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THERMAL STUDIES OF METAL-QUINONE COMPLEXES
Role of aqua coligations with copper(II) in coordination of 2-hydroxy-1,4-naphthoquinone

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Abstract

Copper(II) complexes of lawsone (2-hydroxy-1,4-naphthaquinone, Lw) with variety of aqua ligation *viz.* Cu-1, $[Cu(Lw)_2(H_2O)]_2$; Cu-2, $[Cu(Lw)_2(H_2O)_2]$ and Cu-3, $[Cu(Lw)_2(H_2O)_2]_2$ have been synthesized. The role of water as counter ligand on coordination propensity of redox active lawsone in naphthoquinone/naphthosemiquinone (NQ/NSQ) forms is quantified by studies of pyrolytic reactions, using non-isothermal TG and DTA techniques, coupled with IR studies. Mixed (NQ) (NSQ) ligation in Cu-1 and Cu-3 required energy of activation, E_a ~67 kJ mol^{-1} of (NQ) and ~41 kJ mol^{-1} of (NSQ). Comparable energies of aqua ligand (~43 kJ mol^{-1}) with NSQ ligand in Cu-1 and Cu-3, dictate charge distributions in lawsone coordinations. A large difference between E_a of aqua and *p*-NQ ligand indicates coordination of lawsone in its fully oxidised quinone form in Cu-2. From thermoanalytical studies schematic oxidative decomposition mechanisms are proposed for Cu-1 and Cu-3. From pyrolytic reactions enthalpies are estimated by DTA technique.

Keywords: aqua coligations, hydroxy naphthoquinone, quinones

Introduction

Binuclear metallohydrolases is one of the emerging class of enzymes [1], where hydrolytic cleavage of peptide of phosphate ester bonds take place. In these metalloenzyme water is in vicinity of binuclear metallobiosite containing phenolate (tyrosine) residue which is essential for its biological activity. In other class of copper containing enzymes like oxidases, dioxygen is reduced to water and *o*-diphenols oxidize to *o*-quinones [2]. In molecular mechanism of electron

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transfer, the role of intermediates resulting in product *viz.* semiquinone, Cu(II)/Cu(I) species in di/trinuclear configuration and water is not yet clear. Although the role of counter ligand in charge distribution of transition metal complexes of *o*-quinones is widely studied [3–5], the coligation of water in quinone complexes is not yet solved [6]. In continuation with our former efforts to establish charge transfers in hydroxy naphthoquinone complexes of copper [7–9], herein we describe with the help of pyrolytic mechanism the effect of water as counter ligand on redox isomeric coordination of lawsone with Cu(II)/Cu(I) metallocenters.

Experimental

Synthesis

All the chemicals used in the preparation of metal chelates are of analytical grade. Lawsone (0.002 M) (2-hydroxy-1,4-naphthoquinone) was obtained from Fluka. Anhydrous methanol was prepared according to procedure reported in literature [10]. Copper(II) acetate monohydrate, copper(II) chloride dihydrate and copper(I) chloride were obtained from Aldrich Chemical Co. Triethyl orthoformate was obtained from BDH.

Cu-1, $[Cu(Lw)_2(H_2O)]_2$: $[Cu(OAc)_2(H_2O)]$ (0.001 M) was dissolved in 100 ml of anhydrous methanol to which 5 ml of triethylorthoformate was added as a dehydrating agent. The solution was deaerated by purging with N_2 gas. Lawsone (0.002 M) was taken in 50 ml of anhydrous methanol to which was added a 10 ml solution of triethylorthoformate and the solution was de-aerated with N_2. Both the solutions were mixed under N_2 atmosphere with constant stirring for 15 min. pH of the solution was adjusted to 6 using 10% sodium acetate ($NaOAc\cdot 3H_2O$) solution in methanol. The product which precipitated immediately was filtered and washed with anhydrous methanol and diethyl ether and dried under vacuum.

Cu-2, $[Cu(Lw)_2(H_2O)_2]$: A procedure similar to Cu-1 was used. Anhydrous copper(II) chloride prepared as described by Jung-Hoso and Boudjonk [11] was used instead of copper(II) acetate as starting copper salt.

Cu-3, $[Cu(Lw)_2(H_2O)_2]_2$: A slight modification of the Cu-1 procedure was used. Copper(I) chloride was used instead of copper(II) acetate monohydrate as source of copper and the reaction mixture was kept overnight at 4°C.

