions of the samples in (DMSO) using a PV 9526 digital conductivity meter . All chemicals were of the highest quality available and used as received . Diacetylmonoxime was prepared according to a method reported in the literature[16,17].

Synthesis of the [H_2L] Ligand

1,4-phenylenediamine (5.4 g, 50 mmol) and 2,3- butenedione monoxime (10.2 g , 100 mmol) were mixed together in absolute ETOH (50 cm^3). After stirring for 3 h. at room temperature , the solution was boiled under reflux for 3 h. The resulting red solution was filtered while hot and concentrated slowly . As this solution cooled, a brown crystalline product precipitated. This product was isolated by vacuum filtration , washed with ETOH and dried in air to give a brown solid crystals yield 10 g (74%) . M.P. 185 .

Synthesis of (H2L) Complexes

[Ni (HL)] Cl. H_2O

A solution of NiCl2. 6H2O (0.2 g , 0.84 mmole) in absolute methanol (10 ml) was added to the ligand solution (0.23 g, 0.84 mmole) in (20 ml) of methanol , and this mixture was refluxed with stirring for 2h. The resulting pink precipitated was filtered off, then washed with methanol and Et2o respectively . Then the pink solid product dried under vacuum to give 0.1 g (70%) yield of the title compound , m.p. 282 .

[Pd (HL)] Cl

An identical work-up procedure using $PdCl_2$ (0.15 g, 0.84mmole) to give 0.21 g (65%) yield of the title complex as a yellow solid , m.p. 296 .

[Pt (HL)] Cl.H_2O

An identical work-up procedure using K_2PtC_{l4} (0.35 g, 0.84 mmole) to give 0.25 g (62%) yield of the title complex as a dark brown solid m.p. 320 .

[Cu (HL)] Cl.H_2O

An identical work-up procedure using $CuCl_2.2H_2O$ (0.14 g , 0.84 mmole) to give 0.24 g (77%) yield of the title compound as a green solid , m.p. 265 c .

[Co (HL)] Cl.H_2O

An identical work-up procedure using $CoCl_2.2H_2O$ (0.2 g , 0.84 mmole) to give 0.33 g (79%) yield of the title complex as a dark green , m.p. 255 .

Results and discussion

The ligand (H_2L) was prepared by reacting 1,4-phenylenediamine with diacetylmono oxime (1:2 molar ratio) in MeOH solution , scheme (1). The structural formula of (H_2L) were verified by elemental analysis (Table 1) , which is in a good agreement with the calculated values and spectroscopic methods , ^{1}H-n.m.r (Table 2) , EI mass spectrometry (Table 3) ,i.r. (Table 4) and u.v.-vis., (Table 5). In the proposed structure of (H_2L) (Figure 1) ,N4 units are available for the complexation of metal ion .

The ^{1}H-n.m.r. spectrum of a DMSO-d_6 ، solution of oxime ligand shows singlets at 1.95 (6 H) , singlets at 2.68 (6H) and multiplet signal at 7.65-8.03 (4H) P.P.m. corresponding to the methyl group adjacent to carbon (C-l) , carbon (C-2) and aromatics proton resonance respectively . The oxime proton signals at =11.4 P.P.M disappear on deuterium exchange [18] .
The mass spectrum of (H_2L) exhibited the molecular ion peak at (m/z 274) , which corresponds to (M)$^+$, other fragments are summarized in (Table 3) .

The (i.r.) spectrum for the free ligand (H_2L) (Table 4) , exhibited two fundamental bands at (1636) and (1485) cm^{-1} due to ν (C=N) stretching for the imine and oxime group respectively [19] . However , these bands are shifted to lower frequencies upon complexation and appeared in the region (1613-1548) and (1430-1383) cm^{-1} in Ni(ll) Pd(ll) , Pt(ll) Cu(ll) , and Co (ll) complexes spectra . This is presumably attributed to the delocalization of metal electron density in to the ligand -system [20]. On the other hand , the strong ν (N-O) stretching bands at (992) and (922) cm-1 for the free ligand are shifted to higher frequencies upon complexation and appeared in the region (1090-1250) cm^{-1} for all the complexes . This is due to the increase in

double bond character of (N-O) [21] , suggesting that coordinated N atoms of the oxime groups with metal ions.

The absence of (O-H) stretching vibrations for the free ligand (H_2L) indicates the formation of intra molecular hydrogen bond between the dioxime oxygen atoms[22] in all the complexes, which was observed in the region (2423-2380) and (1766-1715) cm^{-1} indicating the ligand losses one proton and a hydrogen bonding will be formed. These results are in a good agreement with that reported by Blinc and Hadzi [23] . The weak bands at (536-495) cm^{-1} were assigned to ν (M-N) stretches in the complexes spectra[24]. The broad bands observed in the region (3450-3302) cm^{-1} is due to the ν (O-H) stretching of lattice water [24].

The ligand and its complexes were dissolved in DMF. In the u.v.-vis spectra were observed characteristic peaks of the oxime ligand . The absorption bands are given in (Table 5) .

