Journal of Thermal Analysis and Calorimetry, Vol. 76 (2004) 801–812

THERMAL, MAGNETIC AND SPECTRAL STUDIES OF METAL–QUINONE COMPLEXES

Part II. Media effect on coligation of aqua ligands

S. Salunke Gawali[1,2]*, R. Dalvi*[1]*, Khursheed Ah*[1] *and S. Rane*[1]*

[1]Department of Chemistry, University of Pune, Pune 411 007, India
[2]Laboratoire de Magnétisme et d'Optique, CNRS- Université de Versailles-Saint-Quentin,
45, Avenue des États-Unis, 78035 Versailles cedex, France

(Received August 20, 2003; in revised form December 2, 2003)

Abstract

Syntheses of phthiocol complexes with Cu(II) in inert media resulted in anhydrous monomer Cu-4: $[Cu(NQ)_2]$ and dimer Cu-5: $[Cu(NQ)(NSQ)]_2$, however synthesis in air generates polymeric hydrated Cu-6: $[Cu(NQ)_2(H_2O)_2]_n$. Media and colligation give rise to charge transfers in coordination compounds and lead to different redox ligations of 3-methyl-2-hydroxy-1,4-naphthoquinone. These redox forms are determined from quantitization of activation energies (E_a) of different pyrolytic steps in TG using the rising temperature expression of Coats and Redfern. 'Tyrosinase'-type mechanism is discussed for the redox-type ligation. Characteristic six-line EPR signals of dimeric Cu-5 lead to zero field splitting parameters D=0.01608 cm^{-1} and E=0.01576 cm^{-1}. Cu-6 shows molecular association through hydrogen bonding. Variable temperature magnetic measurement data of Cu-6 from 6 to 300 K is fitted to the polymeric expression of Bonner and Fisher model. The best fit was obtained with antiferrromagnetic exchange coupling constant J=–2 cm^{-1}, g=2.2 having R=$4.2\cdot10^{-4}$.

Keywords: dimer, E_a, polymer, redox forms, zfs (zero field split)

Introduction

In the past 25 years, research has been grown towards the understanding of structural, electrochemical and magnetic properties of quinone complexes. Several reviews appeared in the literature by Pierpont *et al.* in this concern [1–4]. Quinones can bind potentially to metal ions in three different oxidation states, viz. quinone, its one-electron reduced form, semiquinone, and its two-electron reduced form, catechol. Coordination compounds with these different oxidations involve different structural, magnetic and electrochemical properties [3, 4]. The charge distribution in metal quinone complexes is relaxed with the energy balance between the quinone and metal orbitals. Paramagnetic bridging agents can be used in synthesis of polymeric chains and thus lead to formation of molecular-based magnets [5].

---

* Author for correspondence: E-mail: syrane@chem.unipune.ernet.in

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Binding ability of quinones in different oxidation states also allow them to play integral role in biological systems. Copper containing oxidases such as amine oxidases and lysyl oxidase contain quinone as an active cofactor. This quinone cofactor is found to be TPQ (topaquinone) and trihydroxyphenylalanine is reduced form of TPQ (Scheme 1) found in amine oxidase which catalyses the oxidative deamination of primary amines to aldehydes, with the concomitant reduction of molecular oxygen to hydrogen peroxide [6–8]. In the catalytic cycle of the enzyme, semiquinone radical is generated [9]. The Cu^{2+} plays an important role in catalysing the electron transfer between TPQ and dioxygen, and provides binding sites for 1 e^- and 2 e^- reduced dioxygen species to be efficiently protonated and released while preventing the back reaction between the product aldehyde and TPQ [10]. Kaim *et al*. recently reported sensitive valence tautomer equilibrium of paramagnetic copper quinone complexes [11].

In our growing interest towards the biomimetic studies of copper proteins with biologically active ligands such as hydroxy-naphthoquinones, we have first [12] discussed the role of water molecules in the charge distribution of the copper–quinone complexes of 2-hydroxy-1,4-naphthoquinone where we cannot avoid the entry of water molecule in the coordination sphere instead of maintained anhydrous conditions during the synthesis. However, in this second report, we discuss the lability of water molecules in the coordination sphere of copper by using methyl derivative of this ligand. The entry of water molecules can be avoided due to the hydrophobicity of the methyl group and the inert condition used during the synthesis. We also discussed the effect of non-inert condition on coordination using different metal salts as starting materials and the ligand phthiocol (3-methyl-2-hydroxy-1,4-naphthoquinone) which resembles to the cofactor of amine oxidase, TPQ, as shown in Scheme 1.

In this second report, the media effect on aqua colligation of phthiocol in copper complexes is explained by means of TG, DTA together with magnetostructural studies.

