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Supramolecular structure and spectral studies on mixed-ligand complexes derived from β-diketone with azodye rhodanine derivatives

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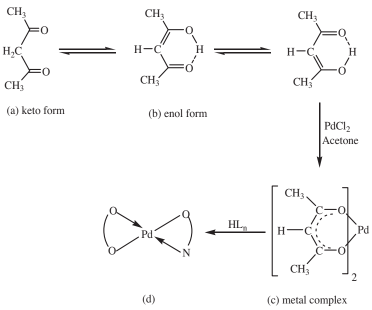
HIGHLIGHTS

- ▶ Structure of mononuclear ternary palladium(II) complexes was established.
- ▶ Square planar geometry around palladium has been assigned in all complexes.
- ▶ Various ligand and nephelouxetic parameter have been calculated for the complexes.
- ▶ The thermal decomposition for complexes were studied.

GRAPHICAL ABSTRACT

Both β-diketonate and azo compound act as bidentate chelating ligands and a square planar geometry around palladium(II) is established forming stable six membered heterocyclic rings.



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ABSTRACT

A novel method to synthesize some mononuclear ternary palladium(II) complexes of the general formula [Pd(L_n)L] (where LH = diketone = acetylacetone, HL_n = azorhodanine) has been synthesize. The structure of the new mononuclear ternary palladium(II) complexes was characterized using elemental analysis, spectral (electronic, infrared and ^{1}H & ^{13}C NMR) studies, magnetic susceptibility measurements and thermal studies. The IR showed that the ligands (HL_n & LH) act as monobasic bidentate through the azodye nitrogen, oxygen keto moiety and two enolato oxygen atoms. The molar conductivities show that all the complexes are non-electrolytes. Bidentate chelating nature of β-diketone and azorhodanine anions in the complexes was characterized by (electronic, infrared and ^{1}H & ^{13}C NMR) spectra. Square planar geometry around palladium has been assigned in all complexes. Various ligand and nephelouxetic parameter have been calculated for the complexes. The thermal decomposition for complexes was studied.

Introduction

1,3-Diketons constitute an important class of ligands in view of their distinct structural properties and high synthetic utility. They exist in two tautomeric forms which have been extensively studied [1]. In the last few decades, mixed ligand complexes have been extensively studied in solution as well as in the solid [2]. Ternary complexes are found to be more stable than binary complexes. Steric effect and lack donation have also been invoked to account for the preferred formation of mixed-ligand complexes [2].

Current interest in the mononuclear metal β-diketonates assemblies of the general composition [Pd(β-diketone)(L_n)] is mainly because of these complexes possess anticancer and insulin mimetic activity [3], specially with β-diketone ligands [4].

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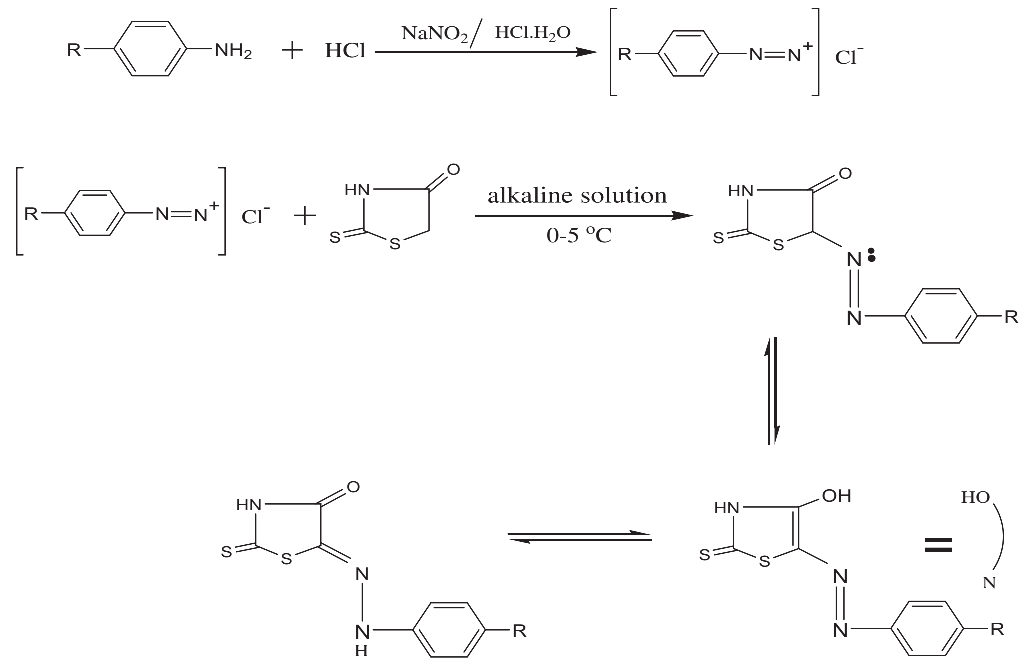
The design and study of well arranged metal containing electron donors ligand is interesting field of chemistry and has attracted the interest of both inorganic and bioinorganic chemists in recent years [1]. The field of mixed-ligand chemistry of metal is developing very rapidly because of its importance in the area of coordination chemistry [5]. Finally design of the mixed-ligand complexes depends upon the stereochemical requirements and coordinating features of metal ion [1,5–8]. The coordination chemistry of square planar metal complexes involving nitrogen donor ligands has excited great interest among chemists in recent years due to the applications of these in catalysis and their relavence to bioinorganic system [1]. The studies of Pd(II) complexes have been widely explored for the versatility of their coordination geometries, technical application and their biochemical significance. Square planar Pd(II) complexes of ligand containing mixed electron donors have been studies extensive, due to their potential applications as molecular materials [9–11].



n = 1, R = OCH_3 (HL_1); n = 2, CH_3 (HL_2); n = 3, H (HL_3); n = 4, Cl (HL_4); and n = 5, NO_2 (HL_5)

The formation mechanism of azodye ligands (HL_n)

Our interest in this is focused for a considerable time on the investigation of coordination chemistry of transition metal with 1,3-diketonate based ligand. To gain more information about the structure and stereochemistry of such type of complex, a detailed investigation on a novel palladium(II) complexes with a ligand involving nitrogen, enolic oxygen as donors has been initiated on our part.