The u-v.-vis . spectrum for free ligand, showed a high intense absorption peak at (317nm) with a shoulder at (268) nm which attributed to (n→*) and (*) transitions respectively [25] . One the other hand, the intense absorption peaks in the u.v. region for the complexes at (271-325) nm were assigned to ligand field transition . However , the spectrum of Pt (II) complex showed additional peak at (342) nm which assigned to charge transfer transition . In all complexes , d-d electronic transitions were observed at Ca. (371-913) nm. Ni (II) complex showed two peaks at(371) nm and (470) nm attributed to (d-d) electronic transition types ($^1A_1g^1B_1g$) and ($^1A_1g \rightarrow {}^1A_2g$) in square planar structure [26] .This is in a good agreement with the results reported by Aly and Co-workers [27] of nickel (II) complexes with imine-oxime ligands. The spectra of Pd(II) and Pt (II) exhibited peaks in the visible region at (400) nm and (436) nm respectively . These peaks were assigned to (d-d) electronic transition type ($^1A_1g^1B_1g$) suggesting a square planar structure around Pd(II) and Pt(II) ion[26]. This is in a good agreement with the results reported by Martin and Co-workers [28] and Alti and Co-workers [29] of Pd (II) and Pt (II) complexes with diphenylglyoxime and dimethylglyoxime. Cu(II) complex showed weak peak in the visible region at (773) nm which is assigned to (d-d) electronic transition

type ($^2B_2 \rightarrow {}^2E$) confirming a distorted tetrahedral structure around Cu (II) ion [26] .The broadening of this band is due to the Jahn-Teller effect . Finally , the spectrum of Co (II) complex showed peaks at (675) nm and (785) nm attributed (d-d) electronic transition type ($^4A_2 \rightarrow {}^4T_{1(p)}$) and ($^4A_2 \rightarrow {}^4T_{1(F)}$) respectively , suggesting a distorted tetrahedral structure around the Co (II) ion[26]. This is in accordance with the results reported by Aly and Co-workers[27] for dimethylglyoximato cobalt (II) complexes .

The magnetic moments of the complexes are shown in (Table 6) . The values of $_{eff}$ lie in the (0.5-0.4) B.M range, indicating diamagnetic properties and a square -planar geometry around the Ni (II) , Pd (II) , and Pt (II) ions[30] . The magnetic moment of the Cu(II) complex is (2.14) B.M, which is near the spin only value for one unpaired electron of the d^9 Cu (II) ion [31] indicating a distorted tetrahedral geometry around the Cu(II) complex. The magnetic moment of the Co(II) complex is (4.1) B.M. corresponding to spin free of three unpaired electrons which are in agreement with those reported for tetrahedral structure of Co(II) complex[32] .

The molar conductance of all the complexes in DMSO, (Table 6) lie in the (50-66) S cm^2 $mole^{-1}$ range , indicating their electrolyte nature with (1:1) ratio[33] .

According to the above data, it is concluded that the proposed geometry for Ni(II), Pd(II) and Pt(II) complexes is square planar , whereas the proposed molecular structure for Co(II) and Cu(II) complexes is a distorted tetrahedral structure.

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Table 1 . Elemental analyses and physical properties of ligand and its complexes

Symbol of compound	Empirical Formula	Mwt .	Yield %	M.P	Colour	Micro analysis Found, (Calc.)%			
						C	H	N	Metal
H_2L		274-33	74	185	Brown	(61.29) 60.00	(6.61) 6.05	(20.42) 20.20	———
C1	[Ni(HL)]Cl.H_2O	385	70	282	pink	(43.62) 43.12	(4.92) 4.80	(14.53) 14.09	(15.32) 14.90
C2	[Pd (HL)] Cl	415.32	65	296	yellow	(40.48) 40.63	(4.09)	(13.49) 12.80	(25.70) 24.84
C3	[Pt (HL)]Cl.H_2O	522.01	62	320	Dark brown	(32.21) 32.04	(3.63) 3.43	(10.73) 10.62	(37.39) 36.81
C4	[Cu(HL)]Cl.H_2O	389.45	77	254	green	(43.17) 42.83	(4.87) 4.75	(14.38) 14.25	(16.32) 16.10
C5	[Co(HL)]Cl.H_2O	385 72	79	256	green	(43.59) 43.12	(4.92) 4.75	(14.52) 14.33	(15.28) 14.90

(Calc) : Calculated

Table 2. ^{1}H-n.m.r dataa for (H_2L) measured in DMSO-d^6 and chemical shift in p.p.m ()

Funct. Group	$_s$ (p.p.m)[b]
-C=N-OH[a]	11.4(s,2H)[C]
C-H(aromatic)	8.03-7.65(m,4H)[d]
CH_3-1	2-68(s,6H)
CH_3-2	1.96 (s,6H)

[a]disappears on D_2O exchange

[b]s chemical shift from TMS

[C]S singlet

[d]m= multiplet

Table 3. EI mass spectral data of (H_2L)

