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THERMAL, MAGNETIC AND SPECTRAL STUDIES OF METAL-QUINONE COMPLEXES

Part III. Radical coordination and hydrogen bonding mediated exchange interaction in copper-hydroxyquinone complex

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The reaction of CuCl with 2HNQ, (viz. 2-hydroxy-1,4-naphthoquinone), in methanol results in $[Cu_2(II,II)(4HNSQ)_2(ONQ)_2(H_2O)_4]$, Cu-3 complex; [where ONQ is the deprotonated oxidized form of ligand (viz. 2-oxido-1,4-naphthoquinone) and 4HNSQ one electron reduced tautomeric form of the ligand (i.e. 4-hydroxy–1,2-naphthosemiquinone)]. The mixed valent redox ligation is confirmed in [9] by us. In present report complex Cu-3 investigated by variable temperature magnetic susceptibility measurements (SQUID), X and Q-band EPR, DSC and CV techniques. A break is observed in the χ_m^{-1} *vs*. T plot ~200 K in Cu-3 which is attributed to a phase transition. In Cu-3 a quintet state (S=2) is populated above 200 K by the molecular association of two exo Cu(II)(4HNSQ) units via hydrogen bonding between Cu(ONQ) unit of endo ligands in dimer. Magnetic susceptibility data is treated with tetramer model with S=1/2,1/2,1/2,1/2. The interdimer triplet-triplet interaction (J) in two [Cu(4HNSQ)] units and intradimer (zJ_1) interaction between [Cu(II)(4HNSQ)] are best fitted with J= –50 cm^{-1} and zJ_1=28 cm^{-1}, respectively, using g=2.2. 'Quintet-triplet' phase transition occurs with an enthalpy change of 31.83 kJ mol^{-1} estimated from DSC. Cu(II)⇔Cu(I) and NSQ⇔CAT redox couples at $E_{1/2}$=0.68 V and $E_{1/2}$ = –1.12 V, respectively are result of exo ligands and Cu(II) ions interaction, while shifts of ligand based peaks viz. NQ→NSQ and NSQ⇔CAT at –0.44 and –0.67 V towards positive potential on complexation are due to electron transfer interactions between endo ligand and Cu(II) ion.

Keywords: *antiferromagnetic coupling, copper complexes, lawsone, model complexes, quinones, triplet state*

Introduction

Quinone cofactors such as topaquinone (TPQ), tryptophan tryptophylquinone (TTQ), lysine tyrosyl quinone (LTQ) derived from post translational modification of either tyrosine or tryptophan are involved in novel biological reactions that range from oxidative deamination to free radical redox reaction in copper containing amine oxidases. In the catalytic cycle of the enzyme there is generation of semiquinone radical [1–3].

The quinonenzyme such as galactose oxidase contains one copper ion at its active site and its function is to oxidize primary alcohol to aldehyde in the presence of dioxygen [4]. The catalytic mechanism of the enzyme involves cycling between two redox states, viz. a Cu(I)-phenol and Cu(II)-phenoxyl radical. Many complexes are prepared as structural as well as functional models having two or more phenolate groups [5].

We had also reported the derivatized hydroxyquinone complexes of manganese acting as functional model of redox active water oxidizing complex (WOC) in photosystem-II [6–8]. Our interest is to reveal functions of galactose and amine oxidases for which its essential to get insight in copper–quinone interactions, because quinones are cofactors at their active sites [3]. To mimic the intermediates of copper–quinone interactions, a redox active 2-hydroxy-1,4-naphthoquinone ligand (Scheme 1) is used in our present studies. In the former reports we established by TG technique role of ancillary ligand like water in Part I [9] for Cu-3 complex. However in Part II [10] we had discussed the media effect on colligation of aqua ligands in Cu-4 to Cu-6 complexes using 3-methyl derivative of 2-hydroxy-1,4-naphthoquinone. In continuation of these studies here we describe the effect of radical coordination and magnetic phase transition property of Cu-3 which is very well supported by DSC.

