

Supramolecular structure, stereochemistry and substituents effect on the spectral studies of novel ruthenium complexes

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H I G H L I G H T S

- ▶ HL_n behaves as a chelating bidentate monobasic ligand.
- ▶ HL_n bonding through azodye (—N=N) and enolic oxygen atom after deprotonation.
- ▶ The ligand field parameters were calculated using various energy level diagrams.
- ▶ The present study revealed octahedral geometry around Ru(III)-complexes.

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Novel complexes of Ru(III) with 5-(4-alkylphenylazo)-2-thioxo-4-thiazolidinone (HL_n) have been prepared and characterized by elemental analysis, thermogravimetric analysis (TGA), ¹H NMR, magnetic susceptibility and electronic spectral techniques. Tentative structures for the complexes are proposed. The important infrared (IR) bands and the main ¹H NMR signals are assigned and discussed relative to the molecular structure. The spectra show that all complexes are octahedral in which chloride is attached to the metal ion. The spectral data were utilized to compute the important ligand field parameters *B*, *β* and *Dq*. The *B*-values suggest a strong covalency in the metal–ligand σ -bond and the *Dq*-values indicate a medium strong ligand field. Results show that the *β*-depends greatly upon the electronegativity of the donor atoms and the ligand structure and also the effect of the *p*-substituent groups. The ligands act as a monobasic (bis/tris-bidentate chelating agent) coordinating through N=N and OH groups by replacement of a proton from the latter group there by forming a six-membered. Stability of these complexes has been investigated and a considerable interest has also been focused on the synthesis of the azo compounds and its metal complex due to its wide potential applications. In *p*-azo-rhodanine intramolecular OH...N hydrogen bonds have detected.

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1. Introduction

The design, synthesis and structural characterization of azo complexes are a subject of current interest due to their structural, magnetic, spectral properties [1]. Currently, a considerable effort is being invested in the development of new chelating ligands, the chelating azo ligands are versatile and they exhibit very rich coordination chemistry, such species occupy an important position in modern inorganic chemistry [2–5]. Much research has been published concerning the use of azo ligands, which incorporate nitrogen and phenolate donors seems appropriate for synthesizing ruthenium complexes [5].

Efforts have been made to carry out detailed studies to synthesize and elucidate the structural and electronic properties of novel families of complexes with rhodanine derivatives as a novel chelating bidentate azodyes models. Rhodanine derivatives are a good series of ligands capable of binding metal ions leading to metal complexes with increasing properties. The high stable potential of rhodanine derivative complexes in different oxidation states increased the application of these compounds in a wide range.

Ligands with potential sulfur, oxygen and nitrogen donors, such as rhodanine and its derivatives are quite interesting which have gained special attention in the last decade, not only because of the structural chemistry and their importance in medical chemistry, but also because these materials are used as a drugs and they are reported to possess a wide variety of biological activities against bacteria, fungi. They are also become a useful model for bioinorganic processes, which has many biochemical and

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pharmacological [6]. Great efforts have therefore been made to synthesize Metal(III) complexes of high biological activity and low toxicity which are readily absorbed.

5-(4-alkylphenylazo)-2-thioxothiazolidine-4-one (HL_n) and their related compounds (Fig. 1) have been extensively used as ligands in transition metal coordination chemistry [7–11]. Ease of synthesis, favorable steric arrangement and variability of donor sites that these ligands possess with suitable constituents, make this family an excellent candidate for constructing new families of complexes which are of great intriguing interest for the coordination chemist.

Although, no structural chemistry or coordinating studies have been reported on ligands containing both azo and rhodanine function groups, data from our laboratory [7–11] have demonstrated that the bidentate azodyes ligands play a key role in making new complexes with transition metal ions. However, little is known concerning the constitution of these complexes, as well as the chemistry involved in their preparation, or the structural and coordination in such complexes. It has been shown from the IR spectral data [7–14] that the hydrogen bonding plays an important role in biological systems. Moreover, Jorgensen and Pranata [15] and El-Sonbati et al. [15,7–13] found out that the stability of multiple hydrogen bonded depends not only on the number of hydrogen bonds but also on the hydrogen bonding pattern. The importance of clarifying the structure and stability of hydrogen-bonded complexes has opened up an area of surface science that has attracted a considerable attention in the environmental chemistry. The present paper describes the preparation, characterization (chemical

analysis, magnetic and spectral studies) of ruthenium complexes of HL_n .

In addition to the above mentioned aims, we will discuss the previous studies of hydrogen bonding [16,17] and compare them with the results of the present paper in order to provide a better explanation and justification to the chemical behavior of such complexes, allowing the reversible formation of aggregates which are non-covalently linked.

