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# Synthesis and Characterization of Trioxime Complexes for Platinum and Palladium Metals

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**Abstract**
A novel trioxime ($LH_1$) ligand bearing hydrazone side group and its complexes for platinum (II) and palladium (II) which have not been described in the literature Previously were synthesized. The trioxime ligand of bearing hydrazone group was synthesized by condensation of anti-glyoximehydrazine ($GH_2$) with Diacetylemonoxime . Ligand forms mononuclear complexes $[Pd(LH_1)CH_3COO]CH_3COO$ and $[M(LH_1)Cl]Cl$ with a metal:ligand ratio of (1:1) with M= $Pt^{(II)}$, $Pd^{(II)}$. The Complexes type of $[Pd(LH_1)CH_3COO]CH_3COO$ and $[M(LH_1)Cl]Cl$ are proposed to be a four-coordination. The ligand is coordinated through nitrogen atoms of oxime groups (C=N-OH) and imine group (C=N), acetate and chloride ion molecules are also coordinated to the metal ion to form complexes with square planer structure. Structural assignments are supported by a combination of $H^1$-NMR , $C^{13}$-NMR ,FT-IR , U.V-visible, elemental analyses (CHN).
**Keywords**: Trioxime, Hydrazone, Metal complex.

## 1. Introduction:

An oxime is a chemical compound belonging to the imines ,with the general formula $R_1R_2C=NOH$ , where $R_1$ is an organic side –chain and $R_2$ maybe hydrogen , forming an aldoxime, or another organic group , forming a ketoxime. Oximes are usually generated by the reaction of hydroxylamine and aldehyde or ketones. Oximes exist as three geomrtric stereoisomers: a syn isomer , an anti isomer and an amphi isomer . Aldoximes, except for aromatic aldoximes, which exist only as anti isomers and ketoximes can be separated almost completely and obtained as a syn isomer and an anti isomer [1-2]. Oximes and their metal complexes are of current interest for their rich physicochemical properties, reactivity patterns and potential applications in many important chemical processes in the areas of medicine [3-4] , bioorganic systems [5-6], catalysis [7,8], electrochemical and electrooptical sensors [9-10].Coordination compounds containing *vic*-dioxime ligands have been known and studied in the beginning of this century [11]. The numerous dioximes and their transition metal complexes have been investigated [12].The high stability of the complexes prepared with vic-dioxime ligands has been extensively used for various purposes including model compounds for vitamin $B_{12}$ or trace metal analysis [13,14].Nunmerous investigations of the reactions between vic-dioximes and metal ions have been reported [15-16] since the initial report on dimethylglyoxime by Tschugaeff [17]. many studies have been camed out into hydrazones, and mono- and di-oximes. Little information related to the derivatives of vic-dioxime with hydrazone side groups was found, in the literature [18] .

## 2. Materials and Instruments:

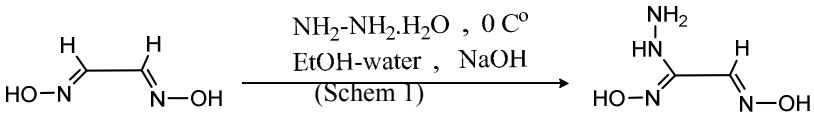
All reagents used were purchased from Aldrich-Sigma , Merck, Riedel, PROLABO and BDH, and used as received. Elemental analyses (CHN)Euro-Vector- CA-3000 ,$^1$H N.M.R spectra(Bruker 400 MHz), I.R. spectra (FT/IR-spectrum-4100 (KBr)), melting points (Buchi SPM-20)and (UV-Visible) Spectrophotometer - Jascow/ V-350 were used to elucidate the structures of the products.

