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 it is 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.
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 \([\text{Cu}^{II} \text{II}(\text{4HNSQ})_{2}(\text{ONQ})_{2} \cdot 4\text{H}_{2}\text{O})]\); Cu-3, complex was discussed previously in Part I. The ligand 2HNQ coordinate in its deprotonated form 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 (\(-60 \times 10^{-6}\) egis 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 mm²) 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 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 N₂.

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 \(\mu_{eff}\) 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

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