Iron(II) Complexes of *ortho*-Functionalized *para*-Naphthoquinones
1. Synthesis, Characterization, Electronic Structure and Magnetic Properties

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Abstract

A series of six high-spin ferrous complexes of *ortho*-functionalized paraquinone ligands of the type $M(L)_2(H_2O)_2$, L = anion of the lawsone derivative, are synthesized where the bound quinone ligands are found to be in their fully oxidized form and the coordinating centers are the C-2 phenolate and the C-1 carbonyl. Thermal studies indicate that the two water molecules are coordinated and their loss leads to the decomposition of the chelates. Variable temperature magnetic susceptibility studies establish the high-spin state of the iron and confirm the quinone formulation of the ligands while Mössbauer data clearly establish the +2 oxidation state for the iron centers. Finally, the electronic absorption data indicate that the six high-spin ferrous complexes described herein are isostructural species including the O_6 chromophore and the cyclic voltammetry confirms that the lawsone ligands are coordinated in their quinone form while the iron centre is at the +2 oxidation state.

Introduction

The bacterial reaction centre has been shown to contain a quinone (Q_A) as primary acceptor which accepts an electron from the reduced bacteriopheophytin dimer (BPh) and transports it further to the subsequent secondary quinone acceptor (Q_B) during the bacterial photosynthesis [1–3]. At this site the two quinones (Q_A and Q_B) which have been shown to be either ubiquinones or menaquinones are 7 Å apart from one high-spin iron(II) ion [4]. EPR measurements [5] and static magnetization studies [6] have shown that both Q_A and Q_B are magnetically coupled to the adjacent ferrous centre. A similar 'ferroquinone complex' (Q_AFe(II)Q_B) has been identified on the acceptor side of photosystem 2 in

chloroplasts [7] where the primary (Q_A) and secondary (Q_B) acceptors of PS2 are plastoquinones. A possible role for the ferrous ion would be to facilitate electron transfer from Q_A to Q_B during which, however, it retains its high-spin nature as determined from the magnetic susceptibility [6] and Mössbauer [8] measurements. In view of this it is necessary to characterize high-spin ferrous complexes covalently linked to quinone ligands and compare their structural characteristics with the biological preparations.

The coordination chemistry of *p*-quinone ligands has not been as extensively developed [9a] as that of corresponding *o*-quinone class [9b]. Iron complexes of some *ortho*-functionalized *p*-quinones like tetrahydroxyanthraquinone [10], chloroanilic acid [11, 12], lawsone [13, 14] and phthiocol [15, 16] have been tentatively characterized in the past. There have also been attempts to synthesize ferrous–semiquinone complexes, the hypothetical intermediates in the electron transport process between Q_A and Q_B [6, 17] employing ortho- and paraquinone ligands which have, however, been unsuccessful and have instead yielded high-spin iron(III) compounds with either a single *o*-semiquinone ligand [18–20] or three semiquinone moieties [19] and binuclear iron(III) complexes with bridging hydroquinone dianions [18b, 20].

In this paper we shall describe the synthesis and characterization of some high-spin ferrous complexes containing two *ortho*-functionalized *p*-quinones which belong to the class of C-3 substituted lawsone (2-hydroxy-1,4-naphthoquinone, **II**) derivatives (Fig. 1). Lawsone is the colouring principle of 'Henna' (*Lawsonia alba*), which can be obtained from its leaves by extraction with mild alkali [21]. Its methyl derivative (**I**) is found to be associated with long grown synthetic cultures of *Mycobacterium tuberculosis* [22] while the presence of chloro derivatives (**III**) is suspected in the plant families Droseraceae [23] and Plumbaginaceae [24]. The other derivatives (**IV**–**VI**) are of synthetic origin.

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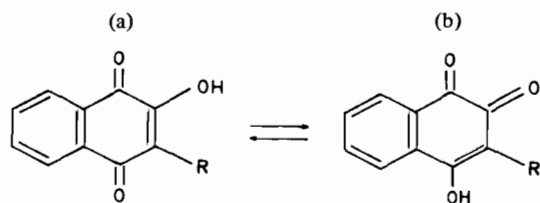
R = CH₃(I); H(Lawsone, II); Cl(III); Br(IV); I(V); NO₂(VI)

Fig. 1. Tautomeric forms of lawsone (**II**) and substituted lawsones (**I** and **III** to **VI**).

Experimental

Materials

All chemicals used for the preparation of the ligands and their metal chelates were of analytical grade. Solvents were purified prior to use according to literature methods [25].

Ligands

Lawsone (**II**) is an Aldrich product while other ligands (**I** and **III–VI**) have been synthesized according to reported procedures [26].