## 3. Experimental:

*Syntheses of anti-chloroglyoxime:[19]
hydroxylamine hydrochloride (0.9 mol) was added dropwise to saturated aqueous solution of $Na_2CO_3$ (0.45 mol) , then chloralmonohydrate (0.3 mol) was added , the mixture was left for whole night then cooled to ( -5 $C^o$) . NaOH saturated aqueous solution (54 gr, in 100 ml distilled water) was added dropwise . the solution was stirred for 20 min and neutralized with diluted sulfuric acid at ( 0 $C^o$) . The precipitate obtained was filtered off and dissolved in diethyl ether .The diethyl ether solution was filtered , evaporated to a small volume and precipitated with hexane . The precipitate was washed with hexane , dried in air then dissolved in diethyl ether and the solution was saturated with gaseous HCl at (0 $C^o$) the reaction mixture was left for 30 min, washed with NaCl saturated aqueous solution and distilled water , dried with $CaCl_2$ and evaporated to dryness. Yield(76.6%) Color; White,m.p.;150 $C^o$ . IR (KBr, $cm^{-1}$): 3296 (O-H), 2890 (C-$H_{aliphatic}$), 1618 (C=$N_{oxime}$), 982 (N-O), 747 (C-Cl). $^1$H-NMR (DMSO, p.p.m.): 12.52, 12.32 s, 2H (=NOH), 8.30 s, 1H (HC=N). $^{13}$C-NMR (DMSO, p.p.m.): 143.01(ClC=N),137.65 (HC=N).
*Synthesis of anti-Glyoximehydrazine ($GH_2$):[19]
A solution of (0.4 g, 10 mmol) NaOH in 1 mL of distilled water was mixed with 10 mL of ethanol and 0.6 mL of hydrazinium hydroxide (80%, d = 1.03 g/mL) and cooled to 0 $C^0$. A solution of anti-chloroglyoxime (1.225 g, 10

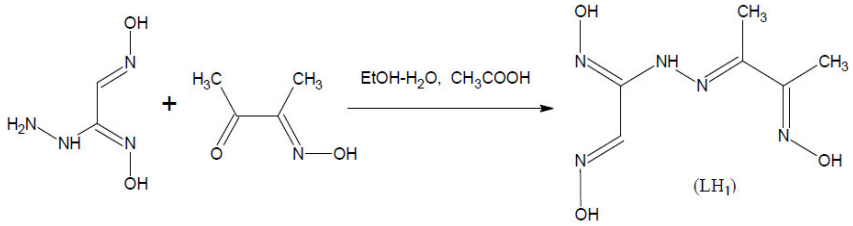
mmol) dissolved in 5 mL of ethanol was added dropwise into the prepared mixture with stirring at the same temperature. At the end of the addition the ligand started to precipitate. Stirring was continued for 15 min at the same temperature to complete the reaction. The precipitate was filtered, washed with cold ethanol and dried in a vacuum oven. Yield was (89.83% ). The compound decomposes easily. After 24 h it may decompose even at room temperature in a vacuum oven. This ligand is soluble in distilled water, DMF, DMSO and pyridine ,the chemical reaction and molecular structure are shown in (schem 1).IR (KBr, $cm^{-1}$): 3368 (O-H), 3326 (N-$H_{amin}$), 3176 (N-$H_{amid}$), 2858 (C-$H_{aliphatic}$), 1622 (C=$N_{oxime}$), 962 (N-N), 925 (N-O).




$GH_2$

*Synthesis of $LH_1$ :[19]