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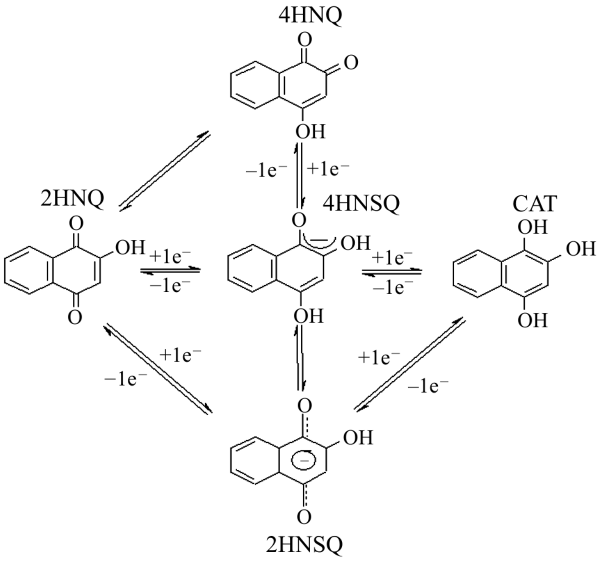

Scheme 1 Various tautomeric redox forms of 2-hydroxy-1,4-naphthoquinone (2HNQ) [11, 12]

Experimental

Synthesis

All the reagents used in the synthesis were obtained from Aldrich Chemical Co. and are used without further purification. 2-hydroxy-1,4-naphthoquinone was obtained from Fluka.

The synthesis of $[Cu_2(II,II)(4HNSQ)_2(ONQ)_2\cdot(H_2O)_4]$; Cu-3, complex was discussed previously [9] in Part I. The ligand 2HNQ coordinate in its deprotonated from viz., ONQ.

Physical techniques

The magnetization curves are recorded using a SQUID magnetometer (Quantum Design MPMS5) operating in the alternative mode at Laboratoire de Magnétisme et d'Optique, CNRS/Université de Versailles (UMR 8634) France. The experimental molar magnetic susceptibilities were corrected for the underlying diamagnetic susceptibility using Pascal constants and temperature independent paramagnetism ($-60\cdot10^{-6}$) cgs units/copper atom [13].

The polycrystalline EPR spectra were recorded on a Varian E-112 spectrometer using 100 kHz field modulation at X-band (9.5 GHz) and Q-band (35 GHz) frequencies.

DSC of Cu-3 was recorded on Mettler DSC-30 coupled with TA-4000 data processor, empty 'Al' crucible was used as a reference.

Cyclic voltammetry (CV), measurements of Cu-3 was performed on BAS-CV-27 assembly in conjunction with an X–Y recorder using the three electrode system with direct correction of the uncompensated cell resistance (iR drop). The three-electrode cell includes a working electrode as a glassy carbon (area 0.23 mm^2) referenced with an Ag/AgCl electrode and platinum wire as an auxiliary electrode. The glassy carbon working electrode was activated according to procedure by Thorp *et al.* [14]. The solvents used in CV studies were purified according to the literature procedure [15] and were always degassed for 10 min before the experiment, 0.1 M tetraethyl ammonium perchlorate (TEAP) was used as supporting electrolyte. Before each CV run, the solution in cell was carefully deaerated with purified N_2.

Results and discussion

Magnetostructural studies of Cu-3

Magnetic measurements were recorded for the complex Cu-3 over the temperature range from 300 to 2 K with 500 Oe applied field. The $\chi_m T$ *vs.* T plot per monomeric unit for simplicity is shown in the Fig. 1.

The $\chi_m T$ value per monomeric unit is observed to be 0.789 emu K mol^{-1} at 300 K and 0.047 at 2 K and the obtained μ_{eff} value is 2.45 B.M. at 300 K and 0.85 B.M. at 2 K. Both the behaviours show net antiferromagnetism in this complex [16]. The $\chi_m T$ continuously decreases on cooling down 2 K. The unusual break was observed in the $1/\chi_m$ *vs.* T plot of Cu-3 around 200 K. Hence the experiments were repeated further between 100 to 300 K region in both heating as well as cooling regimes as shown in Fig. 2 at 2000 Oe applied field. The

