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Synthesis and molecular structure of a zinc complex of the vitamin K₃ analogue phthiocol



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HIGHLIGHTS

• Zinc complex of the vitamin K₃ analogue phthiocol is synthesized and characterized.

- Molecules of 1 show three dimensional network through C–H \cdots O, O–H \cdots O interactions.
- Additional anodic peaks are observed in cyclic voltammogram of phthiocol ligand.

• DFT studies define this redox event as ligand-centered.

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ABSTRACT

The complex [Zn(phthiocol)₂(H₂O)₂]; **1**, where phthiocol is 2-hydroxy-3-methyl-1,4-naphthoquinone, has been synthesized and characterized by elemental analysis, FT-IR, ¹H NMR, UV–vis spectroscopy, thermogravimetric (TG) analysis, electrochemical and single crystal X-ray diffraction studies. The $v_{C=O}$ stretch shifts to lower frequencies upon complexation of phthiocol to Zn^{2+} . ¹H NMR spectra show an upfield shift of the benzenoid ring protons in **1**. There is a bathochromic shift of the LMCT band in the UV-vis spectra of **1**. Single crystal X-ray structure of **1** show distorted octahedral geometry around Zn^{2+} . Two phthiocol ligands are in plane with the metal, while water molecules are trans to this plane. Coordination of deprotonated phthiocol ligands is '*trans, trans*' to Zn^{2+} . Intra as well as intermolecular interactions are observed in **1**. Molecules of **1** show three dimensional network through C—H…O and O—H…O interactions. Additional anodic peaks are observed in cyclic voltammogram of phthiocol ligand ue to oxidation of reduced species formed during reduction. One-electron reduction of **1** is shown to be reversible and DFT studies define this redox event as ligand-centered.

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1. Introduction

Chemistry and coordination chemistry of redox active ligands [1] is of growing importance in recent years because of their multifunctional applications [2], especially to catalytic applications [3]. Naphthoquinones are redox active ligands, as compared to other non-innocent ligands, the coordination chemistry and catalytic applications of these ligands are least explored. However their biological applications for example antiproliferative [4], antifungal [5], antiviral [6], antimalarial [7], etc. are well established. Wide variety of applications of naphthoquinone in biology is due to their redox activity and radical forming abilities [8].

Menadione (2-methyl-1,4-naphthoquinone) is artificial form of vitamin K₃ known for its anticancer activities [9]. Phthiocol (2-hydroxy-3-methyl-1,4-naphthoquinone) is synthesized from menadione and is an hydroxy derivative of vitamin K₃ family members also known for its antifungal [10] and antionconogenic properties [11]. Single crystal X-ray structures show that hydroxy naphthoquinones and their metal complexes are polymeric in nature formed by three dimensional hydrogen bonding network through O-H···O and C-H···O interactions [12]. Molecular associations of naphthoquinones through hydrogen bonding help them to interact with biomolecules and stabilization of reduced forms commonly known as naphthosemiquinone radicals. Besides biological applications of hydroxy naphthoguinones, they can act as a bi or monodentate ligands and could provide redox active functional materials [13], thus synthesis of metal complexes with naphthoquinone ligands are highly encouraged.



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Metal complexes with crystal structures with phthiocol ligands are rare although their synthesis is known [14] only single crystal X-ray structure of Mn complex [15] is known so far, since the structure of phthiocol in 1965 [16]. In present investigation synthesis, characterization, single crystal X-ray diffraction studies and electrochemical properties of zinc metal complex of vitamin K₃ analogue; phthiocol viz. [Zn(phthiocol)₂(H₂O)₂]; **1** are discussed. Intraligand bond lengths of the one- and two-electron reduced forms are computed by density functional theory (DFT). Phthiocol ligand can potentially bind to metal ions in three different oxidation states, viz. naphthoquinone, naphthosemiquinone and catecholate as shown in (Scheme 1).

2. Experimental

2.1. Material and methods

All the chemicals used in the synthesis were analytical grade and used without further purification. Menadione (2-methyl-1,4napthoquinone) have been obtained from Sigma–Aldrich. Zinc acetate was obtained from Qualigens Chemicals, India. Milli-Q water is used in estimation of Zn^{2+} volumetrically [17]. Anhydrous methanol was purified by the literature method [18].

