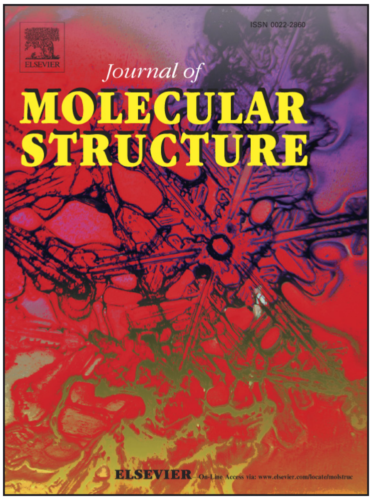

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The first naphthosemiquinone complex of K^+ with vitamin K3 analog: Experiment and Density Functional Theory

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Abstract

Synthesis and characterization of potassium complex of 2-hydroxy-3-methyl-1,4-naphthoquinone (phthiocol), the vitamin K3 analog, has been carried out with FT-IR, UV-visible, ^1H and ^{13}C NMR, EPR, cyclic voltammetry and single crystal X-ray diffraction experiments combined with the density functional theory. It has been observed that naphthosemiquinone binds to two K^+ ions extending the polymeric chain through bridging oxygens O(2) and O(3). The crystal network possesses hydrogen bonding interactions from coordinated water molecules showing water channels along the c-axis. ^{13}C NMR spectra revealed that complexation of phthiocol with the potassium ion engenders deshielding of C(2)signals, which appear at δ=~14.6 ppm) unlike those of C(3) exhibiting up-field signals near δ ~6.9 ppm. These inferences are supported by the M05-2x based density functional theory. Electrochemical experiments further have shown that the reduction of naphthosemiquinone results in only a cathodic peak from catechol. A triplet state arising from interactions between neighboring phthiocol anion lead to half field signal at g= 4.1 in polycrystalline X-band EPR spectra at 133 K.

.

Key Words: Vitamin K3, phthiocol, naphthosemiquinone, hydrogen bonding, ^{13}C NMR, DFT

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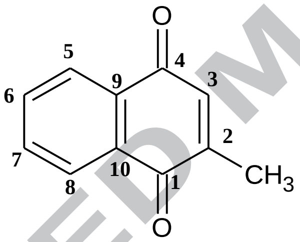
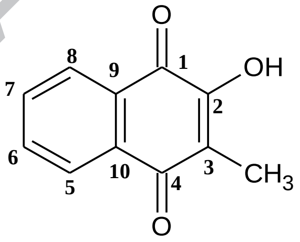
Introduction

Synthesis and isolation of 2-hydroxy-3-methyl-1,4-naphthoquinone was carried out in ether soluble constituents by saponification of acetone soluble fat of tubercule bacillus. The compound [1] crystallizes as yellow prisms with molecular formula $C_{11}H_8O_3$ that melts near 174 °C forming deep red water soluble salts with alkali and other bases. The oxidation of [1] with hydrogen peroxide in alkaline solution yield phthalic acid hence, the pigment was named ‘phthiocol’ [1]. This yellow pigment possesses vitamin K like activity [2]. The phthiocol can be obtained in the laboratory on epoxidation by hydrogen peroxide followed by hydrolysis of vitamin K3 (2-methyl-1,4-naphthoquinone)[3,4] that belongs to the K group vitamin and finds applications in medicine as antitumor, anticancer drug possessing anti-oncogenic [5-7] and antihemorrhagic properties [8-9]. The antihemorrhagic activity of vitamin K group depends on molecular structure [10] and reduction potential [11]. Besides this K group vitamins act as cofactor in blood clotting.



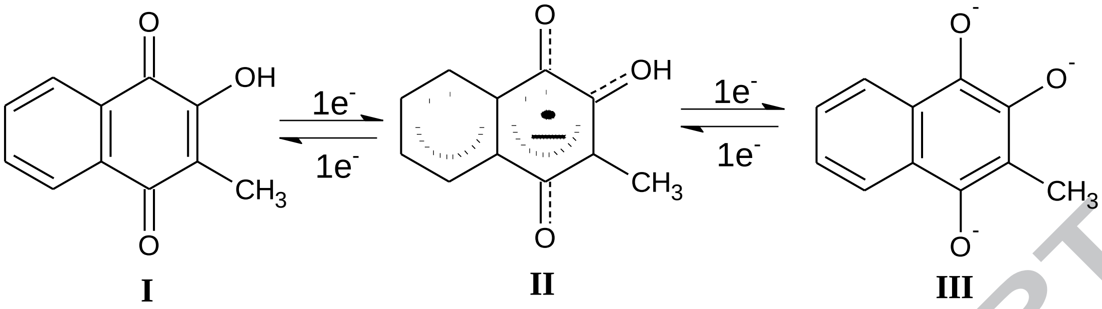
Vitamin K3

Menadione



Phthiocol

Phthiocol binds metal ion with bidentate/tridentate coordination yielding different oxidation states as in: completely oxidized (form I), one electron reduced naphthosemiquinone (form II) and two electron reduced catechol forms (form III), which are shown in Scheme 1. Molecular structures of coordination complexes of phthiocol ligand with the transition metal ions *viz.*, Zn^{2+} [4], Cu^{2+} [13] and Mn^{2+} [15] have been reported. Phthiocol engender coordination polymers with Sm^{3+} and Cd^{2+} ions [16-17]. To the best of our knowledge the hitherto investigation is the first report on characterization of K^+ complex of naphthosemiquinone ligand.



Scheme 1 Redox forms of 2-hydroxy-3-methyl-1,4-naphthoquinone. I, oxidized naphthoquinone form (NQ); II, naphthosemiquinone form ($NSQ^{2-\cdot}$) and III, catechol form (CAT)

Experimental

Analytical grade chemicals are used. Menadione (2-methyl-1,4-naphthoquinone)obtained from Sigma Aldrich was recrystalized in methanol prior to synthesis. Milli-Q water was used in flame photometry experiments. Anhydrous methanol was purified using standard procedure [18].

Synthesis of Phthiocol

The preparation followed a slight modification of the published procedure [3]. Menadione (1.0 g; 5.8 mM) was dissolved in 10 ml methanol and chilled on an ice bath. A solution of 0.2 g of anhydrous Na_2CO_3 and 1 ml of 30% H_2O_2 in 5 ml of water was then added with the reaction mixture maintained at 0 °C. Addition of 100 ml of chilled water precipitates2-methyl-1,4-naphthoquinoneoxide as colorless crystals which were collected by filtration and dried. The solid was treated with 5 ml concentrated H_2SO_4 and allowed to stand for 10 minutes. Subsequent addition of 20 ml water gave a yellow precipitate which was recrystallized with methanol containing a few drops of concentrated H_2SO_4. The crude product was column chromatographed using 5% methanol in toluene.

