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# Substituents effect on the spectral studies on rutheninum(III) complexes of 5(-4'-derivatives phenyldiazo)-3-phenyl-2-thioxo-4-thiazolidinone

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#### Abstract

A novel series of Ru(III) complexes with 5(-4'-derivatives phenyldiazo)-3-phenyl-2-thioxo-4-thiazolidinone (HLn) have been prepared. The ligands and structural composition of complexes were confirmed and characterized by various physico-chemical techniques. The spectral data were utilized to compute the important ligand field parameters B,  $\beta$  and Dq. The effect of Hamett's constant on the ligand field parameters is also discussed. The spectral and magnetic results commensurate an octahedral environment around the Ru(III) ion. The *B*-values suggest a strong covalency in the metal-ligand  $\sigma$ -bond and the Dq-values indicate a medium-strong ligand-field. IR spectra show that the ligand is neutral bidentate forming thereby a six-membered chelating ring and concomitant formation of an intramolecular hydrogen bond. The ligands are present in associated form in solution via intermolecular hydrogen bond and act as neutral bidentate coordinated to ruthenium(III). © 2002 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

El-Dissouky, El-Sonbati and El-Bindary [1-10], the preparation, characterization and spectroscopic properties of some heterocyclic nitrogencontaining aldehydes and their Schiff bases and/or azodyes as well as their transition element complexes have been described. These ligands give complexes which possess a unique stereochemical, magnetic and spectral properties and can be used as analytical reagents in trace element determination. Furthermore, some were found to possess biological activity [11–13].

As part of our studies about simple inorganic models of interest for the development of the bioinorganic chemistry of ruthenium, we have started investigations on Ru(III) complexes with

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5(-4'-derivatives phenyldiazo)-3-phenyl-2-thioxo-4-thiazolidinone (HL*n*) which appear to be suitable models due to the preference of ruthenium(III) for oxygen and nitrogen donors in biological systems.

Recently, our laboratories have initiated a series of studies of the effects of substituents at p-position of the aromatic amine on the stereochemistry of the complexes formed and deduced the relation between Hamett's constants and ligand field parameters.

# 2. Experimental

# 2.1. Synthesis of the ligands

3-Phenyl-2-thioxo-4-thiazolidinone was prepared according to the previously reported method [6,10].

The standard chemical aniline and 4-alkylanilines (alkyl:CH<sub>3</sub>, OCH<sub>3</sub>, Cl and NO<sub>2</sub>; Aldrich Chemical Co.) were used without any further

Table 1						
Analytical	data	of	the	isolated	complexes	

purification. The experimental technique has been described previously [1-10].

# 2.2. Preparation of 5(-4'-derivatives phenyldiazo)-3-phenyl-2-thioxo-4-thiazolidinone (HLn)

In a typical preparation, 25 ml of distilled water containing hydrochloric acid (12 M, 2.68 ml, 32.19 mmol) were added to aniline (0.979, 10.73 mmol) or a 4-alkyl-aniline. To the resulting mixture stirred and cooled to 0 °C, a solution of sodium nitrite (740 mg, 10.73 mmol, in 20 ml of water) was added dropwise. The so formed diazonium chloride was consecutively coupled with an alkaline solution of 3-phenyl-2-thioxo-4-thiazolidinone (31 mg, 10.73 mmol) in 10 ml of pyridine. The orange precipitated, which formed immediately was filtered, washed several times with water. The crude product was purified by recrystallization from hot ethanol, yield 65%. The analytical data confirmed the expected compositions, Table 1. The ligands were also characterized by <sup>1</sup>H-NMR and IR spectroscopy.

