

Oxidative oligomerisation of 2-naphthol by *cis*-bis(glycinato)copper(II)

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Abstract

The reaction of 2-naphthol with *tert*-butylhydroperoxide by *cis*-bis(glycinato)copper(II) oligomerises 2-naphthol. One of the isolated tetramer **A** contains a *tert*-butyloxy group. Similar reaction of 2-naphthol with hydrogen peroxide in the presence of *cis*-bis(glycinato)copper(II) oligomerises 2-naphthol gives tetramer through hydroxylative oligomerisation. The oligomers are bound to oxo-bridged copper cores to give **B** and **C**. These oligomers exhibit thermal sensing property. The oligomer (**B**) converts benzamide to benzoic acid, as well as catalyses oxidation of aromatic aldehydes such as benzaldehyde to corresponding acids. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phenolic compounds in the form of complexes, aggregates and polymers are widely used for molecular recognition [1–4]. They find applications in synthetic chemistry [5] and are constituent of biologically important molecules such as Gossypol [5]. The bromo-naphthols trapped in cyclodextrin molecule show phosphorescence [6,7]. Phenolic and related aggregates having copper(II) ions [8–12] possess the property of thermoelectric switch. The organised aggregates having π -stacks of aromatic rings are able to trap radical [13], ion [2] and decide fate of a catalytic reaction [14–19]. Oxidation of dihydroxy aromatic compounds can give charge-transfer complexes or a quinonic compounds [20]. A charge transfer complex having organised packing with metal ion(s) has interesting electronic properties [21,22]. There has

been increasing interest on the catalytic reactions of phenolic compounds by copper complexes having core of Cu_2O_2 [15–19]. In our recent studies, we had demonstrated that the activated aromatic compounds can be hydroxylated or oligomerised by copper(II) complexes. Foregoing discussion clearly indicates that the understanding of oxidative reactions in terms of product ramification is yet to be achieved. The look for environmentally friendly reagent capable of imparting novel optoelectronic properties to such oligomeric products would continue to be an important issue. The theme of this work is on oligomerisation of 2-naphthol by a bio-related catalyst namely *cis*-bis(glycinato)copper(II) and the physicochemical aspects of the products.

2. Experimental

The *tert*-butylhydroperoxide (70% in water) and naphthols used in this study were purchased from E. Merck Germany and used without further purification.

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2.1. The reaction of 2-naphthol with *tert*-butylhydroperoxide and *cis*-bis(glycinato)copper(II)

2-Naphthol (290 mg, 2 mmol) *cis*-bis(glycinato)-copper(II) monohydrate (48 mg, 0.2 mmol) and *tert*-butylhydroperoxide (0.3 cm³, 70%) were taken together in a mixed solvent of acetonitrile and water (2:1 ratio) and stirred at 70°C for 1 h. The reaction mixture was allowed to cool and the acetonitrile was removed under reduced pressure and the remaining paste was extracted with dichloromethane (25 cm³). The extracted mixture after evaporation of dichloromethane was put over a silica gel column and purified to obtain **A** (isolated yield in pure form 60 mg). Elemental analysis for C₄₃H₃₀O₆ Anal. Calcd.: C, 80.24; H, 4.82. Found: C, 80.42; H, 4.85. ¹H NMR (CDCl₃): 11.9 (s, 1H); 6.2–10 (m, 20H); 1.5–1.8 (m, 9H). IR (film): 3496(s); 2925(s); 1629(s); 1521(w); 1461(w); 1266(w); 1145(w); 810(m); 756(m).

2.2. The reaction of 2-naphthol with hydrogen peroxide and *cis*-bis(glycinato)copper(II)

2-Naphthol (290 mg, 2 mmol), *cis*-bis(glycinato)-copper(II) monohydrate (48 mg, 0.2 mmol) and hydrogen peroxide (1 cm³, 30% v/v) were taken together in a mixed solvent of acetonitrile and water (2:1 ratio) and stirred at 70°C for 4 h. The reaction mixture was allowed to cool and the acetonitrile was removed under reduced pressure and the remaining paste was purified by column chromatography to obtain **B** and **C**. The isolated yield of **B** and **C** in pure form are 25 and 48mg, respectively.