Physical techniques

Elemental analyses of metal complexes for C and H were performed in the microanalytical laboratory of the University of Pune. Metal estimation was carried out using complexometric method [12].

IR spectra of ligand and its metal chelates were recorded in nujol mulls on FTIR 1600 Perkin-Elmer infrared spectrometer.

Thermogravimetric (TG) studies were carried out on a laboratory built thermobalance, details of which have been reported [9]. TG curves of Cu-1 to Cu-3 were recorded with 3–5°C min^{-1} rate, however curve assigned as Cu-1 (a) in Fig. 1 was of Cu-1 compound with slow rate 1.50°C min^{-1}.

Differential thermal analysis (DTA) studies were carried out in static air using a freshly prepared magnesium oxide (particle size=250 mesh, 55–70 microns) [obtained by heating $MgCO_3$ at 800°C for ~6 h] as reference. A sample volume of 150 mm^3 was used.

By placing MgO in sample and reference cups of quartz a DTA was carried out for baseline. DTA plots reported for many standard compounds [13, 14] were also checked in our laboratory. The galvanometer deflections were corrected for baseline and the plots of ΔT were recorded.

Results and discussion

Charge transfers in model compounds of proteins like oxidases are controlled by counter ligands [4, 5]. In such charge transfers solvent plays an important role especially in stabilizing redox forms of quinones [6, 15, 16]. Hence it is essential to study the interaction between metal-quinones with special emphasis to their solvation ability to reveal the tendency of quinones to form solvates [6]. Compositional studies of copper complexes of lawsone (Cu-1 to Cu-3) reveal aqua ligations (Table 1). Such aqua ligations in 2-hydroxy-1,4-naphthoquinones affect the charge distributions which is further confirmed from their magnetic interactions [17, 18].

Table 1 Analytical data of copper(II) complexes of lawsone

Sr. No.	Salt	Complex composition	Yield/	C/	H/	Cu/
			%			
Cu-1	$[Cu(OAc)_2H_2O]$	$[Cu(Lw)_2(H_2O)]_2$	90	54.88	2.79	14.91
				(56.14)*	(2.82)	(14.85)
Cu-2	$[CuCl_2]$	$[Cu(Lw)_2(H_2O)_2]$	55	54.10	3.46	13.67
				(53.83)	(3.16)	(14.25)
Cu-3	CuCl	$[Cu(Lw)_2(H_2O)_2]_2$	60	52.78	3.75	14.16
				(53.83)	(3.16)	(14.25)

* Figure in parentheses indicates calculated values.

Cu-1 is lawsone-bridged dimer, its EPR shows four line feature, typical of dimeric nature, corroborating our dimer formulation [19]. Cu-2 is monomer with lawsone in its 2-oxido-1,4-naphthoquinone form and the trans positions occupied by aqua ligands as established from analogous X-ray crystal structure of iron(II)complex [17, 20]. Cu-3 is also dinuclear with naphthoquinone coordination as evidenced by their magnetic and EPR studies [17]. Presence of water molecules in the coordination sphere of all chelates were confirmed from their IR, TG and DTA studies.

Infrared spectral studies

All chelates show a broad band of medium intensity in the region 3350–3450 cm^{-1} assigned to ν(OH) of H_2O and free ν(OH) of 4-hydroxy-1,2-naphthosemiquinone (as this ligand may be present in tautometric form [21]).

Two types of νC=O absorptions were observed in Cu-1 and Cu-3. The medium intensity band at 1659 cm^{-1} in Cu-1 and Cu-2 is assigned to the coordinated νC=O of NQ, the same band in case of Cu-3 is observed at lower wavenumber (1647 cm^{-1}), probably due to hydrogen bonding of water molecules with phenolic oxygen or cabonyl oxygen of lawsone [22]. However, the strong bands at ~1600 cm^{-1} and ~1564 cm^{-1} observed in Cu-1 and Cu-3 are assigned to ν(C⩦O absorptions. It indicates NSQ ligation [8, 23–25] in Cu-1 due to one electron reduction of NQ moiety. The band at ~1585 cm^{-1} in all complexes is due to νC=C vibrations in *p*-NQ ring as well as in aromatic ring. The characteristic *p*-NQ absorptions are seen at ~1275 cm^{-1} in all complexes. A week band in Cu-2 at 1218 cm^{-1} is due to νC–O absorption of C-2 position in 2-oxido-1,4-naphthoquinone coordination, however in Cu-1 and Cu-3 a strong band is observed at ~1250 cm^{-1} which corresponds to νC⩦O vibration in *o*-NSQ ligand. Based on the above IR studies Cu-1 and Cu-3 possess Cu (*p*-NQ) (*o*-NSQ) type of ligations together with aqua coligations.

