

High-spin Iron(II) Complexes of *ortho*-Functionalized Paraquinones as Models for Quinone Binding Sites in Reaction Centres of Photosynthetic Bacteria

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Abstract

In an attempt to mimic the iron–quinone couple of bacterial reaction center, spectral, magnetic and Mössbauer characterization of seven high-spin iron(II) complexes of the *ortho*-functionalized paraquinones is reported where the quinones are coordinated in their fully oxidized, monoanionic form.

An iron–quinone couple has been shown to accept an electron from reduced bacteriopheophytin (BPh) in the photosynthetic bacterial reaction centre (RC) [1–3]. In this site two quinone moieties are in close proximity to one high-spin iron(II) ion [4–8]. The architectural details of this site have become clear only recently through the X-ray structure determination of the RC of *Rhodospseudomonas viridis* by Deisenhofer *et al.* [9] which together with the hydrophathy plots [10] have indicated the histidine residues to be situated in the first coordination sphere of the ferrous center and the two quinone moieties situated in the close vicinity. In view of the uncertainty about the actual coordination of the quinone species to the metal, it is useful to prepare ferrous complexes containing bound *p*-quinone ligands to compare their structural characteristics with the biological preparations.

Attempts to synthesize high-spin Fe(II) complexes containing quinone ligands as mimicks of the quinone binding sites in the reaction centres of photosynthetic bacteria have been limited to (i) high-spin iron(III) complexes with a single *o*-semiquinone ligand [11]; (ii) high-spin iron(III) compounds containing three *o*-semiquinone ligands

[12]; and (iii) binuclear iron(III) complexes with bridging hydroquinone dianions [13]. However, in no case stabilization of high-spin Fe(II) state was observed.

As a part of more general program concerned with mimicking metalquinone centers in the biological systems we report here the characterization of some iron complexes of *ortho*-functionalized *p*-quinones in which the metal center is stabilized in the high-spin ferrous state while the ligands are coordinated in their fully oxidized quinone form.

The coordinating *p*-quinones used in the present work are derived from Lawsone (Fig. 1a, 2-hydroxy-1,4-naphthoquinone), which is a naturally occurring hydroxy-quinone obtainable from the leaves of *Lawsonia alba* [14]. Due to the tautomeric ortho-quinone form (Fig. 1b), it has the potential of binding the metal ions in three different oxidation states *viz.* quinone, semiquinone and hydroquinone (Fig. 2) similar to other orthoquinone ligands [12, 13, 15–18]. The structural aspects of metalquinone complexation have been summarized by Pierpont and

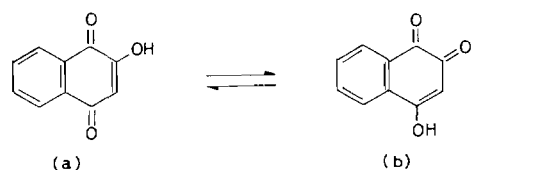


Fig. 1. Tautomerization in lawsone.

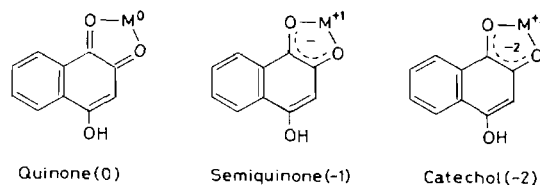


Fig. 2. Electronic structures of the metal–lawsone chelate.

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Buchanan [19]. Accordingly, the three isoelectronic forms of the metal–quinone complexes are interconvertible through intramolecular electron transfers and are accessible through different synthetic routes.

Lawsonite on interaction with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in a degassed methanol solution at pH 6 (uncorrected) in a Schlenk assembly yields a high-spin ferrous complex ($\mu_{300} = 5.10$ B.M.). *Anal. Calc.* for $[\text{Fe}(\text{lawsone})_2(\text{H}_2\text{O})_2]$: C, 54.82; H, 3.22; Fe, 12.75. Found: C, 54.49; H, 3.23; Fe, 12.37%. The monomeric nature of the complex is ascertained from the cryoscopic molecular weight measurements in acetonitrile solvent (Calculated: 438.183. Found: 430.387).

