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Note

INVESTIGATION ON THE INTERACTION OF 2-HYDROXY-3-(3-METHYL-2-BUTENYL)-1,4-NAPHTHOQUINONE (LAPACHOL) WITH COPPER(II) AND IRON(II)

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Sawhney and co-workers [1–5] have investigated the indicator and chelating properties of lapachol. The kinetics of the non-isothermal decomposition of some metal complexes of lapachol have also been listed. This note highlights the solution study of the interaction of Cu(II) and Fe(II) with lapachol, their syntheses and characterization through spectral and thermal studies.

EXPERIMENTAL

All the reagents used were of analytical grade. Solutions of metal ions were made up in distilled water: these solutions were volumetrically or gravimetrically standardised. Lapachol (Aldrich, U.S.A.) was prepared in EtOH. As described by Bjerrum and Calvin [6], the three solutions were maintained at 0.1 M KCl ionic strength, and were pH-metrically titrated with 0.2 M KOH at 20 and 30°C using a Beckman pH-meter, model H-2 calibrated with buffers. 50% (v/v) EtOH–water was kept as medium throughout. Correction for volume for non-aqueous medium was applied according to the method of Van-Uitert and Haas [7].

Isolation of metal complexes was carried out with the addition of sodium lapacholate solution to the metal ion solution with constant stirring. The coloured precipitate was filtered, washed several times with distilled water

TABLE 1

Chemical analysis data

Complex	C(%)		H(%)		Metal (%)	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
$Fe(C_{15}H_{13}O_3)_2 \cdot 2\ H_2O$	63.59	62.73	4.89	5.23	10.34	9.73
$Cu(C_{15}H_{13}O_3)_2 \cdot 0.75\ H_2O$	65.06	64.40	4.90	4.92	11.53	11.36

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and dried at 50°C. For C, H analysis. THERELEK was used (Table 1). A Perkin–Elmer Infra Cord spectrophotometer was employed to record the IR spectra of lapachol and its complexes in nujol. A modern thermogravimetric balance calibrated with calcium oxalate was employed to pyrolyse samples in air using a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Formation functions ($\bar{n}_H$, $\bar{n}$, pL) were calculated using Irving–Rossotti expressions [8]. $\bar{n}_H$ ranged from 0.32–0.96 (20°C) and 0.28–0.88 (40°C), indicating one-step dissociation of lapachol. Linear plots of $\log(1-\bar{n}_H)/\bar{n}_H$ vs. pH and pH vs. $\bar{n}_H$ were employed for evaluating the proton–ligand stability constants (${}^{P}K^{H}$).

Analysis of the formation curves of the systems, showed a difference between $\log k_1$ and $\log k_2$ in the range 0.12–0.43, which fell short of the requirement of the method of interpolation at various $\bar{n}$ values [6] ($\log k_1/k_2 \geqslant 2.5$) and interpolation at various $\bar{n}$ values ($\log k_1/k_2 \geqslant 4$). Therefore, this method could not be applied to these systems to obtain these constants. Values of the constants were obtained by the pointwise calculation method, viz.

$$\log k_n = \mathrm{pL} + \log\left[\frac{\bar{n}-(n-1)}{n-\bar{n}}\right] \tag{1}$$

pH-metric studies gave the stoichiometries of the various complex species formed in solution. The $\bar{n}$ values in both systems nearly reached 2, indicating 1 : 1 and 1 : 2 complexes. Further confirmation came from the pH-metric titrations of mixtures containing 0 : 1, 1 : 1, 1 : 2 and 1 : 3 (metal to ligand) ratios which showed the occurrence of liberation of protons with limiting conditions being reached with the 1 : 3 mixture in both systems, indicating the foregoing experimental conclusions. Chemical analysis also showed that one mole of Cu(II) or Fe(II) combined with two moles of lapachol.

Further, pH-metric titrations revealed the release of a proton during complexation in both systems. So the reaction may be represented by

$$M^{2+} + LH \rightleftarrows ML^{+} + H^{+}$$
$$ML^{+} + LH \rightleftarrows ML_2 + H^{+}$$

where $L = C_{15}H_6O_3$ and $M^{2+} = Cu^{2+}, Fe^{2+}$.

