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Synthesis and Characterization of Chromium(III) Chelates of Some Lawsones

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Chelates of chromium(III) with phthiocol (3-methyllawsone), lawsone (2-hydroxy-1,4--naphthalenedione), 3-chlorolawsone and their 1-oxime derivatives have been synthesized and characterized. They exhibit the general formula $CrL_3 \cdot 3H_2O$ and magnetic moments close to 3.87 B.M. indicating trivalent chromium. IR spectral data suggest that lawsone derivatives exhibit coordinating O͡O system, while lawsone-1-oxime derivatives present N͡O system. Octahedral geometry for chelates has been suggested.

Hydroxynaphthalenediones, which form an integral part of the electron transport chain in photosynthesis [1], as a class of ligands, are capable of coordinating with most of the metal ions. As a part of our programme, concerning the coordination peculiarities of monohydroxynaphthalenediones, we have synthesized and characterized transition metal chelates [2–5] of various 2-hydroxy derivatives of 1,4-naphthalenedione. A literature survey has revealed that very few studies on chromium(III) chelates of these ligands have been carried out [6,7].

The substituent at C-3 in lawsone has a notable effect on the properties of its chelates [8]. The chelating ability of lawsone derivatives is enhanced to a great extent on their oximation [9].

The present paper concerns the synthesis of chelates of chromium(III) with lawsone and its derivatives (Fig. 1).

EXPERIMENTAL

Syntheses: All the chemicals and solvents used were of analytical grade.

Ligands: Lawsone, dichlone (2,3-dichloro-1,4-naphthalenedione) and menadione (2-methyl-1,4--naphthalenedione) were the products of Fluka, A.G., Switzerland. Phthiocol was synthesized from menadione by Fieser's method [10] (m.p. 172°C, lit. m.p. 173°C). 3-Chlorolawsone was prepared from dichlone by substituting one chloro group by a hydroxy group [11] (m.p. 213°C, lit. m.p. 212°C). The lawsone-1-oxime derivatives were synthesized [8] by treating the solution of a lawsone derivative with solution of hydroxylamine hydrochloride. The entire mixture was heated, at *ca.* 60°C, later cooled and neutralized with hydrochloric acid (2 M) untill a complete precipitation of the corresponding lawsone-1-oxime derivative. The melting points were recorded after recrystallization of the ligands from MeOH and were found to be consistent with literature data [11] (phthiocol-1-oxime: 201°C, lit. m.p. 200°C; lawsone-1-oxime: 181°C, lit. m.p. 180°C; 3-chlorolawsone-1-oxime: 187°C, lit.m. p. 188°C).

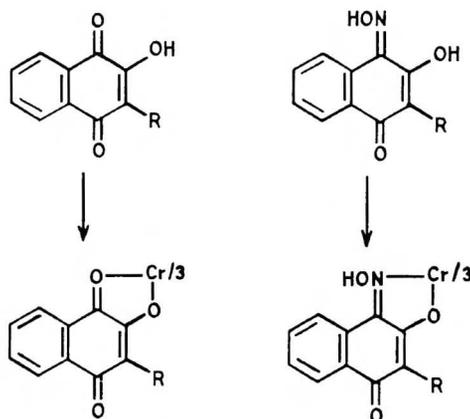* Author to whom all correspondence should be addressed.

**Figure 1.** General structures of lawsones and related ligating systems.

R	Ligand	Abbreviation	R	Ligand	Abbreviation
CH_3	Phthiocol	Phth	CH_3	Phthiocol-1-oxime	Phthoxm
H	Lawsone	Law	H	Lawsone-1-oxime	Lawoxm
Cl	3-Chlorolawsone	ClLaw	Cl	3-Chlorolawsone-1-oxime	ClLawoxm

Chelates: To a solution of the ligand (3 mmol, 0.56 g Phth/0.52 g Law/0.63 g ClLaw/0.61 g Phthoxm/0.57 g Lawoxm/0.67 g ClLawoxm) in aqueous ammonia (3 mmol, 15 mL) was added gradually an aqueous solution of chromium(III) chloride hexahydrate (1 mmol, 0.27 g). The pH of the mixture was adjusted to 6–7, using aqueous ammonia (1:1). The mixture was refluxed for 2 h and then cooled overnight. The resultant precipitate was filtered off, washed with water, followed by MeOH and dried *in vacuo* over $CaCl_2$ at ambient temperature.