2. Experimental

All the chemicals used were of British Drug House quality.

2.1. Synthesis of 5-(4-alkylphenylazo)-2-thioxo-4-thiazolidinone (HL_n) [7–11]

In a typical preparation, 25 ml of distilled water containing 0.01 mol hydrochloric acid were added to aniline (0.01 mol) or *p*-derivatives. To the resulting mixture 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. The colored precipitate, which formed immediately, was filtered through sintered glass crucible, washed several times with water and ether. The crude product was purified by recrystallization from hot ethanol, yield ~40–70% then dried in vacuum desiccator over P_2O_5 .

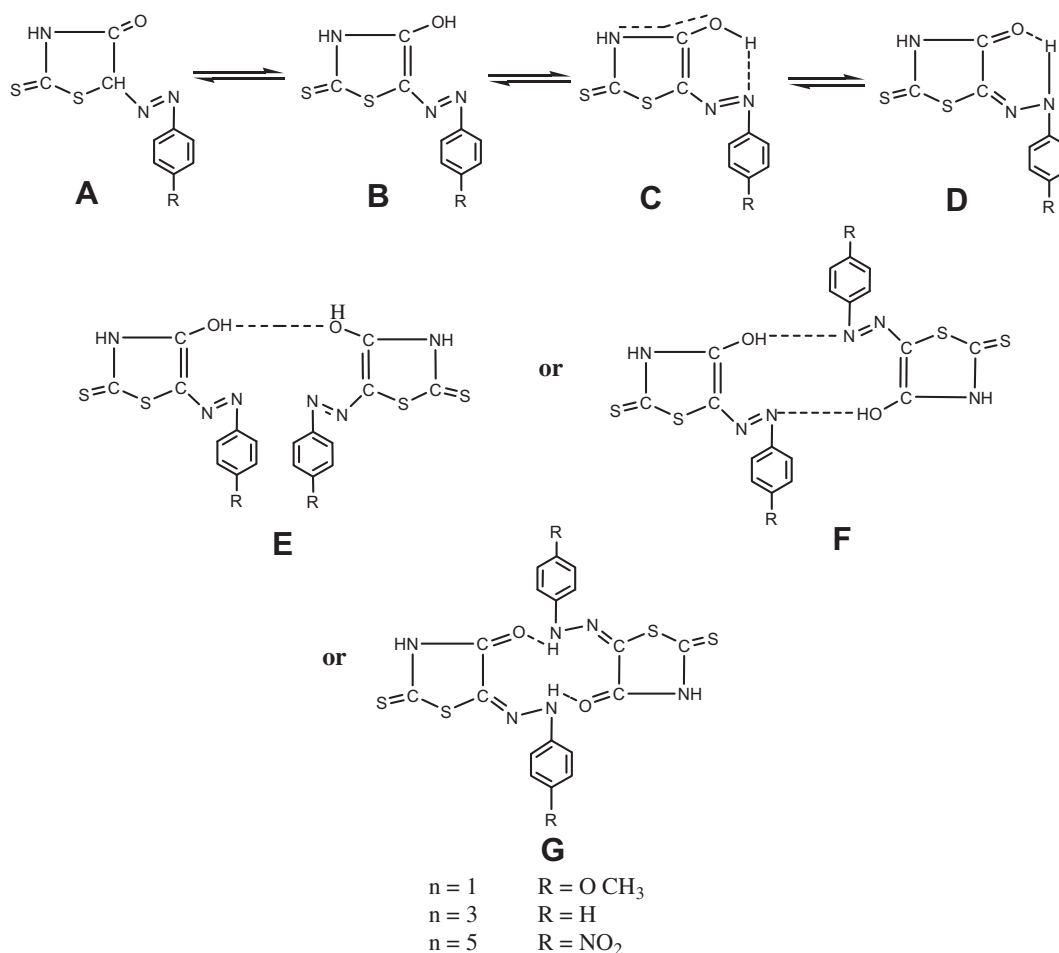
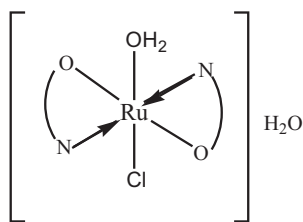


Fig. 1. Structure of ligands.