Complex	Code	Experimental	Composition <sup>a</sup>				
		С	Н	Ν	Cl <sup>b</sup>	M <sup>c</sup>	_
HL <sub>1</sub>	1	65.0 (55.9) 32.7 (32.6)	3.7 (3.8) 2.6 (2.5)	12.5 (12.2) 7.2 (7.6)	_ 18.2 (18.5)	_ 17.2 (17.5)	[HL <sub>1</sub> RuCl <sub>3</sub> OH <sub>2</sub> ]·H <sub>2</sub> O
HL <sub>2</sub>	2	58.7 (58.6) 33.7 (33.6)	3.9 (4.0) 2.6 (2.6)	13.0 (12.8) 7.4 (7.6)	_ 18.7 (18.5)	_ 17.7 (17.5)	[HL <sub>2</sub> RuCl <sub>3</sub> OH <sub>2</sub> ]·H <sub>2</sub> O
HL <sub>3</sub>	3	57.5 (57.5) 32.3 (32.3)	3.5 (3.5) 2.3 (2.2)	13.6 (13.4) 7.6 (8.0)	_ 19.1 (19.4)		[HL <sub>3</sub> RuCl <sub>3</sub> OH <sub>2</sub> ]·H <sub>2</sub> O
$HL_4$	4	52.0 (51.8) 39.9 (40.0)	3.0 (2.9) 2.2 (2.2)	12.4 (12.1) 9.3 (9.7)	- 7.9 (8.2)	_ 11.2 (11.0)	[(HL <sub>4</sub> ) <sub>2</sub> RuCl <sub>2</sub> ]Cl
HL <sub>5</sub>	5	50.1 (50.2) 39.0 (39.0)	2.7 (2.6) 2.3 (2.2)	15.6 (15.7) 12.1 (12.4)	- 7.7 (8.0)	_ 11.0 (11.3)	[(HL <sub>5</sub> ) <sub>2</sub> RuCl <sub>2</sub> ]Cl

0)>11.0 (11.3)>

The stoichiometry of the complexes obtained after drying at 100  $^{\circ}$ C shows the presence of water molecules present. On heating complexes (1–3), the mass loss corresponding to the loss of water molecules present. The presence of coordinated water was confirmed by TGA data, where the loss in weight corresponds to one water molecules for compounds (1–3). No coordinated water molecules were found in the other complexes.

 $^{a}$  HL<sub>1</sub>-HL<sub>5</sub> are the ligand as given in Scheme 1, air stable, non-hygroscopic, high melting points, colored, insoluble in water.  $^{b}$  Estimated gravimetrically.

<sup>c</sup> Estimated on an atomic absorption spectrophotometer.



Scheme 1. General formula and proton numbering of the 5(-4'-derivatives phenyldiazo)-3-phenyl-2-thioxo-4-thiazolidinone.

#### 2.3. Synthesis of the complexes

A stoichiometric amount of  $RuCl_3 \cdot 3H_2O$  (0.01 mol) in ethanol was added to a hot solution of the ligand (0.01 mol in  $HL_1-HL_3$ ) or (0.01 mol; 0.02 mol in  $HL_4$  or  $HL_5$ ) in absolute ethanol and the reaction mixture was boiled under reflux for 1-2 h on cooling at room temperature. The deeply colored precipitates were separated by filtration,

washed with ethanol followed by  $Et_2O$  and finally dried in vacuo over  $P_2O_5$ .

#### 2.4. Elemental analyses

C, H and N were estimated at the Microanalysis Unit at Mansoura and Cairo Universities. The data are given in Table 1.

# 2.5. Results and discussion

Theoretical approaches made by Liang and Lipscomb [14] indicate that the nitrogen atom is more negatively charged than the oxygen atom in the isolated metal ion and consequently, it may account for the coordination of the nitrogen atom rather than the oxygen atom, to the metal ion. Moreover, these authors have found that in the presence of the metal, the bidentate binding conformation with both N and O atoms coordinated to the metal ions is favored.

Our earlier studies on coordination behavior of rhodanine derivatives have shown that this 5(-4'-derivatives phenyldiazo)-3-phenyl-2-thioxo-4-thiazolidinone presents a variety of chelating coordination behavior, depending on the nature of the metal ion and the deprotonation of the ligand.

Microanalytical data as well as sulfur, metal and chloride estimations are in good agreement with stoichiometry proposed for complexes (Table 1). All complexes were found to be nonconducting.

Elemental analysis indicate that the stoichiometry for all these complexes having general formula  $[Ru(HLn)Cl_3 OH_2] H_2O$  (n = 1-3) and  $[Ru(HLn)_2Cl_2]Cl$  (n = 4 or 5). The proposed formulation is supported by IR spectra.

The ligand HLn were obtained in excellent yields, ca. 85%. While the ligands are soluble in coordinating solvent but partially soluble in ethanol. Furthermore, the ligands solution were used as suspension during complexation. As the reaction proceeded, the ligands dissolved completely, as shown by the colour change of the reaction mixture. After ca.  $\approx 2$  h the desired product precipitated as a powder.

Most complexes of the HLn (n = 3-5) were obtained in low yield, possibly due to the low solubility of the ligands. In general, reactions with HLn (n = 1 or 2) were faster and gave better yields than reactions with HLn (n = 3-5). Molar conductance data showed that the metal complexes are non-electrolytes in DMSO [15].