2.2. Characterization studies

2.2.1. FT-IR, elemental analysis, ¹H NMR

Infrared spectra were recorded on a SHIMADZU FT 8400 spectrometer as KBr discs. Elemental analyses were conducted with a Thermo Finnigan EA 1112 Flash series Elemental Analyzer. ¹H NMR spectra were collected on a Varian Mercury 300 MHz in DMSO- d_6 and calibrated to tetramethylsilane.

2.2.2. Thermogravimetric (TG) studies and LC-MS

Thermogravimetric measurements were carried out with a home built instrument previously detailed [19]. Liquid chromatograph mass spectra have been recorded on Shimadzu, LCMS-2010EV.

2.2.3. X-ray crystallography

Single crystals of **1** were grown by slow evaporation of the solution in methanol. Red colored needle type crystal of approximate size $0.17 \times 0.05 \times 0.02 \text{ mm}^3$, was used for data collection on *Bruker SMART APEX* CCD diffractometer using Mo K α radiation with fine focus tube with 50 kV and 30 mA. Crystal to detector distance 6.05 cm, 512×512 pixels/frame, hemisphere data acquisition. Total frames = 1271, Oscillation/frame -0.3° , exposure/frame = 10.0 s/frame, maximum detector swing angle = -30.0° , beam center = (260.2, 252.5), in plane spot width = 1.24, SAINT integration, θ range = 2.09–24.99°, completeness to θ of 24.99° is 99.9%. SADABS correction applied. All the data were corrected for Lorentzian, polarization and absorption effects. SHELX-97 (ShelxTL) [20] was

used for structure solution and full matrix least squares refinement on F^2 . Hydrogen atoms were included in the refinement as per the riding model but the hydrogens of the water molecule were obtained by difference Fourier and were refined during the refinement. Data collection and refinement parameters are listed in Table 1. X-ray analysis revealed the conformation of the molecule it is found that half of the complex molecule is related to another half by symmetry.

2.2.4. DFT studies

All DFT calculations were performed with the ORCA program [21]. Geometry optimized structures of **1**, $[1]^{1-}$ and $[1]^{2-}$ were achieved using the B3LYP method [22,23]. The conductor-like screening model (COSMO) was applied using water as the solvent [24]. The all electron basis sets of triple- ζ quality were those developed by the Ahlrichs group [25]. Auxiliary basis sets were used to expand the electron density in the calculations were chosen the match the orbital basis. The geometry search was carried out in redundant internal coordinates without imposing geometry constraints, and stationary points were characterized via numerical calculations. Spin density plots were obtained using Molekel [26].

2.2.5. Cyclic voltammetric studies

The electrochemical measurements were performed with the help of Metrohm Potentiostat/Galvanostat (Model Autolab PGSTAT 100). A commercial Pt disk electrode (CHI Instruments, USA, 2 mm diameter), Ag wire, and Pt wire loop were used as working, quasireference and counter electrodes respectively. The voltammetric measurements were carried out in an indigenously developed vacuum electrochemical cell having a special provision to transfer the analyte with minimum exposure to the laboratory atmosphere [27]. After fixing the electrodes to the cell 0.239 g of tetra butyl ammonium perchlorate (typically 100 mM in 7 mL solution) was transferred and vacuum dried in situ at 80 °C for an hour. The cell was cooled down to room temperature and brought to atmospheric pressure by relieving the vacuum through high purity argon gas. Predried 5 mL solvent was injected into the cell through silicon septum under argon atmosphere. The blank or controlled voltammograms were acquired in tetra butyl ammonium perchlorate-DMSO mixture prior to the measurements. Sample dispersed in small amount of solvent injected in the cell for further measurement (analyte concentration 1 mg mL⁻¹). At the end of each set of experiments the potentials were calibrated with respect to the normal hydrogen electrode (NHE) using ferrocene as an internal standard.