In the present study we report the synthesis of $[Pd(L_{1-5})(L)]$ complexes from mixed ligands (HL_n & LH). The synthesized compounds have been characterized by analytical and spectral data.

Experimental

Synthesis of ligands

Synthesis of 5-(4-alkylphenylazo)-2-thioxo-4-thiazolidinone (HL_n)

In a typical preparation, 25 ml of distilled water containing 0.01 mol hydrochloric acid were added to aniline (0.01 mol) or a 4-alkylaniline [12–18]. The resulting mixture was stirred and cooled to 0 °C, a solution of 0.01 mol sodium nitrite in 20 ml of water was added dropwise. The formed diazonium chloride was consecutively coupled with an alkaline solution of 0.01 mol 2-thioxo-4-thiazolidinone, in 10 ml of pyridine was filtered through sintered glass crucible, washed several times with water. The formed colored precipitate and ether. The crude product was purified by recrystallization from hot ethanol, yield ~35–65% then dried in vacuum desiccator over P_2O_5.

The resulting formed ligands are: 5-(4-methoxyphenylazo)-2-thioxo-4-thiazolidinone (HL_1), 5-(4-methyphenylazo)-2-thioxo-4-thiazolidinone (HL_2), 5-(4-phenylazo)-2-thioxo-4-thiazolidinone (HL_3), 5-(4-chlorophenylazo)-2-thioxo-4-thiazolidinone (HL_4) and 5-(4-nitro phenylazo) -2-thioxo-4-thiazolidinone (HL_5).

The ligands were also characterized by elemental analysis (Table 1), NMR and I.R. spectroscopy.

General method of synthesis of complexes

Synthesis of bis(1,3-diketonato)palladium(II) complex $[Pd(L)_2]$ (1)

The bis(1,3-diketonato)palladium(II) complex was prepared by reacting a hot solution $PdCl_2$ (0.05 mol) in acetone (20 mL) with a solution of 1,3-diketone (0.01 mol) in ethanol and then was stirred for 45 min. The resulting mixture was concentrated and the solid thus obtained was filtered, dried and recrystallized from hexane (Table 2).

Synthesis of Pd(II) mixed-ligand complexes $[Pd(L_{1-5})(L)]$ (2–6)

The novel solid complexes were prepared by the reaction of calculated amount of ($M:HL_{1-5}:LH$) 1:1:1 ratio of both metal salt and ligands in methanol. The reaction mixture was refluxed for ~10 h. Another method as follows: To the $[Pd(L)_2]$ complex (**1**) (0.05 mol) (50 mL) ethanol was added HL_n (0.05 mol). The solution was al-

Table 1
Elemental analysis (C, H, N)[a], color, yield (%) and melting point (°C) of azorhodanine derivatives (HL_n).

Compound	Color	Yield (%)	M.p. (°C)	Calc. (Exp.)%		
				C	H	N
HL_1 $C_{10}H_9N_3O_2S_2$	Red	37.45	221	44.93 (44.82)	3.39 (3.25)	15.72 (15.85)
HL_2 $C_{10}H_9N_3OS_2$	Dark orange	47.81	231	47.79 (47.88)	3.61 (3.76)	16.72 (16.61)
HL_3 $C_9H_7N_3OS_2$	Pale yellow	42.19	237	45.55 (45.68)	2.97 (2.80)	17.71 (17.85)
HL_4 $C_9H_6N_3OS_2Cl$	Light orange	51.37	248	39.78 (39.65)	2.23 (2.35)	15.46 (15.58)
HL_5 $C_9H_6N_4O_3S_2$	Dark yellow	66.09	245	38.29 (38.42)	2.14 (2.25)	19.85 (19.98)

[a] The excellent agreement between calculated and experimental data suggests the assignment suggested in the present work.

Table 2
Method of preparation, elemental analysis and molar conductance data of Pd(II) complexes[a] (for molecular structure see Fig. 1)[b].

Complexes[c]	Mol. ratio	Calc. (Exp.)%				Λ_M[d]
		C	H	N	S	
$[Pd(L)_2]$ (**1**)	1:2	34.44 (34.24)	5.20 (4.99)	–	–	12.60
$[Pd(L_1)(L)]$ (**2**)	1:1:1	36.64 (36.57)	3.33 (3.38)	9.55 (9.14)	14.32 (13.93)	8.80
$[Pd(L_2)(L)]$ (**3**)	1:1:1	38.13 (37.89)	3.51 (3.38)	9.83 (9.47)	14.82 (14.43)	9.35
$[Pd(L_3)(L)]$ (**4**)	1:1:1	36.40 (36.25)	3.41 (3.25)	10.10 (9.76)	15.25 (14.87)	10.55
$[Pd(L_4)(L)]$ (**5**)	1:1:1	27.46 (27.31)	2.34 (2.28)	7.65 (7.35)	11.65 (11.20)	11.25
$[Pd(L_5)(L)]$ (**6**)	1:1:1	32.96 (32.82)	2.85 (2.74)	12.20 (11.78)	13.84 (13.46)	11.95

[a] Microanalytical data as well as metal estimations are in good agreement with the stoichiometries of the proposed complexes, air stable, non-hydroscopic, high melting temperature and colored.