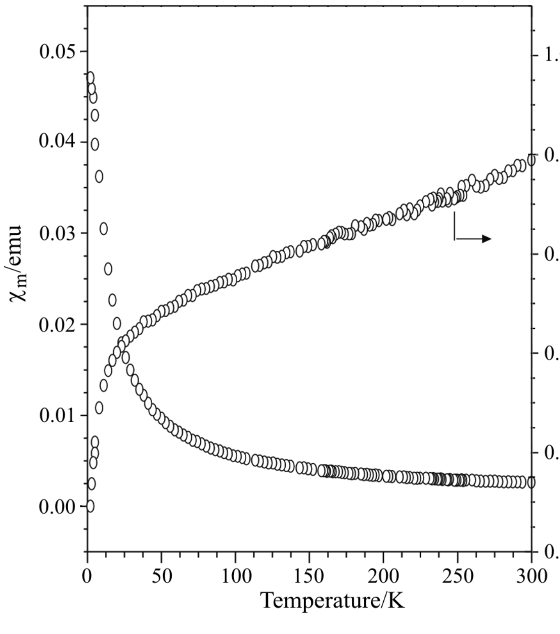

Fig. 1 χ_m and $\chi_m T$ *vs.* T plots of Cu-3 with field applied 500 Oe

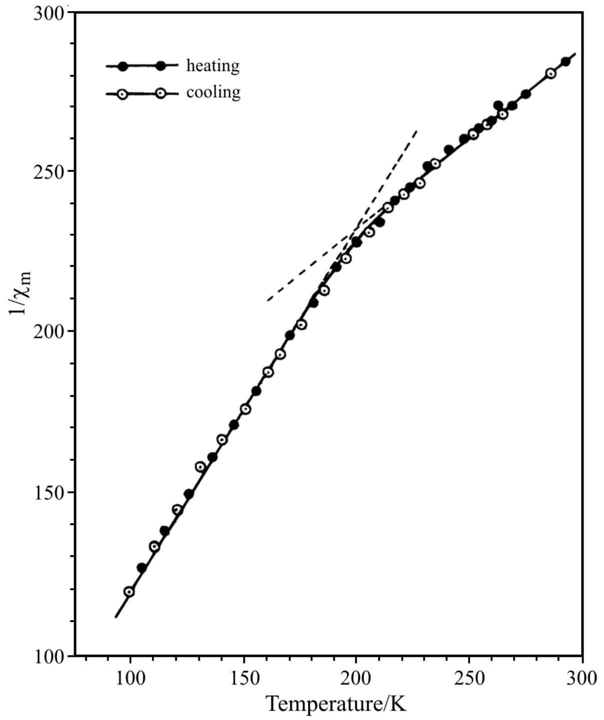

Fig. 2 $1/\chi_m$ *vs.* T plots of Cu-3 applied field 2000 Oe

suspected break occurs around 200 K as to be confirmed by DSC measurements (vide infra).

The observed χ_mT value is more than expected for monomeric Cu(II) complexes (calculated as $\chi_mT=Ng^2\beta^2[S(S+1)/3k]=0.375$ emu K mol^{-1}, where $g=2$, $S=1/2$). The higher value of χ_mT is attributed to the $S=1/2$ spin of Cu(II) and $S=1/2$ spin of the paramagnetic form of the ligand viz. 4HNSQ (Scheme 1). Monomeric as well as dimeric copper complexes with one or two semiquinone ligands are known to have complicated magnetic properties [17–19].

The monomeric complexes of the Cu(II)(SQ)$_2$ type units have complicated spin system with strong Cu(II)–SQ and SQ–SQ spin coupling interactions. The orthogonality of the metal and semiquinone orbitals in the planar molecule results in ferromagnetic [20] interaction between Cu–SQ whereas the SQ–SQ interaction should be antiferromagnetic [21]. Thus such complexes show either net ferromagnetic behaviour or net antiferromagnetic behaviour. The net ferromagnetic behaviour of the complex includes [Cu(py)(3,6-DBSQ)$_2$] complex while the net antiferromagnetic behaviour observed in dimeric [Cu(3,5-DBSQ)$_2$] complex with singlet ground state [22]. On the basis of crystal structure of Cu-2; [Cu(ONQ)$_2$(H$_2$O)$_2$]$_n$ [23–25] we propose the molecular structure of complex Cu-3 as shown in Fig. 3, where the two monomeric units may be interacting with each other through hydrogen bondings of uncoordinated quinone oxygen atoms and hydrogen at C3 position of ONQ quinone group of nearby molecule. Numbers 1 and 3 in Fig. 3 represents the Cu(II) ions and numbers 2 and 4 represents the 4HNSQ ligands, we called the hydrogen bonded ligands as endo-ONQ ligands and the other two as exo-4HNSQ ligands.