2.3. Synthesis

2.3.1. Synthesis of 2-hydroxy-3-methyl-1,4-naphthoquinone (phthiocol)

The preparation followed a slight modification of the published procedure [28]. Menadione (1.0 g; 5.8 mmol) was dissolved in



Scheme 1. Oxidation levels of the phthiocol ligand (I: Naphthoquinone, II: Naphthoqsemiquinone, III: Catechol).

10 mL methanol and chilled on an ice bath. A solution of 0.2 g of anhydrous Na₂CO₃ and 1 mL of 30% H₂O₂ in 5 mL of water was then added and the reaction mixture maintained at 0 °C. Addition of 100 mL of chilled water led to the precipitation of 2-methyl-1,4-naphthoquinoneoxide as colorless crystals which were collected by filtration and dried in air. The solid was treated with 5 mL concentrated H₂SO₄ and allowed to stand for 10 min. The addition of 20 mL water afforded a yellow precipitate which was recrystallized from methanol containing a few drops of concentrated H₂SO₄. The crude product was column chromatographed using 5% methanol in

2.3.1.1. Characterization of phthiocol. Yellow solid, Yield: 0.84 g (84%). FT-IR; (KBr, cm⁻¹): 3371 s, 1660 s, 1591 s, 1392 s, 1276 s, 1211 s, 833 s, 727 s, 684 s, 634 sh. ¹H NMR; (DMSO- d_6 , 300 MHz): δ 1.956 (s, 3H, Ar), 7.969 (d, J = 6.3, 2H, Ar), 7.821 (t, J = 6.15, 2H, Ar), 7.778 (t, J = 6.3, 2H, Ar), 7.989 (d, J = 5.4, 2H, Ar), δ 10.900 (s, Ar—OH). UV–vis; (methanol, λ_{max} , nm): 287, 330, 388, 479. LC-MS (m/z): 188.

2.3.2. Synthesis of 1

toluene.

A solution of zinc acetate (0.22 g; 1.0 mmol) in 10 mL of anhydrous methanol was added drop-wise to phthiocol (0.38 g; 2.0 mmol) dissolved in 25 mL anhydrous methanol over 30 min. with constant stirring. The precipitate of dark red **1** was collected by filtration, washed with methanol, then diethyl ether and dried under vacuum.

2.3.2.1. Characterization of 1. Red solid, Yield: 0.33 g (70%). FT-IR; (KBr; cm⁻¹): 3354 br, 1635 s, 1585 s, 1381 s, 1290 s, 1232 s, 844 s, 734 s, 682 s, 665 s. ¹H NMR (DMSO- d_6 , 300 MHz): δ 1.839 (s, Ar), 7.508 (t, J = 7.8, 2H, Ar), 7.665 (t, J = 6.6, 2H, Ar), 7.758 (d, J = 6.6, 2H, Ar), 7.858 (t, J = 7.2, 2H, Ar). UV-vis; (methanol, λ_{max} , nm): 292, 329, 491. Anal. Data Calc. for [C₂₂H₁₈O₈Zn] (475.76 g): C, 55.54; H, 3.81, Zn, 13.74%. Found: C, 54.95; H, 3.71, Zn, 12.77%.

3. Result and discussion

Coordination of hydroxy naphthoquinone ligands to metal ions will take place by deprotonation of hydroxyl group and it needs basic conditions, this can be achieved by addition of pyridine [29], sodium acetate [30], ammonia [31], 4,4'-bipyridine [32], triethylamine [33], etc. Based on the synthetic conditions the coordination of hydroxynaphthoquinone ligands to metal ions may be either '*cis, cis*' or '*trans, trans*' for example, the coordination of 2-hydroxy-1,4-naphthoquinone (lawsone) to Zn^{2+} is '*cis, cis*' when 1 mmol of triethylamine is used while, '*trans, trans*' coordination is achieved with 2 mmol of triethylamine [29]. Coordination of hydroxynaphthoquinone with metal ions is always '*anti, anti*', when acetate ions are used in reaction mixture [30,12b]. Reaction of zinc acetate with phthiocol at room temperature forms red precipitate of **1**: [Zn(phthiocol)₂(H₂O)₂].