[b] The excellent agreement between calculated and experimental data supports the assignment suggested in the present work.

[c] L_1–L_5 & L are the anions of the ligands HL_1–HL_5 & LH as given in Fig. 1.

[d] Ω^{-1} cm^2 mol^{-1} in DMF.

lowed to stain for 1 h at room temperature with stirring and then refluxed for 12 h on a water bath. The resulting solution was concentrated to almost a quarter of its original volume and kept in desiccator for ~3 days. The color solid separated was filtered off, washed with hot ethanol and dried in an oven at 110 °C; yield 58–68%. The analytical data are given in Table 2.

Measurements

Elemental microanalyses of the separated ligands and solid chelates for C, H, and N were performed in the Microanalytical Center, Cairo University, Egypt. The analyses were repeated twice to check the accuracy of the analyzed data. Palladium was estimated gravimetrically [19]. The ^1H NMR spectrum was obtained with a JEOL FX90 Fourier transform spectrometer with DMSO-d_6 as the solvent and TMS as an internal reference. Infrared spectra were recorded as KBr pellets using a Pye Unicam SP 2000 spectrophotometer. Ultraviolet–Visible (UV–Vis) spectra of the compounds were recorded in nuzol solution using a Unicom SP 8800 spectrophotometer. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy's method. Mercury(II) (tetrathiocyanato) cobalt(II), $[Hg\{Co(SCN)_4\}]$, was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [20] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{\text{eff.}} = 2.84[T\chi_M^{\text{coor.}}]^{1/2}$. TG measurements were made using a Du Pont 950 thermobalance. Ten milligram samples were heated at a rate of 10 °C/min in a dynamic nitrogen atmosphere (70 ml/min); the sample holder was boat-shaped, 10 × 5 × 2.5 mm deep; the temperature measuring thermocouple was placed within 1 mm of the holder. Structural analysis of the powder HL_2 was performed at room temperature by a Philips X-ray diffractometer equipped with utilized monochromatic Cu Kα radiation (λ = 1.5418 Å). The X-ray tube voltage and current were 40 kV and 25 mA, respectively.