A cooled solution (5 $C^0$) of diacetylmonoxime (10 mmol) in (5ml) absolute ethanol was added dropwise into a cooled solution (5 $C^0$)containing (10 mmol) $GH_2$ ,(10ml distilled water) and 3-5 drops $CH_3COOH$ (as catalyst) with constant stirring. After the addition of monoxime was completed, the solution was stirred for an additonal 4 hours at room temperature .The resulting solid compound was filtered off, washed with cold distilled water and ethanol dried in vaccum oven. The chemical reaction and molecular structure are shown in (Scheme 2). Results of the compositional and spectroscopic analyses are as follows :$LH_1$; Yield; (65 %), Color; Cream, m.p.; 154$C^0$. IR (KBr, $cm^{-1}$): 3380 (O-H), 3279 (N-H), 2927 (C-$H_{aliphatic}$), 1600 (C=$N_{oxime}$), 1650 (C=$N_{hydrazone}$), 952 (N-O), 1010 (N-N). $^1$H-NMR (DMSO, p.p.m.): 8.314 s, 1H (-NH), 10.906 ,10.857 ,10.807 s, 3H (-OH), 6.514s , 1H (-CH=NOH) , 1.829,1.892 s, 6H (-$CH_3$). $^{13}$C-NMR (DMSO, p.p.m.) : 143.01 (-NH-C=N-OH) ,137.63 (-CH=N-OH) , 142.02 (MeC=N-OH), 155.49 (MeC=N-NH), 9.72,9.59 (-$CH_3$). For $C_6H_{11}O_3N_5$ (201.183 $g.mol^{-1}$) calculated: 35.82 % C, 5.51 % H, 34.81 % N; found: 35.59 % C, 5.10 % H, 34.20 % N. U.v-vis spectrum(in DMSO) λmax/nm: 290.The chemical reaction and molecular structure are shown in (schem 2).




(Schem 2)

**Preparation of the Transition Metal Complexes of Ligand:**

A solution of a metal salt (1 mmol of $K_2[PtCl_4]$ , $K_2[PdCl_4]$ or $Pd(CH_3COO)_2$ ) in 25 mL of distilled water was added to 1 mmol of the $LH_1$ ligand solution (0.201 g, in 15 mL of ethanol) with stirring. The reaction mixture was kept in a hot water bath (80 $C^o$) for 1 hour. To complete the precipitation. Then the precipitated complex compounds were filtered, washed with hot distilled water and dried at room temperature in a vacuum oven. The structures of complexes are given in (Figure 1) and (Figure 2). Results of the compositional and spectroscopic analyses are as follows:

**[Pt($LH_1$)Cl]Cl**; Yield; (77.5 %), Color; Brown-black , m.p.; 250 $C^o$ (Dec.), IR (KBr, $cm^{-1}$): 3370 (OH), 3270 (NH), 2910 (C-$H_{aliphatic}$), 1547 (C=$N_{oxime}$), 1607 (C=$N_{hydrazone}$), 919 (N-O), 970 (N-N). $^1$H-NMR (DMSO, p.p.m.): 8.30 s, $^1$H (-NH), 12.49, 12.25, 12.26 s, 3H (-OH), 6.60 s, 1H (-CH=NOH), 2.29, 1.81 s, 6H (-$CH_3$). $^{13}$C-NMR (DMSO, p.p.m.): 151.81 (-NH-C=N-OH), 137.63 (-CH=N-OH), 142.67 (MeC=N-OH), 155.62 (MeC=N-NH-), 11.76, 8.42 (-$CH^3$). U.v -vis spectrum (in DMSO) λmax/nm: 230,270 and 365. For $C_6H_{11}Cl_2O_3N_5Pt$ (467.17 $g.mol^{-1}$) ,calculated: 15.42 % C, 2.35 % H, 14.98 % N; found: 14.97 % C, 2.15 % H, 14.11 % N. The complex structure is shown in (Figure 1).