Characterization of Phthiocol

Yellow solid, Yield: 0.84 g, 84%. FT-IR; (KBr, cm^{-1}): 3371, 1660, 1591, 1456, 1392, 1344, 1301, 1276, 1211, 1178, 1074, 1228, 985, 900, 833, 788, 727, 684, 634, 534, 439, 412, 381. ^1H NMR; (DMSO-d_6, 300 MHz) δ/ppm: 1.956 (s, 3H), 7.969 (d, J = 6.3, 2H), 7.821 (t, J = 6.15, 2H), 7.778 (t, J = 6.3, 2H), 7.989 (d, J = 5.4, 2H), 10.900 (s, Ar-OH).^{13}C NMR

(DMSO-d_6, 500 MHz) δ/ppm: 8.97, 120.31, 126.03, 126.04, 130.38, 132.41, 133.7, 134.78, 155.83,181.02, 185.05. UV-Vis; (Methanol, λ_{max}, nm): 295, 324, 479. UV-Vis; (Methanol, λ_{max}, nm): 287, 330, 388, 479. Anal. data calc. for [$C_{11}H_8O_3$] (188.17 g): C, 70.21; H, 4.29 %. Found: C, 70; H, 20 %, LC-MS (*m/z*): 188.

Synthesis of Phth-K_2

1mM of phthiocol (0.188 g) was dissolved in 15 ml anhydrous methanol. 1 mM of KOH (0.560 g) was dissolved in 10 ml of anhydrous methanol. The two solutions were mixed with constant stirring for 20 minutes at 26°C. The pH of the solution was found to be close to 7. The products precipitated products were filtered and washed with diethyl ether and dried under vacuum. The synthesis of Phth-K_2 was carried out at the room temperature (26°C). The mole ratio of naphthoquinone and KOH was retained to 1:1. The concentration of K^+ ions was determined by flame photometry. Thermogravimetric (TG) analysis confirmed the presence of adsorbed as well as coordinated water molecules in the title complex. The residue following complete decomposition of organic entity was found to be K_2O.

Characterization of Phth-K_2

Red orange solid, Yield: 0.22 g, 73 %. FT-IR (KBr; cm^{-1}): 3381, 3215, 1670, 1589, 1521, 1392, 1350, 1280, 1230, 1124, 952, 844, 734, 682, 621, 553, 422. ^1H NMR (DMSO-d_6, 500 MHz) δ/ppm: 1.748 (s, 3H), 7.799 (d, *J* = 7.5, 2H), 7.680 (d, *J* = 7.0, 2H), 7.560 (t, *J* = 7.5, 2H), 7.742 (t, *J* = 7.5, 2H). ^{13}C NMR (DMSO-d_6, 500 MHz) δ/ppm: 9.54, 113.41, 124.43, 124.59, 129.43, 131.52, 132.07, 136.12, 170.44, 178.57, 185.97.UV-Vis; (Methanol, λ_{max}, nm): 295, 324, 479. Anal. data calc. for [$K_2C_{11}H_7O_3$] 2.5 H_2O, (310.41 g): C, 42.56; H, 03.89 %., Found: C, 42.82; H, 03.86 %.

Physical Measurements

Elemental analysis was carried outon Thermo Finnigan EA 1112 Flash series elemental analyzer. The concentration of K^+ in Phth-K_2 was determined on SYSTRONICS flame photometer 128. AR grade KCl was standard for flame photometry analysis. UV-Visible spectra of phthiocol ligand and the K^+ complex were recorded on SHIMADZU UV 1650 in methanol between 200 to 800 nm.^1H and^{13}C NMR spectra of compounds were recorded in DMSO-d_6, on Varian 500 MHz NMR spectrophotometer with the tetramethylsilane (TMS)as a reference. Liquid chromatograph mass spectrum of phthiocol was recorded on Shimadzu, liquid chromatograph mass spectrophotometer,LC-MS-2010EV with ESI as the source was used for ionization

Cyclic voltammetry studies

Electrochemical measurements were performed with CHI 6054E electrochemical analyser equipped with a commercial platinum disc electrode (CHI Instruments, USA, 2 mm diameter), $AgNO_3$wire and platinum wire loop which serve as working, reference and counter electrodes, respectively. After fixing the electrodes to the cell 0.513 g of tetra butyl ammonium perchlorate (100 mM in 15 mL solution) was transferred to cell through high purity argon gas. The blank or controlled voltammograms were acquired in tetra butyl ammonium perchlorate–DMSO mixture prior to measurements. Sample dispersed in small amount of solvent injected in cell for further measurement (analytic concentration 5 mg/15 mL). At the end of each set of experiments the potentials were calibrated with respect to the normal hydrogen electrode (NHE) using the ferrocene as internal standard.

Single Crystal X-ray Crystallography

Single crystal of Phth-K_2 was grown by slow evaporation of the solution in methanol. Red coloured needle type crystal of approximate size 0.12 x 0.10 x 0.01 mm^3, was mounted for data collection on *Bruker SMART APEX* CCD diffractometer employing Mo K_α radiation with fine focus tube of 50 kV and 30 mA. Crystal to detector distance 6.05 cm, 512 x 512 pixels/frame, multirun data acquisition, four data sets. Total frames = 1829, Oscillation / frame -0.3º, exposure / frame = 25.0 sec / frame, maximum detector swing angle = –30.0º, beam centre = (260.2, 252.5), in plane spot width = 1.24, SAINT integration, θ range = 1.10 to 24.75º, completeness to θ of 24.75 º is 99.7 %. SADABS correction applied.

All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL) [19] was used for structure solution and full matrix least squares refinement on F^2. Carbon atom C(2)was thermally not stable and refined isotropically. Hydrogen atoms were included in the refinement as per the riding model, the hydrogens of the water molecule and those of O(2)H were thus determined by difference fourier and refined subsequently. Data collection and refinement parameters are listed in Table 1.

Computational Method

The anion and Phth-K_2 were optimized using the analytical gradient method relaxing all the geometric parameters simultaneously. The density functional theory based on dispersion corrected exchange correlation functional M06-2x [20] from the Minnesota group, with the internally stored 6-31+G(d,p) basis set was employed. The Gaussian-09 program [21] was used. Optimizations were performed with the SCF= ‘ultrafine’ grid option. The vibrational frequencies were computed analytically using the second derivatives of energy from the hessian matrix. The harmonic frequencies thus obtained were scaled by a factor of 0.9541 as recommended for the M06-2x functional [22].All the normal vibration frequencies turned out to be real (no frequency was imaginary) hence, the optimized structures were confirmed to be local minima on the potential energy surfaces. The ^{1}H and ^{13}C NMR chemical shifts were computed by subtracting respective shielding constants from those of the tetramethylsilane (TMS) which was used as the reference within the framework of the gauge-independent atomic orbital (GIAO) method. The influence of solvent on^{1}H and ^{13}C NMR chemical shifts was modeled through self-consistent reaction field (SCRF) theory employing the polarized continuum model (PCM) in the presence of DMSO (solvent).