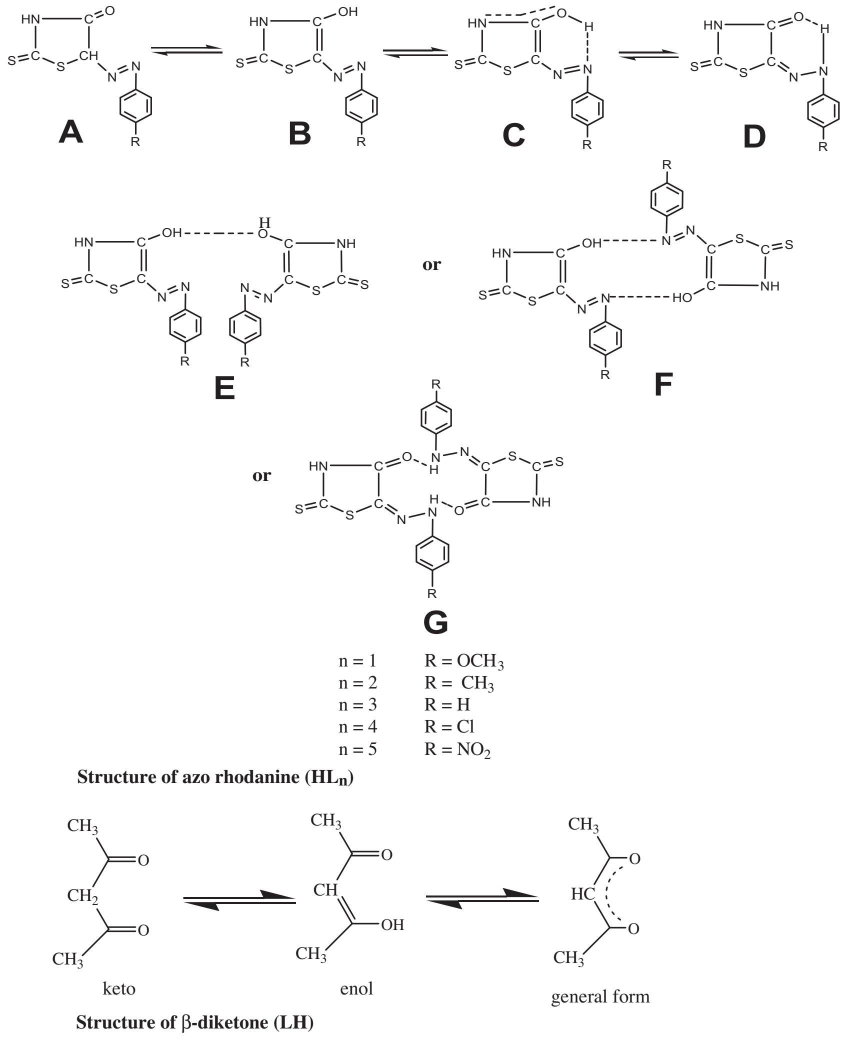
Results and discussion

The azo group can act as a proton acceptor in hydrogen bonds [11,15,21]. The role of hydrogen bonding in azo aggregation has been accepted for some time. Intramolecular hydrogen bonds involving OH group with the –N=N– group increased their stabilities through chelate ring structure [7,16,18]. The strength of the hydrogen bond of compounds depends on the nature of substituents present in the coupling component from the aryl azo group. Chelating rings formed by NH…N bonds are less stable than corresponding rings formed by OH…N bonds [8,21]. The U.V. spectra of acetylaminoazobenzene showed that the chelate ring is stable in dioxan and in methanol solvents, whereas the chelate ring in 2-hydroxy-4-methylazobenzene is stable in dioxan and hydroxylic solvents. Chelate rings involving NH…N=N bonds in azo compounds (e.g. 2-amino-4-dimethylaminoazo benzene) have been treated theoretically and have been studied in the IR and UV. Spectra where both five and six membered chelate rings with NH…N bonds have been suggested [22]. The intramolecular hydrogen bond in 1-phenylazo-2-naphthol was found to be stronger than in the 2-hydroxyazobenzene, due to the attachment of the –OH group to a larger resonance system thereby increasing the acidity [23].

In general, most of the azo compounds give spectral localized bands in the wavelength range 47,620–34,480 and 31,250–27,000 cm^{-1}. The first region is due to the absorption of the aromatic ring compared to ^1B_b and ^1L_b of mono substituted benzene and the second region is due to the conjugation between the azo group and the aromatic nuclei with intermolecular charge transfer resulting from π-electron migration to the diazo group from electron donating substituents [24].

All five ligands HL_1–HL_5, gave satisfactory elemental analysis (Table 1). The molecular structures of these ligands are such that they can exist in three tautomeric forms as shown in Fig. 1. Detailed solution and solid states studies of these ligands were carried out to establish their geometry.

As shown in Table 1, the values of yield (%) and/or melting point (°C) is related to the nature of the *p*-substituent as they increase according to the following order *p*-($NO_2 > Cl > H > CH_3 > OCH_3$). This can be attributed to the fact that the effective charge increased due to the electron withdrawing *p*-substituent (HL_4 and HL_5) while it decreased by the electrons donating character of (HL_1 and HL_2).



n = 1 R = OCH_3
n = 2 R = CH_3
n = 3 R = H
n = 4 R = Cl
n = 5 R = NO_2

Structure of azo rhodanine (HL_n)

Structure of β-diketone (LH)

Fig. 1. Schematic representation of the tautomeric form of the ligands.

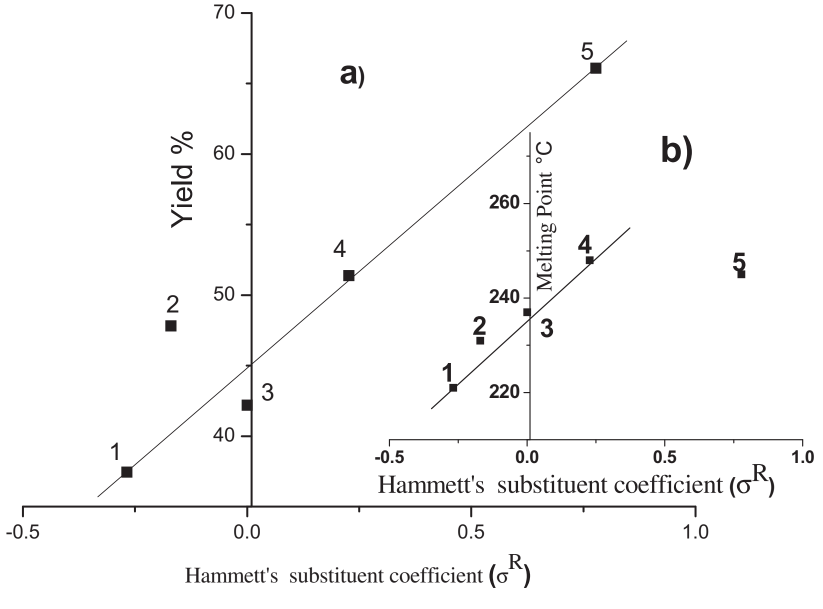


Fig. 2. The relation between Hammett's substitution coefficient (σ^R) *vs.* (a) Yield % and (b) Melting point °C of ligand (HL_n).

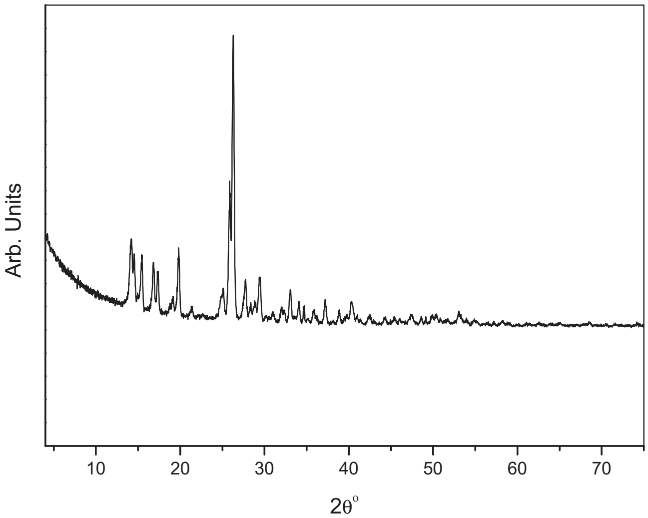


Fig. 3. X-ray diffraction pattern for HL_2 powder form.

This is in accordance with that expected from Hammett's constant (σ^R) as in Fig. 2, correlate the yield (%) and/or melting point (°C) values with (σ^R), it is clear that all these values increase with increasing σ^R.