The resulting formed ligands are: 5-(4-methoxyphenylazo)-2-thioxo-4-thiazolidinone (HL₁), 5-(4-methylphenylazo)-2-thioxo-4-thiazolidinone (HL₂), 5-(4-phenylazo)-2-thioxo-4-thiazolidinone (HL₃), 5-(4-chlorophenylazo)-2-thioxo-4-thiazolidinone (HL₄) and 5-(4-nitrophenylazo)-2-thioxo-4-thiazolidinone (HL₅).



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

2.2. Preparation of the complexes

2.2.1. Monochlorobis[5-(4-alkylphenylazo)-2-thioxothiazolidin-4-one] ruthenium(III) hydrate, $[Ru(L_n)_2Cl.OH_2]H_2O$ (1–3)

$RuCl_3 \cdot 3H_2O$ (0.01 mol) in EtOH (20 mL) was added to a solution of HL_n (HL₁, HL₃ and HL₅) (0.022 mol) in EtOH (25 mL) weakly acidic solution. Microcrystalline solid immediately precipitated and the reaction mixture was heated under reflux for 30 min with stirring. After cooling to room temperature, filtering and washing with EtOH and Et₂O, the solid was dried in vacuum over P₄O₁₀.

2.2.2. Tris[5-(4-alkylphenylazo)-2-thioxothiazolidin-4-one]rutheniumtrihydrate, $[Ru(L_n)_3]3H_2O$ (4–6)

$RuCl_3 \cdot 3H_2O$ (0.01 mol) in EtOH (20 mL) was added to HL_n (HL₁, HL₃ and HL₅) in EtOH (20 mL) weakly alkaline solution and the reaction mixture was stirred under reflux for 2 h. During this period a crystalline solid precipitated. After cooling to room temperature, filtering and washing with EtOH followed by Et₂O, the solid was dried in vacuum over P₄O₁₀.

2.3. Physico-chemical 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. The ¹H-NMR spectrum was obtained with a JEOL FX90 Fourier transform spectrometer with DMSO-d₆ 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 Unicam 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 [18] and Pascal's constants. Magnetic moments were calculated using the equation, $\mu_{eff} = 2.84[T\chi_M^{coor}]^{1/2}$. 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. The halogen content was determined by combustion of the solid complex (30 mg) in an oxygen flask in the presence of a KOH–H₂O₂ mixture. The halide content was then determined by titration with a standard $Hg(NO_3)_2$ solution using diphenyl carbene as an indicator. The conductance measurement was achieved using Sargent Welch scientific Co., Skokie, IL, USA.

3. Results and discussion

3.1. General

The azo group can act as a proton acceptor in hydrogen bonds [8,13,19]. 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 [8,13,19,20]. 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 [21,22]. The U.V. spectra of acetaminazobenzene 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 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 [23]. 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 [24].

In general, most of the azo compounds give spectral localized bands in the wavelength range 47620–34480 and

Table 1
Analytical and physical data of azorhodanine derivatives.

Compound ^a	Empirical formula	Yield%	M.p. °C	Calc. (Exp.)%		
				C	H	N
HL ₁	C ₁₀ H ₉ N ₃ O ₂ S ₂ Red	37.45	221	44.93 (44.82)	3.39 (3.25)	15.72 (15.85)
HL ₂	C ₁₀ H ₉ N ₃ OS ₂ Dark Orange	47.81	231	47.79 (47.88)	3.61 (3.76)	16.72 (16.61)
HL ₃	C ₉ H ₇ N ₃ OS ₂ Pale Yellow	42.19	237	45.55 (45.68)	2.97 (2.80)	17.71 (17.85)
HL ₄	C ₉ H ₆ N ₃ OS ₂ Cl Light Orange	51.37	248	39.78 (39.65)	2.23 (2.35)	15.46 (15.58)
HL ₅	C ₉ H ₆ N ₄ O ₃ S ₂ Dark Yellow	66.087	245	38.29 (38.42)	2.14 (2.25)	19.85 (19.98)

^a The analytical data agree satisfactory with the expected formulae represented as given in structures HL₁–HL₅. Air-stable, colored, insoluble in water, but soluble in hot ethanol, and soluble in coordinating solvent.

31,250–27,000 cm^{-1} . The first region is due to the absorption of the aromatic ring compared to ${}^1\text{B}_u$ and ${}^1\text{L}_b$ 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.

3.2. Characterization of the ligands

All ligands HL_n , 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 $^\circ\text{C}$ is related to the nature of the *p*-substituent as they increase according to the following order $p\text{-(NO}_2 > \text{Cl} > \text{H} > \text{CH}_3 > \text{OCH}_3)$. 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). This is in accordance with that expected from Hammett's constant (σ^R) as in Fig. 2, correlate the yield% and/or melting point $^\circ\text{C}$ values with (σ^R), it is clear that all these values increase with increasing σ^R .