Various analytical tools are used to determine the oxidation states of redox active ligands *viz*. frequency of $v_{C=O}$ by FT-IR spectroscopy [1b,e] and C—O bond length by single crystal X-ray diffraction studies, etc., however sometimes they may lead to misleading results, for antiferromagnetic interaction between the semiquinone radicals [34]. Oxidation states of hydroxy naphthoquinone ligands could also be determined by thermogravimetric analysis [19]. To reveal the oxidation states of phthiocol ligands in **1** characterization is performed by FT-IR, thermogravimetric analysis, single crystal X-ray diffraction and electrochemical studies. The molecular and electronic structures of the one- and two-electron reduced forms are evaluated by DFT studies.

3.1. Characterization of 1

The FT-IR spectra of phthiocol and complex 1 are overlaid in Fig. 1. The peak at \sim 3290 cm⁻¹ in the spectrum of **1** is characteristic of coordinated water as opposed to water trapped in the KBr matrix that manifests as a considerably sharper peak at 3400 cm⁻¹ in the spectrum of phthiocol. The considerable width of this peak obscures the v_{C-H} stretches of the aromatic protons >3000 cm⁻¹ in **1**. These are clearly visible in the spectrum of free phthiocol together with the corresponding vibrations of the C(3)—CH₃ substituent \sim 2900 cm⁻¹. The v_{C=0} vibration at \sim 1635 cm⁻¹ of phthiocol bound to Zn²⁺ in **1** is shift \sim 25 cm⁻¹ to lower energy than the free entity. The $v_{C=C}$ vibrations $(\sim 1587 \text{ cm}^{-1})$ also shift to slightly lower energy upon complexation of phthiocol. A new band observed at \sim 1550 cm⁻¹ is of delocalization of charge between $v_{C=C}$ and $v_{C=O}$ after coordination of the free phthiocol ligand [34]. The p-naphthoquinone vibration in 1 is observed ${\sim}1290\,cm^{-1}$, an increase of ${\sim}10\,cm^{-1}$ compared to phthiocol ligand (~1280 cm⁻¹). Similarly the $v_{C(2)-0}$ vibration is shifted 21 cm⁻¹ to higher energy.

¹H NMR spectrum of phthiocol show two singlet due to -OH and C(3)–CH₃, two doublets due to C(5)H and C(8)H, and two triplets due to C(6)H and C(7)H (Fig. 2). The singlet peak due to -OH disappears upon coordination of a Zn²⁺ ion forming **1**. There is upfield shift of 0.11–0.23 ppm observed for the benzenoid ring protons in **1** compared to free phthiocol.

UV-vis spectra for phthiocol and **1** were recorded between 200 and 800 nm in methanol, with both exhibiting three bands (Fig. S1). Two excitation in the UV region at 292 nm and 329 nm for **1** are assigned as $\pi \rightarrow \pi^*$ transitions of quinonoid and benzenoid rings, respectively. The latter shows a modest hyposochromic shift in **1** compared with free phthiocol. The single peak in the visible region at 479 nm for phthiocol and shifted to 491 nm in **1** has been previously described as the $n \rightarrow \pi^*$ charge transfer (CT) transition [35]. There is a bathochromic shift observed to the band ~491 nm in **1** due to ligand-to-metal charge transfer (LMCT).

Formula weight	475.73
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 5.015(1)$ Å, $\alpha = 90^{\circ}$
	$b = 12.447(3)$ Å, $\beta = 98.280(3)^{\circ}$
	$c = 15.785(4)$ Å, $\gamma = 90^{\circ}$
Volume	975.1(2) Å ³
Ζ	2
ho	1.620 g/cc
Absorption coefficient	1.310 mm^{-1}
F(000)	488
Crystal size	$0.17 \times 0.05 \times 0.02 \text{ mm}^3$
Theta range for data collection	2.09-24.99°
Index ranges	<i>−</i> 5 <= <i>h</i> <= 5, <i>−</i> 14 <= <i>k</i> <= 14, <i>−</i> 18 <= <i>l</i> <= 12
Reflections collected	4803
Independent reflections	1698 [<i>R</i> (int) = 0.0335]
Completeness to theta = 24.99°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9806 and 0.8052
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1698/0/151
Goodness-of-fit on F^2	1.168
Final R indices [I > 2sigma(I)]	$R_1 = 0.0510, wR_2 = 0.1038$
R indices (all data)	$R_1 = 0.0686, wR_2 = 0.1092$
Largest diff neak and hole	0.508 and $-0.249 e^{A^{-3}}$

C22H18O8Zn

Table 1

Empirical formula

Crystal structure data and structure refinement for 1.