Because of the high similarity of the X-ray diffraction, XRD, patterns for all powders of HL_n ligands, we will suffice by mentioning the XRD patterns of HL_2 as representative results for the rest of the ligands. The XRD patterns of the as-synthesized HL_2 powder, measured at room temperature, are shown in Fig. 3. The XRD pattern of the powder (Fig. 3) show many peaks which indicate the polycrystalline nature of the as-synthesized HL_2 ligand.

On the basis of elemental analysis, the Pd(II) ion complexes of ligand were assigned to posses the compositions and molecular formulae listed in Table 2. The results reveal that the ligands (HL_n) and LH behaves as monobasic bidentate towards the Pd(II) ion.

The formation of the complexes may be represented by the following reactions:

$$PdCl_2 + LH \rightarrow [Pd(L)_2] + 2HCl \quad (1)$$

$$PdCl_2 + HL_{1-5} + LH \rightarrow [Pd(L_{1-5})(L)] + 2HCl \quad (2\text{-}6)$$

$$[Pd(L)_2] + HL_{1-5} \rightarrow [Pd(L_{1-5})(L)] \quad (2\text{-}6)$$

where L_{1-5} = deprotonated HL_1, HL_2, HL_3, HL_4, HL_5 and L = β-diketone.

The molar conductance values for the Pd(II) complexes (10^{-3} M) are determined in DMF and these values are found to be low (8.75–18.20 Ω^{-1} cm^2 mol^{-1}) indicating non-electrolytic nature and there is no counter ion present outside the coordination sphere of palladium complexes [24–27]. The elemental analyses data concern well with the planned formulae for the ligands and also recognized the $[Pd(L)_2]$ and or $[Pd(L_{1-5})(L)$ composition of the Pd(II) chelates].

β-Diketones and related derivatives are considered a class of very important ligands in the growth of coordination chemistry. Their complexes have been thoroughly studied. Due to the presence of two oxygen donor atoms and facile Keto-enol tautomerism (Fig. 4a and b) they easily coordinate with metal ions after deprotonating the enolic hydrogen atom and provide stable metal complex (Fig. 4c) with six-membered chelate ring.

Due to the weak metal–oxygen bond usually found in metal acetylacetonates [28]. Diab and El-Sonbati et al. [1,5–8] discuss and found that a relatively stronger ligand can replace the acetylacetonato group to give a new and/or novel type of complex. Replacement of one or both acetylacetonato groups depends upon the ligand to metal acetylacetonates (e.g. $[MO_2(acac)_2]$, M = V, Mo, W, U) ratio taken, number of donating groups present in the ligand and electronic as well as steric properties of the ligand replacing acetylacetonato group. In this way metal acetylacetonates can acts as starting materials to design various types of complexes with varying structural and chemical properties [29,30].

Spectral measurements

^1H NMR spectra

The ^1H NMR spectra of HL_n shows signal for CH (~4.42 ppm), favoring formation of an intramolecular hydrogen bond with the N=N (azodye) group. Electron-withdrawing substituents reduce the intramolecular hydrogen bond as indicated by the marked shift

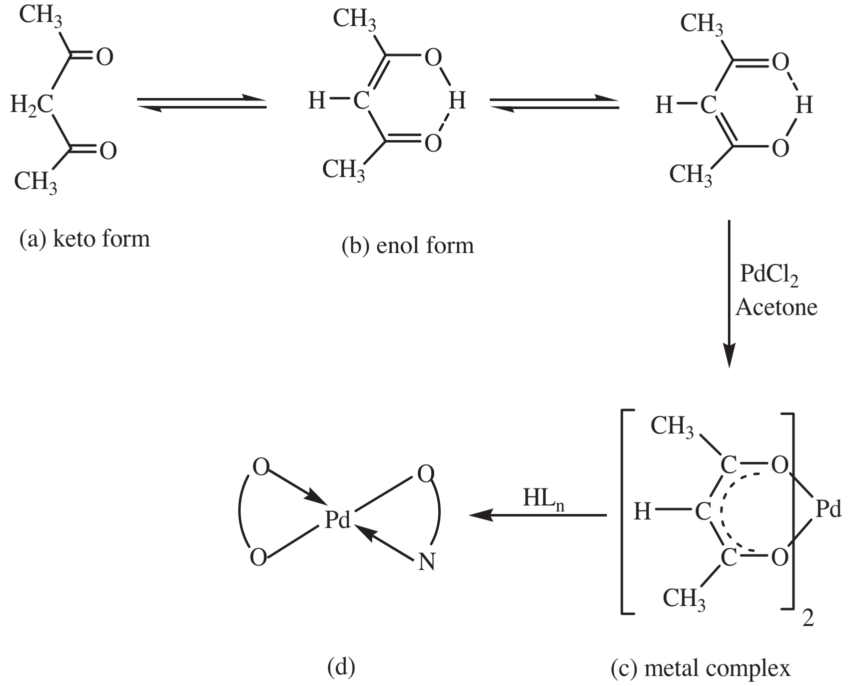


Fig. 4. Proposed structure of keto (a), enol (b), bis(β-diketonato)Pd(II) (c), and its metal complex with electron donors mixed ligands (d).

Table 3
^{1}H NMR spectral data (δ ppm) for palladium(II) complexes.