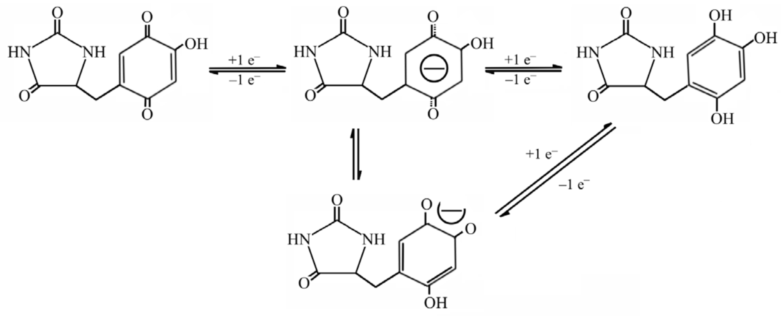
Experimental

Synthesis

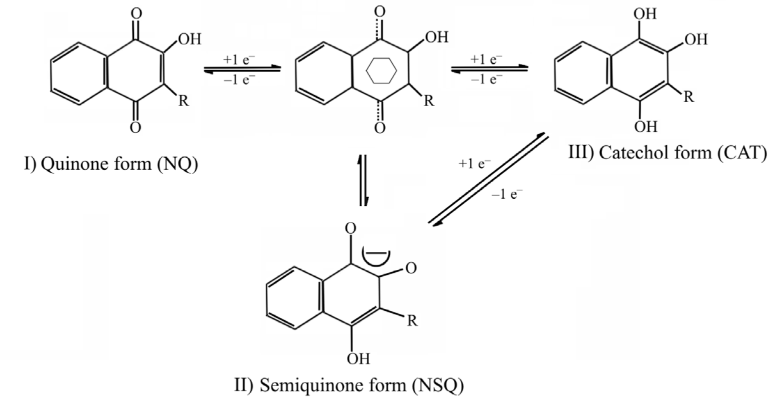
All reagents used in the synthesis are obtained from Aldrich Chemical Co. and are used without further purification.

Ligand phthiocol is prepared according to procedure of Fieser [13]. Anhydrous copper(II) chloride is prepared for synthesis of Cu-5 and Cu-6 as described by Jeung–Hoso and Boudjonk [14]. 1 mmol metal salt [$Cu(OAc)_2{\cdot}H_2O$ in Cu-4; anhydrous $CuCl_2$ in Cu-5 and Cu-6] was dissolved in 100 mL of anhydrous methanol to which 5 mL of triethylorthoformate was added as a dehydrating agent. 2 mmol of phthiocol ligand was dissolved in 50 mL of anhydrous methanol to which 10 mL of triethylorthoformate was added. In case of Cu-4 and Cu-5 the metal salt and ligand solutions were mixed with each other under N_2 atmosphere with constant stirring for 15 min. But in Cu-6 the two solutions were mixed with each other under O_2 atmosphere instead of inert N_2 atmosphere with constant stirring for 15 min. pH of the solution was adjusted to 6 using deaerated 10% sodium acetate trihydrate

Redox active forms of TPQ



Redox active forms of 2-hydroxy-1,4-naphthoquinone and their derivative ligands



Scheme 1 Redox forms of TPQ and 2-hydroxy-1,4-naphthoquinone ligands where R=–CH_3=phthiocol and R=–H=lawsone

solution in anhydrous methanol. The product precipitated (dark brown for Cu-4; red brown for Cu-5; and red for Cu-6) immediately was filtered and washed with anhydrous methanol and diethyl ether and dried under vacuum.

Analytical data calculated for:

Cu-4; $C_{22}H_{14}CuO_6$: C, 60.34; H, 3.22; Cu, 14.51 found C, 59.40; H, 3.63; Cu, 14.60

Cu-5; $C_{22}H_{14}CuO_6$: C, 60.34; H, 3.22; Cu, 14.51 found C, 60.64; H, 3.38; Cu, 14.54

Cu-6; $C_{22}H_{18}CuO_8$: C, 55.75; H, 4.25; Cu, 13.40 found C, 55.75; H, 4.16; Cu, 13.20

Physical techniques

Elemental analyses were obtained on HOSLI C, H analyser in the Department of Chemistry, University of Pune. Nitrogen analysis was done on Carlo Erba instruments (C, H, N, S and O) EA1108 elemental analyser at National Chemical Laboratory, Pune-8 India.

TG of Cu-4 to Cu-6 and DTA of Cu-6 were done on the laboratory constructed instruments, details of which were reported else where [12, 15, 16].

Infrared spectra were recorded in nujol mull/KBr pellet on FTIR 1600 Perkin Elmer infrared spectrometer.

The X-band powder EPR spectra of complexes were recorded on JES 2XG ESR spectrometer. The Q-band EPR spectrum of Cu-5 was recorded on Varian V-4502-12 EPR spectrometer.

The magnetisation curves are recorded using a SQUID magnetometer (Quantum Design MPMS5) operating in the alternative mode at Laboratoire de Magnétisme et d'Optique, Université de Versailles, Versailles, France. Diamagnetic corrections, estimated from Pascal constants were used when calculating the molar magnetic susceptibilities [17, 18].