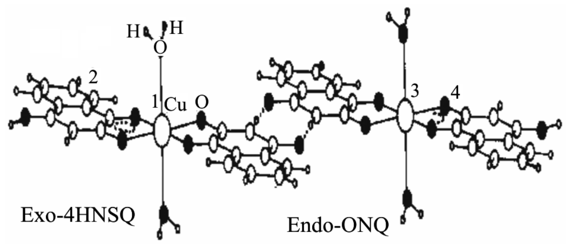

Fig. 3 Proposed molecular structure of Cu-3

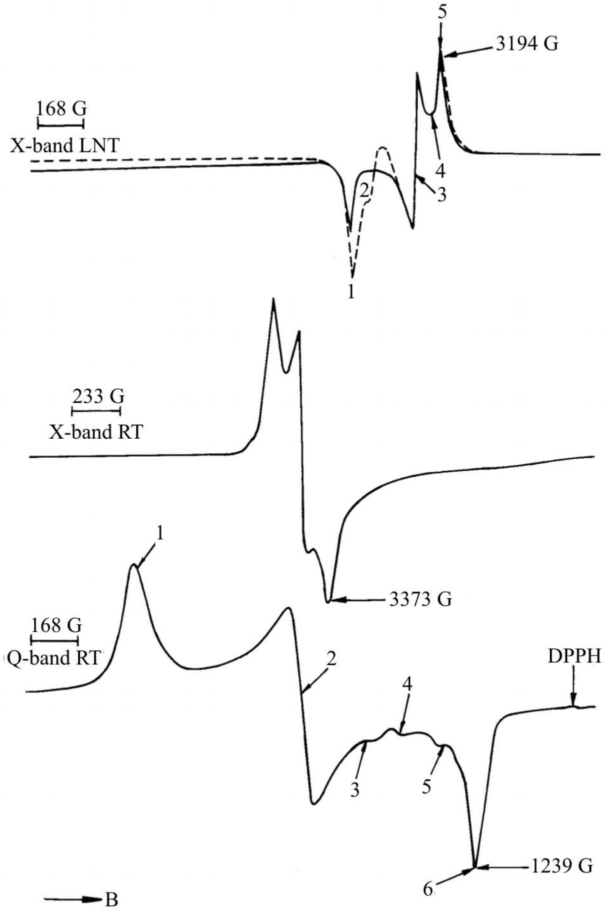

Fig. 4 X-band EPR spectra at 77 and 300 K (--- – in toluene) Q-band EPR spectrum at 300 K of Cu-3

Thus intramolecular interactions in each Cu(II)–4HNSQ monomeric unit of dimer are of ferromagnetic type, this created triplet ground state of the monomer again interacts with each other through intermolecular hydrogen bond. The two monomeric units, then interact with each other through antiferromagnetic coupling with singlet ground state and higher triplet and quintet in a fashion similar to the description of coupling in [n-Bu$_4$N]$_2$[Cu(dcmdtcroc)$_2$] [26]. The newly created quintet and triplet states will be populated at higher temperatures. The break in χ_m^{-1} *vs*. *T* plot (Fig. 2) ~200 K may be due to the breaking of the orthogonality of the two Cu(II)–4HNSQ units from each other and/or change in cell parameters may break the interacting pathway of the two triplets which leads to the enthalpy change (infra DSC studies). We observed a small change in volume at 161 K in the crystal structure of Cu-2 indicating large changes in hydrogen bonding distances, such a small change in the volume of the analogous complex Cu-3 may be a distinct possibility and hence be the cause of phase transition in Cu-3. Such a break can result in isolated triplet state due to intramolecular magnetic interaction at low temperature with singlet as the excited state. As the metal-quinone complexes are known to be having balanced orbital energies so that the shifts in charge distribution may be induced thermally, this phenomenon is accompanied by changes in the enthalpy and entropy and temperature dependent equilibria between the metal and reduced form of the quinone ligands [26]. It is very difficult to quantify precisely the magnetic interactions of this complex as there are intramolecular interaction between Cu(II)–4HNSQ of the monomeric unit and intermolecular interactions between Cu(II)–Cu(II), 4HNSQ–4HNSQ, Cu(II)–4HNSQ – Cu(II)–4HNSQ of the dimeric unit ultimately leading to complicated magnetic structure of the complex. Usual Bleaney Bowers equation for *S*=1/2, 1/2 spin pair interaction fails to fit to monomeric susceptibility data of this complex. We applied a qualitative treatment to the dimeric susceptibility data of complex Cu-3 with a tetrameric model (Eqs (i) and (ii)) [28, 29] of spin *S*=1/2, 1/2, 1/2, 1/2 between 200 and 300 K,

$$\chi_m = \frac{Ng^2\beta^2[F(T)]}{kT - 2zJ_1[F(T)]} \qquad \text{(i)}$$

$$[F(T)] = \frac{6\exp(-4J/kT) + 10}{9\exp(-4J/kT) + 2\exp(-6J/kT) + 5} \qquad \text{(ii)}$$

