Stereochemistry of new nitrogen-containing heterocyclic aldehydes. XII. Supramolecular structures and properties models of ruthenium with quinoline azodyes

A.S. Al-Shihri[a], M.M. Khalil[b] and A.Z. El-Sonbati[c]

[a]Department of Chemistry, Faculty of Science, King Khalid University, Abha, P.O.Box 9004, Saudi Arabia

[b]Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

[c]Chemistry Department, Faculty of Science (Demiatta), Mansoura University, Demiatta, Egypt

Novel bis- and tris-complexes of ruthenium(III) with 5-(4'-derivative phenyldiazo)-8-hydroxy-7-quinolinecarboxaldehyde (HL*n*) have been characterised on the basis of elemental and thermal analysis, IR, magnetic and electronic spectral analysis as well as conductivity measurements. Electronic spectra show that all complexes are octahedral with chloride are attached to the metal ion in a 1:2 (metal:ligand) ratio. The spectral data were utilised to compute the 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. It is apparent that the β values depend greatly upon the electronegativity of the donor atoms and the ligand structure and also the effect of the *p*-substituent groups. IR spectra indicate that the ligand is bidentate forming a six-membered chelating ring with concomitant formation of an intramolecular hydrogen bond. The ligands are present in associated form in solution via intermolecular hydrogen bonding. The effect of Hammett's constant on the ligand field parameters is also discussed.

Keywords: ruthenium azodyes, Hammett's constants, ligand field parameters

Introduction

The preparation, characterisation and spectroscopic properties of some heterocyclic nitrogen-containing aldehydes and their Schiff bases and/or azodyes as well as their transition metal complexes have been described.[1,2]

Due to the diverse properties of quinoline azodyes and their wide application in many field (medicine, analytical chemistry…*etc*.), we have witnessed an increased interest in the study of their complexing affinities toward different transition metals.[1,2] Since we could not find literature information on Ru(III) complexes with 5-(4'-derivatives phenyldiazo)-8-hydroxy-7-quinolinecarboxaldehyde (HL*n*), we have undertaken their preparation and characterisation.

This study is part of a general investigation on Ru(III) complexes with HL*n*, which appear to have potential as anticancer agents.[1–4]

In this paper, the results of IR, electronic spectroscopic studies together with magnetic measurement are presented and discussed. Correlations of Hammett's constants with ligand field parameters were also examined.

Experimental

All the chemical used were of BDH quality. 8-hydroxy-7-quinolinecarboxaldehyde (oxine) was prepared by the method outlined by El-Sonbati.[5]

Preparation of azo compounds

Aniline or its *p*-substituted derivatives (10 mmol) was dissolved in hydrochloric acid (20 mmol/ 25 ml distilled H_2O). The hydrochloric compound was diazotised below -5°C with a solution of sodium nitrite (0.8 g, 10 mmol, 30 ml distilled H_2O). The diazonium chloride was coupled with an alkaline solution of oxine (1.7 g, 10 mmol) in 20 ml of ethanol. The crude dye was filtered off and crystallised from dimethyl formamide, then dried in a vacuum desicator over P_2O_5.

Synthesis of the complexes

Ru(III) complexes were prepared by a general method. A stoichiometric amount of $RuCl_3.3H_2O$ (0.01 mol) in EtOH was added to a hot solution of the ligands (0.02 mol and/or 0.03 mol) in absolute EtOH and the reaction mixture was boiled under reflux with stirring for 2–3 h. On slow evaporation of EtOH the described complex was obtained as microcrystals. In some cases complete precipitation was achieved by addition of Et_2O to the cold reaction mixture. The deeply coloured precipitates were separated by filtration, washed with cold EtOH followed by Et_2O and finally dried *in vacuo* over anhydrous CaO for two weeks.