Complexes

The ligands (**I** to **VI**, 0.002 mol in each case) were dissolved in a minimum amount of methanol (~100 ml) while $FeSO_4$, $7H_2O$ (0.001 mol) was dissolved in a minimum amount of distilled water (25 ml). The ligand and metal ion solutions were taken up in a Schlenk assembly maintained under nitrogen and were degassed with oxygen-free nitrogen gas for 10 min. The metal ion solution was added dropwise onto the ligand solution maintained slightly warm and under stirring. The pH of the reaction mixture was adjusted between 5 and 6 with a few drops of degassed 10% acetate solution and measured with a combined glass electrode (GK 2401C) dipped into the reaction mixture through one of the necks of the reaction flask. On completion of the reaction (usually after 6 h) the mixture was allowed to cool overnight and filtered under vacuum. The resulting complexes were washed with water and cold methanol and dried under vacuum. They were finally transferred to a vacuum dessicator in a glove bag under oxygen-free nitrogen gas. The complexes are designated as **1** to **6** where the numbers correspond to respective ligands as indicated in Fig. 1.

Physical Measurements

Elemental analyses were carried out at the micro-analytical laboratory of the University of Poona. The metal was estimated by complexometric titration with EDTA.

IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer coupled with a Perkin-Elmer Infrared Data station. Samples were run as CsBr pellets prepared under nitrogen in a dry-box.

Thermogravimetric measurements were carried out on a STA 409 NETZSCH Geratebau Gmbh Thermal Analyser in air atmosphere, using about 25 mg of sample, with a heating rate of 5° per min. The thermobalance was calibrated using calcium oxalate for TG runs and aluminum trioxide for the DTA experiments.

Variable-temperature magnetic susceptibility data were obtained on polycrystalline samples with a Faraday type magnetometer equipped with a continuous flow Oxford Instruments cryostat. Magnetic field strengths between 4 and 6 kG were employed. The independence of the magnetic susceptibility from magnetic fields up to 12 kG was checked in the whole temperature range. Mercuritetrathiocyanato cobaltate was used as a susceptibility standard. The absolute accuracy on the measurement of the temperature was ±0.2 K. The relative accuracy on the apparent weight increase when the magnetic field is applied was significantly better than 1%. Diamagnetic corrections were applied using Pascal's constants.

Mössbauer data were obtained with a conventional constant acceleration drive coupled to a ND 100 multichannel analyser operating in time mode. A 5 millicurie ⁵⁷Co source was used and the isomer shifts were measured with respect to natural α-iron foil.

UV–Vis spectra were recorded in DMF on a Hitachi-220A spectrophotometer.

Cyclic voltametry (CV) measurements were performed with a home made (CNRS, Toulouse) microcomputer controlled instrument 'DACFAMOV 05' using the three electrode technique with direct correction of the uncompensated cell resistance (iR drop). Current *versus* potential plots and Ep_c, Ep_a, ΔE, ip_c and ip_c/ip_a values resulting from the processing of the plots by the computer (Apple IIe) were recorded on an Epson MX82F/T plotter. The three electrode cell includes a HDME (+200–3000 mV range) or an EDI type platinum rotating electrode (0 + 1500 mV range), a platinum wire auxiliary electrode and a saturated calomel reference electrode. All DMF solutions were prepared in a dry-box and a purified argon atmosphere was maintained in the cell during CV measurements.

Results and Discussion

Synthesis and Compositional Studies

The interaction of ferrous sulphate heptahydrate ($FeSO_4$, $7H_2O$) with different lawsone derivatives in methanol–water (4:1 v/v) under nitrogen atmosphere employing Schlenk assembly yields complexes **1** to **6** which are various shades of red–brown except that of the nitro derivative which is green. The analytical data (Table 1) indicate a general composition of

TABLE 1. Analytical Data and Conductivities of $[Fe^{II}(L)_2(H_2O)_2]$ Complexes of Lawsone Derivatives

Complex	Colour	Yield (%)	Decomposition temperature[a] (°C)	Elemental analysis: found (calc.) (%)					Λ_M in methanol (cm^2 ohm^{-1} mol^{-1})
				C	H	N	Halogen	Metal	
1	brownish-purple	85	254	58.51 (56.68)	4.02 (3.89)			11.87 (11.98)	17.12
2	dark-brown	90	276	54.49 (54.82)	3.23 (3.22)			12.37 (12.75)	19.38
3	reddish-brown	70	214	46.14 (47.37)	2.38 (2.39)		14.25 (13.99)	10.85 (11.01)	13.18
4	reddish-brown	95	248	40.49 (40.31)	2.09 (2.03)		27.03 (26.82)	10.07 (9.37)	20.37
5	reddish-brown	83	231	34.73 (34.92)	1.86 (1.76)		37.02 (36.90)	8.34 (8.12)	22.58
6	green	85	196	46.20 (45.48)	2.47 (2.29)	5.37 (5.30)		10.86 (10.57)	28.43

[a] Obtained from TG curves.