**[Pd($LH_1$)Cl]Cl**; Yield; (91.8 %), Color; Red , m.p.; 195 $C^o$ (Dec.), IR (KBr, cm-1): 3369 (OH), 3272 (NH), 2922 (C-$H_{aliphatic}$), 1590 (C=$N_{oxime}$), 1625 (C=$N_{hydrazone}$), 943 (N-O), 1000 (N-N). $^1$H-NMR (DMSO, p.p.m.): 7.43 s, 1H (-NH), 12.46, 12.24, 12.25 s, 3H (-OH), 6.87 s, 1H (-CH=NOH), 2.08, 2.12 s, 6H (-$CH^3$). $^{13}$C-NMR (DMSO, p.p.m.): 151.60 (-NH-C=N-OH), 137.63 (-CH=N-OH), 142.98 (MeC=N-OH), 154.06 (MeC=N-NH), 12.86, 11.76 (-$CH^3$). U.v-vis spectrum (in DMSO) λmax/nm: 280 and 325. For $C_6H_{11}Cl_2O_3N_5Pd$ (378.48 $g.mol^{-1}$) calculated: 19.03% C, 2.90% H, 18.49 % N; found: 18.62 % C, 2.30 % H, 17.6 % N. The complex structure is shown in (Figure 1).

**[Pd(LH$_1$)CH$_3$COO]CH$_3$COO**; Yield; (88 %), Color; Red-Brown , m.p.; 197 C$^o$ (Dec.), IR(KBr, cm$^{-1}$): 3368 (OH), 3269 (NH), 2922 (C-H$_{aliphatic}$), 1590 (C=N$_{oxime}$), 1624 (C=N$_{hydrazone}$), 1474(OH$_{carboxylic\ acid}$) , 1376(CO$_{carboxylic\ acid}$), 943 (N-O), 1000 (N-N).$^1$H-NMR (DMSO, p.p.m.): 7.43 s, 1H (-NH), 12.26, 12.27, 12.49 s, 3H (-OH), 6.87 s, 1H (-CH=NOH), 2.08, 2.13 s, 6H (-CH$_3$), 2.22 (-CH$_{3\ acetate}$). $^{13}$C-NMR (DMSO, p.p.m.): 151.59 (-NH-C=N-OH),137.63 (-CH=N-OH), 142.98 (MeC=N-OH), 154.06 (MeC=N-NH), 12.87, 13.61 (-CH$_3$), 13.92(-CO-CH$_3$), 170.12(-C=O). U.v.-vis. spectrum (in DMSO) λmax/nm: 270 and 326. For C$_{10}$H$_{17}$O$_7$N$_5$Pd (319.18 g.mol$^{-1}$) calculated: 37.62 % C, 5.32 % H, 21.93 % N; found: 3624. % C, 4.98 % H, 21.17 % N. The complex structure is shown in (Figure 2).Some physical properties, elemental and analytical data of the LH$_1$ ligand and its complexes are given in (Table 1).

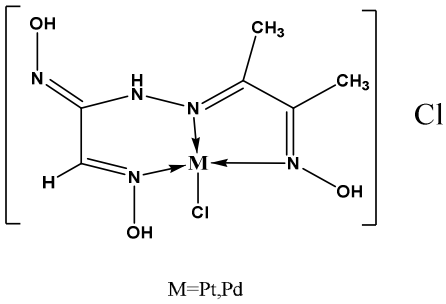



**Figure 1**

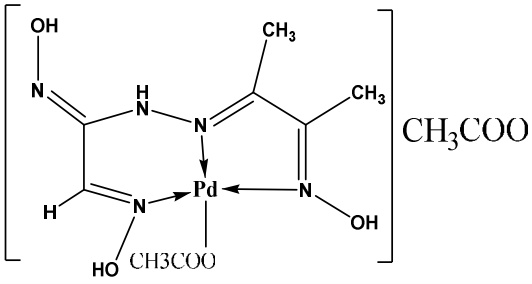



**Figure 2**

**Table 1**: physical properties, elemental and analytical data of the LH$_1$ ligand and its complexes.

| Compound formula | M.P. | yield | Color | Calculated (found)% of | | |
|---|---|---|---|---|---|---|
| | C$^o$ | | | C | H | N |
| LH$_1$ | 154 | 65% | cream | 35.82(35.59) | 5.51(5.10) | 34.81(34.20) |
| [Pt(LH$_1$)Cl]Cl | 250 (dec.) | 77.5% | Brown-black | 15.42(14.97) | 2.35(2.15) | 14.98(14.11) |
| [Pd(LH$_1$)Cl]Cl | 195(dec.) | 91.8% | Red | 19.03(18.62) | 2.90(2.30) | 18.49(17.6) |
| [Pd(LH$_1$)CH$_3$COO]CH$_3$COO | 197(dec.) | 88% | Red-brown | 37.62(36.24) | 5.32(4.98) | 21.93(21.17) |