Results and Discussion

Single Crystal X-ray Crystallography

Single crystal X-ray data for Phth-K_2 was collected at room temperature. The molecular structure, ORTEP diagram has been depicted in Fig.1. Crystallographic data is summarized in Table 1. Selected bond distances are reported in Table 2. An extensive data has further been given in the Table S1 of the ESI† of supporting information. As shown in Fig. 1 the potassium ion shows distorted octahedral geometry and coordinates to *four* phthiocols and a H_2O molecule. The extending polymeric chain resulted through binding of phthiocol to metal ion *via* O(1), O(2) and O(3) as depicted in Fig.2. The potassium oxygen contact distances in distorted octahedron around K^+ vary from ~2.6 to 2.8 Å [23-33]. The phthiocol facilitating hydrogen bonding interactions [(i) O(2)-H=0.96(7)Å, H···O(5)=1.75Å, O(2)···O(5)=2.71(1)Å, ∠O(2)-H···O(5) = 179(7)°, (-1+x,y,z), (ii)O(4)···O(5)=2.82(2)Å] (Fig.3)engender water channels along the ‘c’ axis as depicted in Figure.

The C=O bond distances in the phthiocol complex are displayed in Table 2 are relatively large compared to those observed in the complexes of phthiocol [4]. The C-C and C=O bond distances of quinones are sensitive to oxidation state of ligands in their complexes [34-41]. The bond distances in redox susceptible quinonoid ligands, have proven useful to identifying the oxidation number of phthiocol in the complexes. The C=O distances in catecholate complexes have been observed to be 1.32-1.39Å, whereas the C-C bond distances in hexatomic carbon ring closer to those of aromatic systems with the average of these being in the range 1.39-1.41 Å. The respective C=O and C-C bond distances in semiquinone complexes usually are found to be1.28Å-1.31 Å and 1.42Å -1.45 Å.

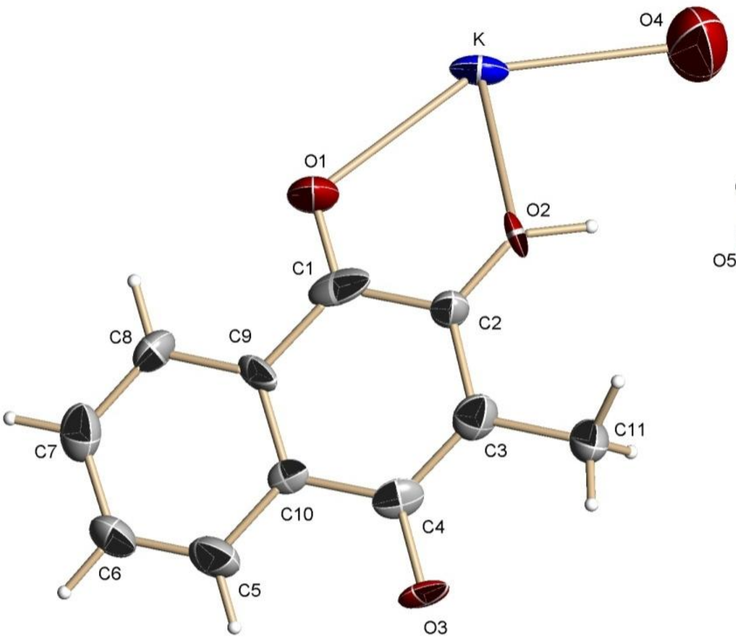


Fig.1 ORTEP diagram of Phth-K_2. Ellipsoids are drawn at 50 % probability

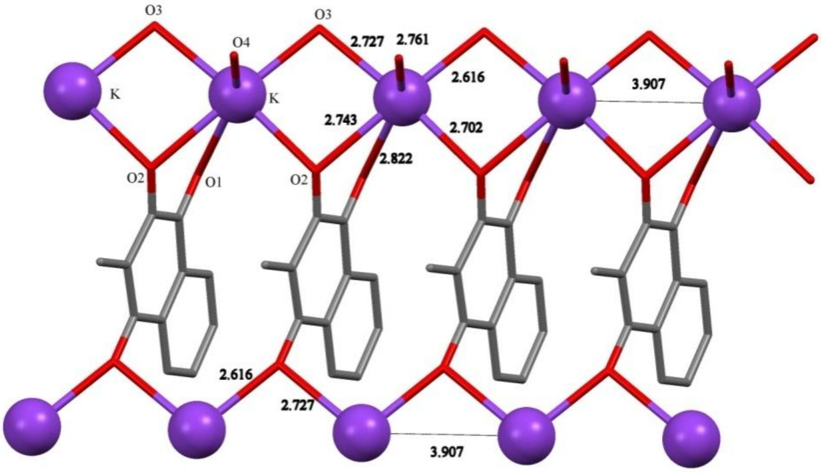


Fig.2 Polymeric chain of 'K^+' formed due to bridged ligands in Phth-K_2

Compared to these data, the neutral quinones complexes possess the carbonyl and C-C bond distances to be ~1.23 Å and ~1.53 Å in [34-41]. Nonetheless, the bond distances do not distinguish metal-quinone antiferromagnetic interactions and the quinonoid C=O distances in 2-oxido-1,4-naphthoquinone anion are observed to be longer[42]. Furthermore charge delocalization engenders relatively long C(2)-O(2) and C(4)-O(3) bonds. Besides the

C(1)-O(1) bond distance in the oxidized form of phthiocol anion are nearly unchanged and turn out to be 1.23 Å [43]. Thus it may be conjectured that variation in oxidation state of naphthoquinone emerge with its signature in C(1)-O(1) bond distances.