Results and discussion

Thermal analysis

The TGA and DTG analyses of $[Ru(Ln)_3]$ show a three-step weight loss in air. The first occurs in the range 250–280°C. The $Ru(NCO)_3$ formed is stable up to *ca* 330°C. whereupon decomposition occurs. Conversion Ru_2O_3 is complete at *ca* 375^{0}C. Ru_2O_3 is stable up to 407°C. In each temperature range, the DSC curve shows an endothermic peak. There is qualitative 1:1 correspondence between DSC and DTG curves for all complexes, indicating that each thermal effect is accompanied by a corresponding mass loss. For $[Ru(Ln)_2Cl]$ the initial weight loss occurs in the range 250–380°C and Ru_2O_3 is formed. The DSC curves also show an endothermic peak in this range. Ru_2O_3 is found to be stable up to *ca* 415°C and then it converts into RuO_2 in the temperature range 410–450°C. The organic part of the chelate gradually burned away and the crucible became empty within the temperature range 485–580°C. The degradation of the organic part of the chelate was an endothermic reaction, which resulted in carbon as residue.

Characterisation of the azo compounds

^{1}H NMR spectra

The ^{1}H NMR spectra show a broad signal for C_8–O*H*. This favours formation of an intramolecular hydrogen bond with the CO group. Electron-withdrawing substituents reduce the intramolecular hydrogen bond as indicated by the marked shift of the hydroxyl signal to a 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 due to the C_8–OH protons at 9.60–10.25 ppm are not affected by dilution and disappear in the presence of D_2O. The shifts are in the sequence : *p*-NO_2 > *p*-Cl > H > *p*-OMe > *p*-CH_3. the multiples at *ca* 8.80 ppm can be assigned to the proton of the pyridine ring.[2,7]

By tracing the IR spectra of the azo compounds, no νNH_2 stretching vibrations are apparent. This supports the formation of azodye ligands. The mode of bonding of the HLn to the metal ions was elucidated by comparing the IR spectra of the complexes with literature data of related systems. The positions of the most relevant and characteristic bands are due to: (i) carbonyl oxygen, (ii) azo-nitrogen, (iii) C_8-OH and (iv) the CN_{Py} group.

The spectra exhibit a medium to strong band in the region 1400–1500 cm^{-1} which could be assigned to the N=N stretching vibration.[7] The C=C stretching vibrations of the phenyl ring at 1500–1600 cm^{-1} are due to the symmetric and asymmetric vibrations, respectively. The investigation of Rossmey and Mecke[8] on deuterated phenolic derivatives showed that the higher frequency band would be

---

* Correspondence. E-mail: elsonbatish@yahoo.com

related to δOH, whereas the band at around 1100 cm^{-1} can be due to νC–OH. The higher value of the δOH absorbtion may account for the existence of hydrogen bonding. Califan and Luttke[9] found that the OH in hydroxyl compounds suffered a blue shift when the OH group is involved in a hydrogen bond.

On turning our attention to the IR spectra of hydrogen containing azo compounds such as HL*n* (Scheme 1), the N=N stretching mode showed a series of medium to weak bands at 1435, 1490 and 1525 cm^{-1}. These bands, together with the very broad bands centered at *ca* 3530 cm^{-1} and *ca* 2900 cm^{-1} suggest a six-membered chelate skeleton. The hydrogen bonding in this compounds could be classified into types according to the position of the OH group, *vis*. (i) intramolecular hydrogen bonding between the C_8–OH and CO and/or CN (Scheme 1A); and (ii) intermolecular hydrogen bonding resulting from the C_8–OH group through two molecules (Scheme 1B) and/or C_8–OH with CN (Scheme 1C) or CO (Scheme 1D) through two molecules. This could be confirmed by the appearance of the high frequency band (*ca* 3530 cm^{-1}) as a result of intermolecular hydrogen bonding and that at lower frequency (*ca* 2900 cm^{-1}) due to the intramolecular hydrogen bonding.

Coggeshall,[10] Diab and El-Sonbati[11] found three kinds of bond–OH structures on the basis of the frequencies: (i) only the oxygen is in the bridge while the hydrogen is free; (ii) a polymer chain is formed in which both hydrogen and oxygen atoms participate in the hydrogen bond; and (iii) dimer associates are formed.

The IR data of HL*n* exhibit a weak band at *ca* 1655 cm^{-1}. This is a criterion for νC=O of the aldehydic group. A very strong band at 1585±10 cm^{-1} is apparent and assignable to νC=C of the phenyl ring. Vibrational bands at 2900 cm^{-1} of medium appearance and a broad at 3400–3550 cm^{-1} are apparent in the off-group region. This indicates two types of hydrogen bonding: (i) an intramolecular one between OH and aldehydic group (Scheme 1A); and (ii) an intermolecular one between OH and aldehydic group through two molecules (Scheme 1D).