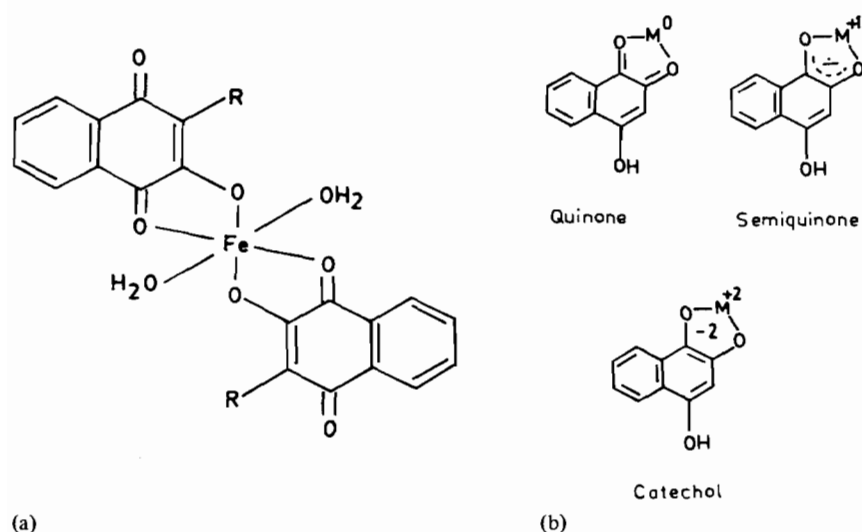(a)   (b)

Fig. 2. (a) Schematic representation of the postulated structure of complexes 1 to 6. (b) Isoelectronic forms of *ortho*-functionalized *p*-quinone--metal complexes.

$M(L)_2(H_2O)_2$ where L = the anion of any one of the lawsone derivatives. The compounds are devoid of any solvated molecules. Their conductivities in methanol indicate them to be non-electrolytes; they are insoluble in non-polar solvents like n-hexane, benzene, etc. but soluble in polar solvents such as methanol, ethanol, dimethyl sulfoxide, dimethylformamide and acetonitrile.

Complexes 1 to 6 involve the paraquinone tautomeric form of the *ortho*-functionalized lawsone ligands and have the $[Fe^{II}(quinone)_2(H_2O)_2]$ general formulation (Fig. 2a). Other formulations involving the orthoquinone tautomeric form of these ligands (Fig. 2b) can be ruled out on the following bases: (i) the oxidation state of the iron reactants is +2 and the ferrous state is retained in the resulting complexes (*cf.* magnetic susceptibility and Mössbauer spectroscopy sections); (ii) no other species is oxidized in the reaction medium; (iii) the quinone oxidation state of the ligands is retained on coordination while deprotonation and coordination of the 2-hydroxyl oxygen atom occurs (*cf.* IR section).

TABLE 2. Significant IR Absorptions[a] of Iron(II) Complexes of Lawsone Derivatives

Metal complexes						Assignment
1	2	3	4	5	6	
3282	3345	3351	3379	3425	3393	ν(OH), coordinated water
3181b	3190b	3235b	3283b	3267b	3223b	
(3335mb)	(3180mb)	(3263mb)	(3203wb)	(3201mb)	(3201mb)	(ν(OH), phenolic)
1665sh	1628sh	1654m	1656m	1652m	1640m	ν(C=O) free
(1675sh,	(1672,	(1658m,	(1670s,	(1670s,	(1690 -	
1656sb)	1640s)	1635s)	1630m)	1644m)	1600sb)	
1618s	1607shb	1620s	1628s	1623s	1594sb	ν(C=O) chelated
(−)	(−)	(−)	(−)	(−)	(−)	
1585, 1552	1582, 1562	1584, 1550s	1560, 1550s	1579, 1545s	1587, 1556m	ν(C=C) activated
(1580m)	(1580b)	(1580s)	(1580)	(1580mb)	(1580s)	by carbonyl
1334s	1338s	1323m	1319m	1316m	1326sh	ν(OH) coordinated water
1230s	1245s	1228s	1228m	1226s	1233s	ν(C–O)
(1208s)	(1225mb)	(1221s)	(1213s)	(1212m)	(1219sh)	
594mb	611wb	616, 580mb	600, 575mb	589, 565mb	596, 582sb	ν(M–O)
(−)	(−)	(−)	(−)	(−)	(−)	

[a]Positions in cm^{-1}. s = strong; m = medium; w = weak; sh = shoulder; b = broad. Frequencies in parenthesis correspond to ligands.