Fig. 1. FT-IR spectra of phthiocol and 1.



Fig. 2. Representation of 1 with ligand numbering scheme.

Nonisothermal TG curve of phthiocol and 1 in air are shown in Fig. 3 and thermodynamic data is given in Table S1. Bottei et al. have been reported data for Zn, Co, Ni and Cu complexes with quinone after correcting for adsorbed water [36]. The decomposition of phthiocol ligand occurs in two stages with a decomposition ratio of 71:29 over the temperature range 52–557 °C. For 1, the first step at 100 °C releases adsorbed water, whereas the second step accounts for the loss of coordinated H₂O molecules below 200 °C. Water molecules are unavoidably adsorbed during sample preparation despite the rigorous drying of the samples under vacuum beforehand. The decomposition of phthiocol ligands in final step in 1 occurs between 287 and 565 °C. The plateau beyond 565 °C stems from the constant mass of residual ZnO. Decomposition of the phthiocol ligands occurs gradually and in single step (step III in Fig. 3), hence the coordination both phthiocol ligands are in same oxidation level, namely the fully oxidized form (form I, Scheme 1) of phthiocol, as reduced ligands often shows abrupt mass losses in non-isothermal thermogravimetric studies [30,31]. Thus, a thermogravimetric study reveals the coordination of phthiocol ligands to Zn²⁺ are in the same oxidation level.



Fig. 3. Thermogram of phthiocol and 1.

3.2. X-ray crystallography

1 crystallizes in monoclinic space group $P2_1/n$. Fig. 4 shows ORTEP diagram of **1** and details of crystallographic data is shown in Table 1. The Zn^{2+} ion is octahedrally coordinated through O(1)and O(2) of two phthiocol ligands, the fifth (O(4)) and sixth(O(5))coordination site is occupied by two water molecules (Fig. 2). Coordination of phthiocol monoanion are 'trans, trans' in 1 [33]. The water molecules occupy axial position and are perpendicular to plane of phthiocol ligands. The Zn–O distances varies with O(1), O(2) and O(4), Zn–O(1) is longest distance of 2.136(3) Å (Table 2). The carbonyl bond distances C(1)—O(1) is 1.227 Å and C(2)—O(2)1.291 Å, this distances fall under oxidized form of phthiocol ligand and are similar to Cu, Zn complexes of hydroxynaphthoquinone ligands [12b,c]. Most affected distance is carbonyl C(4)–O(3), observed to be longer 1.246 Å, this distance is fall in naphthosemiquinone form (form II, Scheme 1) of the ligand or it is results of delocalization of charge density [34]. Bond angle of O(4)—Zn—O(2)and O(4)—Zn—O(1) is more than 90° .

The fascinating fact of hydroxynaphthoquinone ligands and the metal complexes is their hydrogen bonding network. The oxygens of quinonoid ring *viz*. O(2) and O(3), often forms bi or multifurcated O—H···O hydrogen bonding network. In few cases the hydrogen's of benzenoid ring forms C—H···O type of hydrogen bonding, moreover the benzenoid and quinonoid rings can also forms π - π stacked chains. Three dimensional hydrogen bonding network of hydroxynaphthoquinone ligands holds the molecules together and these molecules can have opportunity to interact with one another.