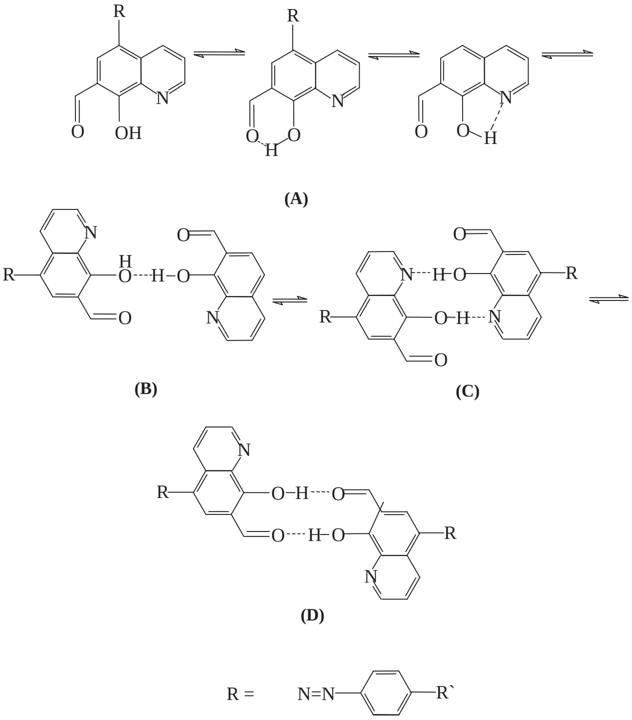
Bonding atoms and stereochemistry

The most important bands in the IR spectra of the complexes are assigned to vibrations of the ligands in accordance with published data.[1-3,11] The most important bands of the infrared spectra of the complexes and of the ligands are also included for comparison. The main differences are those related to OH and CO vibrations, suggesting that coordination has been effected. The analytical data (Table 1) of the prepared ruthenium complexes proved their existence in the following stoichiometries:

(1) 1:3 stoichiometry for Ru-quinoline azodyes (**1–5**).

(2) 1:2 stoichiometry is present in Ru-quinoline azodyes (**6–10**).

The geometry and mode of bonding in these complexes are deduced from infrared, electronic spectra and the magnetic susceptibility measurements. The IR data of the complexes are compared to that of the free ligand as follows:



R` = OCH_3 (*n*=1), CH_3 (*n*=2), H (*n* = 3), Cl (*n* = 4) and NO_2 (*n* = 5)

Scheme 1 General formula and proton numbering scheme of the HL*n*.

Phenolic group vibration

The complexes show no band assignable to phenolic [ν(OH)] but the band at *ca* 1260 cm^{-1} due to ν(C–O) in the quinoline azodye (HL*n*) is significantly shifted to higher frequencies suggesting bonding from the oxygen atom to ruthenium.

Carbonyl group vibration

A strong band at *ca* 1655 cm^{-1} in the ligands is characteristic of the CO group. In all the complexes; this band is shifted towards lower frequency region by *ca* 5–10 cm^{-1} indicating coordination of the ligand carbonyl oxygen atoms.

Azomethine group vibration

The characteristic band of the CN_{Py} ring, observed at 1625 cm^{-1}, is little changed indicating the nitrogen atom of the quinoline does not take part in coordination.[1-3]

Table 1 Analytical data of isolated complexes (for molecular structure see Scheme 2)