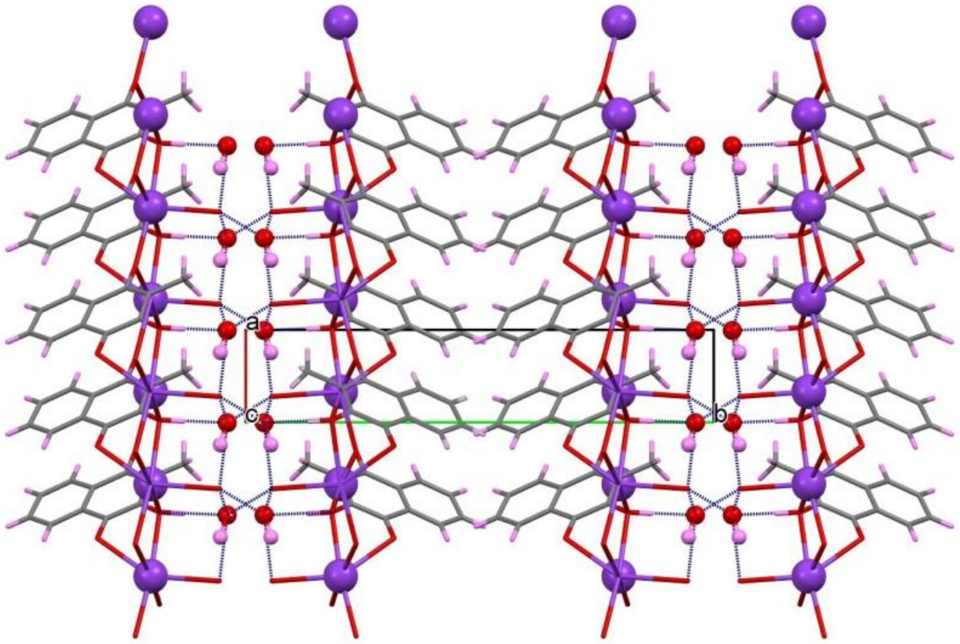


Fig.3 Packing viewed down 'c' axis. The ligand forms channels with water molecule hydrogen bonded to the ligands in Phth-K_2

Selected bond distances in phthiocol complex [4] and free phthiocol [43] are compared in Table 3. The C=O bond distances in Phth-$K_2$are longer than the corresponding ones in the oxidized form of phthiocol. A comparison of catecholate and quinone has shown that the carbonyl bond distances in the latter are relatively short. Observed C(2)-C(3) distances (1.44Å) thus show intermediate C-C and C=C character. Thus, the presence of dianion phthiocol radical as form II (*cf.* Scheme 1) in the titled K^+ naphthosemiquinone complex is evident. These inferences have further been supported by the EPR and electrochemical experiments.

Electronic structure

Optimized structure along with selected bond distances (in Å) of Phth-K_2 complex from the M06-2x/6-31+G(d,p) theory has been displayed in Fig.4

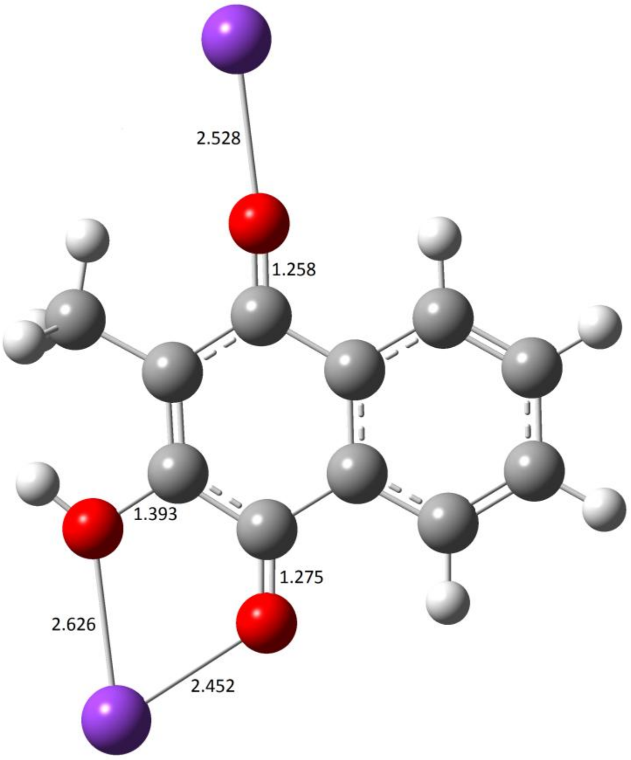


Fig. 4 Optimized geometry of the Phth-K_2 complex

Phth-K_2 structure obtained from the M06-2x based density functional theory is in consonant with that observed in the single crystal X-ray experiments. The separation between K^+ and carbonyl oxygens O(1) and O(2) was predicted to be ~ 2.54 Å in the complex.

^{1}H and ^{13}C NMR,FT-IR and Electronic Spectra

^{1}H NMR spectra revealed *six* peaks for isolated phthiocol compared to *five* for the Phth-K_2 as displayed in Fig.S1 in ESI†. A singlet due to –OH, and -CH_3, doublet from C(5)H and C(8)H and triplet of C(6)H and C(7)H can also be noticed. Further the Phth-K_2 protons on C(5) to C(8)and those from the methyl group exhibit upfield signals compared to the phthiocol anion. It may further be remarked here that the complexation of phthiocol anion with the metal can be monitored by measurements of the^{13}C NMR chemical shifts. The corresponding NMR signals in Phth-K_2 complex (Fig.5) engender upfield signals for C(1), C(3), C(5), C(6), C(7), C(8), C(9) and C(10)). As opposed to this the signals due to (CH_3, C(2), C(4))deshielding in the ^{13}C NMR spectra in thePhth-K_2complex.It is therefore, evident that the complexation with the metal ion influences C(2) and C(3) signals significantly. A large shielding of C(3) signals (δ_C 6.9 ppm) in the spectra further suggests paramagnetic interaction.

As far as the methyl protons are concerned, the δ_H values from the M06-2x/6-31+G(d.p) theory given in Table 4 refer to mean of those of individual protons in the group. Theoretically calculated chemical shifts by and large, agree well with those observed in the experiment.Experimental^{13}C NMR chemical shifts further led to following inferences. The C(4),C(1) and C(2) signals from 184 ppm to 170 ppm, are largely deshielded. A large up-field signal of the methyl carbon (δ_c 9.5 ppm) has also been observed. As shown in Table 4, the calculated chemical shifts are in accordance with the experiment. The largest shielding of C(3) predicted from the present density functional theory concurs with the experimental data.

The infrared spectra in 3400cm^{-1} -2800 cm^{-1} region of phthiocol (Fig.S2 in ESI†) shows a band at 3371 cm^{-1} arising from coupling of-OH and -CH stretchings, which becomes broader on complexation. Two sharp peaks near 1591 cm^{-1} and 1660 cm^{-1}of the anion were assigned to carbonyl stretching [44]. The complexation of phthiocol has further been accompanied by emergence of bands near1521 cm^{-1}, 1589 cm^{-1} and 1670 cm^{-1} instead. A sharp peak ~1521 cm^{-1}assigned to those of carbonyl group of naphthosemiquinone phthiocol [45].