Both intra and intermolecular hydrogen bonding interactions are observed in **1** (Table 3). Interestingly C(11)—H(11B) group is involved in C—H···O type intramolecular hydrogen bonding interaction with oxygen of C(4)—O(3). Bifurcated hydrogen bonding is observed to oxygens O(2) and O(3) of phthiocol anion in **1**. Each complex unit is linked to ten other monomeric units through intermolecular O—H···O, C—H···O hydrogen bondings. The acceptor oxygens are O(2) and O(3) and hydrogen's of water molecules O(4)—H(1), O(4)—H(2), C(5)H and C(8)H are hydrogen donors.

3.2.1. Hydrogen bonding interaction through O(2)

1 forms polymeric chain via O—H···O hydrogen bonding between the coordinated water molecules and quinonoid oxygen O(2) of phthiocol ligand (Fig. 5a). The monomeric units are hydrogen bonded through O(4)—H(1)···O(2) leads to one dimensional polymeric chain. This polymeric chain is stabilized by intermolecular C—H··· π interaction [C(11)H(11)···C(1), 3.62 Å, \angle 149.61°], between the neighboring phthiocol anions on the same side of the chain. The intra chain Zn···Zn distance was found to be 5.015 Å,



Fig. 4. ORTEP diagram of 1, ellipsoids are drawn at 50% probability.

 Table 2

 Selected bond distances for geometry optimized structures.^a

Bond	[1] ⁰		[1] ¹⁻	$[1]^{2-}$
	Exptl	Calcd	Calcd	Calcd
Zn-O(1)	2.136(3)	2.175	2.145	2.102
Zn-O(2)	2.136(3)	1.969	2.008	2.091
Zn-O(4)	2.096(3)	2.332	2.374	2.198
Zn-O(5)	2.096(3)	2.299	2.212	2.223
O(1) - C(1)	1.227(5	1.237	1.237	1.238
O(2) - C(2)	1.292(4)	1.295	1.273	1.254
C(1) - C(2)	1.509(5)	1.500	1.510	1.517
C(1)-C(9)	1.472(5)	1.466	1.396	1.446
C(2) - C(3)	1.363(5)	1.375	1.455	1.425
C(3) - C(4)	1.449(5)	1.457	1.475	1.486
C(3)-C(11)	1.497(5)	1.498	1.484	1.464
C(4) - C(10)	1.494(6)	1.506	1.496	1.491
C(4) - O(3)	1.245(5)	1.227	1.219	1.214
C(5)-C(6)	1.370(6)	1.392	1.391	1.393
C(5)-C(10)	1.389(5)	1.389	1.388	1.387
C(6)-C(7)	1.380(6)	1.393	1.394	1.401
C(7)—C(8)	1.381(6)	1.388	1.386	1.384
C(8)-C(9)	1.385(6)	1.396	1.398	1.404
C(9)—C(10)	1.397(6)	1.401	1.408	1.419

^a O(4) and O(5) are water ligands; C(11) the 3-methyl group.

which is similar to $[Cu(Lw)_2(H_2O)_2]_n$ [12b]. Each chain is further intermolecularly hydrogen bonded to four neighboring chains (Fig. S2) through O—H···O interaction of two trans water molecules and the oxygens O(3) of the two trans phthiocol anions and through C—H···O type of hydrogen boning [C(5)—H(5)···O(2) and C(8)—H(8)···O(2)]. This forms three dimensional polymeric network of **1** molecules.

3.2.2. Hydrogen bonding interaction through O(3)

The O—H···O hydrogen bonding through carbonyl (C(4)—O(3)) of the quinonoid moiety and the coordinated water molecules form a square shaped molecular assembly (Fig. 5b). Each of molecules **1** in a square is almost perpendicular to other with Zn···Zn distance

Table 3

Analysis of potential	hydrogen	bonds o	f 1
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Sr.	D—H···A	D—H	$H{\cdot}{\cdot}{\cdot}A$	$D{\cdots}A$	$D \!\!-\!\! H \!\!\cdot \!\cdot \!\cdot \!A$
no.		(Å)	(Å)	(Å)	(°)
1	$O(4) - H(1) \cdots O(2)^{a}$	0.72(5)	2.01(5)	2.720(5)	172(4)
2	$O(4) - H(2) \cdots O(3)^{b}$	0.75(6)	2.05(6)	2.782(4)	168(6)
3	$C(8) - H(8) \cdots O(3)^{c}$	0.93(1)	2.616(1)	3.545(4)	176(7)
4	$C(5) - H(5) \cdots O(2)^{d}$	0.93(1)	2.647(2)	3.445(2)	144(3)
5	C(11)	0.96(1)	2.389(3)	2.792(5)	105(3)
	$-H(11B) \cdot \cdot \cdot O(3)^{intra}$				

^a 1 - x, -y, -z.