Non-isothermal TG studies

Stochiometries of pyrolytic reactions of Cu-1 to Cu-3 and Cu-1(a) at different steps are ascertained (Table 2, Fig. 1). Kinetic parameters can be calculated from the dynamic TG curve using various expressions [26], with the help of computer program developed in our laboratory on the rising temperature expression of Coats and Redfern [27]. We quantitized the energy of activation for different functional groups (Table 3). All hydrated chelates show three step decompositions. The first step in all complexes leads to dehydration. But in case of Cu-1 together with $2H_2O$ molecules loss, half of lawsone ligand is lost. Such fractional losses of ligands are observed in case of copper(II) amine complexes [28]. From clean step II E_a/Lw, is 41 kJ. Considering the additive property of E_a's for step I in Cu-1, [108 kJ=$2H_2O$+0.5Lw=$2H_2O$+(0.5*41) $\therefore$ $2H_2O$=87kJ], E_a of H_2O molecules is 44 kJ mol^{-1}.

Table 2 TG data for Cu-1 to Cu-3 and Cu-1(a) complexes

Complex	Step No.	Temp. range/ °C	Mass losses/ %	Probale composition of group lost	Residue
Cu-1	I	60–110	11.00 (14.33)*	$2H_2O$+0.5Lw	$[Cu_2(Lw)_{3.5}]$
	II	220–360	42.06 (40.47)	2Lw	$[Cu_2(Lw)_{1.5}]$
	III	430–530	28.68 (30.35	1.5Lw	Cu_2O**
Cu-1(a)	I	60–110	5.00 (4.21)	$2H_2O$	$[Cu(Lw)_2]_2$
	II	220–390	39.00 (40.46)	2Lw	$[Cu(Lw)]_2$
	III	440–640	39.00 (40.46)	2Lw	Cu_2O**
Cu-2	I	60–110	11.00 (8.08)	$2H_2O$	$[Cu(Lw)_2]$
	II	220–380	42.00 (48.54)	1.25Lw	$[Cu(Lw)_{0.75}]$
	III	440–520	28.00 (29.12)	0.75Lw	CuO
Cu-3	I	140–170	9.00 (8.08)	$4H_2O$	$[Cu(Lw)_2]_2$
	II	230–320	33.00 (38.83)	2Lw	$[Cu(Lw)]_2$
	III	340–550	42.71 (38.83)	2Lw	Cu_2O**

* Figures in parenthesis indicate calculated values.
**Residue as described in the text. (Scheme-1 and Scheme-2)

These comparable energies lead to competition of H_2O coordination with lawsone, this is confirmed by the slow rate decomposition (1.5°C min^{-1}) of the same Cu-1 compound (refer Cu-1(a) in Table 2 and Fig. 1). In Cu-1(a), step I corresponds to loss of two H_2O molecules and step II corresponds to loss of two lawsone molecules. E_a for lawsone in step II is 40 kJ mol^{-1} and from first step E_a for H_2O is calculated as 45 kJ mol^{-1}. However loss of another pair of lawsone molecules in the step III (Cu-1(a)) needs activation energy 68 kJ mol^{-1} of lawsone.