Table S7 in ESI† reports vibrational frequencies of the isolated $K_2C_{11}H_{12}O_5$ complex and those in Phth$^{2-\bullet}$from the MO6-2x based density functional theory. A band near 1536 cm^{-1} in the calculated spectra assigned to C=O stretching vibration comprising of strong coupling from different internal coordinates corresponds to a broad band near the 1521 cm^{-1} and thus suggests the presence of Phthiocol in semiquinone form in the complex [45]. Moreover, computational studies revealed that C=O stretching vibration is diffused in different normal vibrations from 1621 cm^{-1} -1508 cm^{-1}(*cf.* Table S7 of ESI†). It has further been predicted that the OH stretching near3718 cm^{-1} of the anion shifts to the lower wave number (3688 cm^{-1}) with a concomitant increase in its intensity on complexation.

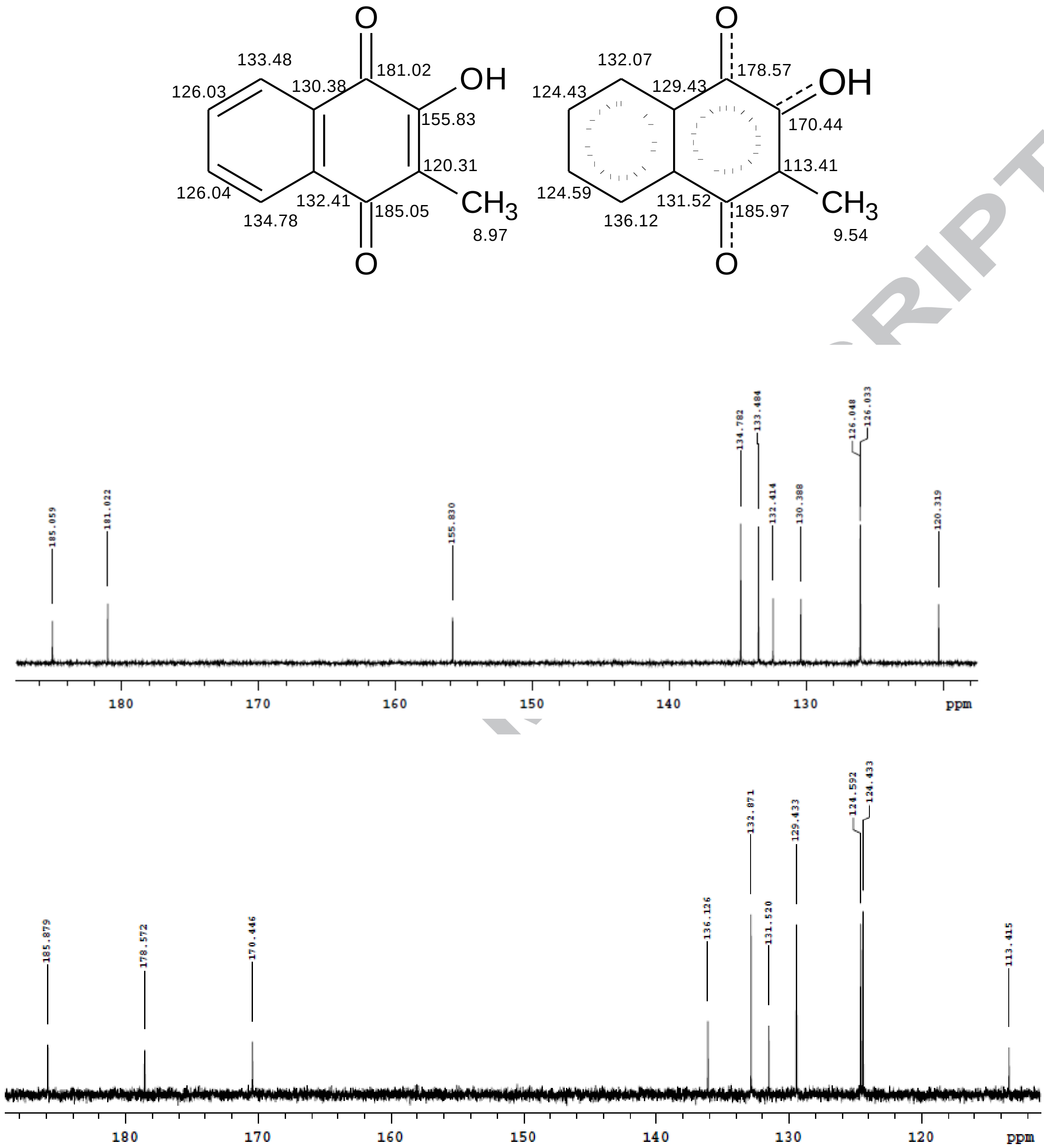


Fig.5 ^{13}C NMR spectra of free phthiocol (top) and Phth-K_2 (bottom)

UV-Visible spectra of phthiocol and Phth-K_2 in methanol are displayed Fig.S3 in ESI†. Two bands centered ~327 nm were assigned to π→π* transition of quinonoid and benzenoid rings, respectively [4, 46-47] are observed. The ~329 nm peak in Phth-K_2 show hyposochromic shift. A single broad band in the visible region arises from n→π* transition.

Table 1 Crystal data for Phth-K_2.

Empirical formula	$K_2 C_{11}H_{12}O_5$
Formula weight	263.31
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*Pc*
Unit cell dimensions	a = 3.9070(4) Å, α = 90°.
	b = 18.510(2) Å, β = 111.347(2) °.
	c = 8.6690(8) Å, γ = 90°.
Volume	583.92(10) $Å^3$
Z	2
Density (calculated)	1.498 g/cc
Absorption coefficient	0.461 mm^{-1}
F(000)	274
Crystal size	0.12 x 0.10 x 0.01 mm^3
Theta range for data collection	1.10 to 24.75°.
Index ranges	-4<=h<=4, -21<=k<=21, -9<=l<=9
Reflections collected	4579
Independent reflections	1950 [R(int) = 0.0790]
Completeness to theta = 24.75°	99.7 %
Max. and min. transmission	0.9949 and 0.9480
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1950 / 5 / 169
Goodness-of-fit on F^2	1.274
Final R indices [I>2sigma(I)]	R1 = 0. 1046, wR2 = 0.1728
R indices (all data)	R1 = 0.1252, wR2 = 0.1800
Absolute structure parameter	0.12(14)
Largest diff. peak and hole	0.391 and -0.481 e.$Å^{-3}$

Table 2 Selected structural parameters (bond- lengths in Å] and -angles in °in Phth-K_2.