Infrared Absorption Data

Infrared spectroscopy has played an important role in the coordination chemistry of metal–quinone compounds particularly in the identification and assignment of the correct quinone oxidation state based on the characteristic spectral features. The free C=O stretching frequency of 1,4-naphthoquinone is observed at 1675 cm^{-1} while that of 1,2-naphthoquinone occurs at 1678 and 1661 cm^{-1} as a doublet [27]. It has been shown that when o-quinone ligands coordinate with the transition metal ions in their fully oxidized state the carbonyl bands are generally retained [28] in the region 1600–1680 cm^{-1}. A one-electron reduction of the quinone to the semiquinone shifts the carbonyl band by about 100–150 cm^{-1} on coordination [29]. Further reduction to the dianion of the hydroquinone shifts this band to even lower frequency (total shift with respect to parent quinone being about 200 cm^{-1}) and an additional strong band at ~1250 cm^{-1} is also noted by Brown et al. [30].

For the assignment of the infrared spectra of the present complexes we have largely relied upon the data obtained on the related naphthoquinones and their metal complexes. It has been established that substitution of any ionizable group in the quinonoidal part of the p-naphthoquinones gives rise to the presence of 'bifurcated H bonds' [31] at least in the solid state [32, 33]. For example, lawsone (II) exhibits two bands in its solid state mull spectra where the broad absorption at lower wave number (3180 cm^{-1}) is due to intramolecular H bonding

while the shoulder absorption at 3300 cm^{-1} corresponds to intermolecular H bonded association [34]. The magnitude of either of the type of bonding in absence of any additional interactions is normally influenced by the inductive effects of C-3 substituents. Thus, the electron donating substituents are found to favour the intramolecular H bonds while electron accepting groups tend to induce more the intermolecular associations [35, 36]. In case of the orthohydroxyquinones there is a distinct possibility of tautomerization of the ligands into their 4-hydroxy-1,2-naphthoquinone forms (Fig. 1b) during complexation with metals, a problem not encountered in solid state reactions but a reality in solutions [34, 37].

Our assignments of the significant peaks in the IR spectra of iron(II) complexes of lawsone derivatives are shown in Table 2. The C-3 substituted lawsone derivatives studied in the present investigation generally exhibit a broad and medium absorption in the region 3180–3335 cm^{-1} attributable to intra- and intermolecular H bonds. On complexation this absorption disappears, which indicates coordination through C-2 hydroxyl, and is replaced by a broader absorption between 3280 and 3430 cm^{-1} corresponding to the hydroxyl stretches of the coordinated water molecules [38].

The substitutions at C-2 and C-3 positions in the 1,4-naphthoquinone nucleus are known to split the carbonyl absorption at 1675 cm^{-1} due to unequal carbonyl bond strengths as a result of inductive

TABLE 3. Temperature Ranges, Decomposing Chromophores and their Calculated/Observed Percent Losses for $[Fe^{II}(L)_2(H_2O)_2]$ Complexes of Lawsone Derivatives

Stage	Decomposing chromophore	Complexes					
		1	2	3	4	5	6
I	CH_3	121–141[a] 3.32[b] (3.32)[c]					
II	$2(H_2O)$	141–160 7.10 (7.73)	147–219 8.21 (8.22)	121–208 6.72 (7.11)	147–213 6.18 (6.05)	153–175 5.73 (5.24)	
							147–184[e] 94.12 (89.43)
III	2(X-Lawsone)	160–298 77.20 (77.72)	219–326 40.32 (39.75)	208–279 39.35 (41.14)	213–395 83.50 (84.92)	175–352 86.00 (87.24)	
			326–567 39.58 (39.75)	279–379 37.91 (41.14)			
IV	Residue	298 15.74 (15.23)[d]	567 15.68 (16.40)	379 20.37 (13.49)	395 13.12 (11.91)	352 10.51 (9.56)	184 7.48 (13.44)

[a]Temperature range.   [b]% wt. ion observed.   [c]% wt. ion calculated.   [d]% wt. ion calculated for FeO.   [e]$2(H_2O) + 2$
(ligand moieties).

effects [27, 39]. Such splitted carbonyls can be seen in the present ligands in the region 1600–1690 cm^{-1}. These are shifted to lower wavenumbers on complexation. The amount of shift is found to be about 20 cm^{-1} for ligands with electron attracting substituents (e.g. halides and nitro) while those with electron releasing substituents (such as methyl) show shifts twice that amount. The shifted carbonyls are found to activate the adjacent C=C skeletal in-plane vibration of the conjugated aromatic ring to the extent that its intensity exceeds that of the carbonyl stretch itself [40]. Such activated C=C vibrations can be seen in the present compounds between 1545 and 1587 cm^{-1}. However, in no case are the shifts of the same magnitude as found for the semi-quinone compounds indicating thereby that coordination in our complexes is essentially through the deprotonated 2-hydroxy-1,4-naphthoquinone form of the ligands. This is corroborated by the magnetic susceptibility data discussed later on.