Table 2 shows a decreasing trend in the values of $\log {}^{P}K^{H}$, $\log k_1$ and $\log k_2$ for the Fe(II)–lapachol system with increasing temperature; this shows that low temperatures favour complexation because of the decreased number of collisions with the decrease in kinetic energy of the molecules and, hence, their stabilities are lowered. For the Cu(II)–lapachol system, high temperature favours the reaction as $\log k_1$, $\log k_2$ increased with temperature. The

TABLE 2

Proton–ligand stability constants of lapachol, stability constants and thermodynamics of Cu(II) and Fe(II)–lapachol systems

Metal ion		Temp. (°C)		ΔG^0 (kcal mole^{-1})		ΔH^0 (kcal mole^{-1})	ΔS^0 (cal mole^{-1} deg^{-1})
		20	40	20°C	40°C		
Cu^{2+}	log $^{P}K^{H}$	6.45	5.69				
	log k_1	3.74	3.96 [a]				
		3.80	4.02 [b]				
	mean	3.77	3.99				
	log k_2	3.17	3.29 [a]				
		3.67	3.77 [b]				
	mean	3.42	3.53				
	log k_1k_2	7.19	7.52	−9.64	−10.77	+7.55	+58.53
Fe^{2+}	log k_1	3.68	3.83 [a]				
		3.89	3.35 [b]				
	mean	3.78	3.59				
	log k_2	3.16	2.61 [a]				
		3.67	3.56 [b]				
	mean	3.41	3.08				
	log k_1k_2	7.20	6.72	−9.66	−9.62	−10.98	−4.35

[a] Correction term method.

[b] Pointwise calculation method.

more negative values of the change in free energy (ΔG^0) accompanying complexation between Fe(II) and lapachol showed the reaction to be a spontaneous process; the reverse occurred in the Cu(II)–lapachol system. The endothermic nature of the Cu(II)–lapachol system provided an explanation for the increase in the formation constants with the rise in temperature.

The exothermic nature of the reaction between Fe(II) and lapachol ($\Delta H^0 = -10.90$ kcal mole^{-1}) gives support to the foregoing inferences. The negative entropy of the reaction of Fe(II) with lapachol indicates that it is enthalpy-controlled only. The values of $-\Delta H^0$ (10.98) for the Fe(II)–lapachol system probably indicates a considerable degree of covalency in the metal-to-ligand bond which presumably involves metal-to-oxygen bonding. The negative entropy is due to solvent effect.

The IR spectra of lapachol and its Cu(II) and Fe(II) complexes show a broad absorption band at ~ 3400 cm^{-1} indicating O–H stretching. Another strong absorption at 1657 cm^{-1} assigned to the C=O group in the compound is shifted to 1600 and 1590 cm^{-1} in the spectra of Cu(II) and Fe(II) complexes, indicating metal–oxygen bonding in the complexes.

A study of the pyrolysis of the Cu(II) and Fe(II) complexes indicated no loss in weight up to 68 and 120°C, respectively, after which weight loss was initiated. Two water molecules [Fe(II) complex] and 0.75 water molecules [Cu(II) complex] were lost in the respective temperature ranges of 120–200°C,

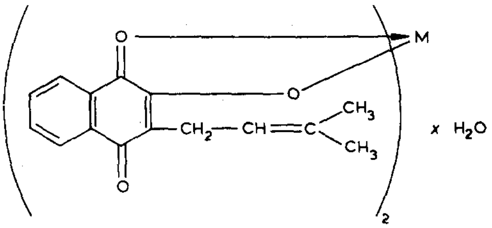
TABLE 3

Pyrolysis data

Stable phase (Temp. range)	Loss and temp. range	Loss		Metal oxide	
		Found (%)	Calcd. (%)	Found (%)	Calcd. (%)
$Fe(C_{15}H_{13}O_3)_2 \cdot 2\ H_2O$ (up to 120°C)					
$Fe(C_{15}H_{13}O_3)_2$ (200–224°C)	$2\ H_2O$ 120–200°C	6.82	6.27		
Fe_2O_3 (⩾ 480°C)	$2(C_{15}H_{13}O_3)$ 224–480°C)	86.36	86.11	13.64	13.89
$Cu(C_{15}H_{13}O_3)_2 \cdot 0.75\ H_2O$ (up to 68°C)					
$Cu(C_{15}H_{13}O_3)_2$ (108–132°C)	$0.75\ H_2O$ (68–108°C)	2.10	2.42		
CuO (⩾ 740°C)	$2(C_{15}H_{13}O_3)$ (132–780°C)	84.62	85.84	15.38	14.16

indicating the presence of coordinated water in the Fe(II) complex, and 68–108°C, indicating lattice water in the Cu(II) complex. Above 200 and 108°C, the organic molecules began to decompose and this was complete at 480 and 780°C, respectively: oxide formation followed. The pyrolysis data are shown in Table 3.

The foregoing studies give the probable structure of the complexes as



where M = Cu(II), $x = 0.75$ or M = Fe(II), $x = 2$.

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