Results and discussion

From the crystal structure of amine oxidase of *E. Coli* [19] Knowles and co-workers concluded that the axial water is proximal to C2 position of TPQ. Proton relaxation measurements suggest that there are no H-bonds from protein residues to coordinated water molecules. It indicates that these water molecules may be labile [20] and they have some role to play in the mechanism of this enzyme. Several reports appear in literature as structural and functional models for this enzyme [21]. In our first report of copper-complexes with 2-hydroxy-1,4-naphthoquinone ligands [12] we observed that we cannot avoid the entry of water molecules in the coordination sphere, thus water molecules are not labile. If we could increase the hydrophobicity of our ligand by introducing methyl group and with media effect such as O_2 atmosphere we can introduce aqua ligands in the coordination sphere along with hydroxy naphthoquinone ligands. Thermal technique very well reveals the coordination of aqua ligands.

Non-isothermal TG and DTA studies

The stoichiometries of pyrolytic reactions of Cu-4 to Cu-6 at different steps are ascertained in Fig. 1 and Table 1. The kinetic parameters can be calculated from the dynamic TG curves using various expressions [22] with the help of computer program developed in our laboratory on the rising temperature expressions of Coats and Redfern [23]. The activation energies for different functional groups were presented in Table 2. Presence of water molecules in the coordination sphere of transition metal complexes of orthoquinones is long time query due to their uncertainty [1]. In our first report [12] the presence of NSQ form in copper lawsone complexes viz. Cu-1 and Cu-3 is due to the similar activation energies of water and lawsone ligands. In case of methyl substituted phthiocol complexes viz. Cu-4 to Cu-6, Cu-4 and Cu-5 are anhydrous and are decomposing in two steps only. Although the decomposition is in two steps and similar infrared bands are observed for them, the fractional mass losses of Cu-4 and Cu-5 are different (Table 1), indicating their different individual coordinating redox nature. The fractional decomposition of ligand phthiocol in Cu-4 and

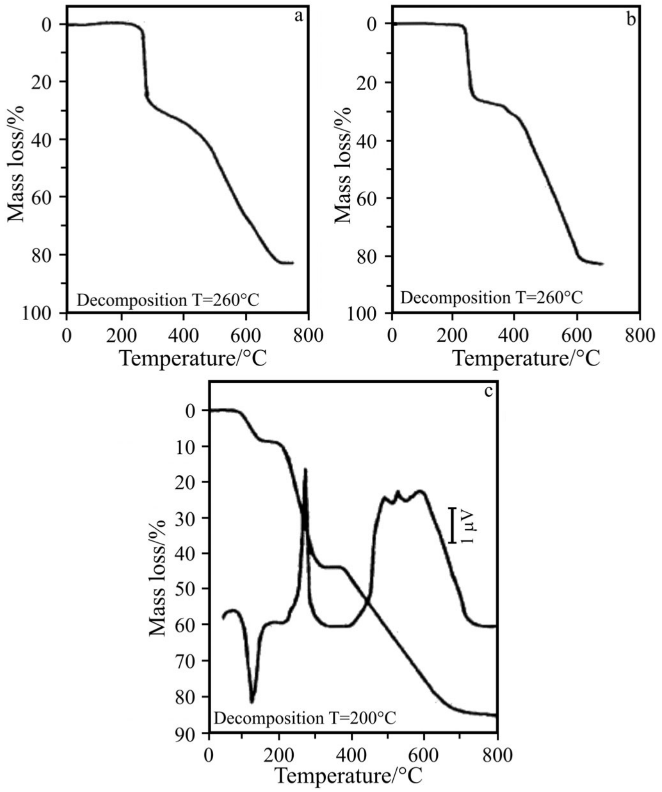


Fig. 1 TG of a – Cu-4, b – Cu-5 and c – Cu-6; DTA plot of Cu-6

Cu-5 are similar to Cu(II) amine complexes [24]. For Step I in Cu-4 and Cu-5 complexes it needs very high energy of activation as compared to Step II (Table 2). From the Step II the activation energy calculated is ~60 kJ mol^{-1} in Cu-4 and ~40 kJ mol^{-1} in Cu-5. As these energies of activation are comparable with NQ coordination form of the ligand in case of Cu-4 and NSQ coordination form of the ligand in case of Cu-5 according to our former report [12].