The present complexes also exhibit splitting of the aromatic ring stretching vibrations at ca. 1587 and 1545 cm^{-1}, respectively, while the deformation mode of the hydroxyl stretch of the coordinated water molecules can be seen in our compounds in the 1316–1338 cm^{-1} range. The $\nu(C-O)$ frequency at ca. 1215 cm^{-1} is found to undergo upward shift by ca. 20 cm^{-1} on complexation indicating increase in

the bond order and confirming the participation of C-2 hydroxyl in coordination.

In the far-IR spectra of these complexes vibronically pure (or least coupled) $\nu(M-O)$ frequencies can be assigned in the 575–617 cm^{-1} range [41].

Thermal Studies

Pierpont and Buchanan [9b] have noted a marked tendency amongst the metal complexes of o-quinone ligands to form solvates which are non-stoichiometric. The thermogravimetric profiles of the synthesized complexes were, therefore, recorded to establish their compositional differences as well as to ascertain the nature of associated water (coordinated or lattice) molecules.

From the observation of these profiles a generalized pattern (Table 3) becomes quite apparent in the thermal decomposition of these chelates. There are no endothermic losses in TG and DTA curves of any of these compounds corresponding to the loss of lattice water even up to 140 °C indicating their unsolvated nature which is in agreement with the IR data. The first stage of the decomposition in almost all of the compounds (except complex 1 for which the methyl groups seem to decompose earlier in the range 121–141 °C) corresponds to the loss of two water molecules which begins between 140 and 153 °C and continues over a temperature range of variable

TABLE 4. Effective Magnetic Moments of Complexes 1 to 6 at 300, 97, 47, 24 and 5 K

Complex		μ_B/Fe (BM)				
		300 K	97 K	47 K	24 K	5 K
1	$Fe^{II}(3\text{-}CH_3L)_2 \cdot 2H_2O$	4.97	4.85	4.75	4.61	4.22
2	$Fe^{II}(L)_2 \cdot 2H_2O$	5.16	5.15	5.17	5.20	4.80
3	$Fe^{II}(3\text{-}ClL)_2 \cdot 2H_2O$	5.14	5.15	5.08	4.92	4.28
4	$Fe^{II}(3\text{-}BrL)_2 \cdot 2H_2O$	5.14	5.04	5.07	4.99	4.58
5	$Fe^{II}(3\text{-}IL)_2 \cdot 2H_2O$	5.11	5.11	5.08	4.85	4.02
6	$Fe^{II}(3\text{-}NO_2L) \cdot 2H_2O$	5.22	5.33	5.31	5.19	5.07

extent. It can be argued that the decomposition temperatures for the loss of corresponding water molecules for these similar complexes may be indicative of the strength of the chelate structure generated by the O_4 donor set since it has been established by Burger [42] that the increase in the strength of the metal–donor atom bond exhibits a decreasing trend in the decomposition temperatures of other donor ligands. The incorporation of electron-releasing substituents in the lawsone nucleus indeed leads to more stable chelate structure thereby weakening the *trans*-axial bonds with the aquo ligands, which are, therefore, lost at lower temperatures. On the other hand, the electron-attracting substituents tend to increase the decomposition temperatures of the axial aquo ligands slightly, although these increases are not as much dramatic as noted in case of electron-releasing substituents.

The loss of the coordinated water molecules is found to lead to the decomposition of the chelate structure indicated by an accelerated loss in the TG curve. The corresponding DTA profiles for these complexes show that this step of the decomposition is a very complex process consisting of several stages and assignment of the individual decomposing group becomes extremely difficult. However, it can be pointed out that ligands bearing the electron-attracting substituents exhibit a more complex pattern of decomposition. The loss of the chelate structure results in the conversion of the compounds to their oxides as shown in Table 3. Compared to the ferrous–lawsonate, the oxide formation temperatures of the other chelates are on the lower side (in the range of 300–400 °C). The extreme lowering observed for the nitro chelate (*ca.* 184 °C) could be an attractive proposition for the preparation of the useful iron oxides.

Magnetic Data

It has been pointed out that μ_{eff}/mol values for molecules containing two or more paramagnetic centres per molecule, are an expression of the summation of the susceptibilities of the constituent parts. The observed moments can, therefore, be used as the

diagnostic tools in formulating these complexes as containing the quinone, semiquinone or catecholate ligands where only the semiquinone form of the ligand is paramagnetic [9b]. The magnetic moments of the metal–quinone compounds containing such paramagnetic semiquinone ligands have been interpreted in terms of the spin–spin coupling of the metal and quinone centres at the first approximation and intermolecular exchange interactions for more complete description of the crystal structures by Hendrickson *et al.* [43].