The complexes derived from other ligands of lawsonite series also exhibit a similar molecular composition, the analytical data for whom are included in Table I. The identical nature of the metal–lawsonates synthesized under conditions similar to the present ones has earlier been noted by Bottei *et al.* [20].

The lawsonite complex exhibits a normal magnetic behaviour down to 5 K ($\mu_{\text{eff}} = 5.08$ B.M.) attributable to a small ZFS term, although iron-quinone complexes with subnormal magnetic moments are known which have been explained on the basis of the antiferromagnetic interactions between the paramagnetic semiquinone ligands and the central metal ion [13]. Hendrickson *et al.* have shown that the unpaired spin density in these complexes

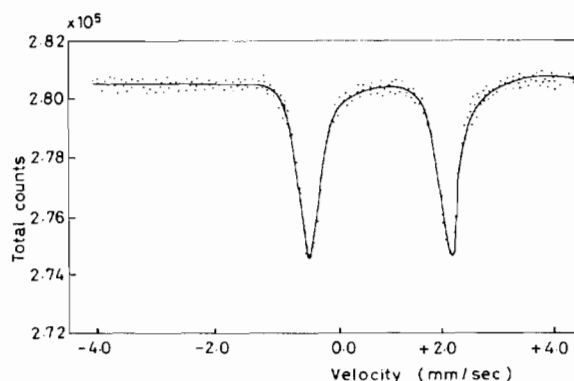
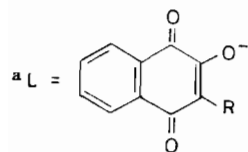


Fig. 3. Mössbauer spectrum of $[\text{Fe}(\text{lawsone})_2(\text{H}_2\text{O})_2]$ at 300 K.

resides in a molecular orbital localised over the ligand as revealed by the EPR and the variable temperature magnetic susceptibility measurements [21]. The Mössbauer spectrum (Fig. 3) recorded for the complex, $[\text{Fe}(\text{lawsone})_2(\text{H}_2\text{O})_2]$, at 300 K and 77 K are similar giving isomer shift of 1.09 mm/s and quadrupole splitting of 2.44 mm/s, characteristic of high-spin iron(II) ion. Similar parameters are obtained for other complexes of lawsonite series (Table II). Fingerprinting the infrared spectra reveals that the coordinating centres in these ferrous complexes are the C-1 carbonyl (shift from 1660 to 1610 cm^{-1}) and C-2 hydroxyl (disappearance of

TABLE I. Analytical data for $[\text{Fe}^{\text{II}}(\text{L})_2(\text{H}_2\text{O})_2]$ Complexes^a

	Colour	Yield (%)	Elemental analysis ^b				
			C	H	N	Halogen	Metal
R = H	Dark brown	90	54.49 (54.82)	3.23 (3.22)	–	–	12.37 (12.75)
CH ₃	Brownish purple	85	57.51 (56.68)	4.02 (3.89)	–	–	11.87 (11.98)
Cl	Reddish brown	70	46.14 (47.37)	2.38 (2.38)	–	14.25 (13.99)	10.85 (11.01)
Br	Reddish brown	95	40.49 (40.31)	2.09 (2.03)	–	27.03 (26.82)	10.07 (9.37)
I	Reddish brown	83	34.37 (34.92)	1.86 (1.76)	–	37.02 (36.90)	8.34 (8.12)
NO ₂	Green	85	46.20 (45.48)	2.47 (2.29)	5.37 (5.30)	–	10.86 (10.57)
NH ₂	Violet blue	78	50.78 (51.31)	3.34 (3.45)	5.93 (5.98)	–	11.80 (11.93)



^b Figures in parentheses are calculated values.