The pyrolytic decomposition of Cu-6 is in three steps viz. loss of coordinated water molecules [25] in Step I and one phthiocol ligand in each Step II and Step III, respectively. The presence of water molecules in Cu-6 are due to media effect as it is synthesized under O_2 atmosphere. The activation energies calculated for phthiocol ligands in Step II and Step III are ~60 to 80 kJ mol^{-1} and are assigned to NQ coordination form of the ligand. If one can compare the activation energies of water and phthiocol ligands in Cu-6 we find that the energies were not comparable, thus the water molecules coordinated will not actively participate in charge distribution within NQ ligands in Cu-6, but we can avoid the entry of water molecules in coordination sphere with application of anhydrous condition as in Cu-4. Lability of aqua ligands can be varied on media effect in these complexes. Thermal stabilities of complexes are indicated from their decomposition temperatures. Anhydrous Cu-4/Cu-5 decomposes at ~260°C while Cu-6 shows decomposition at ~200°C. As coligated aqua ligands volatilize at relatively low temperature [26], the polymeric structure through H-bonding of aqua ligands in Cu-6 collapses at relatively low temperature compared to Cu-4.

Table 1 TG data for Cu-4 to Cu-6 complexes

Complex	Step No.	Temp. range/°C	Masss losses/%	Probable comp. of group lost	Residue
Cu-4	I	210–320	32.00 (32.05)*	0.75Phth	$[Cu(Phth)_{1.25}]$
	II	360–700	51.00 (53.43)	1.25Phth	CuO
Cu-5	I	220–280	26.00 (25.64)	0.60Phth	$[Cu(Phth)_{1.4}]$
	II	340–610	57.00 (59.84)	1.4Phth	CuO
Cu-6	I	90–160	9.00 (7.60)	$2H_2O$	$[Cu(Phth)_2]$
	II	210–280	35.00 (39.49)	1Phth	[Cu(Phth)]
	III	380–700	40.00 (39.49)	1Phth	CuO

*Figures in parenthesis indicate calculated values.

DTA of Cu-6 shows endothermic peaks due to expulsion of water molecules and oxidative decomposition of the phthiocol ligands as exothermic peaks. The enthalpies of the ligands in the successive step of heat absorption or evolution can be calculated assuming the Gaussian curve analysis [27, 28]. The enthalpy calculated for $2H_2O$ molecules in Cu-6 are comparable with that of water molecules in the lawsone complexes (1.8909 kJ mol^{-1}) [16].

Infrared spectral studies

The absence of absorption band in 3600 to 3200 cm^{-1} range in compound Cu-5 indicates its anhydrous nature; however a strong broad absorption band ~3262 cm^{-1} in Cu-6 is assigned to $\nu_{(OH)}$ frequency of either intra/intermolecular H-bonded water molecules. $\nu_{C=O}$ vibrational band in Cu-6 is observed at 1651 cm^{-1} where as for Cu-5 it is seen at 1636 cm^{-1} both indicate carbonyl coordination in fully oxidized form of the ligand. In Cu-5 an absorption at 1595 cm^{-1} can be assigned for $C\overset{\cdots}{-}O$ of NSQ form [29]. The coordination of the ligands in these complexes can be further revealed by magnetic studies. Typical paranaphthoquinone vibrations are seen at 1286 cm^{-1} (s) in Cu-6 however those are reduced to ~1278 cm^{-1} in Cu-5 due to reduced *p*-NQ form of the phthiocol ligand. δ_{H_2O} is observed at 1613 cm^{-1} in Cu-6. Bending in plane vibrations are seen at 1355 cm^{-1} as a strong band in Cu-6, which is assigned to hydroxyl group, this vibrational band is absent in Cu-5.

Magnetostructural studies

EPR Studies

The EPR spectra and EPR parameters are presented in Fig. 2, respectively. Although the EPR of Cu-4 is discussed in detail earlier [12, 29], we have presented it here for comparison with Cu-5 and Cu-6. The X-band EPR of Cu-6 is typical of axial symmetry [30] with elongated tetragonal distortion having g factors $g_{\|}=2.36$ and $g_{\perp}=2.08$. Since $g_{\|}>g_{\perp}$ the unpaired electron is residing in the $d_{x^2-y^2}$ orbital of copper [30–32]. The calculated $G(G=(g_{\|}-2)/(g_{\perp}-2))$ is 4.5; hence the principal axis of the complex is parallel with the field.

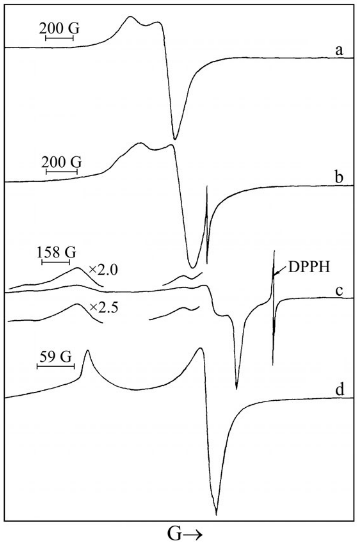


Fig. 2 X-band EPR spectra at 300 K of a – Cu-4, b – Cu-5, d – Cu-6 and c – Q-band EPR spectrum of Cu-5 at 300 K