Compound[a,b]	Code	Structure	Expt (calcl.)%			Cl[c]	$\mu_{eff.}$[d]
			C	H	N		
HL_1			66.5 (66.6)	4.2 (4.2)	13.7 (13.5)		
HL_2			70.1 (70.0)	4.5 (4.6)	14.4 (14.6)		
HL_3			69.3 (69.3)	4.0 (3.9)	15.2 (15.0)		
HL_4			61.6 (61.5)	3.2 (3.2)	13.5 (13.3)		
HL_5			59.5 (59.6)	3.0 (3.1)	17.5 (17.4)		
$[Ru(L_1)_3]$	1	**2A**	60.0 (60.1)	3.4 (3.5)	12.0 (12.4)	–	1.89
$[Ru(L_2)_3]$	2	**2A**	62.9 (63.0)	3.7 (3.7)	12.8 (13.0)	–	1.86
$[Ru(L_3)_3]$	3	**2A**	61.9 (62.0)	3.1 (3.2)	13.8 (13.6)	–	1.84
$[Ru(L_4)_3]$	4	**2A**	55.7 (55.8)	2.5 (2.6)	12.0 (12.2)	–	1.79
$[Ru(L_5)_3]$	5	**2A**	54.0 (54.1)	2.6 (2.5)	15.6 (15.8)	–	1.81
$[Ru(L_1)_2Cl]$	6	**2B**	54.5 (54.5)	3.1 (3.2)	11.0 (11.2)	4.9 (4.7)	1.64
$[Ru(L_2)_2Cl]$	7	**2B**	57.0 (56.9)	3.5 (3.4)	12.0 (11.7)	5.2 (5.0)	1.62
$[Ru(L_3)_2Cl]$	8	**2B**	55.8 (55.8)	2.8 (2.9)	12.4 (12.2)	5.0 (5.2)	1.59
$[Ru(L_4)_2Cl]$	9	**2B**	50.9 (50.7)	2.5 (2.4)	11.4 (11.1)	5.0 (4.7)	1.49
$[Ru(L_5)_2Cl]$	10	**2B**	49.3 (49.3)	2.4 (2.3)	14.7 (14.4)	4.8 (4.6)	1.53

[a] HL_1–HL_5 are the ligand as given in Scheme 1 and L_1–L_5 are the anions.

[b] Deprotonation is confirmed by evolution of hydrochloric acid during complex formation and are assessed quantitatively by the pH-metric technique and by a spot test technique and its characteristic colour.

[c] Estimated gravimetrically.

[d] Per metal ion and measured at room temperature.

Aromatic vibration

The medium intensity band appearing around 1555 cm^{-1} in the ligand, can be assigned to the aromatic [ν(C=C)] vibrations, is little changed indicating non-participation of π-electron cloud in the M–L bond formation.[12]

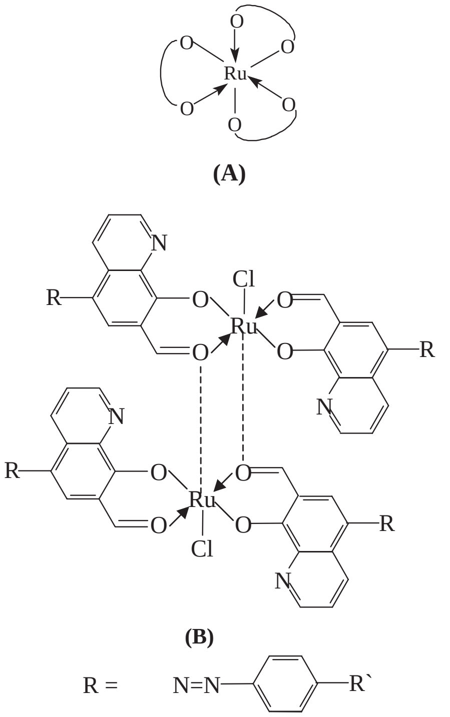
Metal-ligand vibrations

In all the present complexes, the bands with medium and weak intensity in the IR region, 570–590 [ν(Ru–O)] and 310–330 cm^{-1} [ν(Ru–Cl)] [3] indicate the presence of a terminal coordinated chloride ion[6] and also confirm the octahedral stereochemistry of the ligands around the ruthenium metal ion.

Thus, we conclude that the ligand (HL*n*) has two coordinating sites, the carbonyl oxygen and the phenolic oxygen atom. Two geometrical isomers are possible for the tris complexes (**1–5**), the first being the *cis*-isomer with a threefold rotation axis and the second being the *trans*-isomer with a lower symmetry (Scheme 2A). It is interesting to note that complexes (**6–10**) do not exhibit bands characteristic of coordinated water molecules. Therefore, in these complexes, interaction of ruthenium(III) ion with the free electron pairs of the oxygen atoms of a neighbouring complex molecule confers coordination saturation in the octahedral configuration (Scheme 2B).