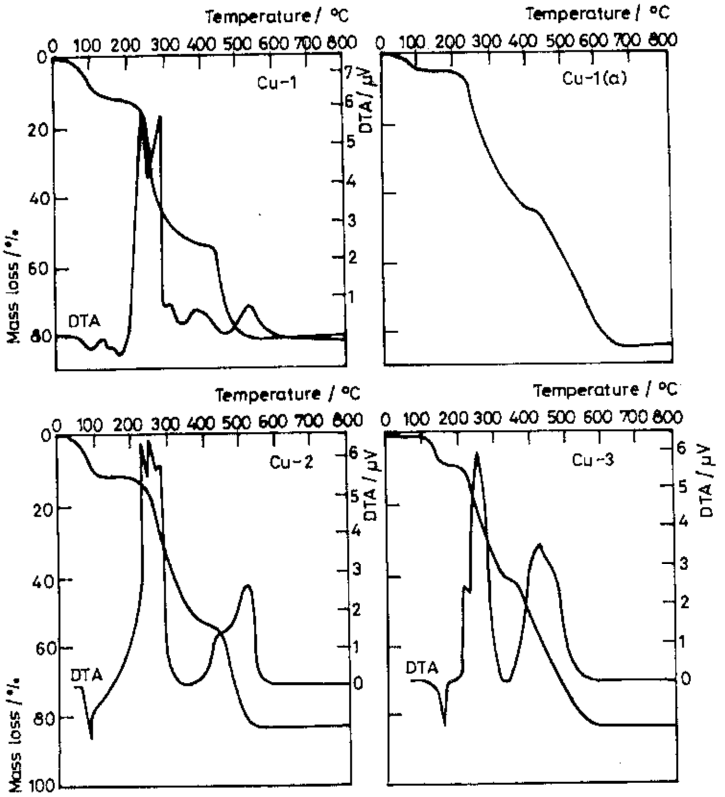


Fig. 1 TG, DTA of Cu-1 to Cu-3 (heating rate 3–5°C min^{-1}; TG profile of Cu-1(a) (heating rate 1.5°C min^{-1})

This indicates that there are two types of coordinations of lawsone in Cu-1 complex, *viz.* NQ and NSQ. Similar coordination behaviour for lawsone is observed in Cu-3 dimeric complex. The ligand loss in step III (with E_a= 42 kJ mol^{-1} of Lw) has comparable energies with coordinated water molecules *viz.* 44 kJ mol^{-1} of H_2O which are lost in step I. However another set of coordinated lawsone pair lost in step II requires higher E_a (66 kJ mol^{-1} of Lw) for evolution. These results indicate that the aqua ligation dictates the charge distribution in lawsone coordination. It results in (NQ) (NSQ) type of ligation in each monomeric unit of dimeric Cu-1 and Cu-3 compound. NSQ coordination is the result of charge transfer in naphthoquinone, only when there is comparable energies of NSQ and counter ligand *viz.* water. If there is a charge difference between E_a of coligand H_2O (76 kJ mol^{-1}) and naphthoquinone (98 kJ mol^{-1} of Lw) as seen in Cu-2 pyrolysis reaction, then counter ligand does not affect electronic structure of lawsone in Cu-2 and hence it results in $Cu(NQ)_2(H_2O)_2$ composition. Based on the TG studies, the oxidative pyrolytic mechanisms are proposed in

Scheme-1 and Scheme-2 for Cu-1(a) and Cu-3, respectively. The main features of the scheme are as follows.

1. Mass loss in step I and step II involves loss of pair of terminal ligands *viz.* H_2O and either monomeric or dimeric hydroxy-naphthoquinone ligands, respectively. The tendency of hydroxy-naphthoquinone ligands to form dimeric compounds is well documented [29–31].

2. During oxidative degradation of lawsone, metal centre is reduced to Cu(I) species which is shown in step II (220–390°C).

3. In step III bridged lawsone ligands are probably evolved resulting in metallic copper which oxidizes to Cu_2O residue due to atmospheric oxygen.

Table 3 Activation energies from dynamic TG of complexes Cu-1 to Cu-3 and Cu-1(a)

Complex	Step No.	Probale group lost	Order	E_a/ kJ	E_a/ kJ mol^{-1}
Cu-1	I	$2H_2O$+0.5Lw	2.25	108	43/H_2O
	II	2Lw	1.35	83	41/NSQ
	III	–	–	–	–
Cu-1 (a)**	I	$2H_2O$	1.44	90	45/H_2O
	II	2Lw	1.92	79	40/NSQ
	III	2Lw	2.28	136	68/NQ
Cu-2	I	$2H_2O$	2.28	151	76/H_2O
	II	1.25Lw	2.29	123	98/NQ
	III	–	–	–	–
Cu-3	I	$4H_2O$	1.57	175	44/H_2O
	II	2Lw	1.49	131	66/NQ
	III	2Lw	1.37	84	42/NSQ