The X-band EPR spectrum of Cu-5 shows multiline features in $g_{\|}$ region ($g_1=2.34$, $g_2=2.26$, $g_3=2.13$, $g_4=2.09$, $g_5=2.04$). The Q-band spectrum is more elaborated and more resolved, due to its field dependence it shows six lines ($g_1=2.31$, $g_2=2.22$, $g_3=2.11$, $g_4=2.08$, $g_5=2.07$, $g_6=2.04$). These six lines are due to stacking of two monomeric units together with different forms of ligand coordination (viz. form II i.e. naphthoquinone form and form III i.e. naphthosemiquinone form) as discussed in supra TG and IR studies. Each of the monomeric unit shows a rhombic spectrum of three lines with $g_x \neq g_y \neq g_z$. Intensities with these two sets of three lines will depend upon the concentrations of each monomeric unit in the crystal packing.

From the six lines in the Q-band spectrum of Cu-5, the zero field splitting (zfs) parameters are calculated from following expressions (Eq. (1)) [33, 34]. D is found to be 0.01608 cm^{-1} and E=0.01576 cm^{-1}.

1. $B_{x1}=g_e/g_x[(B_0-D'+E')(B_0+2E')]^{1/2}$
2. $B_{x2}=g_e/g_x[(B_0+D'-E')(B_0-2E')]^{1/2}$
3. $B_{y1}=g_e/g_y[(B_0-D'-E')(B_0-2E')]^{1/2}$
4. $B_{y2}=g_e/g_y[(B_0+D'+E')(B_0+2E')]^{1/2}$
5. $B_{z1}=g_e/g_z[(B_0-D')^2-(E')^2]^{1/2}$
6. $B_{z2}=g_e/g_z[(B_0+D')^2-(E')^2]^{1/2}$

$$B=(h\nu/\mu_B g_e),\ D'=D/(\mu_B g_e),\ E'=E/(\mu_B g_e) \tag{1}$$

where B is magnetic field, h is Planck constant; μ_B is Bohr magneton of electron and g_e gyromagnetic ratio of free electron. D is less than 0.3 cm^{-1} hence we have not observed the half field transition ($D<h\nu$) [35, 36] in the EPR spectrum of Cu-5. From the D value the metal–metal distance is calculated from the following expression, and found to be 5.10 Å (Eq. (2)) [33].

$$D_{AB}=0.433\ g_{AB}^2/r_{AB}^3 \tag{2}$$

where AB are two copper centers, g is the average gyromagnetic ratio and r is the distance between two copper centers.

The stacking effect observed in Cu-5 is similar to Cu-1 [37] complex. As Cu-5 contains bulky methyl group substituted at C3 position of the phthiocol ligand the Cu–Cu-distance is increased from 5.02 Å (observed in copper complex of 2-hydroxy-1,4-naphthoquinone [38]) to 5.10 Å.

Magnetic susceptibility studies

Cu-4 shows magnetic moment of 1.73 μB.M. and is similar observations for many monomeric copper complexes [29, 37].

Variable temperature magnetic susceptibility measurements were performed on polycrystalline powder of Cu-6 between 5 to 300 K, the plots are shown in the form of χ_m and $\chi_m T$ *vs.* T (Fig. 3). μ_{eff} value is observed as 1.97 B.M. in Cu-6 and it decreases slowly on cooling and approaches to 1.49 B.M. at 5 K, and its $\chi_m T$ value is 0.48 emu K mol^{-1} at 300 K and it decreases to 0.27 emu K mol^{-1} at 5 K. This behaviour suggests the weak antiferromagnetic interactions in this Cu-6 [39] compound. Usual Bleaney Bowers equation used for calculating copper–copper interaction between dimeric copper complexes [40] fails to fit the magnetic data of Cu-6. The susceptibility data are well fitted with Bonner Fisher model (Eq. (3)) [39, 41] assuming the linear chain of array of monomeric units.

$$\chi_m=Ng^2\beta^2/kT(0.25+0.074975x+0.07523x^2/1.0+0.9931x+0.172135x^2+0.757825x^3)$$
$$\text{with } x=|J/kT| \tag{3}$$

where χ_m – molar magnetic susceptibility, N is Avogadro number, g – gyromagnetic ratio, β – Bohr magneton of electron, k – Boltzmann's constant, and J – exchange coupling constant, T – respective temperature.

The best fit is obtained with $J=-2\ \mathrm{cm}^{-1}$ $g=2.2$ and the agreement factor $R=4.2\cdot 10^{-4}$ ($R=\sum[(\chi_m)_{obs}-(\chi_m)_{cal}]^2/\sum[(\chi_m)_{obs}]^2$). The molecular association of monomeric units through hydrogen bonding of water molecules leads to polymeric nature of Cu-6 which is resulted in weak antiferromagnetic interaction within Cu(II) centers.