Magnetic measurements

The magnetic moments were measured at room temperature using the Gouy method and $\mu_{eff.}$ values are listed in Table 1. They correspond to a spin quantum number S = $^1/_2$ as expected for the low-spin configuration t^5_{2g} Ru^{3+} with one unpaired electron in an octahedral environment. For complexes (**1**)–(**5**) the observed magnetic moments are slightly higher than the spin only value for one unpaired electron (1.73 BM.), which can be explained by slight spin–orbit coupling as is common in such cases. For complexes (**6**)–(**10**) the measured effective magnetic moment $\mu_{eff.}$ are lower than the spin only value. This might be indicative of an exchange interaction between two neighbouring ruthenium ions of d^5 configuration in polymeric structures.



R` = OCH$_3$ (*n*=1), CH$_3$ (*n*=2), H (*n* = 3), Cl (*n* = 4) and NO$_2$ (*n* = 5)

Scheme 2 Molecular structures proposed for (A) monomeric and (B) polymeric forms.

Table 2 Electronic spectra and ligand field parameters (cm^{-1}) for octahedral ruthenium(III) complexes (for structures see Table 1)

Complex	Bands (ob.)	Assignments	ν_2/ν_1	10Dq	B	β	C	F_2	F_4
1	13620 17700 18380	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$	1.30	26010	510	0.629	2040	801.4	58.2
2	13530 17530 18700	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$	1.30	25500	500	0.623	2000	785.7	57.1
3	13650 17600 18800	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$	1.29	25184	493.8	0.614	1975	776	56.4
4	13100 16900 18200	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$	1.29	2397	475	0.597	1880	738.6	53.7
5	13440 17350 18600	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$	1.29	24929	488.8	0.60	1955.2	768.3	55.9
6	14280 18180 19800	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$	1.27	24863	487.5	0.665	1950	766.1	55.7
7	14080 17890 19800	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$	1.27	24291	476.3	0.637	1905.2	748.5	54.4
8	14000 17700 20050	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$	1.26	23588	462.5	0.613	1850	726.8	52.9
9	14800 18150 22700	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^4T_{1g}$	1.23	21359	418.8	0.565	16752	658.1	47.9
10	14500 18050 21500	$^2T_{2g} \rightarrow {}^4T_{1g}$ $^2T_{2g} \rightarrow {}^4T_{2g}$ $^2T_{2g} \rightarrow {}^2A_{2g}, {}^4T_{1g}$	1.25	22634	443.8	0.593	17752	697.4	50.7

[a] Numbers as given in Table 1.