^b 1/2 + x, 1/2 - y, 1/2 + z.

^c x, 1/2 + y, 1/2 - z.

^d 1/2 - x, 1/2 + y, 1/2 - z.

of 10.631 Å. This distance is on higher side as compare to Cu and Fe complexes of 2-hydroxy-1,4-naphthoquinone [12b,37].

3.3. Electrochemical studies

Cyclic voltammogram of phthiocol studied in DMSO with tetrabutyl ammonium hexafluorophosphate as a supporting electrolyte by Gonzalez [38]. Reduction of phthiocol takes place by electron transfer followed by protonation reaction, thus the reduction take place via ECE-DISP1-DISP2 mechanism [39]. Reduction studied with tetrabutyl ammonium perchlorate as a electrolyte (Fig. 6 (top)) shows two additional anodic peaks IIIa and IVa at +0.45 V and 1.00 V vs NHE (Table 4) respectively. These peaks are due to reoxidation of reduced phthiocol.

A quasireversible cathodic peak is observed for 1 at -0.52 V vs NHE, this peak is assigned to one electron reduction of phthiocol anion. Peak positions of Ic and Ia in 1 are shifted to more negative potentials while IIc and IIa shifted to positive potentials compared to free phthiocol ligand. More than a single process occurred during reduction, anodic peaks (IIIa and IVa) are the result of oxidation of electrochemical products formed during reduction. Biradicals in zinc quinone complexes are stable and show characteristic triplet signal in X-band EPR spectra [40]. Peak current is reduced in 1 as compared to phthiocol ligand although same concentration is used for the experiments.

3.4. DFT studiesss

The observed quasireversible redox processes for **1** have been investigated by density function theoretical (DFT) calculations. The ground state geometry of **1** was geometry-optimized using the spin-unrestricted Kohn-Sham density functional B3LYP in the gas phase. The salient Zn-O and intraligand bond distances are in very good agreement with the experimentally determined metrics as listed in Table 3. They depict two co-planar phthiocol monoanions bound to an octahedral central Zn²⁺ ion as shown by the short C(4)–O(3) distance of 1.227 Å typical of a ketone moiety. The C(1)–O(1) bond of 1.237 Å is slightly longer as a consequence of metal coordination, whereas the C(2)–O(2) distance is the longest of the at 1.295 Å as was original a hydroxyl substituent prior to complexation, and hence more closely held to the Zn^{2+} ion. The two Zn–OH₂ bond distances are ~0.24 Å longer in the optimized structure (Fig. S3), which highlights the intricate array of intermolecular interactions found in the crystal structure excluded in the optimization.

The one-electron reduction of **1** to the monoanionic form $[1]^{1-}$ was deemed quasireversible by electrochemistry. The geometry about the Zn^{2+} ion remains octahedral however the phthiocol ligands are now pitched with a dihedral angle ~25° relative to each other (Fig. S4). There is a modest contraction of the Zn–O(1) bond whereas the Zn–O(2) bond lengthens as a resonance mechanism scatters charge throughout the quinonoid ring as portrayed in



Fig. 5. (a) Polymeric chain formed by quinonoid oxygen O(2) and coordinated H₂O molecules. (b) O-H···O hydrogen bonding network in 1.



Fig. 6. Cyclic voltammograms of phthiocol (top) and 1 (bottom) at indicated scan rates.