The coordination of hydroxy-naphthoquinone ligands in various oxidation states like NQ and NSQ redox forms can be strategically coordinated with control of starting material cofactors and media. 'Aqua' ligands play significant role in proposing electronic structures at active coordination site of oxidases. Let us see how starting metal cofactors

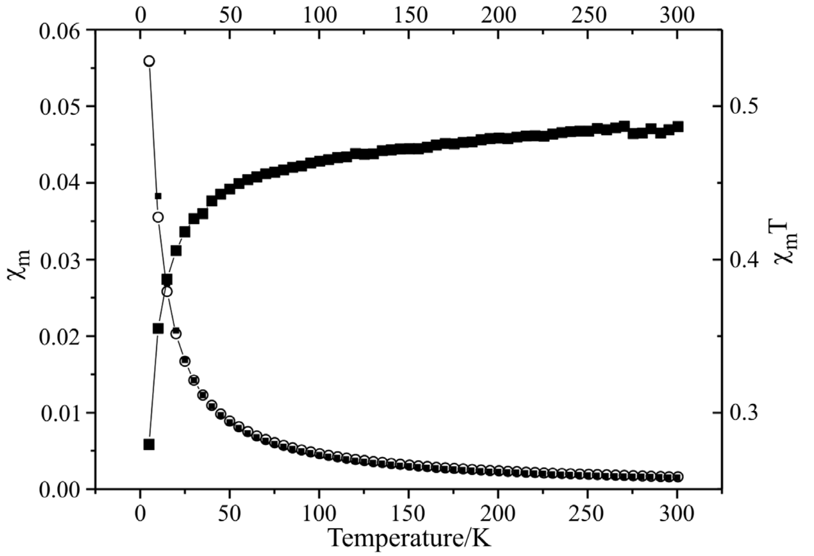


Fig. 3 ○ – χ_m and ■ – $\chi_m T$ *vs.* *T* plots of Cu-6 (The solid line indicates fitted curve)

help to generate required electronic structures in copper–quinone complexes. We have used $(Cu(OAc)_2H_2O)_2$ as metal cofactor for preparation of Cu-4. In $(Cu(OAc)_2H_2O)_2$ ~pH 4 two copper(II) ions are separated at distance of ~2.64 Å [35] bridged by OAc^- ligand is well known. As the 2-hydroxy-1, 4-naphthoquinone ligand (*R*=H in Scheme 1) has ~same pKa value as that of the OAc^- (pKa=4) ligand the copper complex formed with this ligand used the dimeric framework of $(Cu(OAc)_2H_2O)_2$ metal salt and the OAc^- ligands will be replaced simultaneously. However in Cu-4, the methyl substituent at C3 position (*R*=CH_3 in Scheme 1) of phthiocol is electron donating, hence pKa of phthiocol is higher than OAc^- ligands thus acetate ligand will not be replaced by phthiocol ligands simultaneously, once the acetate ligands totally free from the metal salt in solution there will be entry of phthiocol ligands hence there is no entry of water molecules in axial position in the coordination sphere of copper in Cu-4. An inert condition used also avoids the entry of water molecules in the coordination sphere of Cu-4 and also the energy of activation varies that of phthiocol and water molecules (Table 2).

The starting material used for Cu-5 and Cu-6 is anhydrous $CuCl_2$. Cu(II)chloride possesses distorted rutile structure in solid-state [36] with Cu–Cl bond lengths in square planar geometry are 2.30 Å and axial bond length of 2.95 Å. In anhydrous and hydrophobic media chlorobridged copper ions may disproportionate oxidation state of copper as Cu(I)/Cu(II) such as $[CuCl_2]^{-1}/[CuCl_2]$ [36] and on addition of $NaOAc\cdot 3H_2O$ solution intramolecular charge transfer between metal-NQ ligand may lead to Cu(II)(NSQ) species formation and simultaneously stacking of monomeric units in Cu-5.

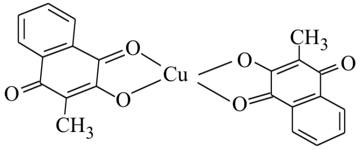
Table 2 Activation energies from dynamic TG of complexes Cu-4 to Cu-6

Compound	Step No.	Probable group lost	Order	E_a/kJ	E_a/kJ mol^{-1}
Cu-4	I	0.75Phth	1.95	400	533
	II	1.25Phth	1.38	73	58/NQ*
Cu-5	I	0.6Phth	1.02	300	501
	II	1.4Phth	0.89	59	42/NSQ
Cu-6	I	$2H_2O$	1.14	71	$35H_2O$
	II	1Phth	1.62	65	65/NQ
	III	1Phth	2.12	75	75/NQ