with the interactive Hamiltonian of the two ground triplet states which can be presented as

$$\hat{H} = -J(S_1S_2+S_3S_4)+zJ_1(S_1S_2)(S_3S_4)$$

where S_1 and S_3 are *S*=1/2 spins of Cu(II) ions and S_2 and S_4 are *S*=1/2 spins of the 4HNSQ radical ligands, *J* defines the inter dimer exchange i.e. between the two triplet states and zJ_1 defines the intra dimer exchange i.e. within triplet state. The best fit obtained with *g*=2.2, $J=-50$ cm^{-1} and $(zJ_1)=28$ cm^{-1}. These values are similar to our former report [30]. Thus the intramolecular interaction between the Cu(II)–4HNSQ is ferromagnetic and the intermolecular interaction between [Cu(II)-4HNSQ]$_2$ is antiferromagnetic and the dominating magnitude of molecular interactions resulted in net antiferromagnetism in Cu-3.

X- and Q-band powder RT and X-band LNT in toluene EPR spectra of Cu-3 are represented in Fig. 4. Six lines Q-band feature of Cu(II) dimer is characteristic of orthorhombic symmetry. The field positions and *g*-factors were shown in Table 1. Using transition field expressions [10, 31].

Axial and equatorial zero field split parameters are quantitised as *D*=0.04947 cm^{-1} and *E*=0.01035 cm^{-1} (Table 2). Unequal intensities of six lines lead to various population of different states in high magnetic field (Q-band), and is not due to spin orbit coupling [32] but due to intrinsic dipolar spin-spin interaction among four electrons of the Cu(II)(4HNSQ) [33] pair states. Five-line feature in LNT X-band spectrum is characteristic of triplet state [33]. The shift of transition in X- and a Q-band RT spectra is a function of distance R between individual triplet centres and the triplet fine structure.

Table 1 Anisotropic *g* tensors from EPR of Cu-3

Band	Microwave frequency/GHz	Temperature/K	g_1	g_2	g_3	g_4	g_5	g_6
X	9.439	300	2.31	2.14	2.05	2.00		
X	9.070	77	2.40	2.15	2.09	2.03		
X*	9.070	77	2.40	2.30	2.15	2.09	2.03	
Q	35.150	300	2.37	2.18	2.11	2.09	2.05	2.02

*values in toluene

Table 2 Line position assignments and the magnetic parameter values of Cu-3

Microwave frequency/GHz	H_{x1} and g_{x1}	H_{y1} and g_{y1}	H_{z1} and g_{z1}	H_{x2} and g_{x2}	H_{y2} and g_{y2}	H_{z2} and g_{z2}	D/cm^{-1}	E/cm^{-1}
35.15	12391	11481	10601 (10725)	12201	11971	11861 (11669)	0.04947	0.01035
	2.027	2.188	2.370 (2.342)*	2.059	2.099	2.118 (2.153)		

*figures in parenthesis indicate calculated values

The shifts are characterized by an increase of the D_T (T=triplet) value and decrease of the E_T value of the triplet spin pair state [34] as compared to individual triplet centres 1, 2 and 3, 4 (Fig. 3) viz. Cu(II), 4HNSQ states [33]. Hence $D>E$ obtained from Q-band RT EPR spectrum. X-band RT spectrum shows intense signal having g_4=2 (Table 1) may be due to 4HNSQ radical.

The triplet state is populated from liquid nitrogen temperature to high temperature. It shows ferromagnetic exchange interaction between Cu(II)(4HNSQ) species accounted as triplet state in monomeric unit. However dynamic quintet-triplet antiferromagnetic interaction occurs only in high temperature region above ~200 K. Latter antiferromagnetic interaction may be explained by explicitly considering the vibronic coupling leading to valence delocalisation in a continuous i.e. dynamic and united manner. This is supported by observations in some instances of new electronic transition polarized along the A–H...B axis [35]. In Cu-3 directional side by side hydrogen bonds between two endo-ONQ units as shown in Fig. 3 are responsible for magnetic phase transition when those are disrupted.