The room temperature magnetic susceptibility data for the present compounds (μ_{eff} = 4.97 to 5.22 BM, Table 4) evidence high-spin S = 2 systems [44]. The variable temperature magnetic susceptibility data summarized in Table 4 show a small decrease in μ_B/Fe for complexes 2, 4 and 6. This decrease is situated between 20 and 4 K which indicates that it originates in a small zero field splitting term. The decrease in μ_B/Fe with decreasing temperature for complexes 1, 3 and 5 begins at higher temperature and is more gradual and slightly more pronounced. It can be attributed to weak intermolecular antiferromagnetic interactions, either alone or together with a small zero field splitting term.

Although these magnetic susceptibility data could agree with formulations involving the orthoquinone tautomeric form of the ligands, we have already noticed that these formulations disagree with the IR data that indicate the presence of the unreduced but deprotonated (and therefore mono-anionic) lawsone ligands. Furthermore, the Mössbauer data described in the following section unequivocally confirm that these complexes are high-spin iron (II) compounds ruling out definitely the formulations involving lawsone ligands chelated in the semiquinone or hydroquinone oxidation state. On the other hand these magnetic susceptibility results do agree with the Fe^{II}(quinone)$_2$ formulation schematized in Fig. 2a.

Mössbauer Data

The Mössbauer spectra were obtained for the present series of complexes at 300 and 77 K whenever necessary. In each case, the spectrum consists of

TABLE 5. Mössbauer Data[a] for [Fe^{II}(L)$_2$(H$_2$O)$_2$] Complexes of Lawsone Derivatives at 300 K

Complex	δ (mm/s) ±0.02	ΔE_Q (mm/s) ±0.04
1	1.13	2.43
2	1.21	2.44
3	1.17	2.44
4	1.22	2.16
5	1.12	2.53
6	1.21	2.61

[a] Relative to natural Fe foil.

a single quadrupole-split doublet. Each doublet was least-squares fit with two Lorentzian lines, each constrained to have the same area. The resulting isomer shift and quadrupole splitting parameters at 300 K are given in Table 5.

All complexes have very similar ^{57}Fe Mössbauer data consistent with high-spin iron(II) centres [45, 46]. The isomer shift (δ) is *ca.* 1.2 mm/s relative to iron foil and the quadrupole splitting (ΔE_Q) is *ca.* 2.35 mm/s. Both are nearly temperature-independent indicating the absence of any second order Doppler shift. Similar Mössbauer parameters have been observed by Tuchagues and Hendrickson [18b] in the case of the ferrous complexes of tetradentate Schiff base ligands derived from the condensation of salicylaldehyde and various diamines. These authors have noted an extreme sensitivity to air for some of these ferrous complexes in the solid state showing a partial but Mössbauer-detectable conversion to ferric compounds. Comparatively the present complexes of lawsone series of ligands are fairly robust and show no detectable changes in the oxidation state during the measurements.

Some useful observations can be made on the Mössbauer parameters obtained for the present series of complexes where electron-releasing or electron-attracting substituents are introduced in the bound quinone ligands. In the iron(II) complexes with quinone ligands having more or less pronounced π-acceptor character, an increase in the covalence of metal—ligand bond can promote d-electron transfer from the non-σ bonding orbitals of the central atom to the π-acceptor orbitals of corresponding symmetry of the ligand. For high-spin Fe(II) complexes, this should lead to a higher symmetry of the d shell because the $d^6(t^4_{2g}e^2_g)$ electronic configuration of the central ferrous atoms gradually approaches the spherically symmetric $d^5(t^3_ge^2_g)$ configuration characteristic of the high-spin iron(III) atom [47, 48]. In the case of high-spin iron(II) complexes with coordination spheres of similar symmetry, the decreasing order of isomer shift and quadrupole splitting shall

agree approximately with the increasing degree of covalence of the complexes, *i.e.* with the nephelauxetic sequence [49].

First of all, in the present series of complexes the isomer shift values have not undergone considerable reduction as observed for the salicylaldoxime or dimethylglyoxime complexes of iron(II) where the back-coordination phenomenon is well-established [50]. This suggests that there is a negligible extent of electron-transfer in the M → L direction which would have put electron density on the quinone ligand attributing to it the status of semiquinone species. It supports our formulation of these compounds as the high-spin ferrous complexes containing fully oxidized quinone species.