2.2.1. Analytical data of **B**

Elemental analysis for C₉₀H₅₉O₁₂Cu₂, Anal. Calcd.: C, 74.07; H, 4.87. Found: C, 74.96; H, 5.23. IR (film): 3469(s); 2925(m); 2825(m); 1629(s); 1521(s); 1461(s); 1266(s); 1219(s); 1145(s); 809(s); 755(s). FAB mass (*m/e*): 663; 647; 584; 516; 444; 413; 391; 363; 355; 351; 281; 255; 221; 207; 167.

2.2.2. Analytical data of **C**

Elemental analysis for C₁₂₀H₇₆O₁₅Cu₂, Anal. Calcd.: C, 76.47; H, 4.04. Found: C, 76.93; H, 4.72. IR (film): 3182(s); 1626(s); 1606(s); 1475(s); 1371(s); 1273(s); 1201(s); 815(s); 756(s). FAB mass (*m/e*):

663; 584; 565; 444; 391; 355; 323; 302; 281; 255; 226; 207; 176; 154; 136; 107; 95; 83; 69; 55.

A mixture of 1,4-naphthalenediol (400 mg, 2.53 mmol) and *cis*-bis(glycinato)copper(II) (6.2mg, 0.027 mmol) with hydrogen peroxide (1 cm³, 30%) was stirred at room temperature for 15 min. On removal of the solvent from this reaction mixture under reduced pressure gave a black mass (413.6 mg). Elemental analysis found: C, 68.64; H, 5.72. ¹H NMR (DMSO-d₆): 9.3(s); 7.9(dm); 7.4(m); 7.1(s); 6.65(s). IR (film): 3300(bs); 1700(s); 1600(s); 1325(s); 1300(s); 1150(s); 1125(s); 900(s); 800(s). ESR: 2975 G (*g* = 1.86); 1375 G (*g* = 1.14). The reactivity of this compound was studied in situ for oxidation of aldehydes. A typical oxidation reaction studied is as follows. To a well stirred mixture of benzaldehyde (318 mg, 3 mmol) and hydrogen peroxide (0.5 cm³, 30%), the catalyst (20 mg) was added and stirred at 80°C for 2 h and product was analysed by GC, extracting the reaction mixture with dichloromethane (2 cm³).

3. Results and discussions

The reaction of 2-naphthol with *tert*-butylhydroperoxide is catalysed by *cis*-bis(glycinato)copper(II) monohydrate leading to tetrameric product (**A**) (Eq. (1)). The presence of the *tert*-butyloxy group on the oligomer suggests it to pass through an initial transfer of butyloxy group from *tert*-butylhydroperoxide. A similar reaction of 2-naphthol with catalytic amount of *cis*-bis(glycinato)copper(II) monohydrate in the presence of hydrogen peroxide gives compounds (**B**) and (**C**) through hydroxylation cum oxidative coupling reaction (Eq. (2)). The compound **B** contains a Cu₂O₂ core held by two tetramers of 2-naphthols and the axial ligands are 2-naphthol and water. While **C** contains three units of tetramers which hold two copper centres. In the case of **C**, out of the three tetramer units one is a neutral one and others are in oxo-form. The compounds are characterised by their elemental analysis, IR, FAB mass, ESR spectra and magnetic moment. The oligomer having four naphthalene units is formed through hydroxylation cum C–O bond formation of hydroxylated β-naphthol with unreacted 2-naphthol. Similar hydroxylation cum oligomerisation of *p*-phenylphenol is catalysed by Cu₂O₂ dimeric core [15]. The FAB mass spectra of the compound