DSC studies of Cu-3

An exothermic peak in DSC (differential scanning calorimetry) plot (Fig. 5) supports with magnetic phase transition in Cu-3 like that of the spin crossover complexes [36–38] and complexes exhibiting thermochromism [39, 40] as concluded from supra magnetic susceptibility studies. The exotherm observed in heating curve of DSC plot at 197.4 K is result of an enthalpy and entropy variations consistent with expected quintet-triplet spin transition as discussed above. ΔH (Eq. (iii)) obtained from DSC exotherm is 31.83 kJ mol^{-1}

$$\Delta S_t=\Delta H/T_t \qquad \text{(iii)}$$

ΔS_t entropy variation [41] at transition is 161.26 J K^{-1} mol^{-1}. From enthalpy and entropy variations Gibbs free energy ΔF is estimated as 63.66 kJ mol^{-1}. Similar free energy 65.75 kJ mol^{-1} is reported from thermogravimetry data for evolution of ONQ coordinated form in decomposition of complex Cu-3 [9] in Part I. The irreversibility of the exotherm in heating and cooling regimes is due to order-disorder type of phase transition [42]. Exotherm is a consequence of breaking of hydrogen bonds in endo-ONQ ligands (Fig. 3) which disturbs the electronic state of the Cu-3 that leads to separation in two monomeric units [Cu(II)(4HNSQ)(ONQ)(H$_2$O)$_2$] of dimer forming a triplet state at low temperature. Hence probable spin transition mechanism may be as follows:

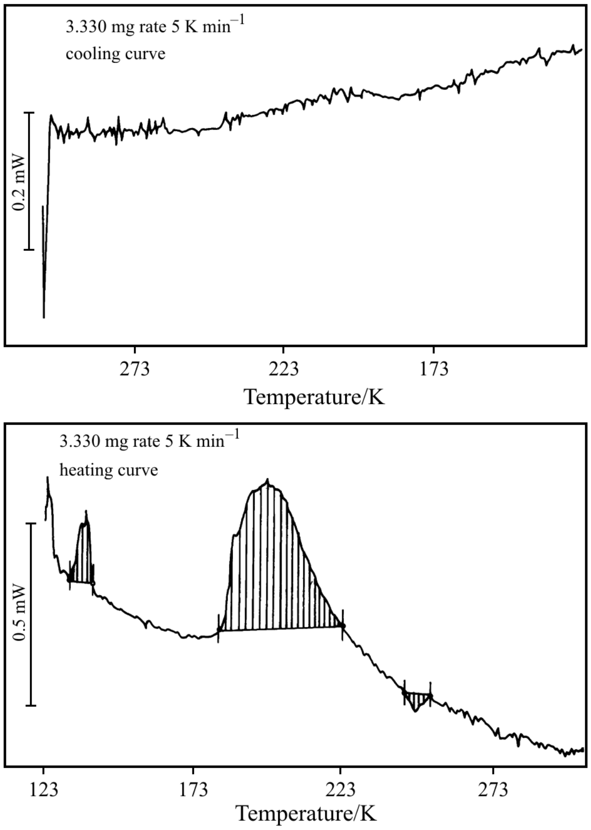

Fig. 5 Heating and cooling curves in DSC plots of Cu-3

$$[Cu_2(II,II)(4HNSQ)_2(ONQ)_2(H_2O)_4]$$

(S=1,1 spin pair, leading to S=0,1,2 states)

$$\downarrow$$

$$2[Cu(II,II)(4HNSQ)(ONQ)(H_2O)_2]$$

(S=1/2,1/2 spin pair, S=1 triplet state)

Recently calorimetric studies on antiferromagnetic 'KNiCl$_3$ family' infers the structural phase transitions rather than magnetic phase transitions [43], however our Cu-3 leads to magnetic phase transition due to dimer to monomer structural variations confirmed from supra magnetic and DSC studies.

Electrochemical studies of Cu-3

Two reversible redox couples (Fig. 6) are seen in the cyclic voltammogram of Cu-3 at $E_{1/2}$=0.68 V and $E_{1/2}$=–1.12 V which can be assigned for Cu(II)$\leftrightarrows$Cu(I) and 4HNSQ$\leftrightarrows$CAT reversible electron transfers and are result of exo-(4HNSQ) ligand and metal interactions, respectively. However respective ONQ→ONSQ (one electron reduced form of ONQ) and ONSQ→CAT irreversible E_{PC} peaks at –0.44 and –0.67 V are result of endo-(ONQ) ligand coordinated with metal and endo hydrogen bonded ligand-ligand interactions, respectively [44]. Because former ONQ→ONSQ peak is