Bonds	Bond lengths [Å]	Bonds	angles [°]
K-O(3)#1	2.616(7)	O(3)#1-K-O(2)#2	88.4(2)
K-O(2)#2	2.702(7)	O(3)#1-K-O(3)#3	93.94(19)
K-O(3)#3	2.727(7)	O(2)#2-K-O(3)#3	173.2(2)
K-O(2)	2.743(7)	O(3)#1-K-O(4)	96.5(3)
K-O(4)	2.761(9)	O(2)#2-K-O(4)	89.1(3)
K-O(1)	2.821(7)	O(3)#3-K-O(4)	96.9(3)
K-C(4)#3	3.412(8)	O(2)-K-O(4)	89.8(3)
K-C(2)#2	3.474(9)	O(3)#1-K-O(1)	116.4(2)
O(1)-C(1)	1.230(10)	O(2)#2-K-O(1)	87.5(2)
O(2)-C(2)	1.248(10)	O(3)#3-K-O(1)	85.8(2)
O(2)-K#4	2.702(7)	O(2)-K-O(1)	57.3(2)
O(2)-H	0.96(7)	O(4)-K-O(1)	146.8(3)
O(3)-C(4)	1.268(10)	O(1)-C(1)-C(2)	118.9(10)
C(1)-C(2)	1.462(13)	O(1)-C(1)-C(9)	119.4(10)
C(1)-C(9)	1.482(12)	C(2)-C(1)-C(9)	121.7(8)
C(2)-C(3)	1.441(13)	O(2)-C(2)-C(3)	123.4(8)
C(3)-C(4)	1.407(14)	O(2)-C(2)-C(1)	119.4(8)
C(5)-C(6)	1.351(13)	C(3)-C(2)-C(1)	117.2(8)
C(5)-C(10)	1.370(12)	C(7)-C(8)-H(8)	120.1
C(6)-C(7)	1.386(13)	C(9)-C(8)-H(8)	120.1
C(7)-C(8)	1.375(13)	C(10)-C(9)-C(8)	120.7(8)
C(8)-C(9)	1.383(12)		
C(9)-C(10)	1.375(12)		

Symmetry transformations used to generate equivalent atoms:

#1 x-2,y,z-1 #2 x-1,y,z #3 x-1,y,z-1 #4 x+1,y,z #5 x+2,y,z+1 #6 x+1,y,z+1

Table 3 Bond distances (in Å) of Phth-K_2 and [Zn(Phthiocol)$_2$(H_2O)$_2$] from the experiment and M06-2x/6-31+G(d,p) theory.

Bond	Phth-K_2		Phthiocol		[Zn(Phthiocol)$_2$(H_2O)$_2$]	
	Expt.	DFT	Expt.	DFT	Expt.	DFT
C(1)-O(1)	1.230(10)	1.275	1.228(2)	1.212	1.227(5)	1.241
C(2)-O(2)	1.248(11)	1.393	1.346(2)	1.341	1.292(4)	1.303
C(4)-O(3)	1.268(10)	1.258	1.224(2)	1.220	1.245(5)	1.222
C(1)-C(2)	1.462(13)	1.431	1.486(2)	1.501	1.509(5)	1.501
C(2)-C(3)	1.441(14)	1.379	1.352(2)	1.352	1.363(5)	1.368
C(3)-C(4)	1.407(14)	1.442	1.477(2)	1.481	1.449(5)	1.469
C(1)-C(9)	1. 482(12)	1.456	1.477(2)	1.489	1.472(5)	1.470
C(4)-C(10)	1.461(12)	1.470	1.493(2)	1.497	1.494(6)	1.505

Table 4 Comparison of ^{1}Hand ^{13}C NMR chemical shifts of Phthiocol anion and PhthK$_2$ complex from the experiment and M06-2x/6-31+G(d,p) theory. The numbers in parenthesis refer to those obtained from theory.

Types of carbons/protons	Phth-K2 δ_H	Phth-K2 δ_c	Phth δ_c
C(1)		178.57 (170.12)	181.02 (152.68)
C(2)-OH	(3.7)	170.44 (154.65)	155.83 (154.94)
C(3)-CH$_3$	1.748 (2.1)	113.41 (121.24)	120.31 (107.54)
C(4)		185.97 (180.73)	185.05 (166.04)
C(5)H	7.680 (9.2)	136.12 (141.65)	134.78 (139.61)
C(6)H	7.560 (8.5)	124.59 (139.42)	126.04 (113.61)
C(7)H	7.742 (8.3)	124.43 (140.06)	126.03 (120.40)
C(8)H	7.799 (8.7)	132.07 (139.64)	133.48 (138.11)
C(9)		129.43 (143.87)	130.38 (145.51)
C(10)		131.52 (142.56)	132.41(137.61)
CH$_3$		9.54 (15.54)	8.97 (9.13)

Electron Paramagnetic Resonance and Electrochemical Studies

EPR spectra of polycrystalline Phth-K$_2$ were recorded at the room temperature (298 K) and at 133 K (Fig.S4 and Fig.S5 in ESI†). A broad signal near g = 2.00 and a weak triplet near g ~ 4 was observed. The Phth-K$_2$ being polymeric a triplet state possibly generated from ferromagnetic interactions between neighboring radical spins in the complex [48]. With 1:1 mole ratio of KOH to phthiocol used in synthesis the hydroxyl group of Phth-K$_2$getsdeprotonated:

$$\mathrm{Phth}^{-} + \mathrm{Phth} \rightleftharpoons 2\mathrm{Phth}^{-\bullet}$$

Disproportionate reaction between anionic phthiocol and protonated phthiocol generates naphthosemiquinone dianion in Phth-K$_2$. A similar mechanism was suggested in case of the 2-hydroxy-1,4-naphthoquinone [42]. It should be pointed out here that the generation of the anion radical from menadione in the presence of alkali through disproportionate reaction was conjectured earlier in the literature [48-57]. Alkali metal NaOH, KOH, KF are used in solvent

(0.1 NaOH, methanol/water, ethanol/water, ethanol (abs), methanol, DMSO, THF) generate the anionic radical of menadione ($MNQ^{-\bullet}$). The observed 'g'value in the presence of salt in different solvents was found to be 2.00045± 0.00002. The hydroquinone reacts with potassium fluoride (KF) in methanolic solution producing the dipotassium salt. A disproportionate reaction yields radical through:

$$MNQ^{2-} + MNQ \rightleftharpoons 2MNQ^{-\bullet}$$

Cyclic voltammogram of Phth-K_2in DMSO (Fig.6 and Fig.S6 in ESI†) reveals Cathodic quasi-reversible peak ~0.52 V vs NHE in free phthiocol [58]. No such a peak observed in Phth-K_2. The observed cathodic peak at ~1.10 V assigned to naphthosemiquinone (form II in Scheme 1) stem from catechol (form III in Scheme 1) reduction. Anodic irreversible peak at +0.88 V assigned to the reoxidation of coordinated phthiocol in Phth-K_2 [58, 62]. Electrochemical studies hence, ascertain coordination of phthiocol in one electron reduced naphthosemiquinone form.