It has been shown for iron complexes possessing covalent character that substitution of electron-attracting or electron-releasing groups do not produce any clear-cut differences in the Mössbauer spectra, due probably to the combined effects of the coordinate σ bond and back-coordination [50—53]. However, the Mössbauer parameters included in Table 5 indicate that substitution of electron-releasing groups on the quinone ligands tends to increase the covalence of M—L bond and thereby decrease the isomer shift values. The reverse trend is observed with the electron-attracting substituents with exception of the bromo substituent. Thus, on the whole for the present series of complexes, both isomer shift and quadrupole splitting seem to follow the orders of nephelauxetic series and metal—ligand covalencies.

Electronic Absorption Data

The electronic spectra of the ligand anions of *ortho*-functionalized *p*-quinones studied previously [27, 34] have indicated that they generally exhibit intense charge transfer bands in the region 350—500 nm (with ε values of 10^3 l mol^{-1} cm^{-1}). The d—d transitions falling in this region are therefore expected to receive contributions from the charge transfer bands. In some cases the asymmetrical nature of the bands in the above region itself indicates such mixing-in effects where low intensity component on the longer wavelength side is probably a d—d transition as suggested by Wicklund and Brown [54] on the basis of the electronic spectra of the transition metal catechol complexes.

It has been shown that the electronic ground and excited states for high-spin iron(II) complexes are $^5T_{2g}$ and ^5E_g respectively and a single absorption band usually observed for these compounds corresponds to 10 Dq parameter. However, due to Jahn—Teller distortion and the effective low symmetry (D_{4h}) the excited state is further splitted into $^5A_{1g}$ and $^5B_{1g}$ states where the actual splitting of the energy states is given by the relation [(8/3)dσ] being positive when $^5A_{1g} > ^5B_{1g}$ [55]. The ground term $^5T_{2g}$ also undergoes splitting in the tetragonally

TABLE 6. Assignments of Principal Electronic Absorptions and Spectrochemical Parameters of $[Fe^{II}(L)_2(H_2O)_2]$ Complexes

Complex	Bands[a] λ_{max} (cm^{-1})	ϵ (1/cm/mol)	Assignments (transitions)	Dq (cm^{-1})	$(8/3)d\sigma$
1	11235	1034	$^5B_{2g}(D) \rightarrow {}^5B_{1g}(D)$	1123	1487
	12722	846	$^5B_{2g}(D) \rightarrow {}^5A_{1g}(D)$		
	20000	4488	CT		
2	11260	1288	$^5B_{2g}(D) \rightarrow {}^5B_{1g}(D)$	1126	1727
	12987	1118	$^5B_{2g}(D) \rightarrow {}^5A_{1g}(D)$		
	21740	5501	CT		
3	11364	934	$^5B_{2g}(D) \rightarrow {}^5B_{1g}(D)$	1136	1230
	12594	907	$^5B_{2g}(D) \rightarrow {}^5A_{1g}(D)$		
	20284	5516	CT		
4	11364	868	$^5B_{2g}(D) \rightarrow {}^5B_{1g}(D)$	1136	1294
	12658	833	$^5B_{2g}(D) \rightarrow {}^5A_{1g}(D)$		
	20408	5007	CT		
5	11236	853	$^5B_{2g}(D) \rightarrow {}^5B_{1g}(D)$	1123	1109
	12345	805	$^5B_{2g}(D) \rightarrow {}^5A_{1g}(D)$		
	20408	4878	CT		
6	12658	134	$^5B_{2g}(D) \rightarrow {}^5B_{1g}(D)$	1265	
	24876	5946	CT		
	25907	6030	CT		

[a]All the spectra have been recorded in DMF (1×10^{-3}) solution; d–d = metal based transition; CT = charge transfer transition; ϵ = molar extinction coefficient; Dq = ligand field splitting parameter.

distorted environment into $^5B_{2g}$ and ^5E_g components where the transition $^5B_{2g} \rightarrow {}^5B_{1g}$ gives a direct measure of 10 Dq [56].

Our assignments of the electronic transitions in the present series of complexes are shown in Table 6. The 10 Dq values obtained for the present complexes are close to the ones observed for high-spin iron(II) complexes containing O_6 donor sets [57]. The nearly identical 10 Dq values observed for all the complexes support their isostructural nature while the positive sign of the $(8/3)d\sigma$ values indicate that the order of the splitting as discussed above is essentially valid.

Cyclic Voltammetry

The cyclic voltammograms of lawsone ligands and their respective iron(II) complexes were recorded using the three electrode system (HDME, Pt wire and SCE) in DMF with 0.1 M $(C_4H_9)_4NPF_6$ as the supporting electrolyte. Lawsone (II) which can be considered as the parent compound of the present series exhibits cathodic peaks at −376 and −1432 mV, respectively, of which the former corresponds to the one electron reduction of the quinone to semiquinone anion and the latter to the conversion of semiquinone to catecholate dianion. Such an assignment is in agreement with reports of Jaworski *et al.* [58] and Peover [59] on the reduction of 1,4-naphthoquinone derivatives in DMF and studies by Sawyer *et al.* [60] on the catechol compounds.