Complex*	^{1}H NMR
1	5.44(s, 1H, CH acac), 2.28(s, 6H, acac)
2	7.09–7.49(m, 4H, arom), 5.54(s,1H, acac), 2.32(s,6H, acac), 3.9(s, 3H, L_1)
4	7.15–7.54(m, 5H, arom), 5.76(s, 1H, acac), 2.35(s,6H, acac)
6	7.18–7.63(m,4H, arom), 6.68(s, 1H, acac), 2.38(s, 6H, acac)

* Numbers as given in Table 2.

of the hydroxyl signal to higher field in the p-NO_2 and p-Cl compounds. Electron-donating substituents give the opposite effect, arising from the increasing basicity of the azo-nitrogen. The broad signals assigned to the OH protons at ~11.36–11.88 ppm are not affected by dilution. The previous two protons disappear in the presence of D_2O. Absence of –CH proton signal of the ligand moiety indicated the existence of the ligand in the azo-enol form. According to Diab and El-Sonbati et al. [12–17], hydrogen bonding leads to a large deshielding of the protons. The shifts are in the sequence: p-(NO_2 > Cl > H > OCH_3 > CH_3). In the meantime, the ^{1}H NMR of the HL_1/HL_2 exhibits signals at δ(ppm) [3.3(s,3H,CH3)]/[3.9(s,3H,OCH3)]. The aromatic protons have resonance at 7.10–7.45 ppm for the ligands. No signal was observed in the ^{1}H NMR spectra of the complexes (**1–6**) in the region Δ 15.0–10.0 ppm (observed due to –OH proton) which indicated deprotonation and bonding of β-diketone and azo compounds to palladium. A multiplet of phenyl protons was appeared in the region δ 7.69–7.15 ppm. A singlet at $\delta = \sim 2.28$ ppm (6H) indicated the methyl protons of acac while the methane proton of acac was observed as a singlet at $\delta = \sim 5.44$ ppm (1H) [31]. The signal positions observed in the spectra for other complexes are given in Table 3.

^{13}C NMR spectra

The ^{13}C NMR spectra of all the ligands contain signal in the range of 153.3–167.2 ppm due to the presence of carbon which is doubly bonded to nitrogen, a downfield shift in peak position is observed in the ranges of 157–173 and 188–193 ppm in complexes and this evidence confirms that the ligands coordinate through nitrogen and oxygen (HL_n & LH) atoms. No appreciable change is seen in the peak position corresponding to aromatic and CS proton of rhodanine in the complexes. This also supports the CS is not coordinate to the metal center in case of all the metal complexes having the ligand as HL_n. Also, the singlet peaks at 55.45 ppm is due to the methoxy (OCH_3) carbon in HL_1. Thus, the ^{1}H and ^{13}C NMR spectra, confirms the monobasic bidentate nature of the ligands, which has already been suggested by the IR spectral studies, discussed above. On the basis of the above discussion, following structures have been suggested for the metal complexes (Fig. 4).

Hydrogen bonding

The infrared spectra of HL_n give interesting results and conclusions. The ligands (HL_n) displays two bands at ~3200–3040 cm^{-1} due to asymmetric and symmetric stretching vibrations of N–H group and intramolecular hydrogen bonding NH…O systems (Fig. 1-D), respectively. When the OH group (Fig. 1-C) is involved in intramolecular hydrogen bonding, the O…N and N…O bond distances are the same. But, if such mechanism is happened in case of intermolecular hydrogen bond, the O…O and O…N bond distances are differ.

The broad absorption of a band located at ~3400 cm^{-1} is assigned to νOH. The low frequency bands indicate that the hydroxy hydrogen atom is involved in keto ⇔ enol (A ⇔ B) tautomerism through hydrogen bonding (Fig. 1-C). Bellamy [32] made detailed studies on some carbonyl compounds containing –NH-group. The ΔυNH values were used to study the phenomena of association.

The infrared spectra of ligands shows a medium broad band located at ~3460 cm^{-1} due the stretching vibration of some sort of hydrogen of hydrogen bonding. El-Sonbati et al. [12–17] made detailed studies for the different types of hydrogen bonding which are favorable to exist in the molecule under investigation:

(1) Intramolecular hydrogen bond between the nitrogen atom of the –N=N- system and hydrogen atom of the hydroxy hydrogen atom (Fig. 1-C). This is evident by the presence of a broad band centered at 3460 cm^{-1}.
(2) Hydrogen bonding of the OH…N type between the hydroxy hydrogen atom and the N–Ph group (Fig. 1-C).
(3) Intermolecular hydrogen bonding is possible forming a cyclic dimer through NH…O=C (G), OH…N=N (F) or OH…OH (E) (Fig. 1).

The presence of a broad band located at ~3200 cm^{-1} is strong indication of υNH (Fig. 1-D). In general, the low frequency of such region from its normal position is, again due to hydrogen bonding property gathered with keto ⇔ enol tautomerism.

In general, hydrogen bonding involving both NH and OH groups are proton donors and both –N and –O atoms are proton acceptors. It is of interest since much multiplicity of proton donor and acceptor sites are prevalent in biological systems. Both intra- and intermolecular OH…N and NH…O may form leading to a number of structures in simultaneous equilibrium.

*IR spectra of [Pd(L)$_2$] (**1**)and [Pd(L_n)(L)] (**2–6**) complexes*

The bonding of the metal ion to the ligands can be clarified by comparing the IR spectra of the complexes with those of the ligands.