# 2.6. Mode of bonding

The infrared spectra of ligands exhibit strong to medium broad bands in the frequency range  $3240-2900 \text{ cm}^{-1}$ . These bands can be attributed to intramolecular hydrogen bonded-OH group [7].

Table 2

Electronic absorption spectra and ligand field parameters (cm<sup>-1</sup>) of Ru(III)-azodyes complexes

Complex <sup>a</sup>	Observed bands	Assigments	$v_2/v_1$	Dq	В	β	$Z^{\mathfrak{b}}$	С	$F_2$	$F_4$
4	15280 18680 22250	$ {}^{2}T_{2g} \rightarrow {}^{2}A_{2g} (v_{1})  {}^{2}T_{2g} \rightarrow {}^{2}T_{1g} (v_{2})  {}^{2}T_{2g} \rightarrow {}^{2}E_{g} (v_{3}) $	1.22	2028	398	0.64	0.68	1592	625.4	45.5
1	16667 18867 23255	Do	1.13	2167	425	0.68	0.80	1700	667.9	48.6
3	16270 17540 20399	Do	1.08	2126	417	0.66	0.76	1668	655.3	47.7
2	16390 19800 23810	Do	1.21	2139	419	0.67	0.77	1676	658.4	47.9
5	15380 18867 23245	Do	1.23	2038	400	0.64	0.69	1600	628.6	45.7

<sup>a</sup> 24400-27700 ligand and C.T.

<sup>b</sup> 33333–35000 aromatic transition  $\pi \rightarrow \pi^*$ .



Fig. 1. The variation of *p*-substituted Hamett's constants with: (a) Dq; (b) *B*; (c)  $\beta$ ; and (d)  $Z^*$ .

Furthermore, all ligands exhibit a strong band at  $1735-1720 \text{ cm}^{-1}$ . This is due to  $\nu$ C=O [8]. The discussed infrared features beside the band appeared at  $1610-1595 \text{ cm}^{-1}$  can guide to assume the presence of C=N structure through resonating phenomena [8]. Such class of compounds is with different types of hydrogen bonding [16,7–9]:

- 1. H-bonding of the type O–H…N between the –OH group and –N=N– group (1C).
- 2. H-bonding of the type N–H…O between the –NH group and C=O group (1D).
- Intermolecular hydrogen bonding of the O-H…N (E) or N-H…O (F) type of one molecule to another one. The (2) case is more favored than (1). This is due to the presence of a broad band located at 870-970 cm<sup>-1</sup> which could be taken as a good evidence for the intermolecular hydrogen bonding. This is illustrated in Scheme 1.

The following features for some of the prepared complexes are observed:

- 1. The infrared spectra of the free ligands show no characteristic absorption assignable to  $NH_2$ function. This confirms the formation of the azo compounds.
- 2. The strong band observed at  $1135-1140 \text{ cm}^{-1}$  may be assigned to v(N-N) vibration modes [16] is affected on complexation. It is blue shifted and appeared as a weak band.
- In all complexes 3490-3150 cm<sup>-1</sup> is observed. Such region is attributed to different probabilities: (a) it is due to either free OH or NH; (b) bonded-OH group or -NH group; or (c) due to the presence of coordinated water molecules.
- 4. The spectra of ligands do not show absorption characteristic of the N=N function owing to the formation of the hydrazone. The sharp, medium intensity band of C=N (hydrazone) appears at 1610–1595 cm<sup>-1</sup> for ligands.
- 5. The spectra exhibits a very strong band at  $1720 \text{ cm}^{-1}$ . This is a powerfull indicative to vC=O. However, the broad band located at 3420 cm<sup>-1</sup> leads to characterize the vNH rather than hydrogen bonded–OH with N=N. This is rather confirmed from the observation of Karabatoser [17] where the hydrazone form is more than the azo structure for similar compounds.

This is also proved by the appearance of N=N in splitted strong spectral bands at 1440 and 1530 cm<sup>-1</sup> combined with the tracing of a strong bands at 1225 cm<sup>-1</sup> characteristic to NH stretching vibration. All these data with lack of the  $\nu$ C–O of enol in the IR spectrum leads us to assume the structure (1D) for this compounds.

6. Introduction of a hydrazo group instead of N=N leads to: (i) a change in the coordination mode of the azo group from the azo-nitrogen to the amine nitrogen (NH); (ii) stabilization of the chelate ring by intermolecular hydrogen bonding between hydrogen of water of this chelate ring and the basic oxygen of the six-membered chelate ring and the basic oxygen of the six-membered chelate ring of an carbonyl group (Scheme 1).