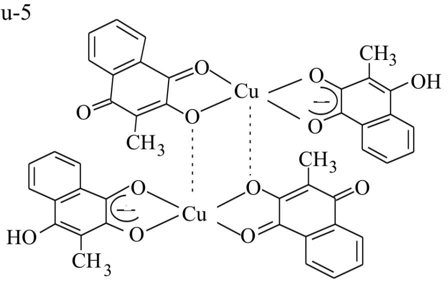
*Ref. 16

In Cu-5 and Cu-6 phthiocolate complexes media dictate charge transfers in the coordination sphere around Cu(II). They undergo 'tyrosinase' type activity in inert N_2 and non-inert O_2 atmosphere [42]. In inert atmosphere the 2-hydroxy group of the naphthoquinones shows dimerisation tendency [43]. Hence two electron transfer leads to 50% reduction of ligands in coordination sphere and bulky hydrophobic methyl group does not allow water molecules to enter in coordination sphere which gives rise to $[Cu(NQ)(NSQ)]_2$ coordination in Cu-5 as it is confirmed from its suprathermal, IR and magnetic studies. In Cu-6, O_2 oxidizes probably the reduced form of phthiocol and gets itself reduced to water. And this water may be coordinated at axial

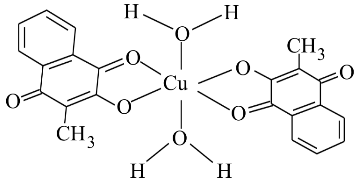
Cu-4



Cu-5



Cu-6



position, as the equatorial positions have been blocked by phthiocol ligands. Thus in O_2 atmosphere, oxidation of reduced organic cofactor phthiocol leads to [Cu $(NQ)_2(H_2O)_2$] coordination in Cu-6.

All the supra studies lead to above probable molecular structures of Cu-4 to Cu-6 complexes.

* * *

SAS is thankful to UGC, India for awarding SRF and Ministry of Research Government of France for awarding visiting fellowship and Prof. F. Varret of Laboratoire de Magnétisme et d'Optique, CNRS/ Université de Versailles (UMR 8634) 45 Avenue des Etats-Unis 78035 Versailles cedex France for Variable Temperature Magnetic Measurement, SYR is grateful to the CSIR, New Delhi, India (01(1686)/00/EMR-II) for the grant.

References

1 C. G. Pierpont and R. M. Buchanan, Coord. Chem. Rev., 38 (1981) 45.
2 C. G. Pierpont and C. W Lange, Prog. Inorg. Chem., 41 (1994) 331.
3 C. G. Pierpont, Coord. Chem. Rev., 216–217 (2001) 99.
4 C. G. Pierpont, Coord. Chem. Rev., 219–221 (2001) 451.
5 a O. Kahn, in Modular Chemistry, Ed.: J. Michl, Dordrecht 1997, p. 287.
b D. A. Shultz, A. K. Boal, D. J. Farmer, M. G. Holmon, J. R. Kitchin, D. B. Miller and G. N. Mol, Mol. Cryst. Liq. Cryst., 305 (1997) 303.
c E. J. Rittenberg, A. M. Arif, J. S. Miller and E. J. Brandon, Inorg. Chem., 37 (1998) 3376.
d Caneschi, D. Gatteschi, J. P. Renard, P. Rey and R. J. Sessoli, J. Am. Chem. Soc., 111 (1989) 785.
e H. O. Stumpf, L. Ouahab, Yu Pei, P. Bergerat and O. Kahn, J. Am. Chem. Soc., 116 (1994) 3866.
f M. Ruf, B. Noll, M. Groner, G. T. Yee and C. G. Pierpont, Inorg. Chem., 36 (1997) 4860.
6 J. P. Klinman, Chem. Rev., 96 (1996) 2541.
7 M. Fontecave and J.-L. Pierre, Coord. Chem. Rev., 170 (1981) 125.
8 M. Mure, S. A. Mills and J. P. Klinman, Biochemistry, 41 (2002) 9269.
9 D. M. Dooley, M. A. McGuirl, D. E. Brown, P. N. Turwski, W. S. McIntire and P. F. Knowles, Nature, 349 (1991) 262.
10 S. Kishishita, T. Okajima, M. Kim, H. Yamaguchi, S. Hirota, S. Suzuki, S. Kuroda, K. Tanizawa and M. Mure, J. Am. Chem. Soc., 125 (2003) 1041.
11 J. Rall, M. Wanner, M. Albrecht, F. M. Hornung and W. Kaim, Chem. Eur. J., 5 (1999) 2802.
12 S. Y. Rane, S. D. Gawali, S. B. Padhye, A. S. Kumbhar and P. P. Bakare, J. Therm. Anal. Cal., 55 (1999) 249.
13 L. F. Fieser, J. Biol. Chem., 133 (1940) 391.
14 J. Hoso and P. Boudjonk, Inorg. Chem., 29 (1990) 1592.
15 S. Y. Rane, J. P. Salvekar, N. V. R. Dass, P. S. Kaduskar and P. P. Bakare, Thermochim. Acta., 191 (1991) 255.
16 S. Y. Rane, S. B. Padhye, G. N. Natu, A. H. Kumar and E. M. Khan, J. Thermal Anal., 35 (1989) 2331.
17 A. Earnshaw, Introduction to Magnetochemistry, Academic Press, N.Y. 1968.