3.3. ${}^1\text{H}$ NMR spectra

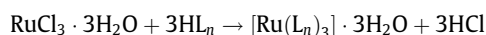
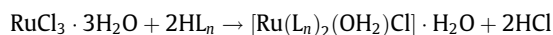
The NMR spectroscopy was used to differentiate stereoisomers. El-Sonbati et al. [7–13,17,20] investigated the NMR spectra of azo rhodanine and its derivatives with various transition metal salts. The ${}^1\text{H}$ NMR spectra are in agreement with the proposed structures. Signal for CH (~ 4.42 ppm), favoring formation of an intramolecular hydrogen bond with the $\text{N}=\text{N}$ (azodye) group. Electron-withdrawing substituents reduce the intramolecular hydrogen bond as indicated by the marked shift of the hydroxyl signal to higher field in the *p*- NO_2 compounds. Electron-donating substituents give the opposite effect, arising from the increasing basicity of the azonitrogen. 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 $-\text{CH}$ proton signal of the ligand moiety indicated the existence of the ligand in the azo-enol form. According to El-Sonbati et al. [7–13,17,20], hydrogen bonding leads to a large deshielding of the protons. The shifts are in the sequence: $p\text{-(NO}_2 > \text{H} > \text{OCH}_3)$. In the meantime, the ${}^1\text{H}$

NMR of the HL_1 exhibits signals at $\delta(\text{ppm})$ [3.9 (s, 3H, OCH_3)]. The aromatic protons have resonance at 7.10–7.45 ppm for the ligands. The chemical shifts, δ ppm owing to NH proton (of rhodanine) remain practically unchanged in the complexes, indicating that (NH of rhodanine) nitrogen does not involved in ligand coordination to the metal. Absence of CH proton signal of the rhodanine azo moiety indicated the existence of the ligand in the azo-enol form.

On the basis of all the above spectral data, an internally hydrogen bonded azo-enol structure has been proposed for the ligand (Fig. 1).

3.4. Structural of the metal complexes

Microanalytical data as well as metal and chloride estimations are in good agreement with stoichiometry proposed for complexes (Table 2) and their nature was found to be dependent on the mole ratio of the reactants and the pH of the reaction medium.



where $\text{L}_{1,3,5}$ = deprotonated HL_1 , HL_3 , HL_5 .

The molar conductance of 10^{-3} M of solutions of the ruthenium(III) complexes in DMSO is calculated at 25 ± 2 $^\circ\text{C}$. It is concluded from the results that $\text{Ru}(\text{III})$ chelates under investigation were found to have molar conductance values of the compounds (1:2)/(1:3)($\text{M}:\text{L}_n$) shows that they are non-electrolytic. This indicates that the anions are involved in the coordination sphere. [25]. This is in accordance with the fact that conductivity values for a non-electrolyte are below $50 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ in DMSO solution [26]. Such a non-zero molar conductance value for each of the complex in the present study is most probably due to the strong donor capacity of DMSO, which may lead to the displacement of anionic ligand and change of electrolyte type [25].

3.5. IR spectra and the mode of bonding in the complexes

The bonding of the metal ion to the ligand can be clarified by comparing the IR-spectra of the complexes with those of the ligands. In the light of the data of elemental analysis, it is expected that the light of the data of elemental with equivalent anions.

The broad/strong absorption of a band located at ~ 3450 – 3434 and at ~ 1710 – 1695 cm^{-1} region assigned to the $\nu(\text{NH})$ stretching vibrations mode and carbonyl stretching vibrations are expected to occur in this region. The three bands in the 1600 – 1500 cm^{-1} region are characteristic for most six-membered aromatic ring system. The frequencies for the $\text{N}=\text{N}$ stretching lie in the region 1440 – 1435 cm^{-1} . The region between 1500 and 900 cm^{-1} is due $\text{C}=\text{N}$ stretching, $\text{N}-\text{H}$ in plane or out of plane bending and out-of-plane $\text{C}-\text{H}$ bending vibrations [17]. The symmetric and anti-symmetric ($\text{C}=\text{C}$) stretching vibration modes are expected to exist in this region. 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 ($\text{N}=\text{N}$) group. However, considering the planarity of the ligand, it is unlikely that this ligand could be tetradentate on a single metal center. Hence, this ligand is expected to be bidentate and the three favorable possibilities of donor sites are: (i) the carbonyl oxygen and (ii) the nitrogen atom of azo ($\text{N}=\text{N}$) group or (i) the carbonyl oxygen and (ii) the CS. The coordination of the ring nitrogen (NH) is unlikely due to the zwitterions [27] formation, thereby lowering the electron density on N. The ring thion (CS) in this ligand is found to be inert towards coordination to metal as revealed by the appearance of the $\nu(\text{C}=\text{S})(\text{ring})$ mode at almost the same position.