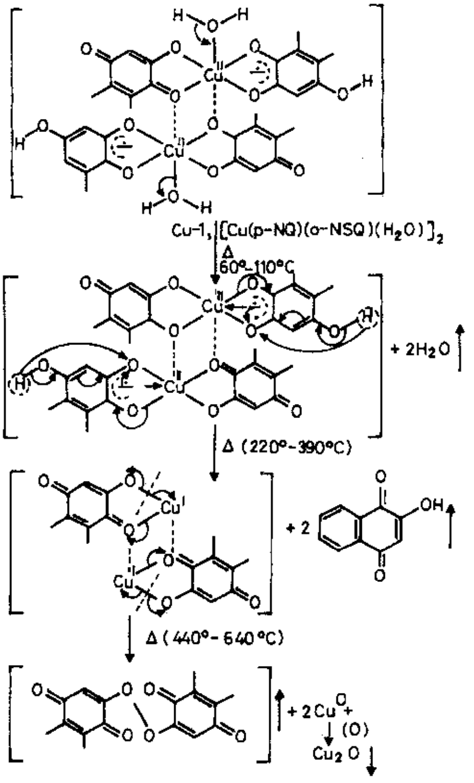
* III absurd results are obtained for E_a, not incorporated in Table
**Cu-1(a) Heating rate 1.5°C min^{-1}

Table 4 Heat of reaction values for Cu-2 and Cu-3 from DTA

Complex	Step No.	ΔH / kJ g^{-1}	ΔH / kJ mol^{-1}
Cu-2	I	0.2099	1.8909
	II	2.0863	288.9905
Cu-3	I	0.5076	2.2865
	II	2.6279	227.5034
	III	6.1978	536.5457

DTA studies

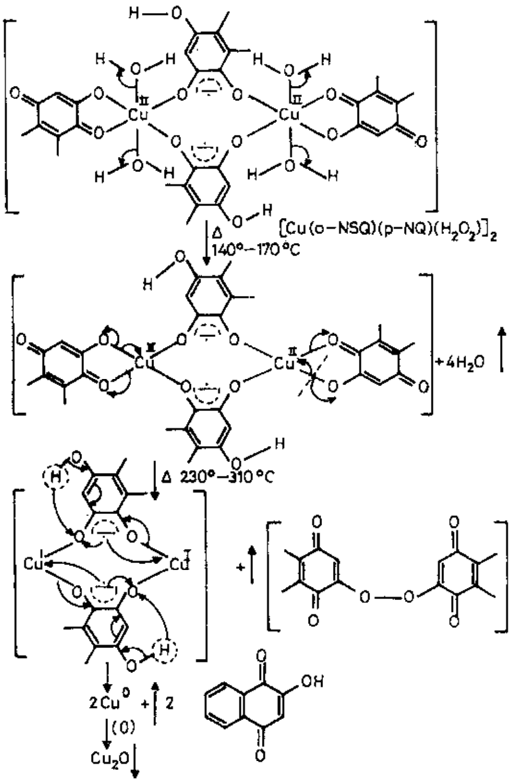
Figure 1 shows DTA curves indicating endothermic evolution of aqua ligands in step I and oxidative exothermic reaction for lawsone ligand degradation. It supports the proposed oxidative pyrolytic mechanisms in Scheme-1 and Scheme-2.



Scheme 1

From the area of DTA peak heat of reaction per step can be calculated. Area of DTA peak was determined by considering simple Gaussian shape [13]. Heat of reactions kJ g^{-1} are shown in Table 4. From TG trace of Cu-3 step II and step III correspond for loss of two lawsone molecules in each step. If we compare the enthalpies of pyrolytic reactions for those steps, for step III, ΔH kJ g^{-1} evaluated is more than two times compared to step II.

It suggests that two different redox forms of ligation *viz.* NQ and NSQ for step II and step III may be possible in Cu-3, which is in accordance with its former TG results (Scheme-2). In case of Cu-2, the heat of reaction calculated for one molecule of lawsone is comparable to enthalpy of NQ form of step II in Cu-3. Hence we conclude that in Cu-2, $[Cu(NQ)_2(H_2O)_2]$ coordination is present



Scheme 2

while in Cu-3, [Cu(NQ)(NSQ)(H_2O)$_2$]$_2$ coordination is possible from their TG and DTA studies. In case of counter aqua ligands more heat is absorbed per mole of water during dehydration of Cu-3 compared to Cu-2. It supports that aqua ligation in Cu-3 and Cu-1 dictate the charge transfers in hydroxy naphthoquinones during dimer formation, but in monomeric Cu-2, ionic bonding prevails to localized 2-oxido-1,3-naphthoquinone coordination.

* * *

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Nomenclature

CAT	catechol
E_a	energy of activation
Lw	lawsone
NQ	naphthoquinone

NSQ	naphthosemiquinone
OAc	acetate
SQ	semiquinone

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