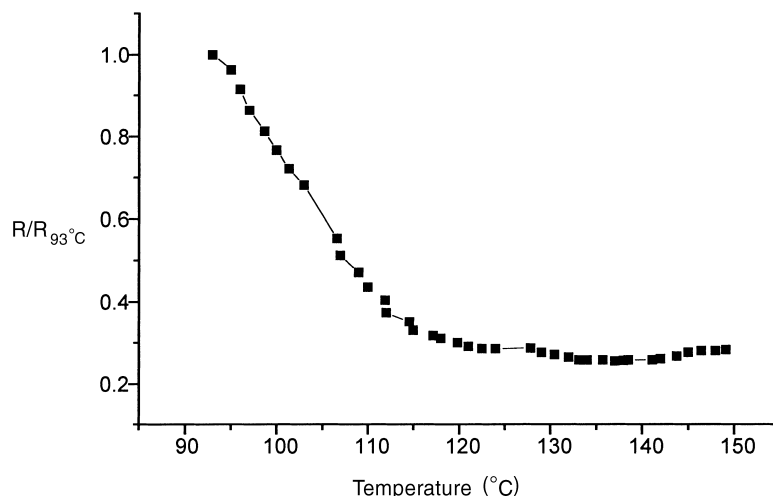
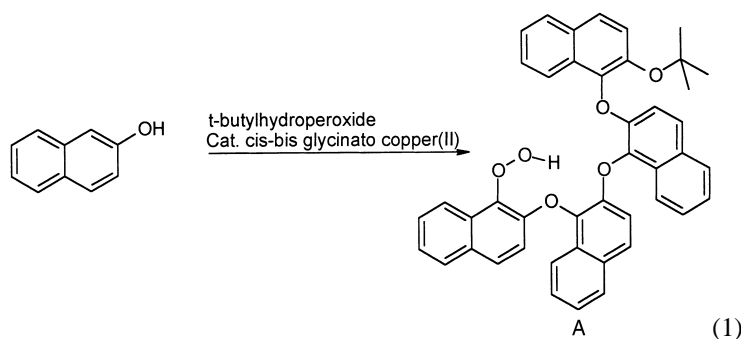
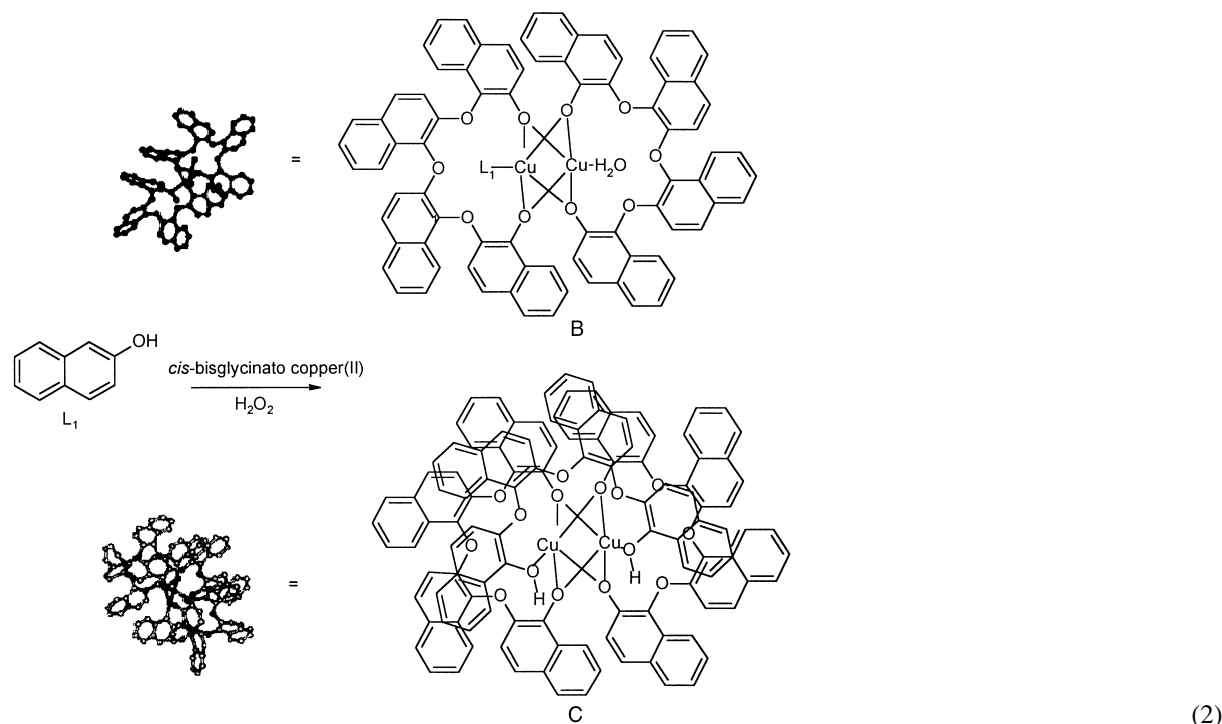