The infrared spectra of HL_n give interesting results and conclusions. The ligands gives two bands at ~ 3200 – 3040 cm^{-1} due to

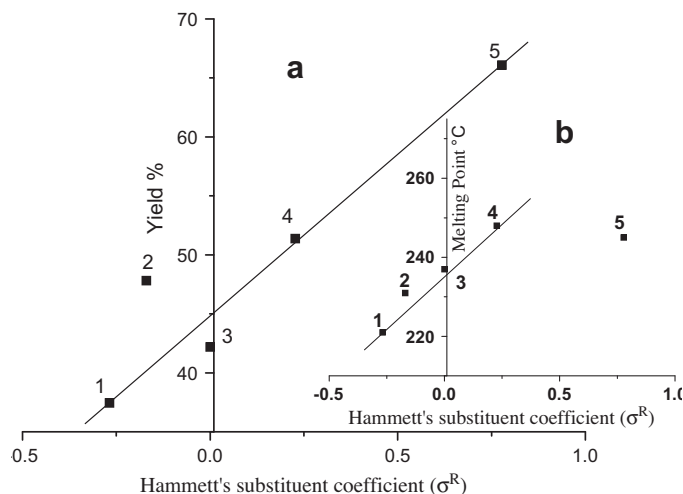


Fig. 2. The relation between Hammett's substitution coefficient (σ^R) vs. (a) Yield% and (b) Melting point $^\circ\text{C}$ of ligand (HL_n).

Table 2
Elemental analysis data and magnetic moment of complexes^a (for molecular structure see Fig. 1).^b

Complexes ^c	Exp. (Calc.)%				Cl
	C	H	N	S	
[Ru(L ₁) ₂ (OH ₂)Cl]H ₂ O (1)	34.20 (34.06)	2.95 (2.84)	12.33 (11.92)	18.34 (18.17)	5.22 (5.04)
[Ru(L ₃) ₂ (OH ₂)Cl]H ₂ O (2)	33.68(33.51)	2.53 (2.48)	13.29 (13.03)	20.04 (19.86)	5.68 (5.51)
[Ru(L ₅) ₂ (OH ₂)Cl]H ₂ O (3)	30.03 (29.98)	2.05 (1.94)	15.77 (15.54)	17.87 (17.76)	5.32 (4.93)
[Ru(L ₁) ₃]3H ₂ O (4)	37.88 (37.77)	3.24 (3.15)	13.44 (13.22)	20.34 (20.15)	–
[Ru(L ₃) ₃]3H ₂ O (5)	37.64 (37.54)	2.88 (2.78)	14.82 (14.60)	22.44 (22.25)	–
[Ru(L ₅) ₃]3H ₂ O (6)	32.56 (32.46)	2.21 (2.10)	16.97 (16.83)	19.54 (19.24)	–

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

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

^c L₁, L₃, L₅ are the anions of the ligands HL₁–HL₅ as given in Fig. 1.

asymmetric and symmetric stretching vibrations of N–H group and intramolecular hydrogen bonding NH...O systems (Fig. 1D), respectively. When the OH group (Fig. 1C) is involved in intramolecular hydrogen bond, 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 $\sim 3400\text{ cm}^{-1}$ is assigned to νOH . The low frequency bands indicate that the hydroxy hydrogen atom is involved in keto $\rightleftharpoons$ enol ($A\rightleftharpoons B$) tautomerism through hydrogen bonding (Fig. 1C). Bellamy [28] made detailed studies on some carbonyl compounds containing –NH-group. The $\Delta\nu\text{NH}$ values were used to study the phenomena of association.

On the other hand, the OH group (Fig. 1B) exhibits more than one absorption band. The two bands located at 1330 and 1370 cm^{-1} are assigned to in-plane deformation and that at 1130 cm^{-1} is due $\nu\text{C}=\text{OH}$.

However, the 860 cm^{-1} band is probably due to the out-of-plane deformation of the –OH group. On the other hand, the two bands located at 650 and 670 cm^{-1} are identified as $\delta\text{C}=\text{O}$ and NH.

Similar to the other investigated compounds, the different modes of vibrations of C–H and C–C band are identified by the presence of characteristic bands in the low frequency side of the spectrum in 600–200 cm^{-1} .