## 4.RESULTS AND DISCUSSION:

In this study, a novel trioxime (LH$_1$) compound bearing hydrazone side group and its new metal complexes with Pt(II) and Pd(II) were synthesized. The trioxime ligand LH$_1$ of bearing hydrazone side group was synthesized by reacting *anti*-glyoxime hydrazine (GH$_2$) [19] with diacetylmonoxime. Ligand forms mononuclear complexes [Pd(LH$_1$)CH$_3$COO]CH$_3$COO and [M(LH$_1$)Cl]Cl ,with a metal:ligand ratio of 1:1 with M=Pt(II) and Pd(II). Novel ligand was characterized by a combination of $^1$H-NMR, $^{13}$C-NMR, FT-IR, UV-vis and elemental analytical techniques. The structure of the complexes were characterized by $^1$H-NMR, $^{13}$C-NMR , FT-IR, UV-vis and elemental analyses. In the IR spectrum of the hydrazone-oxime compound, an O-H stretching vibration was observed at 3380 cm$^{-1}$ for LH$_1$ as a broad absorption. FT-IR data of the ligands and their complexes are given in (Table 2).

**Table 2:** Characteristic IR bands of the LH$_1$ ligand and its metal complexes (cm$^{-1}$, KBr).

| Comp. | ν(N-H) | ν(O-H) st | ν(C-H) CH$_3$ | ν(C-H) alphatic | ν(C=N) oxime | ν(C=N) hydrazone | ν(N-O) | ν(N-N) | ν(O-H) carboxylic acid | ν(C-O) carboxylic acid |
|---|---|---|---|---|---|---|---|---|---|---|
| LH$_1$ | 3279$_s$ | 3380$_s$ | 3043$_w$ | 2927$_m$ | 1600$_m$ | 1650$_w$ | 952$_s$ | 1010$_s$ | – | – |
| [Pt(LH$_1$)Cl]$^+$ | 3270$_m$ | 3370$_s$ | 3012$_w$ | 2910$_m$ | 1547$_m$ | 1607$_w$ | 919$_w$ | 970$_m$ | – | – |
| [Pd(LH$_1$)Cl]$^+$ | 3272$_m$ | 3369$_s$ | 3025$_w$ | 2922$_m$ | 1590$_m$ | 1625$_w$ | 943$_w$ | 1000$_m$ | – | – |
| [Pd(LH$_1$)CH3COO]$^+$ | 3269$_m$ | 3368$_s$ | 3025$_w$ | 2922$_w$ | 1590$_m$ | 1624$_w$ | 943$_w$ | 1000$_m$ | 3182$_s$ | 1376$_s$ |

In the IR spectral data of the ligand ,the characteristic bands of C=N$_{hydrazone}$ and C=N$_{oxime}$ were observed at 1650 cm$^{-1}$ and 1600 cm$^{-1}$ respectly for LH$_1$ . N-H and N-O stretching vibration bands of the ligand were shown at 3279 and 952 cm$^{-1}$. These values are in accord with the previously reported oxime derivatives [19].Ligand forms mononuclear complexes [Pd(LH$_1$)CH$_3$COO]CH$_3$COO and [M(LH$_1$)Cl]Cl ,with a metal:ligand ratio of 1:1 with M=Pt(II) and Pd(II). The Pt(II) and Pd(II) complexes of the ligand are proposed to be square planar. The C=N$_{oxime}$ and C=N$_{hydrazone}$ stretches decrease from 1600 cm$^{-1}$ and 1650 cm$^{-1}$ in the free ligand to 1547-1607 cm$^{-1}$ , 1590-1625 cm$^{-1}$ and 1590-1624 cm$^{-1}$ in [Pt(LH$_1$)Cl]Cl , [Pd(LH$_1$)Cl]Cl and [Pd(LH$_1$)CH$_3$COO]CH$_3$COO complexes respectly . The intensity of characteristic stretching and bending vibrations of the free ligand were shifted and lowered on complex formation, and that indicates the nitrogen atoms of the C=N groups participate in the complex