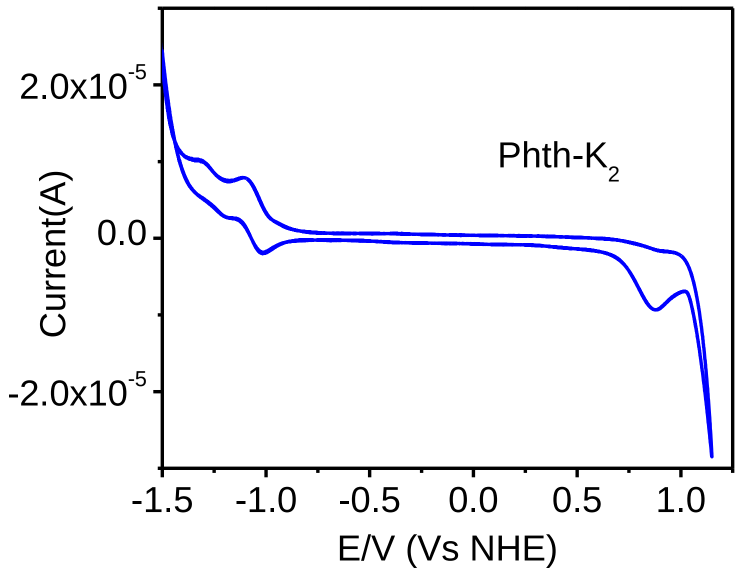


Fig.6 Cyclic voltammogram of Phth-K_2 at 0.1 V/s scan rate.

Conclusions

A room temperature stable Phth-K_2 complex was synthesized with phthiocol binds to K^+ ions in naphthosemiquinone form. The complex was characterized by FTIR, ^1H and ^{13}C NMR, EPR, electrochemical, single crystal X-ray diffraction experiments. Polymeric Phth-K_2 shows metal ion located in the vicinity of four phthiocol neighbours. Naphthosemiquinone generated in disproportion reaction of catechol and oxidised form of phthiocol ligand. Half field signal observed ~g=4 at 133 K in the X-band EPR spectra of polycrystalline Phth-K_2, attributed to ‘triplet state’ consequent to ferromagnetic interactions of neighbouring spins of phthiocol.

Supporting information available

Fig. S1 to S7, crystallographic Tables S1 to S7. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and may be obtained on request quoting the deposition number 1034515from the CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44 1223 336 033; E-mail address: deposit@ccdc.cam.ac.uk).

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References

[1] R.J. Anderson, M. S. Newman, J. Biol. Chem., 103 (1933) 197-201.

[2] E.G. Ball, J. Biol.Chem., 106 (1934) 515-524.

[3] L.F. Fieser, J. Biol.Chem., 133 (1940) 391-396.

[4] L. Kathawate, S. Sproules, O. Pawar, G. Markad, S. Haram, V. Puranik, S. Salunke-Gawali, J. Mol. Struct., 1048 (2013) 223-229.

[5] S. Rane, K. Ahmed, S. Salunke-Gawali, S. B. Zaware, D. Srinivas, R. Gonnade, M. Bhadbhade, J. Mol. Struct., 892 (2008) 74–83.

[6] J.M. Jamison, J. Gilloteaux, M. Venugopal, J.A. Koch, C. Sowick, R. Shah, J.L. Summers, Tissue. Cell, 28 (1996) 687-701.

[7] C. Chen, Y.Z. Liu, K.S. Shia, H.Y. Tseng, Bioorg. Med. Chem. Lett., 12 (2002) 2729–2732

[8] J.A. Duin, J.A. Jongejan, Annu. Rev. Biochem. 58 (1989) 403-406.

[9] D.M. Dooley, M.A. McGuirl, D.E. Brown, P.N. Turkowski, W.S. Mcintire, P.F. Knowles, Nature, 349 (1991) 262-264.

[10] C.M. Jackson, Y. Nemerson, Ann. Rev. Biochem. 49 (1980) 765-811.

[11] S.A. Petrova, M.V. Kolodyazhny, O.S. Ksenzhek, J. Electroanal. Chem., 277 (1990) 189-196.

[12] O.S. Ksenzhek, S.A. Petrova, M.V. Kolodyazhny, S.V. Oleinik, Bioelectrochem. Bioenerg., 4 (1977) 335-543.

[13] S. Salunke-Gawali, R. Dalvi, K. Ahmed, S. Rane, J. Therm. Anal. Cal, 76 (2004) 801–812.

[14] S. Salunke-Gawali, S.Y. Rane, K. Boukheddaden, E. Codjovi, J. Linares, F.Varret, P.P. Bakare Ind. J. Chem.43A (2004) 2563-2567.

[15] M.P. Mulay, P. L. Garge, S.B. Padhye, R.L. Haltiwanger, L.A. deLearie, C.G. Pierpont, J. Chem. Soc., Chem. Commun.,(1987) 581-582.

[16] P. Shinde, S. Nilakhe, V. Shinde, B.A. Kulkarni, V.R. Sapre, M.P. Wadekar, J. Appl. Chem., 7 (2014) 33-40.

[17] S. Gaikwad, R. Kankariya, D. Shah, J. Appl. Chem., 3 (2014) 164-169.

[18] W.L. Armarego, D.D. Perrin, D.R. Perrin Purification of Laboratory Chemicals, Pergamon Press. London, (1998) 260.

[19] G.M. Sheldrick, SHELX-97 Program for crystal structure solution and refinement, University of Göttingen, Germany, 1997.

[20] Y. Zhao, D.G. Truhlar, Theor. Chem. Acc., 12 (2008) 215-241.

[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H Nakatsuji, M Caricato, X Li, H.P Hratchian, A.F Izmaylov, J Bloino,G .Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr, J.E Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R Kobayashi, J Normand, K. Raghavachari, A Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A. J. Austin,. R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A Voth, P. Salvador, J.J Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. J.Cioslowski, D.J. Fox,. Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford CT, 2009.

[22] M. L. Laury, M. J. Carlson, A. K. Wilson, J. Comput. Chem. 33 (2012) 2380-2387.

[23] S. Margadonna, K. Prassides, Y. Iwasa, Y. Taguchi, M.F. Craciun, S. Rogge, A.F. Morpurgo, Inorg. Chem., 45 (2006) 10472-10478.

[24] I. Fernandez, F. Breher, P. S.Pregosin, Z. Fei, P. J. Dyson, Inorg. Chem., 44 (2005) 7616-7623.