18 L. N. Mulay and E. A. Bourdreaux, Theory and Applications of Molecular Paramagnetism, Wiley, N.Y. 1970.

19 M. R. Parsons, M. A. Convery, C. M. Wilmot, K. D. S. Yadav, V. Blakely, A. S. Corner, S. E. Phillips, M. McPherson and P. F. Knowles, Structure, 3 (1995) 1171.

20 D. M. Dooley, M. A. McGuirl, C. E. Cote, P. F. Knowles, I. Singh, M. Spiller, R. D. Brown and S. H. Koening, J. Am. Chem. Soc., 113 (1996) 754.

21 a A. Sokolowski, B. Adam, T. Weyhermuller, A. Kikuchi, K. Hildebrandt, R. Schnepf, P. Hildebrandt, E. Bill and K. Wieghardt, Inorg. Chem., 36 (1997) 3702.
b Y. Wang, J. L. Dubois, B. Hedman, K. O. Hodgson and T. D. P. Stack, Science, 279 (1998) 537.
c M. D. Snodin, L. Ould-Moussa, U.Wallmann, S. Lecomte, V. Bacher, E. Bill, H. Hummel, T.Weyhermuller, P. Hildebrand and K.Wieghardt, Chem. Eur. J., 5 (1999) 2554.
d P. Chaudhari, M. Hess, T. Weyhermuller and K. Wieghardt, Angew. Chem. Int. Ed. Engl., 38 (1999) 1095.
e P. Chaudhari, M. Hess, J. Muller, K. Hildebrand, E. Bill, T. Weyhermuller and K. Wieghardt, J. Am. Chem. Soc., 119 (1999) 9599.
f Y. Shimazaki, S. Huth, S. Horota and O. Yamauchi, Inorg. Chim. Acta, 331 (2002) 168.

22 M. E. Brown, D. Dollimore and A. K. Galway, Comprehensive Chemical Kinetics, C. F. H. Tipper Ed., Elsevier, Amsterdam, 22 (1980) 74.

23 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.

24 L. S. Prabhumirashi, G. N. Natu and J. K. Khoje, J. Thermal Anal., 35 (1989) 1097.

25 a S. A. Abdel-Latif and H. B. Hassib, J. Therm. Anal. Cal., 68 (2002) 983.
b R. Kurpiel-Gorgol and W. Brzyska, J. Therm. Anal. Cal., 71 (2003) 539.

26 K. Berger, Coordination Chemistry: Experimental Methods, Butterworth, London 1973 p. 330.

27 W. W. Wendlant, Thermal Methods of Analysis, 2nd Ed. Wiley, N.Y. 1974, p. 184.

28 A. Blazek, Thermal Analysis, Van Nostrand, Reinhold 1973, p. 170.

29 S. Y. Rane, S. B. Padhye, E. M. Khan and P. L. Garge, Synth. React. Inorg. Met. Org. Chem., 18 (1988) 609.

30 B. J. Hathway and D. E. Billing, Coord. Chem. Rev, 5 (1970) 143.

31 B. J. Hathway and A. A. G. Tomlinson, Coord. Chem Rev., 5 (1970) 1.

32 B. J. Hathway, Struct. Bonding (Berlin), 57 (1984) 55.

33 A. Bencini and D. Gatteschi, EPR of exchange coupled systems, Ed. Springer, Berlin 1990.

34 G. A. Goodman and J. B. Raynor, Adv. Inorg. Chem. Radio. Chem., 13 (1970) 135.

35 R. L. Datta and A. Syamal, Elements of Magnetochemistry, 2nd Edition 1993, p. 197.

36 J. D. Lee, Concise Inorganic Chemistry, ELBS, Chapman and Hall Publishers, 5th Ed. 1996.

37 S. Y. Rane, S. Gawali, S. Padhye, S. Date and P. Bakare, Indian J. Chem., 42A (2003) 255.

38 S. Y. Rane, S. D. Gawali, S. B. Padhye, A. S. Kumbhar, P. P. Bakare, S. K. Date and V. G. Puranik, Proc. Indian Acad. Sci. (Chem. Sci.), 108 (1996) 289.

39 O. Kahn, Molecular Magnetism, VCH, New York, Weinheim. Germany and Cambridge, U.K. 1993.

40 B. Bleaney and K. D. Bowers, Proc. Roy. Soc., Sect. A, 214 (1952) 451.

41 J. C. Bonner and M. E. Fisher, Phys. Rev. A 135 (1964) 640.

42 N. Kitajima, Adv. Inorg. Chem., 39 (1992) 1.

43 D. R. Thube, A. Todkary, S. Y. Rane, K. Joshi, S. P. Gejji, S. A. Salunke, F. Varret and J. Marrot, J. Mol. Struct., 622 (2003) 211.