The infrared spectra of ligands shows medium broad band located at $\sim 3460\text{ cm}^{-1}$ due the stretching vibration of some sort of hydrogen of hydrogen bonding. El-Sonbati et al. [12,17,19,20] 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. 1C). 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. 1C).
- (3) Intermolecular hydrogen bonding is possible forming cyclic dimer through NH...O=C (G), OH...N=N (F) or OH...OH (E) (Fig. 1).

The presence of broad band located at $\sim 3200\text{ cm}^{-1}$ is strong indication by νNH (Fig. 1D). In general, the low frequency of such region from its normal position is, again due to hydrogen bond property gathered with keto $\rightleftharpoons$ 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.

Again the three bands located at 1380, 1340 and 1310 cm^{-1} identified as δOH gathered with the two bands at 1240 cm^{-1}

assigned as $\nu\text{C}=\text{O}$ are strong indication to keto $\rightleftharpoons$ enol equilibria. The presence of a medium band at $\sim 1605\text{ cm}^{-1}$ assigned to $\nu\text{C}=\text{N}$ illustrates the tracing of keto structure (Fig. 1D).

By comparing the infrared spectra of free ligands to that of the prepared complexes the following points could be outlined:

- (1) In solution and in the presence of Ru(III) ions these compounds exist in a tautomerism equilibrium [8] $A\rightleftharpoons B\rightleftharpoons C$ (Fig. 1). The internally hydrogen bonded enolic –OH band disappeared in the spectra of the metal complexes, indicating the deprotonation and formation of metal–oxygen bond. This is further supported by the shifting of $\nu(\text{C}=\text{O})$ towards higher frequency as compared to the free ligands (HL_n) due to the conversion of hydrogen bonded structure into a covalent metal bonded structure [28].
- (2) The appearance of $\nu(\text{C}=\text{N})$ and the disappearance of frequency bands of the $\nu(\text{C}=\text{O})$ group in the free ligands (HL_n) suggest that there is no hydrazo-keto transformation; this is similar to that reported in the literature [1,4,5,10–16]. 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 azonitrogen atoms in coordination with metal ion [1,4,5,10–16]. This lowering of frequency can be explained by the transfer of electrons from the nitrogen atom to the metal ion due to coordination.
- (3) In the $\nu(\text{OH})$ water region, the spectra of (1–3) show one relatively strong and sharp band at $\sim 3280\text{ cm}^{-1}$, assignable to coordinated water [19]. The presence of H₂O molecules in coordination spheres of these complexes is further confirmed by the appearance of the rocking mode of the aquo ligand at ~ 850 and 430 cm^{-1} [19]. In the spectra of all complexes (1–6) a strong and broad absorption (~ 3500 –3180 cm^{-1}) indicates the lattice water is present [29], this being supported by results of TG and dehydration methods [29].
- (4) Coordinating of the oxygen and the nitrogen in the chelate ring is supported by the appearance of new bands at 624–668 and 555–575 cm^{-1} , which are assigned to (Ru–N and (Ru–O), respectively. The coordination of halogen in the complexes exhibits a far IR absorbance.
- (5) 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 [1].

Under such condition the ligand (L_n) is behaving as a bidentate monobasic [(O,N)] nature with respect to the evidence above, the structure for the novel complexes are tentatively proposed as shown in Fig. 3.

According to the structure shown in (Figs. 1 and 3) the HL_n ligand takes its usual anionic form (L_n) to chelate Ru(III) through

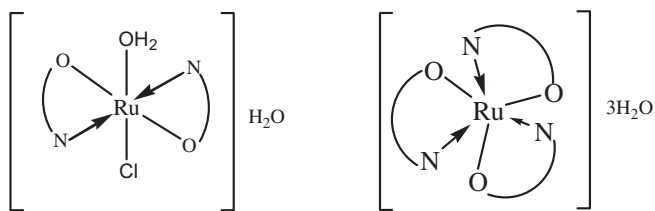


Fig. 3. The structure proposed for Ru(III)-complexes.

N- of azo group with enol group (Figs. 1C and 3) as the potential binding sites. Our sincere effort to obtain single crystals of the complexes went unsuccessful.