Measurements: The percentages of carbon, hydrogen and residue (as Cr_2O_3) [6] were determined using a Hosli-Holland C, H analyser, whereas nitrogen was determined using a Microdumas-Hosli instrument. Chromium was determined on a Perkin–Elmer Model 3100 atomic absorption spectrophotometer with a setting for 4.0 ppm standard at a wavelength of 357.9 nm and using an air-acetylene flame. The thermogravimetric analysis was carried out up to 600°C on a laboratory constructed balance [12] in air. The balance was calibrated using $CaC_2O_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$. For each run a 50–60 mg sample was used with uniform heating rate of 3°C min^{-1}. Magnetic studies were carried out at room temperature, using the Faraday technique, using mercury(II) tetrathiocyanatocobaltate as calibrant. The molecular magnetic susceptibilities were corrected for diamagnetism of the constituent atoms by use of Pascal constants. The electrical conductance measurements were performed in 1×10^{-3} M DMF solutions using a Systronics direct reading conductivity meter model 303 calibrated with potassium chloride solution. The infrared spectra were recorded in Nujol mulls on a Perkin–Elmer FTIR spectrophotometer Model 1600 in the range 4000–450 cm^{-1}. The electronic spectra were obtained in MeOH on a Shimadzu UV 300 double beam spectrophotometer in the range 200–800 nm.

RESULTS AND DISCUSSION

General characterization: The chelate formation occurs by the general reaction:

$$CrCl_3 + 3HL \xrightarrow[\text{pH 6-7}]{\text{Reflux}} CrL_3 \cdot 3H_2O$$
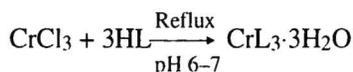
where HL represents the ligand. All products are brownish red and are partially soluble in methanol, water, *etc.* indicating the non-polymeric nature of chelates. The

analytical data confirm the general formula $CrL_3 \cdot 3H_2O$. The low molar conductance values of the chelates indicate their non-electrolytic behaviour [13]. The thermogravimetric profiles in air show a two/three-step weight loss pattern. The first step, at temperatures preceding $\sim 160°C$, corresponds to loss of water molecules. The later step(s) involve oxidative decomposition of the ligand, resulting in Cr_2O_3 as residue [6].

Magnetic Studies: The solid state magnetic susceptibility of the chelates of chromium(III) measured at room temperature indicates their magnetic moments close to spin only value of 3.87 B.M. (Table 1). This value corresponds to three unpaired electrons.

Table 1.

Compound/Empirical Formula/Formula weight	Yield (%)	Λ_M (ohm^{-1} mol^{-1} cm^2)	μ_{eff} (B.M.)
Cr(Phth)$_3 \cdot$3H$_2$O C$_{33}$H$_{27}$O$_{12}$Cr 666.99	66	11.05	3.76
Cr(Law)$_3 \cdot$3H$_2$O C$_{30}$H$_{21}$O$_{12}$Cr 624.99	75	12.25	3.84
Cr(ClLaw)$_3 \cdot$3H$_2$O C$_{30}$H$_{18}$O$_{12}$Cl$_3$Cr 728.49	70	11.45	3.91
Cr(Phthoxm)$_3 \cdot$3H$_2$O C$_{33}$H$_{30}$O$_{12}$N$_3$Cr 711.99	70	12.92	3.78
Cr(Lawoxm)$_3 \cdot$3H$_2$O C$_{30}$H$_{24}$O$_{12}$N$_3$Cr 669.99	78	10.82	3.75
Cr(ClLawoxm)$_3 \cdot$3H$_2$O C$_{30}$H$_{21}$O$_{12}$N$_3$Cl$_3$Cr 773.49	72	10.07	3.80

IR Studies: The IR spectra (Table 2) of the lawsone derivatives show a broad, medium intensity band at *ca.* 3400 cm^{-1}, assigned to ν(O–H) vibrations. In the chelates this band is replaced by a much broader band between 3650–3200 cm^{-1}, which is due to water molecules. The lawsone-1-oxime derivatives exhibit two distinct bands, one in the region 3533–3333 cm^{-1}, the other at 3150 cm^{-1}, due to O–H bonds, associated with phenol and oxime groups respectively. On chelation, the ν(O–H) absorption of the phenol group disappears, indicating coordination through the phenolato oxygen. The broad bands of weak to medium intensity observed in the region 3300–3167 cm^{-1} are due to the oxime group and water molecules.