As can be seen in Table 7, the substituted lawsone derivatives I and III to VI also exhibit two quasi reversible reduction waves attributable to consecutive one electron reductions to the semiquinone and catechol anions. However substituent effects do not lead to linear free-energy relations of the Hammet type [61].

The iron(II) complexes 1 to 6 also exhibit two quasi reversible one electron reductions with cathodic peaks ranging from −371 to −742 mV for the first reduction wave and −1257 to −1600 mV for the second reduction. The metal ion effect on the electrochemical behaviour of the quinone ligands is a shift towards more negative potentials for both reductions concerning complexes 1 to 5 and more positive potentials for complex 6. The magnitude of these shifts is larger for the first reduction compared to the second one. These results indicate that the quinone form of the ligands is more stable than the anionic semiquinone form for complexes 1 to 5 while the reverse is true for complex 6. The presence of the strongly electron withdrawing 3-NO_2 substituent could account for this reversed trend in 6. The smaller shifts observed for the second reduction compared to those observed for the first reduction indicate a further reduction of the potential range in which the anionic semiquinone form of the ligands is stable (on account of the dianionic hydroquinone form). The irreversible reduction of the NO_2 sub-

TABLE 7. Redox Potentials[a] for Lawsone Derivatives and their Iron(II) Complexes

Complex (Ligand)	First reduction		Second reduction	
	Ep_c (mV)	% reversibility (ip_c/ip_a)	Ep_c (mV)	% reversibility (ip_c/ip_a)
1 (3-CH$_3$L)	−742 (−715)	50 (92)	−1600 (−1502)	79 (64)
2 (L)	−675 (−376)	18 (86)	−1507 (−1432)	56 (66)
3 (3-ClL)	−599 (−281)	72 (65)	−1586 (−1374)	60 (96)
4 (3-BrL)	−588 (−263)	95 (17)	−1391 (−1368)	70 (93)
5 (3-IL)	−589 (−305)	92 (22)	−1526 (−1389)	79 (80)
6 (3-NO$_2$L)	−371 (−915)	0 (50)	−1257 (−1593)	56 (35)

[a]Measured at 100 mV s^{-1} in DMF (10^{-3} M) solutions containing 0.1 M TBAHFP as supporting electrolyte, HDME as working electrode with Pt as auxiliary electrode. Potentials are referenced *vs.* Ag/Ag$^+$ electrode and given with iR drop correction.

stituent has been observed both for the free ligand VI and the corresponding complex 6 nearby the semi-quinone ⟷ hydroquinone reduction.

The cyclic voltammograms of 2 and 3 have also been recorded in the 0 to +1000 mV range with an EDI type platinum rotating electrode. Quasi reversible one electron oxidations have been observed at +345 and +450 mV for 2 and 3, respectively, which can be related to the iron(II)—iron(III) oxidation process.

Consequently, the cyclic voltammetry of complexes 1 to 6 confirm that the lawsone ligands are coordinated in their fully oxidized quinone form and that the iron centre is at the +2 oxidation state.

Conclusions

The present work has shown that *ortho*-functionalized *p*-quinone ligands like lawsone and its derivatives are able to stabilize high-spin ferrous complexes of the type [M(L)$_2$(H$_2$O)$_2$], where L is the anion of the lawsone derivative. The diagnostic peaks in the IR spectra are indicative of the *p*-quinones being in the fully oxidized form and the coordination occurring through the C-2 phenolate and the C-1 carbonyl. Thermal studies indicate that the two water molecules are coordinated and their loss leads to the decomposition of the chelates. Variable temperature magnetic susceptibility studies establish the high-spin state of the iron and confirm the quinone formulation while Mössbauer data clearly establish the +2

oxidation state for the central iron ions. The electronic absorption data indicate that the six high-spin ferrous complexes described herein are iso-structural species including the O$_6$ chromophore and the cyclic voltammetry confirms that the lawsone ligands are coordinated in their quinone form while the iron centre is at the +2 oxidation state.

The iron environment in the synthetic complexes is well defined and stable which makes them potential model compounds for studying the effect of quinone oxidation state changes on electronic and magnetic properties of the iron—quinone couple in photosynthetic reaction centres. Work in this direction is presently under way in our laboratories.

Supplementary Material

Figures 3 to 7 showing the actual IR spectra, TG/DTA graphs, Mössbauer spectra, electronic spectra and CV profiles, respectively, can be obtained from the authors.

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