(1) In solution and in the presence of Pd(II) ions these compounds exist in a tautomerism equilibrium [8,18] A ⇔ B ⇔ C (Figs. 1 and 4). In infrared spectra of all the complexes O–H stretching vibrations of β-diketone (LH) and azo compounds (HL_n) was found absent in the region 3600–3200 cm^{-1}. No band was found in 1600–1700 cm^{-1} region indicating the CO group of β-diketone and azorhodanine was not free in the complexes. Two spitted new bands observed at 1597–1565 cm^{-1} [υ(C$\underline{\cdots}$O)] and 1515–1495 cm^{-1} [υ(C$\underline{\cdots}$C)] indicated the chelating nature of β-diketonate ion in the complexes [33]. The υ(C–O)(phenolic) bands appeared in the region 1285–1270 cm^{-1} in free azorhodanine were shifted to higher wavenumber (~20 cm^{-1}) which may be due to bond formation from oxygen to the metal after deprotonation. The absorption bands at ~1500–1480 cm^{-1} are

Table 4
Electronic spectral data (cm^{-1}) of palladium(II) complexes.

Complexes[a]	Spectral bands (cm^{-1})	Transitions	Δ_1	Δ_2	Δ_3	ν_2/ν_1
2	14540 22500 34300	$^1A_{1g} \rightarrow {}^1A_{2g}$ $^1A_{1g} \rightarrow {}^1B_{1g}$ $^1A_{1g} \rightarrow {}^1E_{1g}$	19740	5160	6960	1.214
3	18730 22660 33900	-do-	20830	5130	7180	1.210
4	18920 22840 34800	-do-	21020	5120	5260	1.207
5	19380 23350 35000	-do-	21480	5170	4910	1.205
6	19890 24150 35120	-do-	21990	5460	4460	1.214

[a] Numbers as given in Table 2.

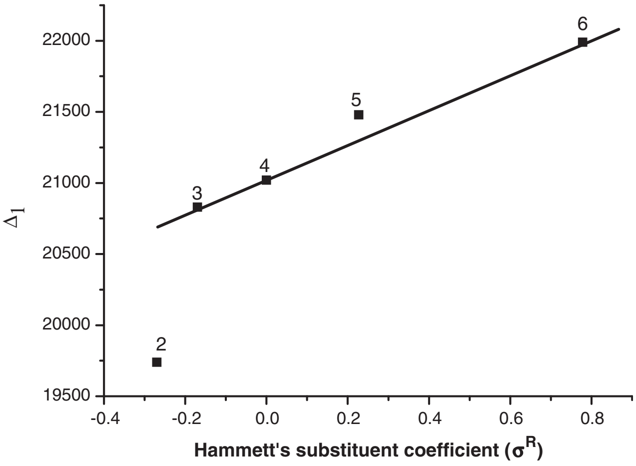


Fig. 5. The relation between Δ_1 *vs.* Hammett's constant coefficient (σ^R).

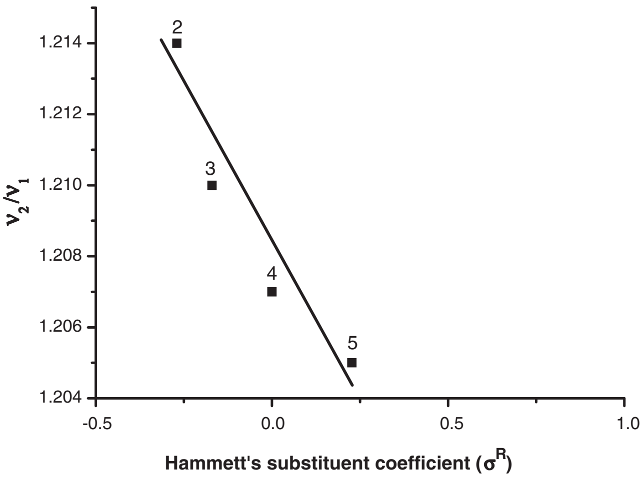


Fig. 6. The relation between ν_2/ν_1 *vs.* Hammett's constant coefficient (σ^R).

attributed to the C=C stretching mode coupled slightly with the C–H in-plane bending mode. The absorption band in the region of 1412–1385 cm^{-1} is assigned to the degenerate and asymmetric deformation vibrations of the methyl group.

(2) The appearance of υ(N=N)(1440–1433 cm^{-1}) and the disappearance of frequently bands of the υ(C=O)(1710–1695 cm^{-1}) group in the free ligands (HL$_n$) suggest that there is no hydrazo-keto transformation; this is similar to that reported in the literature [1,7,15–20]. The N=N stretching frequency of azo group is shifted to lower frequency by ca. 25–35 cm^{-1} due to the involvement of one of the azo nitrogen atoms in coordination with metal ion [1,7,15–20]. This lowering of frequency can be explained by the transfer of electrons from nitrogen atom to the Pd(II) ion due to coordination.

(3) Far infrared spectra of the metal complexes show several non-ligand bands of low intensity appearing in the region 415–460, 435–455 cm^{-1} can be assigned to (Pd–N) and (Pd–O) vibrations, respectively [1,5,15]. Absence of υ(Pd–S) band in the far IR spectra gives added evidence for the non-participation of ring sulfur atom in bond formation.

(4) The variation in the spectral bands of the C–C, C=C, C–N and C–H different modes of vibrations of the complexes lead to that, probably, the aromaticity of the complex is differ from one to other.

(5) Thus, this ligand (HL$_n$) contains four potential donor sites (Fig. 1): (i) the ring nitrogen NH, (ii) the ring CS, (iii) the carbonyl group, and (iv) the nitrogen of azo (N=N) group. However, considering the planarity of the ligand, it is unlikely that this ligand could be a tetradentate on a single metal center. Hence, this ligand is expected to be bidentate and the three favorable possibilities of donor sites are: the carbonyl oxygen and the nitrogen atom of azo (N=N) group or the carbonyl oxygen and the NH ring, and the third possibility between NH ring and CS ring. The coordination of the ring nitrogen (NH) is unlikely due to the zwitterions [34] formation, thereby lowering the electron density on N. The ring thion (CS) in this ligand is found to be inert towards coordination to palladium as revealed by the appearance of the υ(C=S)(ring) mode at almost the same position here merged with υ(C=O)(acac) compared with the υ(C=S)(ring) at 820 cm^{-1} of the uncoordinated ligand after complexation.