3.6. Magnetic moments and electronic spectra

HL_n exhibits bands at $26360\text{--}26280\text{ cm}^{-1}$ (CS) ($n \rightarrow \pi^*$), $30,560\text{--}30,260\text{ cm}^{-1}$ (CO) ($n \rightarrow \pi^*$), $32980\text{--}33180\text{ cm}^{-1}$ (H-bonding and association), $40,250\text{--}39,900\text{ cm}^{-1}$ (phenyl) (Ph-Ph⁺), ($\pi\text{--}\pi^*$) [17] and $29,620\text{--}29,350\text{ cm}^{-1}$ transition of phenyl rings overlapped by composite broad $\pi\text{--}\pi^*$ of azo structure. In the complexes, the ($n \rightarrow \pi^*$) transition shifts to lower energy at 28660 cm^{-1} and the band due to the H-bonding and association is absent as expected. Furthermore, the (CS) ($n\text{--}\pi^*$) transition shifts slightly to lower energy and remains almost constant. The (CO) ($n \rightarrow \pi^*$) transition disappears with the simultaneous appearance of new bands, being attributed to $\pi \rightarrow \pi^*$ (C=C) as a sequences of enolization. The band due to $\pi \rightarrow \pi^*$ transition moves to lower energy. These shifts or disappearance of the bands are indicative of coordinating of the ligands to metal.

The magnetic moments of complexes have been lie in the 1.78–1.99 B.M. range corresponding to one unpaired electron, suggesting a low spin t_{2g}^5 configuration for ruthenium(III) ion in pseudo-octahedral environment [30] (Table 2).

The electronic absorption spectra of Ru(III)-azodye complexes under study Tables 3 and 4, show three groups of bands. The bands

with frequencies above 35000 cm^{-1} ($\pi\text{--}\pi^*$) transitions of the aromatic system. The bands within the $20,000\text{--}35,000\text{ cm}^{-1}$ region represent various types of charge transfer interactions either intraligand or due to $L \rightarrow Ru(III)$ or $Ru(III) \rightarrow L$ charge transfer interactions.

The third group of bands lying below $20,000\text{ cm}^{-1}$ usually exhibits three distinct peaks. These three peaks can be attributed to three spin forbidden d-d transitions corresponding to low spin d^5 complexes of Ru(III) in octahedral environment (t_{2g}^5) is $^2T_{2g}$, which is in accordance with the results of the magnetic moment values Table 2. The first excited doublet levels will be $^2A_{2g}$ and $^2T_{1g}$. The energy difference between these two states ($^2T_{2g}$ and $^2A_{2g}$) is $\{10Dq - 3F_2 - 20F_4\}$ [30] assuming pure quantization. The electronic spectra of these complexes are further rationalized in terms of ligand field parameters and interelectronic repulsion parameters by using some known equation [26] (neglecting the configurational interaction). The values of these parameters, given in (Tables 3 and 4), are comparable to those reported for other ruthenium(III) derivatives involving nitrogen, oxygen donor molecules [29].

The lower values of the Racah interelectronic repulsion parameter B in comparison to the free ion value indicate that strong covalent bonds certainly occur between the ligands and the central metal ion. In other words, the greater the reduction in B the greater the covalency in the metal–ligand bond and the smaller the effective charge experienced by the d-electrons [31]. The overall effect will be an increase in the observed Dq value; high Dq values are usually associated with considerable electron delocalization [32]. Decreasing values of the nephelauxetic ratio β are also associated with a reduction in the effective positive charge of the metal ion and with an increasing tendency to reduction to the next lower oxidation state. For the 4d transition metals, the variations of the Racah interelectronic repulsion parameter with the cationic charge Z^* and the number (q) of electrons in the partly d-shell is expressed by the relation [28].

$$B (\text{cm}^{-1}) = 472 + 28q + 50(Z^* + 1) - 500/(Z^* + 1)$$

Table 3
Electronic absorption spectra and ligand field parameters of $[Ru(L_n)_2Cl.OH_2].H_2O$.

Complex ^a	Observed bands (cm^{-1})	Assignments	ν_2/ν_1	Dq	B	β	Z^*	C	F_2	F_4
1	13333 18018 19230	$^2T_{2g} \rightarrow ^2A_{2g} (\nu_1)$ $^2T_{2g} \rightarrow ^2T_{1g} (\nu_2)$ $^2T_{2g} \rightarrow ^2E_g (\nu_3)$	1.35	2332	585	0.78	0.97	2342	920	66
2	13888 18200 19230	-do-	1.31	2300	539	0.84	0.93	2156	847	61.6
3	14388 17857 19607	-do-	1.24	2264	433	1.02	0.90	1734	681	49

^a Numbers as given in Table 2.

Table 4
Electronic absorption spectra and ligand field parameters (cm^{-1}) of $[Ru(L_n)_3]3H_2O$.