Table 4 Electrochemic	al data (ir	n V) for p	hthiocol	and 1	at a scan	rate of 1	100 mV s ⁻
	$L_{2}(M)$	$I_{a}(M)$	٨E	Це	Ше	AΓ	ша

	Ic (V)	la (V)	$\Delta E_{\rm p}$	llc	lla	$\Delta E_{\rm p}$	Illa	IVa
Phthiocol 1	$-0.40 \\ -0.52$	-0.29 -0.39	0.11 0.13	-1.27 -1.18	-0.94 -1.04	0.32 0.10	0.45 0.50	1.00 1.04

Scheme 1. This is reflected in a shortening of the O(2)–C(2), C(3)–C(11) and C(4)–O(3) bonds with a concomitant elongation of C(1)–C(2), C(2)–C(3) and C(3)–C(4) bonds of the quinonoid ring as each gains and loses some bonding character, respectively, when

the unit is reduced. The benzenoid ring remains largely unaffected by the increase in charge on the phthiocol ligands as foretold by resonance structures (Scheme 1). The distribution of the additional spin is quantified by a Mülliken spin population analysis shown in Fig. 7 consequence of their co-planar arrangement, spin is spread across both ligands with the majority found at C(3). This is in agreement with EPR and theoretical data obtained on one-electron reduced lawsone, an analogue of phthiocol [41].

The second one-electron reduction generates a dianionic species, $[1]^{2-}$, which possesses the same octahedral geometry seen in the other two members of this electron transfer series. Here, the dihedral angle between reduced phthiocol ligands decreases to $\sim 10^{\circ}$ (Fig. S5). This nearly co-planar arrangement provides strong overlap of the oxygen p orbitals with the filled zinc d orbitals facilitating an efficient super exchange pathway. Here, phthiocol radical dianions are strongly coupled via this superexchange mechanism leading to a well-isolated diamagnetic ground state for $[1]^{2-}$. The Zn–O(1) and Zn–O(2) bonds lengthen and shorten, respectively, in accord with reduction of the second phthiocol ligand, and allows the water molecules to bind more closely to the Zn^{2+} ion. Additionally, both C(3)–C(11) and C(4)–O(3) contract while C(1)–C(2) and C(3)–C(4) elongate. Interestingly, C(2)–C(3)becomes shorter which may stem from more co-planar ligands here than in [1]^{1–}. Again, the aromatic C–C distances in the benzenoid ring remains unchanged.



Fig. 7. Mülliken spin population analysis for [1]^{1–} from B3LYP-DFT calculations.

4. Conclusions

 Zn^{2+} complex of phthiocol, a vitamin K₃ analogue [Zn(phthiocol)₂(H₂O)₂]; **1** has been structurally and spectroscopically characterized. Coordination of anionic phthiocol ligands to Zn^{2+} is in oxidized form (naphthoquinone form) as revealed by FT-IR, thermogravimetric analysis and X-ray diffraction studies. UV–vis spectra show a LMCT band ~491 nm, which imparts red color to the complex.

X-ray diffraction studies of **1** show, distorted octahedral geometry around Zn^{2+} . The two phthiocol ligands are co-planar and their coordination to Zn^{2+} is '*trans*, *trans*', while water molecules occupy the two vacant sites and are also '*trans*' to each other. Molecules of **1** show three dimensional network through C—H···O and O—H···O interactions. Cyclic voltammetric studies of phthiocol ligand show additional anodic peaks at +0.45 V and 1.00 V vs NHE. These peaks are due to the oxidation of reduced phthiocol anion. A quasireversible cathodic peak is observed in **1** at -0.52 V vs NHE, this peak is assigned to one electron reduction of phthiocol anion in **1**.

The observed quasireversible redox processes for **1** have been investigated by density function theoretical (DFT) calculations. The ground state geometry of **1** was geometry-optimized using the spin-unrestricted Kohn–Sham density functional B3LYP in the gas phase. The salient Zn–O and intraligand bond distances in very good agreement with the experimentally determined metrics. Bond distances, geometry around Zn²⁺ and phthiocol anion co-planarity of one electron reduction [**1**]^{1–} and two electron [**1**]^{2–} of **1** is discussed.

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Appendix A. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and may be obtained on request quoting the deposition number CCDC 925950 from the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; email address: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.molstruc.2013.05.057.

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