On the basis of all these data, the molecular structure of the Pd(II) complexes could be suggested based on: (i) the absence of anion, (ii) the disappearance of C=O, (iii) the coordination of azo-group.

Under such condition the ligand (HL$_n$/LH) is behaving as a monobasic bidentate [(O,N)(O,O)] with respect to the evidence above, the structure for the novel complexes are tentatively proposed as shown in Fig. 4d.

According to the structure shown in (Figs. 1 and 4) the HL$_n$/LH ligand takes its usual anionic form (L$_n$/L) to chelate Pd(II) through N- of azo group with enol group (Fig. 1-C, Fig. 4) as the potential binding sites.

Magnetic susceptibility measurement and electronic spectra

The magnetic susceptibility measurements show that all the palladium(II) complexes are diamagnetic, as expected of square planar d^8 complexes system. The electronic absorption spectra of the ligands exhibit mainly five bands (A–D, F). The band (A) located at 26360–26280 cm^{-1} can be assigned to the n–π* transition of the CS group. The band (B) within 30560–30260 cm^{-1}; can be assigned to n–π* transition within the CO group. The band (C) within 32980–33180 cm^{-1} could be assigned to the H-bonding and association. The band (D) located at 40250–3990 cm^{-1} could be assigned to Ph–Ph*, π–π*corresponding to the aromatic system. The band (F) located at 29620–29350 cm^{-1}. These latter bands can be assigned to phenyl rings overlapped by composite broad π–π* of azo group which undergoes a blue shift in the complexes due to the polarization within the N=N chromophore caused by the metal–ligand electron interaction during the chelation. The shift of this band in the spectra of the complexes suggest the coordination of nitrogen to metal atom. The band B transition disappears with the simultaneous appearance of new bands, being attributed to π–π* (C=C) as sequences of enolization. Furthermore, the band A transition shifts slightly to lower energy and remains almost constant. In the electronic spectra of Pd(II) complexes, three spin-allowed d–d transitions are expected, corresponding to transitions from the three lower lying d-levels to the empty d_{x2-y2} orbital; two-electron transitions would be very weak and can be neglected. The ground state is $^1A_{1g}$ and the excited states, corresponding to these transitions are $^1A_{2g}$, $^1B_{1g}$ and ^1E_g in order of increasing energy. The electronic spectra of the Pd(II) complexes show four bands are presented in Table 4. The spectra resemble the spectra of four-coordinate square planar complexes of palladium reported earlier [5,6,35,36]. The three orbital parameters, Δ_1, Δ_2, and Δ_3 were calculated using a value of $F_2 = 10$ $F_4 = 600$ cm^{-1} for a Slater–Condon interelectronic repulsion parameters and subsequently the equations suggested by Gray and Ballhausen [37,38]. The separation Δ_1 was the largest, which indicated that the

d_{x2-y2} was strongly antibonding. The ν_2/ν_1 values were also calculated (Table 4) and are in close agreement with data reported earlier for square planar complexes [6,39].

The plot of Δ_1 *vs.* σ [σ = Hammett's constant of R] (Fig. 5) shows a linear relationship between Δ_1, and σ for each chromophore. The Δ_1 values are relatively insensitive to the inductive effect of the phenyl ring substituents and chiefly depend on the stereochemical factors as the redox properties. The Δ_1 values are weaker in the compound (2) in agreement with the more electrondonating character atom, while Fig. 6 is a plot of ν_2/ν_1 (Table 4) *vs.* σ shows inversely proportionality.

Thermal analyses

The thermal decomposition of the studied complexes presented characteristic pathways, depending on the nature of the ligands, as can been see from the TG/DTA curves. All TG and DTA figures of the other compounds have the same trend. There is no loss in the range 100–220 °C which indicates the absence of coordinated or uncoordinated water molecule. DTA curves show no endothermic peaks up to 200 °C confirming the absence of lattice or coordinated water molecule in the complexes [40]. The sharp decomposition corresponding to the loss of organic moiety in complexes can bee seen in the DTA curves which contained one sharp exothermic peak failing in the range of 365–410 °C beyond which no decomposition was observed indicating the formation of stable palladium oxide. The final residue was analyzed by IR spectra and identified as metal oxide corresponds to the calculated value.

Conclusion

In this work, 6 novel heterocyclic azo dyes were synthesized by coupling diazotized rhodanine with p-derivatives aniline. Their structures were confirmed by ^{1}H and ^{13}C NMR, IR and UV–Vis spectra. The absorption data of the synthesized dyes revealed that all dyes exist in the form of two tautomeric species. The present paper reports on the synthesis, characterization and their electronic absorption spectra of mixed ligand (azorhodanine and acetylacetone) and Pd(II) complexes. The synthetic procedure in this work resulted in the formation of ternary complexes in the molar ratio (1:1:1)(M:L_n:L), respectively. Both β-diketonate and azo compound act as monobasic bidentate chelating ligands and a square planar geometry around palladium(II) is established (Fig. 4) forming stable six membered heterocyclic rings. From conductance measurements Pd(II)-complexes are non-electrolytes. The values of ligand field parameters orbital parameters were calculated.

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