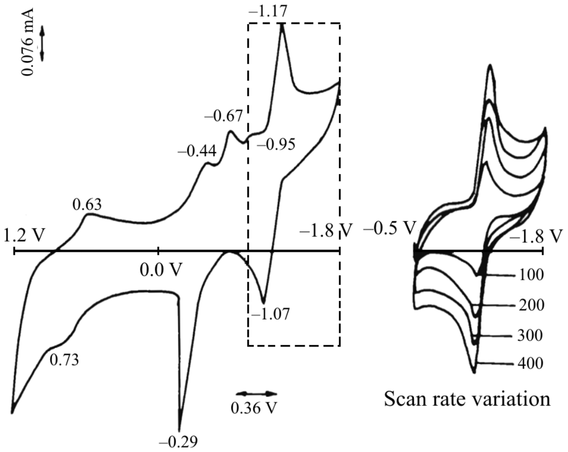

Fig. 6 Cyclic voltammogram of Cu-3

shifted towards positive side compared to pure ligand ONQ→ONSQ peak (E_{PC}=–0.51 V) [45].

The reversible redox couples are in support of variable temperature magnetic susceptibility data where we have established triplet interaction in Cu(II)(4HNSQ) species. The shifts in irreversible ONQ→ONSQ charge transfer set compared to free ligand is in agreement with antiferromagnetic interaction between triplet-triplet states via endo hydrogen bonded naphthoquinone ligands. The ONQ→ONSQ irreversible peak may deposit Cu(0) on electrode which is supported by observation of sharp E_{pa} peak during the reverse scan at –0.29 V with a typical feature of redissolution process [46]. Exo ligands in Cu-3 are coordinated in 4HNSQ form is further supported by very small concentration of ONQ form, which shows ONQ→ONSQ peak at –0.95 V. This shift of ΔE with respect to pure ligand ONQ→ONSQ peak is (0.95 V–0.51 V=0.44 V) of 42 kJ mol^{-1}. This conversion energy in CH_3CN solvent is same as that thermal energy required for the expulsion of ONSQ form of ligand [9], considering zero solvation energy in aprotic solvent. It confirms same electronic structure in Cu-3 in the solid state as well as in aprotic CH_3CN solvent from its electrochemical studies. Finally we conclude that the charge transfer in radical coordination of complex Cu-3 throw light on complicated electron transfer mechanism in quinone enzymes viz. oxidases.

Conclusions

Valence tautomers of 2HNQ ligands are interpreted in non-innocent radical coordination form 4HNSQ and innocent ONQ form with coligation of water molecules in complex Cu-3. Former interaction between Cu(II) and 4HNSQ resulted in triplet state. Quintet→triplet spin transition in Cu-3 at ~200 K reflected in exothermic enthalpy change and also reveals dimeric association of triplets viz. $[Cu(II)(4HNSQ)(ONQ)(H_2O)_2]_2$.