Table 2. Significant IR bands (cm^{-1}) of ligands and chelates.

Compound	ν(O–H)	ν(C=O) Free	ν(C=O) Chelated	ν(C=N)	ν(C–O)	ν(N–O)	ν(C–X)	ν(M–O)
Phth	3333	1658	1635	–	1208	–	–	–
Cr(Phth)$_3 \cdot$3H$_2$O	3417	1634	1579	–	1212	–	–	668
Law	3174	1678	1644	–	1224	–	–	–
Cr(Law)$_3 \cdot$3H$_2$O	3209	1614	1583	–	1245	–	–	669

Table 2 (continuation)

ClLaw	3274	1679	1640	–	1222	–	661	–
Cr(ClLaw)$_3$·3H$_2$O	3254	1634	1557	–	1227	–	682	667
Phthoxm	3333, 3134	1620	–	1588	1204	1060	–	–
Cr(Phthoxm)$_3$·3H$_2$O	3200	1584	–	1517	1227	1106	–	693
Lawoxm	3533, 3174	1631	–	1577	1211	1050	–	
Cr(Lawoxm)$_3$·3H$_2$O	3300	1582	–	1538	1234	1107	–	694
ClLawoxm	3500, 3150	1604	–	1575	1211	1050	694	–
Cr(ClLawoxm)$_3$·3H$_2$O	3233	1579	–	1516	1227	1083	694	673

The lawsone derivatives exhibit bands at *ca.* 1670 cm^{-1} and 1644 cm^{-1}, assigned to free and chelated carbonyl vibrations. The coordination of phenolic oxygen to chromium(III) ion would be expected to reduce density of carbonyl linkage and thus lower v(C=O) frequency [14]. On coordination of chromium(III) with lawsone derivatives, these bands are shifted to a lower frequency (Δ 24–80 cm^{-1}), indicating weakening of C=O bond. The v(C=O) band in lawsone-1-oxime derivatives, observed at 1631–1600 cm^{-1}, is also shifted to lower frequency (Δ 25–49 cm^{-1}).

The band in the region 1224–1200 cm^{-1}, assigned to the C–O stretching vibration shifts to a higher frequency (Δ 4–23 cm^{-1}), indicating strengthening of the C–O bond and the participation of phenolic oxygen in the coordination. The shift magnitude is greater in chromium(III) chelates of lawsone-1-oximes than in corresponding lawsones. The C=N stretching frequency in lawsone-1-oxime derivatives is assigned in the region 1588–1575 cm^{-1} [8]. This band is shifted to lower frequency on chelation (Δ ~60 cm^{-1}), indicating coordination through oximino nitrogen. The strong absorption at *ca.* 1050 cm^{-1}, attributed to the N–O stretching vibration [8], shows shifts notable to a higher frequency (Δ 33–57 cm^{-1}). A new band at *ca.* 675 cm^{-1}, is assigned to (Cr–O) vibrations [15]. In general, the shifts are greater in chromium(III) chelates of lawsone-1-oxime derivatives than in lawsone derivatives. Thus, IR studies indicate the participation of carbonyl oxygen at C-1 and phenolato oxygen at C-2 in coordination in lawsone derivatives (O O system), while that of oximino nitrogen at C-1 and phenolato oxygen at C-2 in lawsone-1-oxime derivatives (N O system). In both cases a five-membered chelate ring is formed.

Electronic Spectral Studies: The ligands show intense bands at 230–268 and 300–380 nm, referred to as benzenoid electron transfer (BET) bands as well as at 272–293 and 392–500 nm, referred to as quinonoid electron transfer (QET) bands [16]. The spectra of chelates, in general, resemble with some modifications the spectra of their corresponding ligands. The chelates are characterized by a broad, intense charge-transfer (CT) bands and most of the absorptions, arising from d-d transitions, are obscured in the visible region by CT bands. The band observed in the region 392–500 cm^{-1} exhibits a red shift after chelation of chromium(III) with lawsone derivatives (Δ 70 nm) or lawsone-1-oxime derivatives (Δ30 nm). These bands observed in the region 415–480 nm are assigned to the ligand-to-metal charge transfer (LMCT) bands [17].

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