formation. There is no O-H….O peaks accrording to IR and NMR spectra as expected for the complexes of formulas shown in Figure 1 and Figure 2.

When the $^{1}$H-NMR spectrum of the ligand in DMSO was examined, peaks corresponding N-OH protons were observed at 10.906,10.857,10.807 s, 3H (-OH) for $LH_1$. The peak of NH proton of ligand appears at 8.314ppm (s, 1H) for $LH_1$. The vanishing of these peaks by addition of $D_2O$ to the ligand solution indicates that the observed resonances are those of the protons of O-H and N-H groups. These values are in accord with the previously reported oxime derivatives [20-21-22]. C-H proton neighbouring to oxime group was observed at 6.514 ppm (s, 1H) for $LH_1$. The signals of $CH_3$ appear at 1.892 ppm (s, 3H) and 1.829 ppm (s, 3H) for $LH_1$. In the $^{1}$H-NMR spectrum, two peaks are present for the O-H protons of the oxime groups. These two deuterium exchangeable singlets correspond to two inequivalent O-H protons that also indicate the anti-configuration of the O-H groups relative to each other.In the $^{13}$C-NMR spectrum of ligand, different signals which were observed at 143.01 ppm for (HNC=N-OH) and 137.63 ppm for (H-C=N-OH) show asymetrically substituted vic-dioximes. $^{13}$C-NMR spectrum of $LH_1$ at two different frequencies in each case, indicates that the vic-dioxime has the anti structure [23-24].The peaks of (MeC=N-N)and (MeC=N-OH) appear at 155.49 ppm and 142.02 ppm for as expected [25]. The signals of $CH_3$ were shown 9.72 and 9.59 ppm for $LH_1$.

The UV-Vis spectral data of $LH_1$ exhibited the characteristic $n \longrightarrow \pi\pi^*$ absorption at (290 nm) in DMSO, due to the imine group. In the electronic spectrum of the complexes ([Pt($LH_1$)Cl]Cl , [Pd($LH_1$)Cl]Cl and [Pd($LH_1$)$CH_3COO$]$CH_3COO$ ,charge-transfer bands and characteristic $n \longrightarrow \pi^*$ transitions due to (C=/N) groups are also observed at (230 ,280 ,270 nm ) in DMSO respectly. A strong absorption at (270 ,325 ,326 nm) respectly , which is assigned to a charge transfer (LMTC) , $n \longrightarrow \pi\pi^*$ type, from the n orbitals of the donor nitrogen atoms(in the ligand) to the metal ion . the third band in the electronic spectrum of the complexe Pt($LH_1$)Cl]Cl at 365nm , due to (d(M)$\longrightarrow$ d( L)) electronic transfer and it doesn't exist in palladium complexes because of the external saturated d orbital in palladium .

**5. conclosion**

in the present work , we have prepared and characterized a novel trioxime ligand ($LH_1$) bearing hydrazone side group and its new complexes with platinum (II) and palladium (II). Mononuclear complexes have a metal:ligand ratio of (1:1) and the ligand is coordinated through nitrogen atoms of two oxime groups (C=N-OH) and imine group (C=N), acetate and chloride ion molecules are also coordinated to the metal ion. On the basis of the above data , it is concluded that the prepared complexes are $dsp^2$ hybridized with square-planar structure.

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