This hydrogen bonding interaction will prevent the hydrazone group from rearranging to the energetically more favorable *N*-coordination mode. This behavior has been observed with other metal azo compounds that contained the substituent C=N–NH instead of C=O in the vicinity of the azo group.

7. The broad, medium intensity band at  $\sim 2900$  cm<sup>-1</sup> in the free ligand is shifted to  $\sim 2400$  cm<sup>-1</sup> on complex formation, a behavior attributed to the OH of the hydrogen bond (O-H…O) [18].

The bands characteristic of coordinated water molecules are observed at ca.  $880 \text{ cm}^{-1}$ , including the rocking, wagging and the metal–oxygen stretching vibrations at 900, 760 and 670 cm<sup>-1</sup>, respectively. Coordination of the carbonyl oxygen and the amine nitrogen in the chelate ring is suported by the appearance of new bands at 640–690 and 570–590 cm<sup>-1</sup>, which are assigned to Ru–N and Ru–O, respectively. The coordinated halogen in the complexes exhibits a far IR absorbance.

# 2.7. Magnetic studies

The experimental values of magnetic moment at room temperature from Ru(III) complexes (4) and (5) (1.56 and 1.37 B.M.), respectively correspond to one unpaired electron indicating inner orbital octahedral geometry around the metal ion. While the magnetic moments of the ruthenium(III) complexes (1)–(3) (Table 1) lie in the 1.86–2.1 B.M. and are markedly higher than the spin-only value of one unpaired electron for low spin  $t_{2g}^5$  ruthenium(III) in an octahedral environment. This positive deviation due to incomplete quenching of the orbital contribution to the magnetic moment [19].

# 2.8. Spectra and geometry of the complexes

The electronic absorption spectra of Ru(III)– azodye complexes under study Table 2, show three groups of bands. The bands with frequencies above  $35\,000 \text{ cm}^{-1}$  ( $\pi$ - $\pi$ \*) transitions of the aromatic system. The bands within the 20 000–35 000 cm<sup>-1</sup> region represent various types of change 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 cm<sup>-1</sup> usually exhibits three distinct peaks. These three peaks can be attributed to three spin forbidden d-d transtions corresponding to low spin d<sup>5</sup> complexes of Ru(III) in octahedral environment  $(t_{2g}^5)$  is  ${}^2T_{2g}^5$ , then the separation between the two low energy spin-forbidden transitions  $v_1$  and  $v_2$  corresponds to 8*B* [20]. The magnitude of this separation is useful in evaluating the electronic repulsion parameter *B*. The values of 10 Dq have been calculated from the relation:

 ${}^{2}T_{2g} \rightarrow {}^{2}A_{2g} = 10 \text{ Dq} - 3F_{2} - 20F_{4} \text{ [21]}$ 

The *B*-values are less than that of the free ion indicating considerable orbital overlap with strongly covalent metal-ligand bond. The nephelauxetic parameter,  $\beta$ , is in the 0.64–0.68 range indicating that HLn is in the middle nitrogen and oxygen donor series. It is apparent that the parameter,  $\beta$ , depends greatly upon the electronegativity of the donor atoms and the ligand structure. According to Jørgensan [22], decrease B-values are associated with a reduction in the nuclear charge on the cation and an increased tendency to be reduced. For 4d metal, the variation of the Racah interelectronic repulsion parameter with the ionic charge,  $Z^*$ , and the number of the electrons in the partly fielded dstate (q) is given by the equation: B = 742 + $28q + 50(Z^* + 1) - 500/(Z^* + 1)$ . The Z\*-values of the ruthenium(III) in the complexes are listed

in Table 2, and lie in the 0.68-0.80 range which is considerably below the formal value of +3.

As can be seen from Table 2, the Racah parameters (Dq, *B*,  $\beta'$ ) and  $Z^*$  values increased from compound 5, 4, 3, 2 to 1. This can be attributed to the fact that the effective charge experienced by the d-electrons decreased due to the electron withdrawing p-substituent (HL<sub>4</sub> and HL<sub>5</sub>) while it increased by the electrons donating character of HL<sub>1</sub> and HL<sub>2</sub>. This is in accordance with that expected from Hamett's constant ( $\sigma^R$ ) (Fig. 1a–d) correlate the Racah parameter with  $\sigma^R$ , it is clear that all these parameters decrease with increasing  $\sigma^R$ .

The above results show clearly the effect of substitution in the para position of the benzene ring on the stereochemistry of both Ru(III) complexes. It is important to note that the existence of a methyl and/or methoxy group enhances the electron density on the coordination sites and simultaneously increases the values of Racah parameters (Table 2).

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