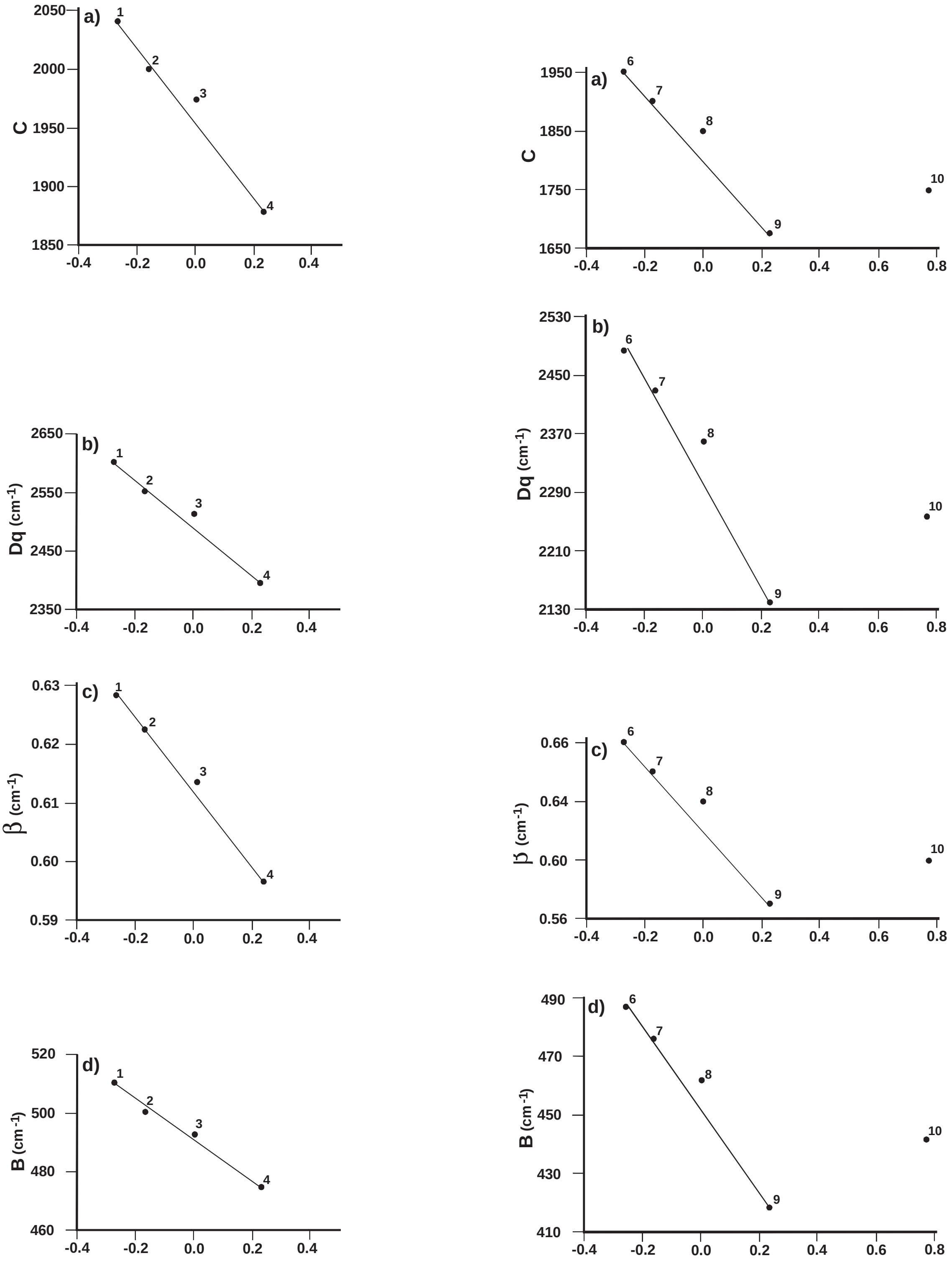


Fig. 1 The variation of p-substituted Hammett's constants; (a) C; (b) Dq; (c) β and (d) B.

Electronic absorption spectra

Ruthenium has the electronic structure corresponding to d^5. The ground state of octahedral ruthenium(III) (t^5_{2g}) is $^2T_{2g}$ which is in accordance with the results of the magnetic moment values in Table 2.

The electronic absorption spectra of the Ru^{3+}-azodye quinoline complexes under study, show three groups of bands. The absorption bands seem always to be of the same pattern through appearing with varied extinctions and changed absorption maxima which can be ascribed to changes in the molecular structure of the ligands leading to varied strength in the azodye quinoline → Ru^{3+} interaction. Of the three regions, the bands with frequencies above 34000 cm^{-1} can be assigned to localised $\pi \rightarrow \pi^*$ transitions of the aromatic system. The bands within the 20000–34000 cm^{-1} region represent various types of C.T. transitions either within the ligand molecule (intraligand CT) or due to L → Ru^{3+} or R^{3+} → L CT interactions. The third group of bands lying below 20000 cm^{-1} usually exhibits three distinct peaks. These three peaks can be attributed to three spin forbidden d–d transitions at *ca* 13000–14400 ($^2T_{2g} \rightarrow {}^4T_{1g}$), 17000–18400 ($^2T_{2g} \rightarrow {}^4T_{2g}$) and 19000–20000 cm^{-1} ($^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$) transitions in increasing order of energy as expected for octahedral symmetry of low spin Ru(III) complexes.[13] The separation between the two low energy spin-forbidden transition corresponds to 6B.[14] 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:[11]

$$^2T_{2g} \rightarrow {}^2A_{2g} = 10\ Dq–3F_2–20F_4$$

However, the electronic spectra may be further rationalised in terms of ligand field parameters (Table 2), which show that the values of the Racah parameter B are less than the free ion value which is an indication of strong covalent bonding between the metal ion and the ligand. The effect of covalent bonding is reflected by the high value of 10Dq. Such values of 10Dq are generally associated with considerable electron delocalisation.[14] The electronic spectra of these complexes are further rationalised in terms of ligand field parameters (10Dq) and interelectonic repulsion parameters (B and C) by using the following equations:[15]

$$^4T_{1g}\ (t^4e) = 10Dq–5B–4C$$
$$^4T_{2g}\ (t^4e) = 10Dq + 3B–4C$$
$$^2A_{2g},\ ^2T_{1g}\ (t^4e) = 10Dq–2B–C$$