Fig. 1. Plot of resistance (R) normalised to resistance at 93°C ($R_{93^{\circ}\text{C}}$) vs. temperature.

(B) shows highest ion peak at 663 and 665. These peaks are assigned to mass ions of L-Cu-O^+ (where $\text{L} = \text{ligand}$) due to two isotopes of Cu . Such fragment is formed through heterolytic cleavage of the complex. The mass at 647 and 649 (m/z) are due to L-Cu^+ . Similarly the signals at 584, 568, 444, 424 (m/z) are due to the subsequent mass loss from this part. The O–H stretching vibration of the compound appears at 3182 cm^{-1} , whereas in 2-naphthol it appears at 2951 cm^{-1} . The characteristic C–O stretch of the complex appears at 1201 cm^{-1} . The complex has a characteristic visible absorption at 472 nm due to dimeric oxo-bridged core of copper(II). The Cu_2O_2 core in biologically related systems [16,17,23,24] has a characteristic absorption in a similar region. The complex has also another absorption at 333 nm from the ligand. It has fluorescence emission at 547 nm on excitation at 401 nm. The magnetic moment of the

complex is field dependant and effective magnetic moment (μ_{eff}) per copper centre of B is 2.23 BM at 25°C for a field of 2 kG. It varies between 2.23–2.62 BM with an increasing trend on increase of field from 2 to 10 kG. This indicates the presence of an exchange coupling in the system. The ESR spectrum of the compound at 25°C has two signals; one at 3025 G ($g = 1.89$) having resemblance to copper(II) centre with distorted tetrahedral geometry [26]. The other signal at 3125 G ($g = 1.95$) is due to a radical stabilised by the copper centre [13] (Fig. 1a). The highest mass of compound (C) is identical to (B) showing it to be due to a fragmented ion. This compound shows only a broad signal at 3025 G ($g = 1.89$) due to copper(II) centres. It has a magnetic moment value of 2.27 BM with a field strength of 10 kG. The value is dependant on the applied field. These results are in support of exchange coupling between the two copper(II) centres.





We have recently found that copper(II) containing dihydroxy aromatics and aminohydroxy aromatic compounds possess property of thermoelectric switch [11,12], i.e. the temperature dependence of the resistance of films prepared from these compounds has a normal Gaussian shape. This means, it increases initially and then decreases exponentially after a limiting temperature. In the present study, it is observed that the electrical resistance of a film prepared from a chloroform solution of **(B)** decreases in the region of temperature 90–150°C (Fig. 2) having resemblance to behaviour of a semiconductor. It has identical ESR spectra at 100°C. The differential scanning calorimetry in the region of 90–160°C has an exothermic process. Thermogravimetry shows that there is about 3.8% weight loss of **(B)** in the region 90–160°C. This weight loss can be correlated to the loss of the solvent molecules from the co-ordination sphere. The compound is thermally unstable above 220°C and decomposes to lose 59% of its weight on heating to 550°C. Based on all these observations we suggest that the decrease in the resistance in the region of 90–160°C occurs due to the loss of the solvent molecules from the co-ordination sphere as well

as from the interstices. The change in co-ordination around copper(II) centre on heating in copper(II) containing hydroquinone aggregate [11] and also in the copper(II) containing dihydroxyphenolic aggregates gives a resistance profile that passes through a normal Gaussian shape [12].