Complex ^a	Observed bands (cm^{-1})	Assignments	ν_2/ν_1	Dq	B	β	Z^*	C	F_2	F_4
4	13888 18200 19230	$^2T_{2g} \rightarrow ^2A_{2g} (\nu_1)$ $^2T_{2g} \rightarrow ^2T_{1g} (\nu_2)$ $^2T_{2g} \rightarrow ^2E_g (\nu_3)$	1.31	2307	495	0.91	0.94	1980	777	56
5	14283 16950 18515	-do-	1.19	2084	408	0.81	0.72	1332	523	38
6	14385 18180 19800	-do-	1.26	1760	345	0.72	0.49	1896	745	54

^a Numbers as given in Table 2.

This gives effective ionic charges of the ruthenium(III) azoquinoline complexes in the 0.49–0.97 range, which are considerably below the formal +3 oxidation state of the metal ion. It is apparent that the nephelauxetic ratio β depends greatly upon the electronegativity of the donor atoms and the ligand structure.

As can be seen from Tables 3 and 4, the Racah parameters (B , Dq , β) and Z^* values increase from compound **1** to **3** and from **4** to **6**. This can be attributed to the fact that the effective charge experienced by the d-electrons decrease due to the electron withdrawing p -substituent (HL_5) while it increased by the electrons donating character of HL_1 .

3.7. Thermogravimetric analysis

In the mean time, the thermal analysis of ruthenium complexes under study was carried out in an attempt to clarify the content and bonding of water in the complexes. The determined temperature ranges, % losses in mass and thermal effect accompanying the changes in the solid complexes on heating are as following:

- (i) The observed loss in mass within the temperature range 125–125 °C could be correlated with the loss of water of hydration from all complexes. At higher temperature (125–225 °C), the coordinated water could be eliminated from complexes (**1–3**).
- (ii) Coordinated Cl could be removed within the temperature range 185–280 °C.
- (iii) Exotherms due to oxidation, decomposition of the complexes and the formation of metal oxides, and
- (iv) The organic part of the chelate gradually burned a way and the crucible became empty within the temperature range 440–580 °C. The degradation of the organic part of the chelate was an endothermic reaction, which resulted in carbon as residue. The decomposition of carbon dioxide was an exothermic reaction [6].

The TG curve for complexes shows similar decomposition with weight losses in two stages. In the first stage, in the temperature range ~280–320 °C is attributed to the weight loss of one molecule of ligands. The total mass loss observed at 480–540 °C was found to be stable metal oxides. The fragmentation patterns of the thermograms agree well with theoretical calculations and support the stereochemical and stoichiometrical assignments..

3.8. Structural interpretation

From all of the above observation and according to the data reported in this paper based on the IR, molar conductivity, spectral and magnetic measurements, the structure of these complexes is given as shown in Fig. 3. The structure proposed for Ru(III)-complexes is octahedral distorted. This indicates that, the ligand (HL_n) behaves as monobasic bidentate chelating ligand and azodye nitrogen and enolic oxygen are the two sites of coordination.

4. Conclusions

The present paper reports on the synthesis, characterization and their electronic absorption spectra of ligand (azo rhodanine) and Ru(III) complexes. The synthetic procedure in this work resulted in the formation of complexes in the molar ratio (1:2)/(1:3)(M:L_n), respectively. In these complexes the azo ligand acts as a monobasic bidentate ligand and coordinated to metal ion through the azo-nitrogen, enolic oxygen atoms forming stable six membered heterocyclic rings. The present study revealed octahedral geometry around Ru(III)-complexes. The strong chelating

ability of HL_n , which contain azodye group, is considered to result in part from the $d\pi$ - $p\pi$ bonding from the metal to the ligand; this π -bonding imparts some aromatic character to the chelate ring. The above results show clearly the effect of substitution in the p -position of the benzene ring on the stereochemistry of Ru(III) complexes. The results also suggest that the existence of a hydroxyl group enhances the electron density on the coordination sites and simultaneously increases the values of Racah parameters of Ru(III) complexes. In conclusion, the results of the present study indicate that the selected (HL_n) ligands are suitable for building a supramolecular structure. Moreover, since the azo compounds experience photochemical isomerization and are, therefore, of interest for applicative purposes [33], complexes of Ru(III) with 5-(4-alkylphenylazo)-2-thioxothiazolidin-4-one(HL_n) moiety may be considered as promising supramolecular, which could be useful in molecular materials. The values of ligand field parameters orbital parameters were calculated. The thermogravimetric analyses confirm the presence of coordinated one water molecule in the complexes (**1–3**).

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