[25] C. Kayser, R. Fischer, J. Baumgartner, C. Marschner, Organomet., 21 (2002) 1023-1030.

[26] I. Kobrsi, W. Zheng, J.E. Knox, M.J. Heeg, H.B. Schlegel, C.H. Winter, Inorg. Chem., 45 (2006)8700-8710.

[27] R.E. Dinnebier, S. Vensky, M. Panthofer, M. Jansen, Inorg. Chem., 42 (2003) 1499-1507.

[28] M. Westerhausen, M.W. Ossberger, P. Mayer, H. Piotrowski, H. Noth, Organomet., 23 (2004**)** 3417-3424.

[29] Y. Shuku, R. Suizu, K. Awaga, Inorg. Chem., 50 (2011) 11859-11861.

[30] S. Gupta, M.V. Kirillova, M.C. Fatima, G. da Silva, A.J.L. Pombeiro, and A.M. Kirillov, Inorg. Chem. 52 (2013) 8601-8611.

[31] K.T. Mahmudov, M. Fatima. G. da Silva, A.M. Kirillov, M.N. Kopylovich, A. Mizar,J.L.P. Armando J. L. Pombeiro, Cryst. Growth. Des. 13 (2013) 5076-5084.

[32] I.A. Guzeia, M.H. Kima, R. Westa, Daltan. Trans. 21 (2013) 3722-3739.

[33] M.U. Anwar, L.N. Dawe, M.S. Alam, L.K. Thompson, Inorg. Chem. 51 (2012) 11241-11250.

[34] C.G. Pierpont, Coord. Chem. Rev., 219-221 (2001) 415-433.

[35] C.G. Pierpont, Coord. Chem. Rev., 216 -217 (2001) 99-195.

[36] M.W. Lynch, R.M. Buchanan, C. G. Pierpont, D.N. Hendrickson, Inorg. Chem., 20 (1981) 1038-1046.

[37] M.W. Lynch, D.N. Hendrickson, B.J. Fitzgerald, C.G. Pierpont, J. Am. Chem. Soc., 106 (1984) 2041-2049.

[38] A.M. Barthram, Z.R. Reeves, J.C. Jeffery, M. D. Ward, J. Chem. Soc. Dalton Trans., (2000) 3162-3169.

[39] A.B.P. Lever, P.R. Auburn, E.S. Dodsworth, H. Masa-aki, W.Liu, M. Melnik, W.A. Nevin, J. Am. Chem. Soc., 110 (1988) 8076-8084.

[40] G.A. Abakumov, V.K. Cherkasov, M.P. Bubnov, O.G. Ellert, Z.B. Dobrokhotova, L. N. Zakharov and Y. T. Struchkov, Dokl. Akad. Nauk., 328 (1993) 12-15.

[41] C.G. Pierpont, H.H. Downs, Inorg. Chem., 16 (1977) 2970-2972.

[42] S. Salunke-Gawali, L. Kathawate, Y. Shinde, V.G. Puranik, J. Mol. Struct. 1010 (2012) 38-45.

[43] J. Gaultier, C. Hauw, Acta.Crystallogr., 19 (1965) 919-926.

[44] T. Satoh, T. Tsuji, H. Matsuda, S. Sudoh, Bull. Chem. Soc. Jpn. 80 (2007) 321-323.

[45] M. Mac, J. Wirz, Photochem Photobiol Sci. 1 (2002) 24-29.

[46] K.Y. Chu, J. Griffiths, J. Chem. Soc., Perkin Trans. 1 (1979) 696-701.

[47] M. Khan, Z. Khan, Spectrochim. Acta. Part. *A*. 61 (2005) 777-790.

[48] C. Frontana and I. Gonzalez, J. Electroanal. Chem., 603 (2007) 155-165.

[49] J.A. Pedersen, J. Chem. Soc., Perkin Trans., 2 (1973) 424-431.

[50] S.C. Sharma, K. Torssell, Acta Chem. Scand., Ser. B, 32 (1978) 437-446.

[51] P. Ashworth, W. T. Dixon, J. Chem. Soc., Perkin Trans., 2 (1974) 739-744.

[52] M.R. Das, H.D. Connor, D.S. Leniart, J.H. Freed, J. Am. Chem.Soc., 92 (1970) 2258-2268.

[53] J.M. Fritsch, S.V. Tatwawadi, R.N. Adams, J. Phys. Chem., 71 (1967) 338-341.

[54] M. Adams, M.S. Blois, R.H. Sands, J. Chem. Phys., 28 (1958) 774-776.

[55] J.L. Huntington, D.G. Davis, J. Magn. Reson., 3 (1970) 456-467.

[56] J.A. Pedersen, Spectrochim. Acta. Part A., 58 (2002) 1257-1277.

[57] H. Joela, P. Lehtovuori, Phys. Chem. Chem. Phys., 1 (1999) 4003-4010.

[58] F.J. Gonzalez, Electroanalysis, 10 (1998) 638-642.

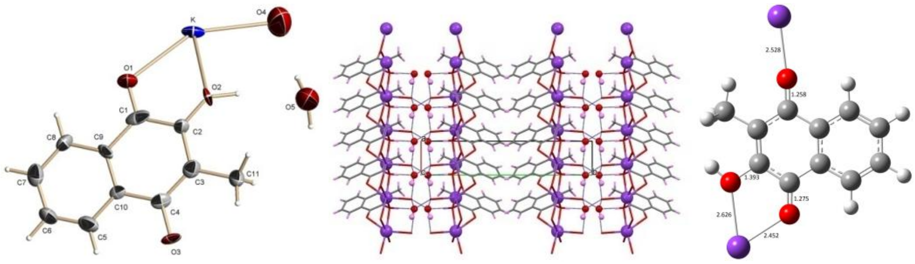
[59] F. González, J. Aceves, R. Miranda, I. González, J. Electroanal. Chem.,310(1991) 293-303.

[60] C. Amatore, J-M. Save´ant, J. Electroanal. Chem.,85(1977) 27-46.

[61] J. L. Ortiz, J. Delgado, A. Baeza, I. González, R. Sanabria, R. Miranda, J. Electroanal. Chem., 411(1996)103-107.

[62] C. Amatore, G. Copobianco, G. Farnia, G. Sandona, J-M. Saveant, M. G. Severin, E. Vianello, J. Am. Chem. Soc., 107(1985) 1815-1824.

Graphical Abstract



Highlights

- The first naphthosemiquinone coordination complex of vitamin K3 analog is reported.
- Hydrogen bonded water channels to the phthiocol are observed.
- Redox couple naphthosemiquinone to catechol is evident in electrochemical studies.
- ^{13}C NMR chemical shifts are in consonant with experiments.