The values of these parameters, given in Table 2, are comparable to those reported for other ruthenium(III) derivative involving oxygen donor molecules.[14] The B-values are *ca* 58–88% of that of the free ion indicating considerable orbital overlap with strongly covalent metal–ligand bonds. In other words, the greater the reduction in B the greater the covalent character in the metal–ligand bond and the smaller the effective charge experienced by the d-electrons.[15] The overall effect of the covalent bonding will be an increase in the observed value of 10Dq. Such an increase in 10Dq values is generally associated with considerable electron delocalisation.[16] Decreasing β values 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 second row transition metals, the variation of the Racah interelectronic repulsion parameter with the cationic charge Z* and the number (q) of electrons in the partly filled d-shell is expressed by the relation[14] below:

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

This gives effective ionic charges of the ruthenium(III) complexes in the 0.97–1.22 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 and will be affected the p-substituent groups.

As can be seen from Table 2, the Racah parameter values increased on passing from **10** 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-substituents of HL_4 and HL_5, while it increased by the electron donating character of the substituents of HL_1 and HL_2. This is in accordance with that expected from Hammett's constants (σ^R) Fig. 1a–d correlates the Racah parameter with σ^R, it is clear that all these parameters decrease with increasing σ^R.

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

In conclusion, the results arising from the present investigations confirm that the selected 5-(4´-alkyl-phenylazo)-8-hydroxy-7-quinolinecarboxaldehyde ligands are suitable for building a supramolecular structure. Moreover, since the azo compounds experience photochemical isomerisation and are therefore of interest for applicative purposes,[17] complexes containing the HL*n* moiety combine features which could be useful in molecular materials. Work is underway on the synthesis and characterisation of further compounds of this family of ligands and toward the development of the materials they produce.

Received 14 May 2003; accepted 10 October 2003
Paper 03/1806

References

1 A.Z. El-Sonbati, A.A. El-Bindary and M.A. Diab, *Spectrochim. Acta Part A*, 2003, **59**, 443.
2 A.Z. El-Sonbati, A.S. El-Shihri and A.A. El-Bindary, *J. Inorg. Organomet. Polym.*, 2003, **13**, 99.
3 A.A. El-Bindary, A.S. El-Shihri and A.Z. El-Sonbati, *Design. Monom. Polym.*, 2003, **6**, 283.
4 S.S. Aleksenko, A.P. Gumenyuk, S.P. Mushtakova and A.R. Timerbaev, *J. Anal. Chem.*, 2001, **370**, 865.
5 A.Z. El-Sonbati, *Spectroscopy Lett.*, 1997, **30**, 459.
6 A.Z. El-Sonbati, A.A. El-Bindary and A.A. Al-Sarawy, *Spectrochim. Acta Part A*, 2002, **58**, 2771.
7 A.Z. El-Sonbati, A.A. El-Bindary, A.F. Shoair and R.M. Younes, *Chem. Pharm. Bull.*, 2001, **49**, 1308.
8 G. Rossmey and R. Mecke, Z. *Electrochem*., 1956, **59**, 866.
9 S. Califan and W. Luttke, *Z. Phys. Chem.*, 1955, **5**, 240.
10 N.D. Coggeshall, *J. Am. Chem. Soc.*, 1947, **69**, 1620.
11 M.A. Diab and A.Z. El-Sonbati, *Polym. Deg. Stab.*, 1990, **29**, 271.
12 K. Laxma Reddy, S. Sri Hari and P. Lingaiah, *Ind. J. Chem.*, 1985, **24A**, 318.
13 R.S. Nyholm and G.J. Sutton, *J. Chem. Soc.* A, 1958, 567.
14 A.Z. El-Sonbati, A.A. El-Bindary and A.F. Shoair, *Spectrochim. Acta* Part A, 2002, **58**, 3003.
15 A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968.
16 C. Preti, G. Tosi and P. Zannini, *Inorg. Nucl. Chem.*, 1979, **41**, 485.
17 Z. Sekkat, C.S. Kang, E.F. Aust, G. Wegner and W. Knoll, *Chem. Mater.*, 1995, **7**, 142 and refs. therein.