Fragment Ions	Mass / charge	Relative abundance
[M] +	274	6.0
[M- { (CH_3-C=NOH)$_2$}] $^+$	158	100
[M- { (CH_3-C=NOH)$_2$ - (CH_3-C=N)}] $^+$	117	67
[M- { (CH_3-C=NOH)$_2$ - (CH_3-C=N)$_2$}] $^+$	76	25
[M- { (CH_3-C=NOH)$_2$ - (CH_3-C=N)$_2$-C}] $^+$	64	4
[M- { (CH_3-C=NOH)$_2$ (CH_3-C=N)$_2$-C_3}] $^+$	40	46

Table 4. Infrared spectral data[a] (wave number ¯v) of the ligand (H_2L) and its complexes

compound	v(O-H)	v(C-H) aliph.	v(C-H) aroma.	v(C=N) imine	v(C=N) oxime	v(N-O)	v (O...H-O)	(O..H-O)	v(M-N)
H_2L	3165(m)	2871(w)	3042(w)	1636 (s)	1485(S)	922(m) 992 (s)	———	———	———
CI	———	2933(w)	3062(w)	1532(m)	1383(w)	1104 (m) 1246 (m)	2423 (w.b.r)	1745 (w.b.r)	531(w)
C2	3450(br.)	2950(w)	3015(w)	1602(m)	1430(w)	1040 (w) 1160(m)	2380 (w.br.)	1750 (w.br.)	495(w) 518(w)
C3	3435(br.)	2926(w)	3060(w)	1548 (m)	1420(w)	1090 (m) 1262 (s)	2394 (w.br.)	1736 (w.br.)	523(w)
C4	3414(br.)	2896(w)	3050(w)	1613(w)	1430 (m)	1004 (s) 1206 (m)	2395 (w.br.)	1766 (w.br.)	536 (w)
C5	3302(br.)	2900(w)	3040(w)	1611(m)	1406(w)	1090(m) 1230 (s)	2412 (w.br.)	1715 (w.br.)	516 (w)

[a] recorded as KBr disc , w : weak (w.br.): weak broad
S: strong m: medium v: stretching
: bending

Table (5) Electronic spectral dataa of (H_2L) and its metal complexes

Compound	nm	$\bar{V}$ wave number cm^{-1}	εmax ($molar^{-1}.cm^{-1}$)	Assignment	Suggested structure
H_2L	268 317	3713 31546	1749 2457	* n→*	
C1	271 319 371 470	36900 31348 26954 21277	1960 1762 481 100	Ligand field Ligand field $^1A_1g \rightarrow {}^1B_1g$ $^1A_1g \rightarrow {}^1B_2g$	Square planar
C2	272 325 400	36765 30769 25000	1558 1904 360	Ligand field Ligand field $^1A_1g \rightarrow {}^1B_1g$	Square planar
C3	318 342 436	31446 29239 22936	2003 1976 750	Ligand field Charge transfer $^1A_1g \rightarrow {}^1B_1g$	Square planar
C4	313 773	31949 12937	2072 191	Ligand field $^1B_2 \rightarrow {}^2E$	Distorted tetrahedral
C5	279 675 785	35842 14815 12738	2440 137 49	Ligand field $^4A_2 \rightarrow {}^4T_1(p)$ $^4A_2 \rightarrow {}^4T_1(F)$	Distorted tetrahedral

[a] recorded in DMF solvent

Table 6. values of magnetic moment $_{eff}$=B.M) and molar conductance of prepared complexes

complexes	$_{eff}$ B.M. expt.	m ($S.cm^2. mol^{-1}$)
C1	0.4	54
C2	0.3	59
C3	0.15	51
C4	2.14	66
C5	4.1	52

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الخلاصة

تضمن البحث تحضير ليكاند جديد نوع (ايمين – اوكسيم) رباعية السن هو بارا – فنيلين ثنائي ايمين -N -N - بيوتان -3- اون اوكسيم من مفاعله مركب 1 ، -4 فنيلين ثنائي الأمين مع مركب 2 ، -3 ثنائي اون أحادي اوكسيم وشخص اليكاند بوساطة التحليل الدقيق للعناصر وأطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية والمرئية والرنين النووي المغناطيسي ومطياف الكتلة ، كما تضمن البحث تحضير سلسلة جديدة من المعقدات من خلال مفاعله الليكاند المحضر مع بعض أملاح العناصر الانتقالية النيكل () ، والبلاديوم () ، والبلاتين () والنحاس() والكويلت () وشخصت المعقدات المحضرة بوساطة التحليل الدقيق للعناصر والامتصاص الذري وأطياف الأشعة تحت الحمراء والأشعة فوق البنفسجية والمرئية وقياسات التوصيلية الكهربائية إضافة إلى دراسة الحساسية المغناطيسية حيث أظهرت القياسات نسبة فلز - ليكاند هي (1:1) وتناسق ايونات الفلزات أعلاه مع الليكاند عن طريق ذرات نتروجين مجاميع الاوكسيم والايمين.

وبأعتماد نتائج التقنيات المستخدمة فأن الشكل الفضائي للمعقدات المحضرة كما يأتي:-

- الشكل الفراغي المتوقع لمعقدات الينكل ()، والبلاديوم () والبلاتين () هو مربع مستو.
- الشكل الفراغي المتوقع لمعقدات النحاس () والكوبلت () هو رباعي السطوح المشوه.