TABLE II. Magnetic and Mössbauer data (300 K) for [Fe^{II}(L)₂(H₂O)₂] Complexes

Compound R =	μ_{eff} (B.M.)	δ (mm/s) ± 0.02	ΔE_{q} (mm/s) ± 0.04
H	5.10	1.21	2.44
CH ₃	5.13	1.13	2.43
Cl	4.92	1.17	2.44
Br	4.97	1.22	2.16
I	4.92	1.12	2.53
NO ₂	5.27	1.21	2.61
NH ₂	4.99	1.07	2.19

the band at 3250 cm⁻¹) respectively (Table III). This together with recent crystal structure data on the bis-pyridine adduct of [Mn(methylawsone)₂(H₂O)₂] [22] and on [Cu(lawsone)₂(H₂O)₂] by Peng *et al.* [23] led us to conclude that the coordination in the present series of compounds is through the deprotonated form of the ligands with considerable delocalization of the bonds between C-2 and C-4 positions. The electronic spectra (in nujol mull) of the lawsone complexes show bands at 10 100 cm⁻¹ [⁵T_{1g}(D) → ⁵B_{1g}(D)] and 8547 cm⁻¹ [⁵T_{2g}(D) → ⁵A_{1g}(D)] cm⁻¹ confirming the high-spin iron(II) state as indicated above. The presence of two coordinated water molecules in these compounds is supported by the percent weight loss in the range 80–120 °C (Calc.: 8.22%. Found: 8.21%) from their thermogravimetric profiles.

The substitution of strong pyridine donor ligands on the metal centres in the metal–quinone complexes have been shown [24] to induce intramolecular electron transfer from the filled metal d-orbitals to the partially filled π* levels of quinone ligands resulting in the reduction of the quinone ligands with concomitant metal oxidation. The ease of such intramolecular electron transfers between the metal centres and quinone ligands has been attributed to the closeness of their energy levels [25]. The synthesis of bis(pyridine) adduct of the ferrous-lawsone complex, however, does not lead to such intramolecular electron transfer as judged from the unchanged magnetic moment ($\mu_{300} = 5.12$ B.M.) and quinone oxidation state (as seen from the IR diagnostic quinone peaks, $\nu(\text{C}=\text{O})$ at 1610 cm⁻¹ and $\nu(\text{C}=\text{C})$ at 1590 cm⁻¹). The pyridine characteristic peaks [26] are seen at 1075, 1056 and 1025 cm⁻¹ in the adduct.

The absence of intramolecular electron transfers probably reflects large differences in the electronic levels of the metal and these *ortho*-functionalized paraquinone ligands.

TABLE III. Significant Peaks^a in the IR Spectra of Iron(II) Complexes of Lawsone Derivatives [Fe^{II}(L)₂(H₂O)₂]^b

R = H	CH ₃	Cl	Br	I	NO ₂	NH ₂	Assignment
3350–3150b	3350–3150b	3350–3150sb	3400–3100mb	3400–3150sb	3400–3200sb	3300w, 3225 m	$\nu(\text{OH})$ (coordinated water)
1650sh	1640sh	1655m	1650m	1645m	1635sh	1640sh	$\nu(\text{C}=\text{O})$ (free)
1605shb	1610s	1620s	1620s	1620s	1580sb	1620s	$\nu(\text{C}=\text{O})$ (chelated)
1580, 1550b	1570, 1550m	1580, 1550s	1580, 1540s	1570, 1535s	1580, 1540m	1570, 1535s	$\nu(\text{C}=\text{C})$ (activated by carbonyl)
1335m	1335s	1320m	1315m	1310m	1325sh	1335s	$\nu(\text{OH})$ (phenolic)
1245s	1225s	1225s	1224m	1225s	1230s	1240s	$\nu(\text{C}-\text{O})$
422	435	425	428	425	437–423	440–420	$\nu(\text{M}-\text{O})$

^aPositions in cm⁻¹; s = strong, m = medium, w = weak, sh = shoulder, b = broad.

^bL = Lawsone anion.

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