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References

1 J. P. Klinman, Biochim. Biophys. Acta, 1647 (2003) 131.
2 W. Kaim, J. Chem. Soc. Dalton Trans., (2003) 761.
3 F. Himo and P. E. M. Siegbahn, Chem. Rev., 103 (2003) 2421.
4 J. W. Whittaker, Chem. Rev., 103 (2003) 2347.
5 M. Fontecave and J.-L. Pierre, Coord. Chem. Rev., 170 (1998) 125.
6 M. S. Karacan, G. Somer, N. Karcan, E. M. Khan, S. Y. Rane, S. I. Allkhverdiev, S. Padhye, V. V. Kilmov and G. Renger, Biochem., 33 (1994) 12210.
7 M. S. Karacan, G. Somer, E. M. Khan, S. Y. Rane, S. I. Allkhverdiev, S. B. Padhye, V. V. Kilmov and G. Renger, Z. Naturforsch, 49C (1994) 587.
8 S. Y. Rane, E. M. Khan, D. R. Thube, S. B. Padhye, S. K. Date and P. P. Bakare, Indian J. Chem., 39 (2000) 1117.
9 S. Y. Rane, S. D. Gawali, S. B. Padhye, A. S. Kumbhar and P. P. Bakare, J. Therm. Anal. Cal., 55 (1999) 249.
10 S. Salunke-Gawali, R. Dalvi, Ah. Khursheed and S. Rane, J. Therm. Anal. Cal., 76 (2004) 801.
11 M. C. Rath, H. Pal and T. Mukherjee, J. Chem. Soc., Faraday Trans., 92 (1996) 1891.
12 V. Arancibia and M. Bodini, Anales De Quimica, 82 (1986) 309.
13 C. J. O'Connor, Prog. Inorg. Chem., 29 (1982) 203.
14 H. H. Thorp, J. E. Sarneski, G. W. Brudvig and R. H. Crabtree, J. Am. Chem. Soc., 111 (1989) 9249.
15 D. D. Perrin, W. L. Armarego and D. R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, London 1966.
16 O. Kahn in Molecular Magnetism, VCH, New York, Weinheim, Germany and Cambridge, UK 1993.
17 C. G. Pierpont and R. M. Buchanan, Coord. Chem. Rev., 38 (1981) 45.
18 C. G. Pierpont and C. W Lange, Prog. Inorg. Chem., 41 (1994) 331.
19 C. G. Pierpont, Coord. Chem. Rev., 219–221 (2001) 451.
20 O. Kahn, Y. Pei and Y. Journaux, Mol. Cryst. Liq. Cryst., 176 (1989) 429.
21 G. A. Fox and C. G. Pierpont, Inorg. Chem., 31 (1992) 3718.
22 S. Thompson and J. C. Calbrese, J. Am. Chem. Soc., 108 (1986) 1903.
23 S. Y. Rane, S. D. Gawali, S. B. Padhye, A. S. Kumbhar, V. G. Puranik, P. P. Bakare and S. K. Date, Proc. Indian. Acad. Sci. (Chem. Sci.), 108 (1996) 289.
24 S. D. Gawali, Magnetostructural Studies in Synthetic Analogs of Copper Quinoprotiens Ph.D. Thesis, University of Pune, India 1999.
25 S. Salunke-Gawali, S. Y. Rane, V. G. Puranik, C. Guyard-Duhayon and F. Varret, Polyhedron, 23 (2004) 2541.

26 N. Venkatlakshmi, B. Varghese, S. Lalitha, R. F. X. Williams and P. T. Manoharan, J. Am. Chem. Soc., 111 (1989) 5748.
27 D. M. Adams and D. N. Hendrickson, J. Am. Chem. Soc., 118 (1996) 11515.
28 R. F. Darke, V. H. Crawford and W. E. Hatfield, J. Chem. Phys., 60 (1974) 4525.
29 M. E. Lines, A. P. Ginsberg, R. L. Martin and R. C. Sherwood, J. Chem. Phys., 57 (1972) 1.
30 S. Y. Rane, S. Gawali, S. Padhye, S. Date and P. Bakare, Indian J. Chem., 42A (2003) 255.
31 EPR of exchange coupled systems, Eds A. Bencini, D. Gatteschi, Springer Verlag, Berlin 1990.
32 R. Huber and M. Schworer, Chem. Phys. Lett., 72 (1980) 10.
33 H. Benk and H. Sixl, Mol. Phys., 442 (1981) 779.
34 D. Snaathorst and C. P. Keijzers, Mol. Phys., 51 (1984) 509.
35 K. Y. Wong and P. N. Schatz, Prog. Inorg. Chem., 28 (1981) 369.
36 H. A. Goodwin, Coord. Chem. Rev., 18 (1976) 293.
37 P. Gutlich, Struct. Bonding., 44 (1981) 83.
38 M. Sorai, K. Kaji, D. N. Hendrickson and S. M. Oh, J. Am. Chem. Soc., 108 (1986) 702.
39 K. Sone, Y. Fukuda in Inorganic Thermochromism. (Inorganic Chemistry Concepts, Vol. 10) Springer, Berlin 1987.
40 A. Nishimori and M. Sorai, J. Phys. Chem. Solids, 60 (1999) 895.
41 T. Sato, F. Ambe, K. Endo, M. Katada, H. Maeda, T. Nakamoto and H. Sano, J. Am. Chem. Soc., 118 (1996) 3450.
42 M. Sorai, J. Chem. Thermodyn., 34 (2002) 1207.
43 K. Yamonaka, N. Nishiwaki, K. Iio, T. Kato, T. Mitsui, T. Tojo and T. Atake, J. Therm. Anal. Cal., 70 (2002) 371.
44 A. A.Vlcek, Coord. Chem. Rev., 42 (1982) 39.
45 S. Salunke-Gawali, S. Y. Rane, K. Boukheddaden, E. Codjovi, J. Linares, F. Varret and P. P. Bakare, Indian J. Chem., 43A (2004), in press.
46 M. M. Whittaker, W. R. Duncan and J. W. Whittaker, Inorg. Chem., 35 (1996) 382.

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