The oxo-bridged cores of manganese are catalytic centres for peroxo bond formation and the Cu_2O_2 cores are believed to be responsible for cleavage of O–O bond in biological system [16]. It is believed that Cu(III) intermediates are involved in such cleavage in biological systems [17,19]. The compound **B** reacts with O–O bonded compounds, hydrogen peroxide and *tert*-butylhydroperoxide in dichloromethane, acetonitrile, etc. The relative rate of such reactions could be ascertained from the decay of the absorption at 472 nm (Fig. 3). This suggests decomposition of the dimeric copper(II)–copper(II) centre on reaction with peroxides. In the reaction of hydrogen peroxide oxygen was not evolved showing a probable involvement of homolytic cleavage. The decrease in the absorbance at 472 nm accompanies an isosebestic point at 420 nm and is indicative of its conversion to another single product in solution. In all the cases, 2-naphthol was

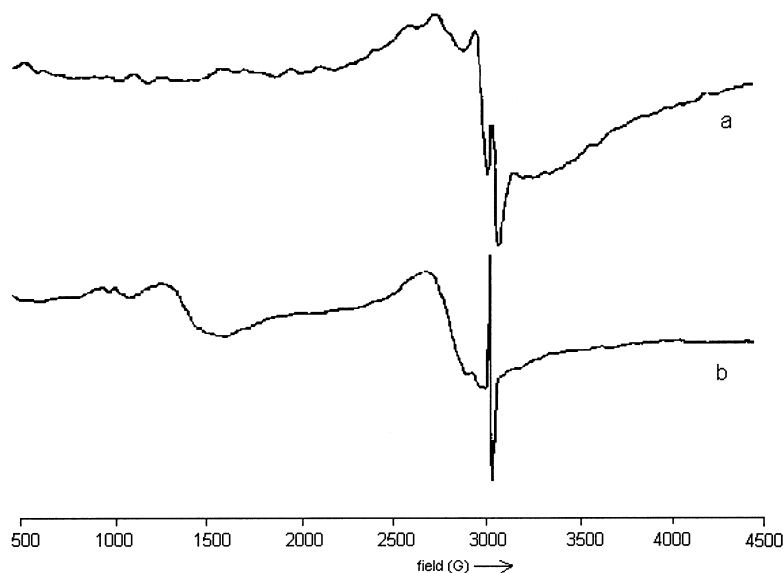


Fig. 2. The ESR spectra at 25°C of (a): (**B**); b: (**D**), at field setting of 2500 G central field, 9.04 GHz microwave frequency and 1500 G sweep width.

obtained after reaction with peroxides. Probably, this was formed during the reaction of peroxide with copper core and it loses the axial 2-naphthol ligand. The relative rates of oxidation are found to be solvent dependant and are in the order of dichloromethane > methanol > acetonitrile. Solvent effect on the rate indicates involvement of hydrogen bonding in the transition state. The decomposition of hydrogen peroxide through cyclic H-bonded intermediate is established

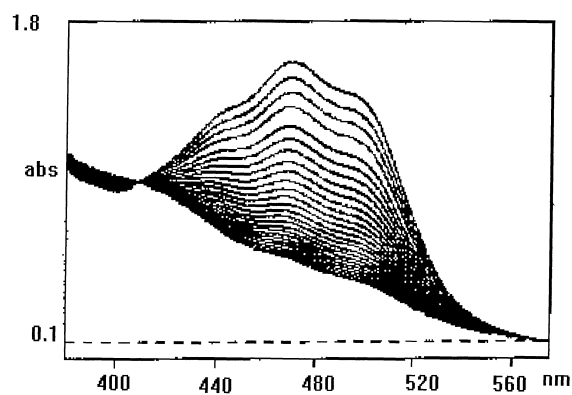


Fig. 3. Decay of absorption at 472 nm at a time interval of 1 min of **B** on reaction with hydrogen peroxide ($[B] = 0.0013$ mmol, $[H_2O_2] = 0.01$ mmol).

[25]. The compound **B** also reacts with reducing agent such as hydrazine hydrate, loses the absorption peak at 472 nm. The absorption at 472 nm of **B** is also bleached on irradiation by a tungsten lamp.

A metal catalysed oxidation of 2-naphthol usually gives binaphthol [5,26]. Binaphthol was not formed in the reaction of the 2-naphthol with *cis*-bis(glycinato)copper(II) monohydrate in hydrogen peroxide and this precludes a C–C coupling product. The dimeric copper compound (**B**) catalyses oxidation of benzaldehyde to benzoic acid in hydrogen peroxide. With these observation the reaction of 1,4-naphthalenediol with hydrogen peroxide was performed with a very low concentration of *cis*-bis(glycinato)copper(II) (0.01 mole%). This reaction yielded a black solid (**D**) and the elemental analysis, NMR, IR suggests it to comprise of a mixture of 1,4-naphthoquinone and 1,4-naphthalenediol. The ESR spectra has a sharp signal at 3250 G ($g = 2.02$) due to a radical and two broad signals at 2975 ($g = 1.86$) and 1375 G ($g = 1.14$) from the copper(II) centre stabilised through a radical (Fig. 1b). The signal 1375 G suggests the radical to be stabilised by the metal centre [27]. The copper concentration in the complex is of the order of $\sim 1\%$. The unit is believed to have a metal stabilised naphtholenediol

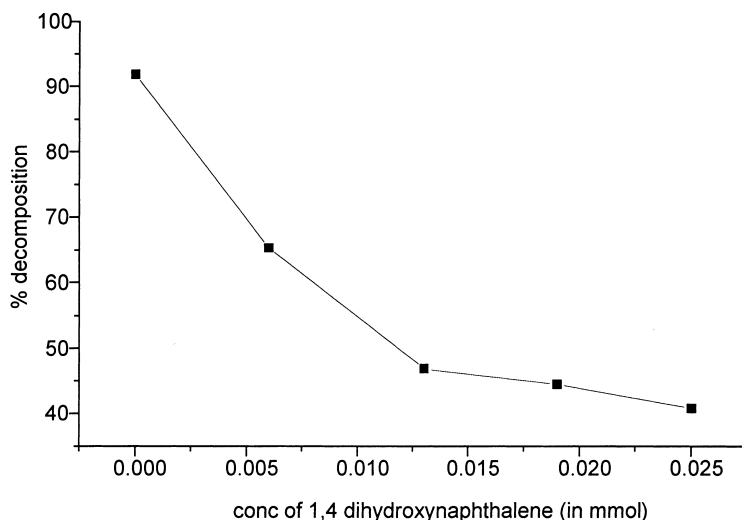


Fig. 4. The percentage decomposition of a constant amount of hydrogen peroxide (4%, 1 cm³) with a fixed amount of *cis*-bis(glycinato)copper(II) monohydrate (0.043 mmol) after 60 min time at 30°C for different concentrations of 1,4-naphthalenediol.

radical whose effect is relayed through a possible π -stacks through a charge-transfer interaction. The extensive π -stacks of charge transfer complex having copper ions are well established [22]. Further support to aggregation is reflected in the DSC, where the melting point of the starting 1,4-naphthalenediol is not observed. Due to paucity of getting suitable crystal for diffraction study, it is difficult to draw a structure fitting the metal ion within this aggregate. The resistance of a film prepared from (**D**) continuously increases in the region of 30–160°C (15-fold) suggesting the disruption of π -stacks in the system on heating. The decomposition of hydrogen peroxide by (**D**) is less as compared to an identical reaction of *cis*-bis(glycinato)copper(II) monohydrate as evident from the observation from the in situ reactivity study of complex (**D**). Thus, with a fixed amount of *cis*-bis(glycinato)copper(II) monohydrate, the decomposition of hydrogen peroxide is reduced as the concentration of 1,4-naphthalenediol is increased (Fig. 4). The catalytic ability to oxidise benzaldehyde to benzoic acid by *cis*-bis(glycinato)copper(II) monohydrate in hydrogen peroxide is also enhanced when the oxidation is performed with catalytic amount of (**D**) containing analogous copper(II) catalyst concentration. Similarly the complex (**D**) has superior catalytic activity than the parent *cis*-bis(glycinato)copper(II)

monohydrate in hydrogen peroxide to oxidise amide bond in benzamide to give benzoic acid.

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